Division of Polymer Chemistry, Inc.

American Chemical Society

Organic/Inorganic Polymer Systems

An Interdisciplinary Workshop

February 12-15, 1995
Inn @ Napa Valley--Napa, California

Workshop organizers: Richard M. Laine
Departments of Materials and Engineering, and Chemistry
The University of Michigan
(313) 764-6203, FAX 763-4788

Bruce Novak
Department of Polymer Science and Engineering
University of Massachusetts at Amherst
Room 701, Lederle Graduate Res. Center
(413) 545-2160, FAX 413-545-0764

With special thanks to: Diane M. Morrill, Business Manager
Division of Polymer Chemistry
1103 Hahn Hall
Virginia Polytechnic Institute
Blacksburg, VA 24061-0212
Phone: (703) 231-3029, FAX: 231-8517

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The Program

Sunday, February 12

4:00-8:00 pm — Registration
8:00-10:00 pm — Reception

Monday, February 13

8:30-8:45 am Introductory Remarks by **Rick Laine**, University of Michigan, Ann Arbor, MI and Bruce Novak, University of Massachusetts, Amherst, MA

Sol-Gel Processing--Multifunctional Materials

8:45-9:35	**Clement Sanchez**	Hybrid Inorganic/Organic Systems with Electrochromic, Photochromic.. Properties
9:35-10:25	**Bruce Dunn**	Optical Applications of Inorganic/Organic Hybrids
10:25-10:45	*Break*	
10:45-11:35	**Douglas A. Loy**	Silsesquioxane Derived Porous Materials
11:35-12:25	**Richard W. Pekala**	Organic/Inorganic Aerogels: Controlling Structure at the Nanometer Scale
12:25-2:00	*Lunch*	

Organic/Inorganic Hybrid Polymers.

2:00-2:50	**Michael Michalczyk**	Star Gels: New Single Component Organic/Inorganic Network Materials
2:50-3:10	*Break*	
3:10-4:00	**Barry Arkles**	Commercial Production of Inorganic/Organometallic Hybrids
4:00-5:30	Poster Session	Abstracts:

Synthesis and Characterization of Carbonate-bridged Polysilsesquioxane Sol-Gels.

Annealing Effects on Solid State Properties of Transition-Metal Coordination Complexes and Networks Based on Diene Polymers with Palladium Chloride.

Reactive Blending via Metal-Olefin Coordination in Diene Polymers---Solid State Properties that Support the Concept of a Network Structure.

Densification Behavior in Organically Modified Silica Systems as a Function of Heat Treatment: A Comparative Study of Bulk Gels and Thin Films Prepared Using Pendant and Bridged Organic Ligands.

Aluminosilicate-Poly(ethyleneglycol) Copolymer Electrolytes and Vanadium Oxide Oxymethylene Bridged Polyethylene Oxide Nanocomposite Electrode Materials.

Wednesday, February 15

Composites

8:45-9:35	Paul D. Calvert	Polymer/Inorganic Composites via Biomimetic Processing
9:35-10:25	Emanuelle Giannellis	Design, Synthesis and Properties of Polymer Matrix Nanocomposites
10:25-10:45	Break	
10:45-11:35	Bruce Novak	Mutually Interpenetrating Organic-Inorganic Networks: Synthesis, Structure and Properties
11:35--	Checkout, departure	

Tuesday, February 14

Organic/Inorganic Hybrid Polymers (cont.)

8:30-8:45	Introductory Remarks by **B. Novak, R. Laine**	
8:45-9:35	**Frank J. Feher**	Rational Synthesis of Si/O and Si/O/M Frameworks
9:35-10:25	**Helmut Schmidt**	Inorganic/Organometallic Hybrid Polymers: Routes to Industrial Applications
10:25-10:45	*Break*	

Inorganic/Organometallic Polymers

10:45-11:35	**Harry Allcock**	Polyphosphazenes, Properties and Application
11:35-12:25	**James E. Mark**	Properties of Inorganic Polymers with Bimodal Chain Distributions
12:25-2:00	*Lunch*	
2:00-2:50	**Len Interrante**	Preceramics Polymers
2:50-3:10	*Break*	
3:10-4:00	**Rick Laine**	Chemicals and Polymers from Silica and Alumina
4:00-5:30	Poster Session/General Discussion	

Abstracts:

Aluminosilicate-Polymer Electrolytes.

Ambient Pressure Aerogels via Organosilyl Derivatization of Polysiloxanes.

Novel, Functionalized Hybrid Materials from Polyhedral Silsesquioxanes and Propargyloxy Derivatives.

Polyphosphazene Solution Properties.

Preparation and Properties of Inorganic-Organic Composite Materials Containing $R_3SiO_{1/2}$, SiO_2 and TiO_2 Units.

Molecular Composites from Vinyl and Hydrido Functionalized Polyhedral Silsesquioxanes.

Sol-Gel Processing

Clement Sanchez	Molecular Design of Hybrid Organic-Inorganic Nano-composites Made via Sol-Gel Chemistry
Bruce Dunn	Optical Applications of Inorganic/Organic Hybrids
Douglas A. Loy	Silsesquioxane Derived Porous Materials
Richard W. Pekala	Organic/Inorganic Aerogels: Controlling Structure at the Nanometer Scale

MOLECULAR DESIGN OF HYBRID ORGANIC-INORGANIC NANO-COMPOSITES MADE VIA SOL-GEL CHEMISTRY

Clément Sanchez

Laboratoire de Chimie de la Matière Condensée - URA 1466
Université Pierre et Marie Curie
Paris -France

OUTLINE

Introduction

→ Rudiments of sol-gel chemistry
Classification of hybrids O-I

Molecular design of class II O-I

→ 1-Siloxane based hybrids (Si-C bonding)

NLO (grafted organic chromophores)
Emission (Rare-earth, Nd^{3+}, Dy^{3+} etc..)
Redox (V^{4+}...V^{5+}), Photochromic (W^{5+}..W^{6+})
Electronic and dielectric (polypyrolle-V^{4+}...V^{5+})

→ 2- Crosslinked Tin-oxo clusters (polymers, difonct-ligands)
(Sn-C bonding, Sn-C + electrostatic bonding)

→ 3- Transition metal based hybrids

Complexing ligands as particle size controllers
Copolymers zirconium oxo-PMMA

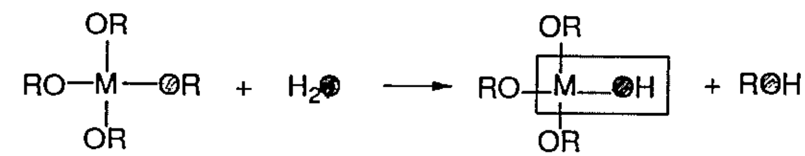
Conclusion

INORGANIC POLYMERIZATION REACTIONS

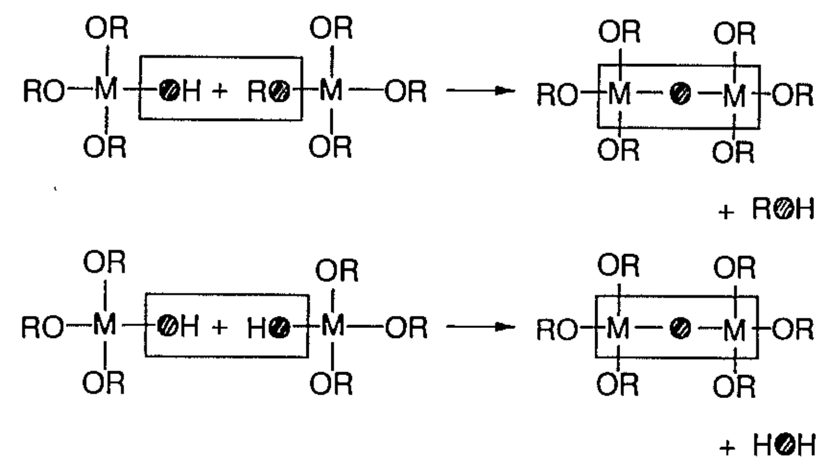
Hydrolysis-Condensation of Metal Alkoxides

Alkoxide : $M(OR)_n$
$M = Si, Ti, Zr, Al$
$R = -CH_3, -CH_2CH_3$

→ Hydrolysis



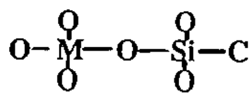
→ Condensation



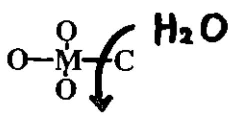
CLASS II HYBRIDS: ORGANIC-INORGANIC COMPONENTS ARE CHEMICALLY BONDED

1- Silanes et stananes

→ 2- Transition metals: bonding via silicium



3- Transition metals (M= Ti^{IV}, Zr^{IV}, Ce^{IV}, V^{V}, W^{VI}..)

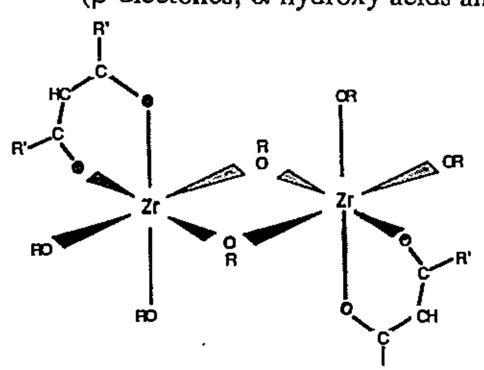


CHEMICAL MODIFICATION OF THE TRANSITION METAL ALKOXIDE

M - OR + H-OX ———> M - OX + ROH

M-OX is a new molecular precursor

OX = Strong complexing ligands
(β-dicétones, α-hydroxy acids and derivatives)



1-Siloxane based hybrids (Si-C bonding)

→ General exemples (alkoxysilanes + metal alkoxides)

Copolymers or nanocomposites ?

Specific exemples of hybrid materials:

NLO (grafted organic chromophores)

Emission (Rare-earth, Nd^{3+}, Dy^{3+} etc..)

Redox (V^{4+}---V^{5+}), Photochromic (W^{5+}--W^{6+})

Electronic and dielectric (polypyrolle-V^{4+}---V^{5+})

HYBRID ORGANIC-INORGANIC MATERIALS

1- ORGANIC AND INORGANIC CHEMISTRY CAN BE COUPLED VIA THE SOL-GEL PROCESS

Room temperature synthesis and Organic solvents
Metallo-organic precursors:

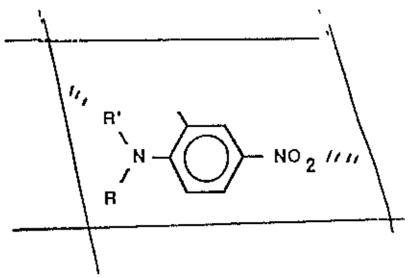
- Metal alkoxides
- Alkoxysilanes
- Complexed alkoxides

2-HYBRID ORGANIC-INORGANIC CAN BE CONVENIENTLY DIVIDED IN

THREE CLASSES

CLASS I

Embedded

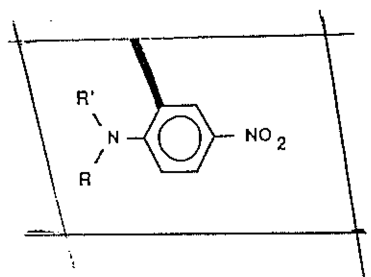


No covalent or ionocovalent chemical bonds

Vd W, H.B, or .electostatic interactions

CLASS II

Grafted



Chemically bonded

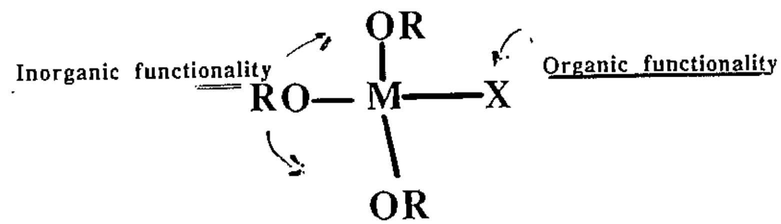
Strong interactions

CLASS III

(C.Sanchez and F. Ribot, New Journal of chemistry, 1994, 10,1037)

MOLECULAR DESIGN OF CLASS II HYBRIDS

The molecular precursor carry both functionalities



X is "not" hydrolyzable

X is a molecule	NETWORK MODIFIER
X is polymerizable	NETWORK FORMER

HYBRID ORGANIC-INORGANIC FILMS FOR OPTICS

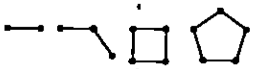
Siloxane chain former — **Metal-oxo crosslinkers**

Alkoxysilanes — **Metal alkoxides**

$Si(OR)_{4-x}R'_x$ x=1,2 — $M(OR)_n$ M= Si, Ti, Zr, Al...V

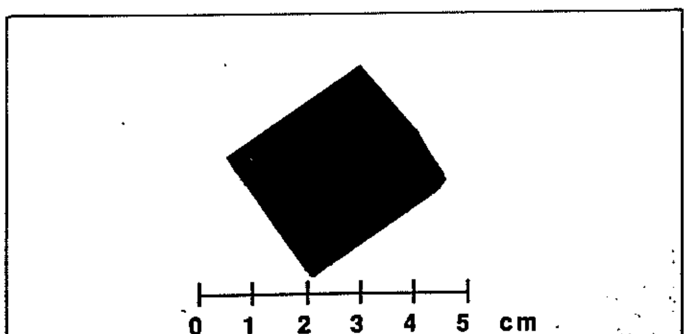
R'= CH_3, Phenyl, H ..

H_2O (catalyst?)



siloxane oligomers → **Sol**

Thick Coatings (1-30 μm)



FILM 90 $(CH_3)_2Si(OEt)_2$ / 10 $Ti(OPr^i)_4$ with Rhodamin 6G

(S.Diré, F.Babonneau, C.Sanchez, J.Livage, J.Mater.Chem., 2 , 239, 1992)

ALKOXYSILANES AS NETWORK MODIFIERS

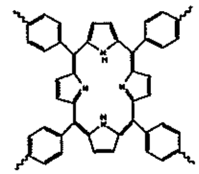
FUNCTIONALITY

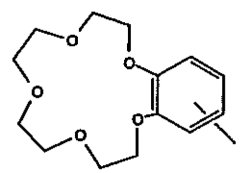
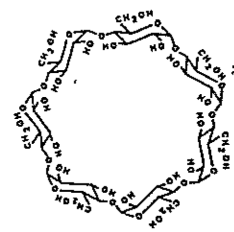
$(OR)_2Si(\underline{R})_2$ — 2D networks (Chain former)

$(OR)_3Si\text{-}\underline{R}$ — 3D networks

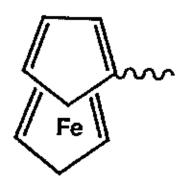
R= CH_3, Phenyl, — mechanical, hydrophobic; refractive index

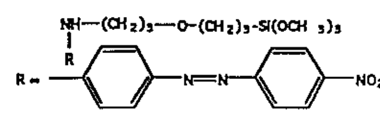
R= $CF_2\text{-}CF_2\text{-}CF_3$ — hydrophobic

R=  — catalyst

R=   — Selective membrane

β-cyclodextrin

R=  — Electrochemical sensor

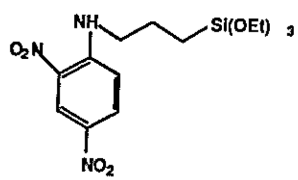
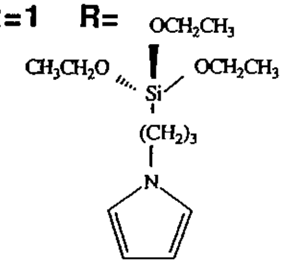
R =  — NLO

SOME PROPERTIES OF SILOXANE-OXIDE MATRICES

Alkoxysilanes $Si(OR)_{4-x}R'_x$ → ← M(OR)n alkoxides

$H_2O(H^+)$ ↓

FILMS

x=2 R= CH_3	Luminescence Photochromic (organic dyes)	M= Si, Zr
→ x=2 R= CH_3, H	luminescence	M= Zr + Ln (III)
x=2 R= CH_3	photochromic	M= W
x=2 R= CH_3	redox	M= V
→ x=1 R= 	NLO	M= Si, Zr
x=1 R= 	electronic	M= Si, Zr, V
x=1 Ferrocene	Electrochemistry	M = Si, Zr

1-Siloxane based hybrids (Si-C bonding)

General exemples (alkoxysilanes + metal alkoxides)

→ Copolymers or nanocomposites ?

Specific exemples of hybrid materials:

NLO (grafted organic chromophores)

Emission (Rare-earth, Nd^{3+}, Dy^{3+} etc..)

Redox (V^{4+}---V^{5+}), Photochromic (W^{5+}--W^{6+})

Electronic and dielectric (polypyrolle-V^{4+}---V^{5+})

Siloxane-oxide based coatings

Hydrolysis and co-condensation of

Alkoxysilanes	**Metal alkoxides**
Siloxane polymer former	Crosslinking reagents (catalyst)
$Si(OR)_{4-x}R'_x$	$M(OR)_4$ M= Si, Ti, Zr,..

H_2O (H+)

Coatings

→ **CONTROL THE EXTENSION OF THE PHASE SEPARATION between siloxane species and metal-oxo species**

→ Nature of the metal M
Nature of the R and R' groups
pH, Water content, time and sequence of mixing

→ ABILITY TO FORM STABLE -Si(R)--O--M BONDS

KINETICALLY STABLE BONDS

AGING TIME before film deposition
(by pass important Φ separation)

COPOLYMERS OR NANOCOMPOSITES

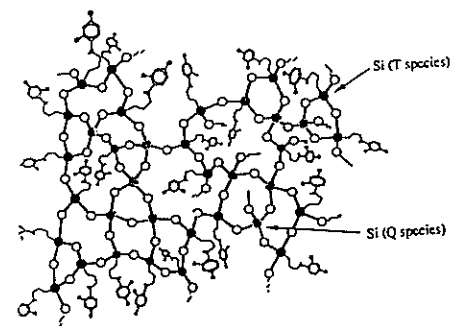
General Trend (^{29}Si, ^{17}O NMR)

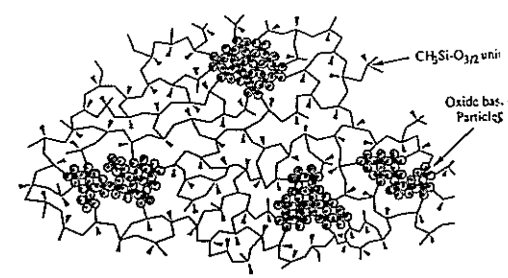
Hydrolysis and condensation of Alkoxysilanes and metal alkoxides

(F. Babonneau et al., MRS Proceedings, 346, 949,1994)

$Si(OR)_{4-x}R'_x + Si(OR)_4$ → COPOLYMERS (SEQUENCING)

$Si(OR)_{4-x}R'_x + M(OR)_4$ (M= Ti, Zr..) → NANO-COMPOSITES





The control of the extend of the phase separation is important for many properties

Mechanical properties, Transparency, Porosity, Hydrophobicity
Residual solvent and OH groups
Specific ACTIVE property (optical, electronic.)

1-Siloxane based hybrids (Si-C bonding)

General exemples (alkoxysilanes + metal alkoxides)

Copolymers or nanocomposites ?

→ Specific exemples of hybrid materials:

→ NLO (grafted organic chromophores)

Emission (Rare-earth, Nd^{3+}, Dy^{3+} etc..)

Redox (V^{4+}---V^{5+}), Photochromic (W^{5+}--W^{6+})

Electronic and dielectric (polypyrolle-V^{4+}---V^{5+})

NLO PROPERTIES

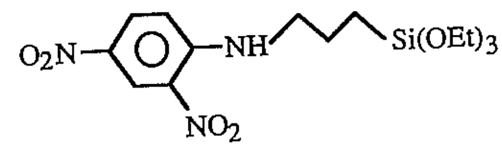
Induced polarisation

$$P = P_0 + \chi^{(1)}.E + \chi^{(2)}.E.E + \chi^{(3)}.E.E.E + \ldots$$

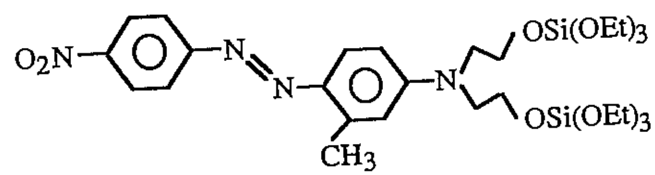
$\chi^{(2)}$ vanishes in centrosymmetric systems

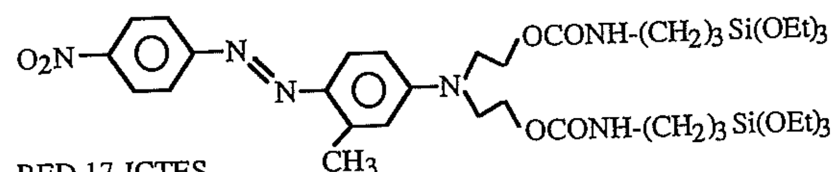
ORGANIC NLO CHROMOPHORES GRAFTED TO HYBRID SOL-GEL MATRICES

TSDP



RED 17-TES





RED 17-ICTES

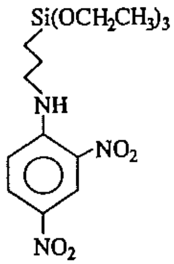
(E. TOUSSAERE, J. ZYSS, P. GRIESMAR, C.SANCHEZ),Non Linear Optics, 1991, 3.
(B.LEBEAU, J. MAQUET,C.SANCHEZ,E. TOUSSAERE, R. HIERLE, J. ZYSS), J. Mater Chem.1994]
(B.LEBEAU, C.GUERMEUR, C.SANCHEZ) [Better Ceramics Through Chemistry VI, 1994]

NLO PROPERTIES OF HYBRID SILOXANE-OXIDES

Hydrolysis and co-condensation of

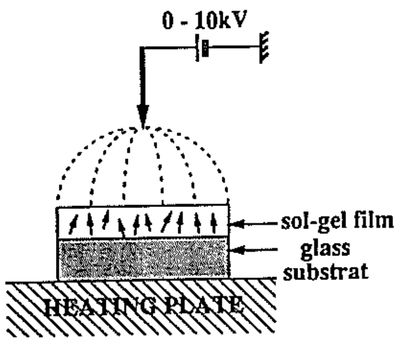
Alkoxysilanes $Si(OR)_3R$ — $H_2O(H+)$ → **FILMS** ← $M(OR)_4$ M=Si

R =

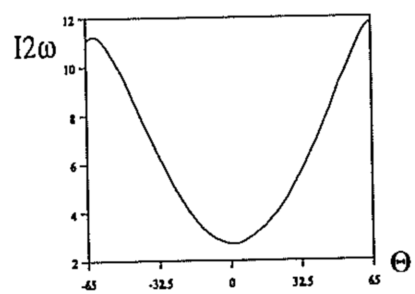


Thickness = 2µm
Refractive index = 1.62

ORIENTATION by CORONA POLING



SHG Response



SHG= 2-10 pm/V

(E. TOUSSAERE, J. ZYSS, P. GRIESMAR, C.SANCHEZ), Non Linear Optics, 1991, 3.
(B.LEBEAU, J. MAQUET,C.SANCHEZ,E. TOUSSAERE, R. HIERLE, J. ZYSS), J. Mater Chem.1994
4, 1155, (1994)

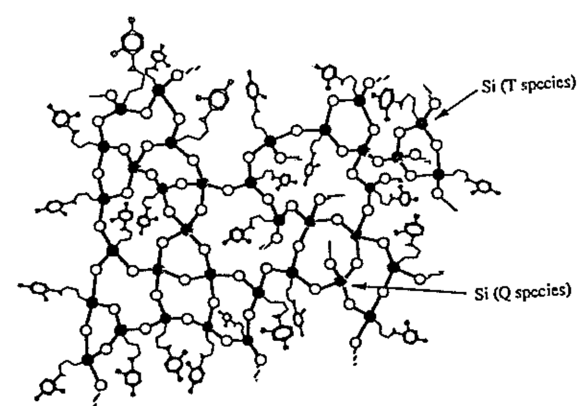
HYBRID SILOXANE- SILICA COPOLYMERS

Hydrolysis and co-condensation of

Alkoxysilanes $Si(OR)_3R$		$Si(OR)_4$
T units	$H_2O(H^+)$ ↓	Q units

- Compatibility between tetrahedral coordinences of T and Q units
- Relatively stable Si-O-Si bonds (hydrolysis ratio)
- Control the cocodensation (^{17}O NMR)

COPOLYMERS $(T\text{-}T)_m\text{---}(Q\text{-}Q)_n$



Liquid and solid ^{13}C, ^{29}Si NMR, SAXS, DSC, EXAFS

POLING OF ORGANIC MOLECULES CHEMICALLY BONDED TO HYBRID GELS

(B.LEBEAU, J. MAQUET,C.SANCHEZ,E. TOUSSAERE, R. HIERLE, J. ZYSS)
[J. Mater Chem.1994]

Second strategy ⟶ **hydrolysis TSDP with H+**

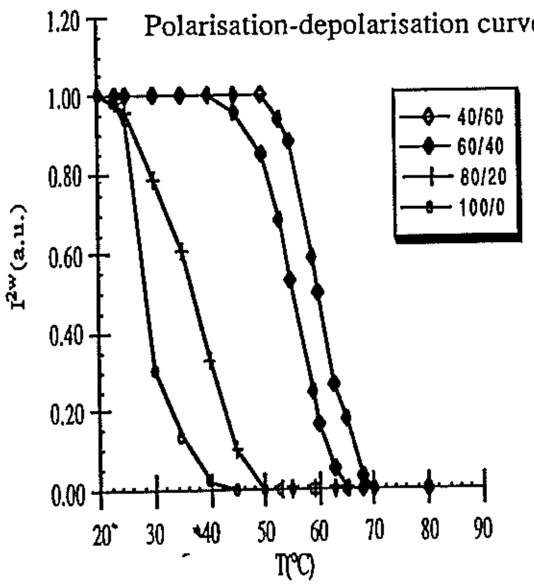
NLO dye TSDP (100–20%)

Crosslinker $Si(OMe)_4$ (0-80%)

Spin coated films
Thickness = 3-4μm
Refractive index = 1.6-1.65

Higher SHG response (10 pm/V) and less relaxation

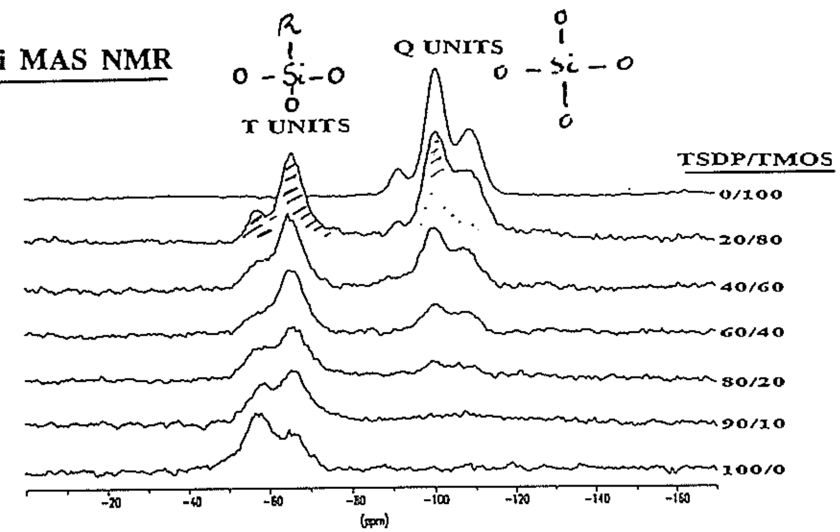
Polarisation-depolarisation curves



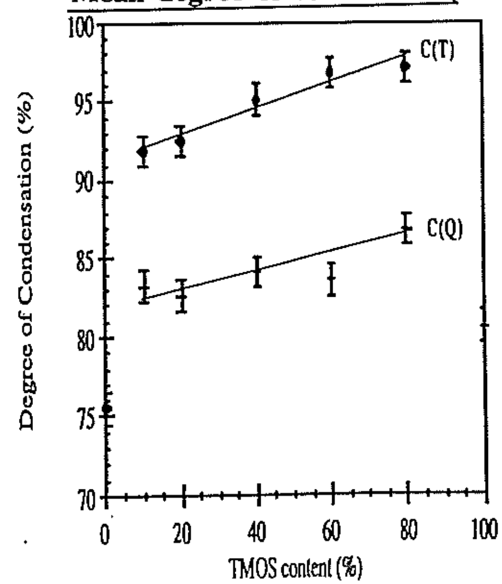
Transition temperature increases with the crosslinker content (TMOS)

RIGIDITY OF HYBRID SOL-GEL MATRICES (T+ Q)

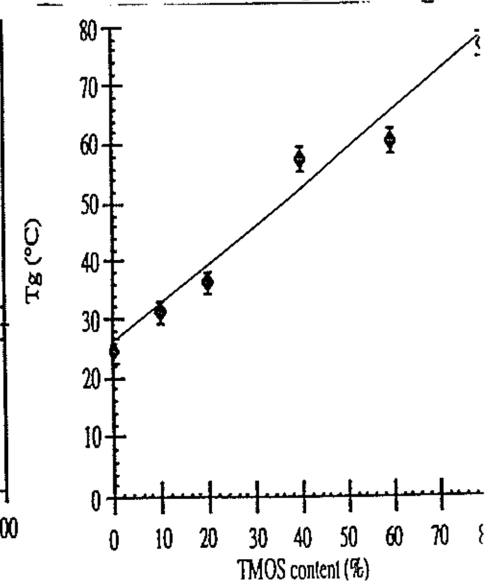
29Si MAS NMR



Mean degree of condensation

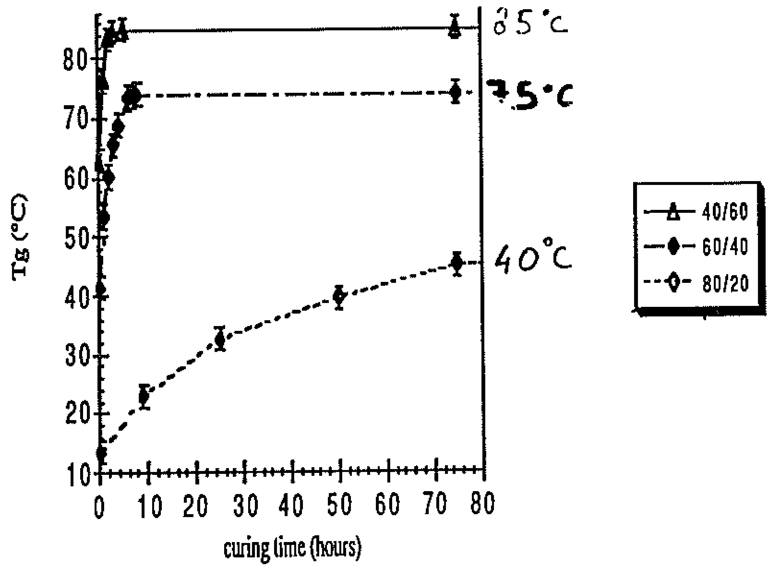


Glass transition temperature Tg



EFFECTS OF CURING

→ Glass Transition Temperature T_g increases upon thermal curing



→ THE TIME TO GET THE PLATEAU DECREASES WITH TMOS CONTENT

STRONG EFFECT OF THE ELECTRICAL FIELD POLING

→ THERMAL CURING UNDER ELECTRICAL FIELD POLING AFFECTS

THE MEAN DEGREE OF CONDENSATION
THE SEQUENCING: $(T\text{-}T)_m$----$(Q\text{-}Q)_n$

→ THE POLING EFFICIENCY DEPENDS ON :

AGEING TIME OF THE SOL
AGEING OF THE COATING BEFORE POLING
COATING THICKNESS

1-Siloxane based hybrids (Si-C bonding)

General exemples (alkoxysilanes + metal alkoxides)

Copolymers or nanocomposites ?

Specific exemples of hybrid materials:

NLO (grafted organic chromophores)

→ Emission (Rare-earth, Nd^{3+}, Dy^{3+} etc..)

Redox (V^{4+}---V^{5+}), Photochromic (W^{5+}--W^{6+})

Electronic and dielectric (polypyrolle-V^{4+}---V^{5+})

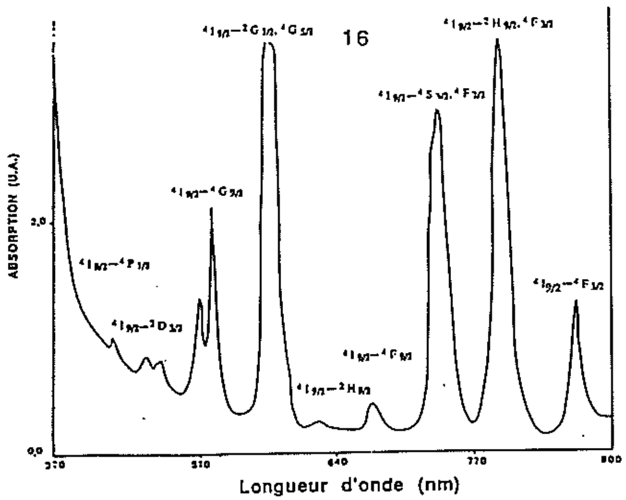
Classical xerogels →

Nd(III) doped Metal Oxide gels

SiO_2, TiO_2 or ZrO_2 based gels

Nd (III) Absorption spectrum

16



→ **Probe the Nd environment** Judd-Ofelt parameters (Ω_2)

$\Omega_2 = 3\text{-}5\ 10^{-20}$ high reactivity with the T.M.O. network

→ **Problems:**

No emission in the gel or xerogel state

$^4F_{3/2}$--------> $^4I_{9/2}$ very sensitive to
$^4F_{3/2}$--------> $^4I_{11/2}$ the presence of OH groups

Thin coatings only (thickness< 1µm)

TiO_2 GELS (M. Lecomte, B. Viana, C. Sanchez, J. Chim. Phys., 1991,88,39)

SYNTHESIS OF HYBRID ORGANIC-INORGANIC COATINGS CONTAINING LANTHANIDES

$H{-}Si(OEt)_2{-}CH_3$ ----H_2O-------> Siloxane Oligomers

refluxed solution containing →
Zr-O-Ln (oxo-alkoxides)

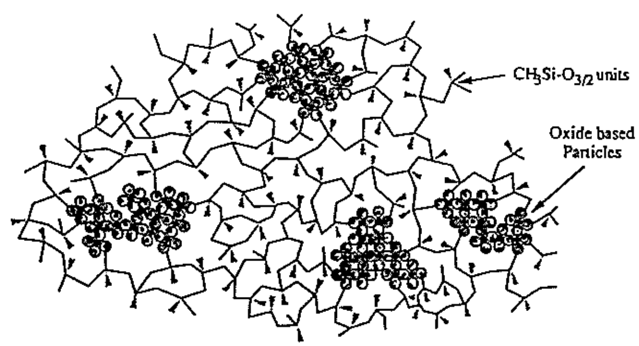
- - - H_2 ?

cleavage of Si-H

SOL

HYDROPHOBIC COATINGS

(FTIR, ^{29}Si MAS NMR, XANES-EXAFS)



NEODYMIUM DOPED HYBRID ORGANIC-INORGANIC COATINGS WITH LUMINESCENT PROPERTIES

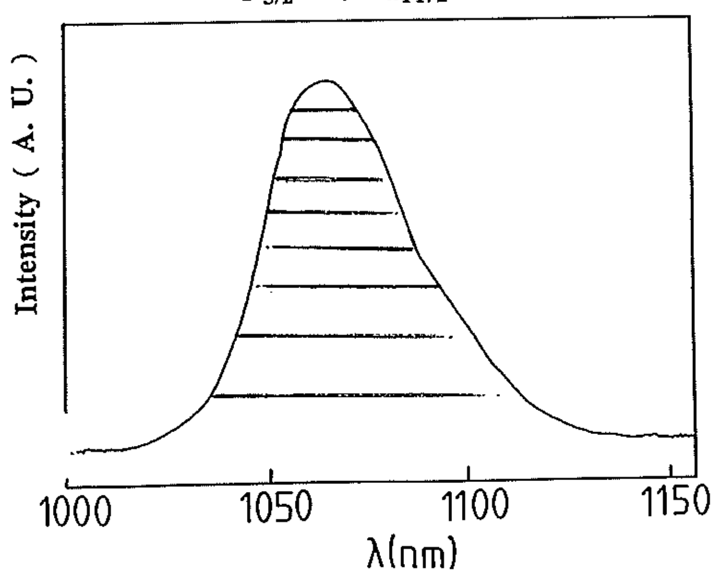
Hydrophibicity of siloxane polymers-------> solvent removal
mimimise OH (FTIR)

Zirconium oxo crosslinkers

- Zr-OH is more acid than Si-OH
- Zr accomodate the high coordinence required by the rare earth

Emission spectra of Nd 3+ inside hydrid coatings

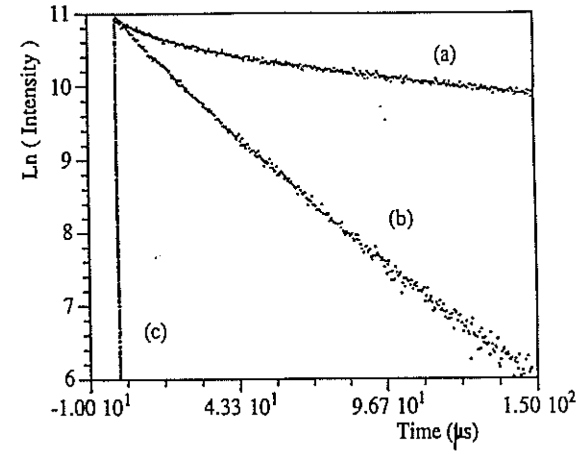
$^4F_{3/2}$ ---> $^4I_{11/2}$



Nd concentration from 4. 10^18 atm/cm3 to 4. 10^21 atm/cm3

LIFE TIME OF Nd EMISSION INSIDE HYBRID SILOXANE -OXIDE COATINGS

The initial parts of the decays are non exponential

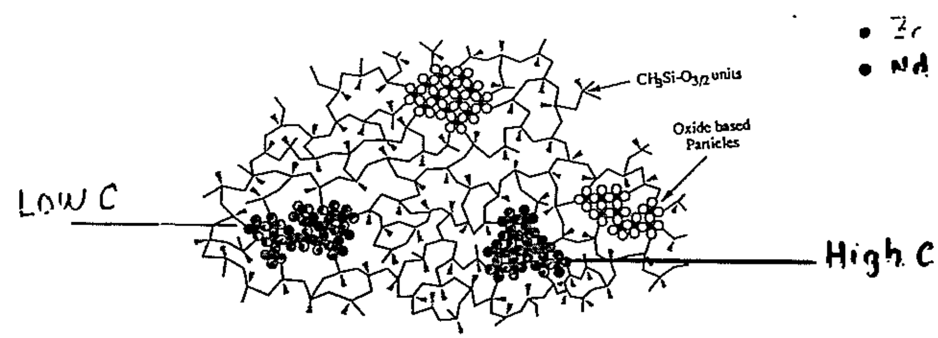


At low Nd^{3+} concentration (4.10^{18} atm/cm^3) τ=160µs

Emission is governed by Nd-Nd cross relaxation

At high Nd^{3+} concentration ($4.\ 10^{21}$ atm/cm^3) τ=200ns

Emission is governed by :
- by the presence of OH
- by Nd-Nd cross relaxation



HYBRID ORGANIC-INORGANIC COATINGS CONTAINING LANTHANIDES

EMISSION WAS RECORDED FOR MANY OTHERS RARE EARTH

Lanthanides : Ln (III): Ln = Nd, Sm, Gd, Dy, Er, Tm, Lu

Ln(III)	excitation (nm)	Strongest emission Red and NIR	Mean emission (nm)	$\tau(\mu s)$
Nd	798	$^4F_{3/2} \rightarrow {}^4I_{9/2}$	880	0.2-160
Sm	532	$^4G_{5/2} \rightarrow {}^6H_{7/2}$	610	27
Dy	355	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	577	14
Er	355	$^4S_{3/2} \rightarrow {}^4I_{13/2}$	580	13
Tm	785	$^4H_4 \rightarrow {}^3H_6$	800	150

References: N. Koslova, B. Viana, C. Sanchez J. Mater Chem 3,(3) 111, (1993)
B. Viana, N. Koslova, P. Aschehoug, C. Sanchez J Mater. Chem (in print)

1-Siloxane based hybrids (Si-C bonding)

General exemples (alkoxysilanes + metal alkoxides)

Copolymers or nanocomposites ?

Specific exemples of hybrid materials:

NLO (grafted organic chromophores)

Emission (Rare-earth, Nd^{3+}, Dy^{3+} etc..)

→ Redox (V^{4+}---V^{5+}), Photochromic (W^{5+}--W^{6+})

Electronic and dielectric (polypyrolle-V^{4+}---V^{5+})

MOLECULAR DESIGN OF SILOXANE-OXIDE HYBRID NETWORKS

(C. Sanchez, R. Alonso, F Ribot, ... JSST 1994) 2, (1,2,3), 161 (1994) 161

Hydrolysis and co-condensation of Alkoxysilanes and Metal Alkoxides with redox properties

chain former — Crosslinker and catalyst

$(OR)_2Si(CH_3)_2$ + $VO(OAmt)_3$

$(H_2O, pH=1)$ or $(H_2O, pH=7)$

SOL

RT DRYING

XEROGEL

Opalescent Green Coatings	Transparent coatings
FAST REDUCTION OF V^{5+} Acidic	SLOW REDUCTION OF V^{5+} neutral

Reduction of V^{5+} into V^{4+} by organics (ROH) and light

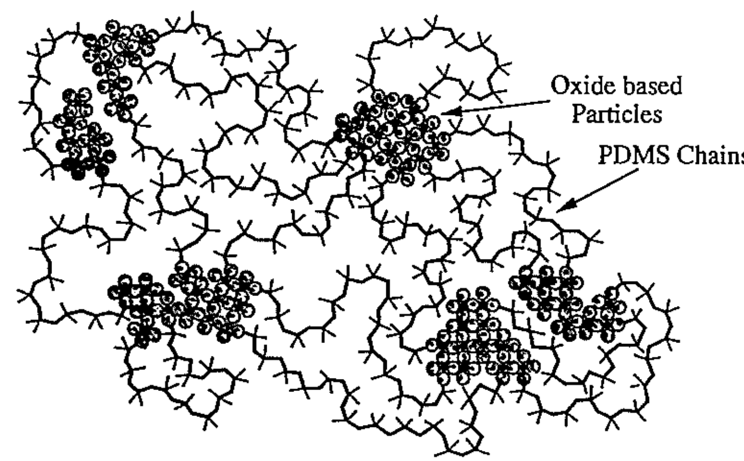
V^{4+} is not commonly found in a tetrahedral oxygen environment

REDOX BEHAVIOR OF SILOXANE-VANADIUM OXIDE HYBRIDS

$(OR)_2Si(CH_3)_2$ + $VO(OAmt)_3$ $(H_2O, pH=1)$

^{51}V NMR, ^{29}Si NMR	V-O-Si bonds are formed in the liquid state
^{51}V NMR	Vanadium in tertrahedral coordinence Vanadium in square pyramidal coordination
EPR	Clusters of V^{4+} in square pyramidal coordinence

- V-O-Si bonds are not stable in acidic media
- No efficient sequestering
- hydrophilic vanadium oxo-polymers (V-OH) tend to segr
- Vanadium can increase its coordinence
- Bad tuning of the hydrophilic/ hydrophobic balance



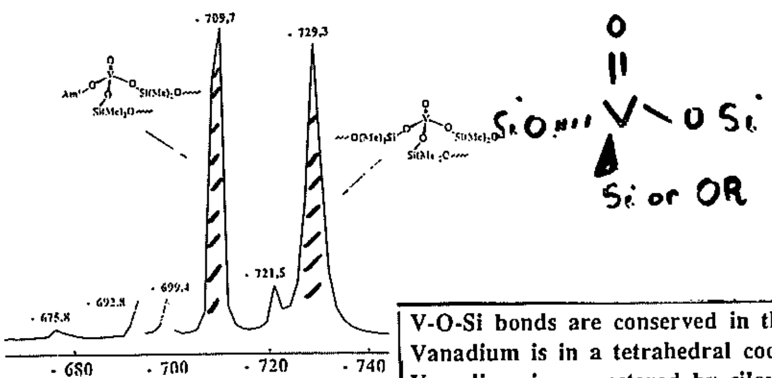
EASY REDUCTION OF V^{5+} — opalescent green coatings

REDOX BEHAVIOR OF SILOXANE-VANADIUM OXIDE HYBRIDS

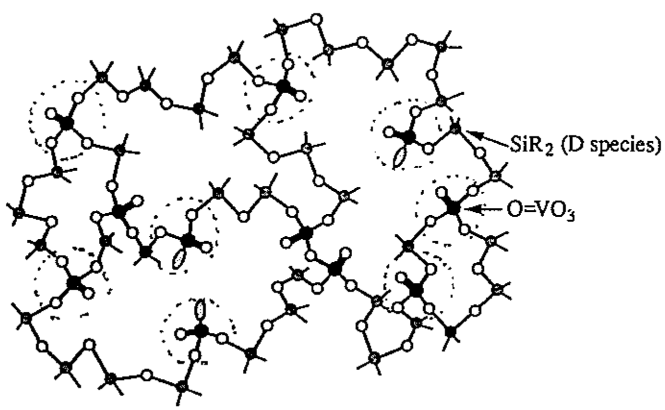
$(OR)_2Si(CH_3)_2$ + $VO(OAmt)_3$
(H_2O, pH= 7)

29Si NMR, 51V NMR   V-O-Si bonds are formed in the liquid state

51V NMR MAS Spectra of the xerogel



V-O-Si bonds are conserved in the gel
Vanadium is in a tetrahedral coordinence
Vanadium is sequestered by siloxane units
Well tuned hydrophilic/hydrophobic balance



DIFFICULT REDUCTION OF V^{5+} Transparent coatings

PHOTOCHROMIC HYBRID GELS

Me / RO-Si-OR / Me + H_2O (HCl)

↓

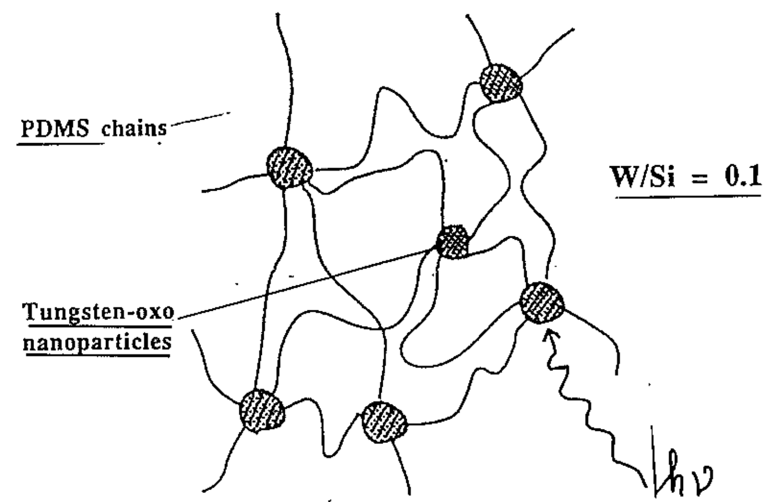
Siloxane oligomers

← $WO(OEt)_4$ + acac

SOL

FILM (30µm)

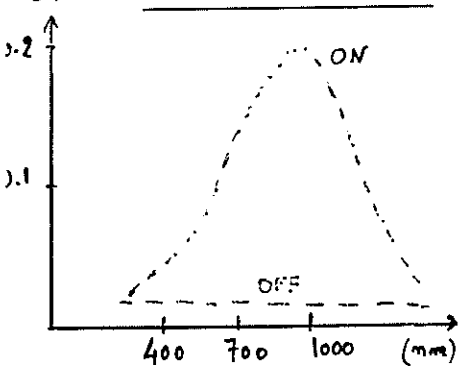
PDMS chains crosslinked with tungsten-oxo nanoparticles



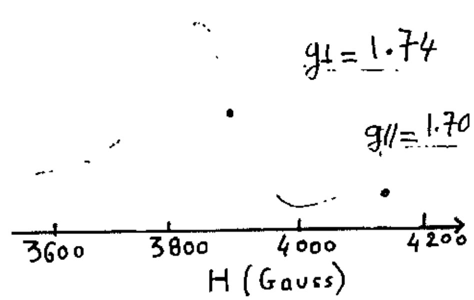
CHARACTERIZATION OF PHOTOCHROMIC HYBRID COATINGS

Upon UV exposure (λ = 365nm) coatings are blue in a few minutes

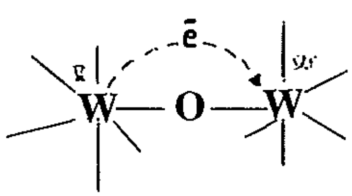
UV-VISIBLE Spectrum



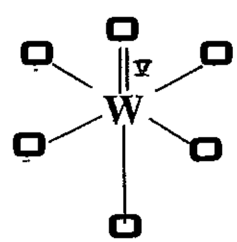
E.P.R. Spectrum (4K)



Intervalence Band Transfert
(λmax = 960nm)



W5+ in axial symetry



Complete bleaching (oxydation of W 5+) occurs in 2 hours

1-Siloxane based hybrids (Si-C bonding)

General exemples (alkoxysilanes + metal alkoxides)

Copolymers or nanocomposites ?

Specific exemples of hybrid materials:

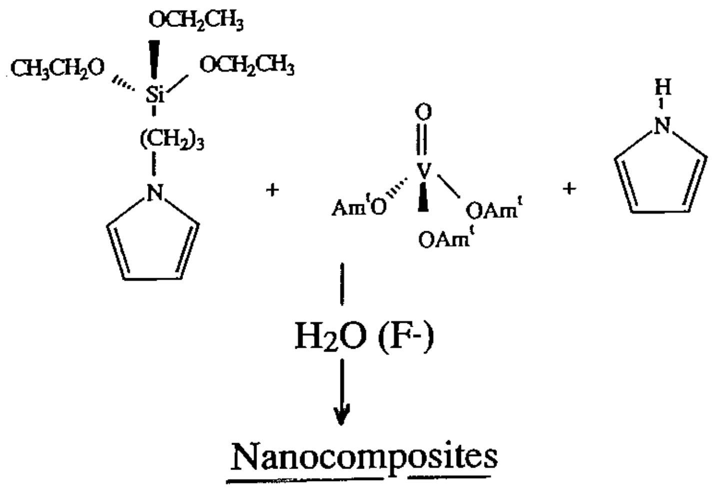
NLO (grafted organic chromophores)

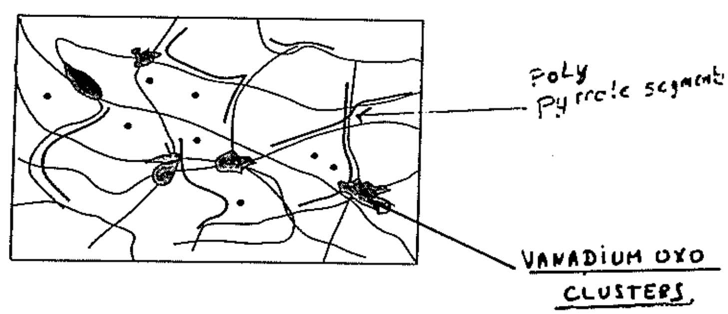
Emission (Rare-earth, Nd^{3+}, Dy^{3+} etc..)

Redox (V^{4+}---V^{5+}), Photochromic (W^{5+}--W^{6+})

→ Electronic and dielectric (polypyrolle-V^{4+}---V^{5+})

HYDRID MATERIALS WITH ELECTRONIC PROPERTIES





Conductivity = 10^{-2}-10^{-4} $\Omega^{-1}cm^{-1}$

$\varepsilon = 5 - 6$

(E. Potiron, J.C Badot, C. Sanchez)

2- Tin-oxo based hybrids (stable Sn-C bonds)

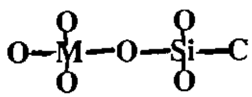
Tin-oxo-hydroxo clusters crosslinked via:

- dicarboxylic ligands (class III hybrids)
- Polybutenyl chains (class II hybrids)

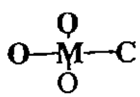
CLASS II HYBRIDS: ORGANIC-INORGANIC COMPONENTS ARE CHEMICALLY BONDED

→ 1- Silanes et <u>stananes</u>

2- Transition metals: bonding via silicium



3- Transition metals (M= Ti^{IV}, Zr^{IV}, Ce^{IV}, V^{V}, W^{VI}..)

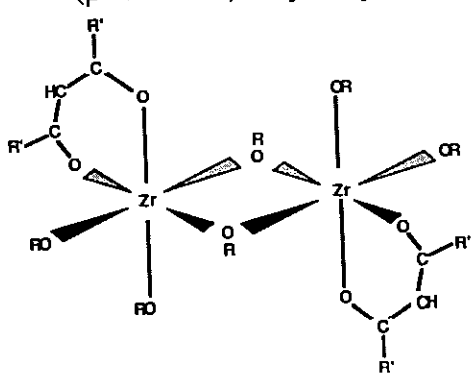


CHEMICAL MODIFICATION OF THE TRANSITION METAL ALKOXIDE

M - OR + H-OX ——> M - OX + ROH

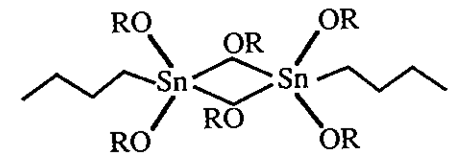
M-OX is a new molecular precursor

OX = Strong complexing ligands
(β-dicétones, α-hydroxy acids and derivatives)

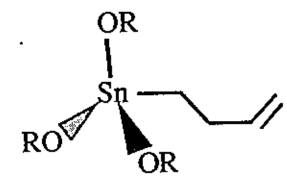


Heterofunctional Tin Alkoxides Precursors

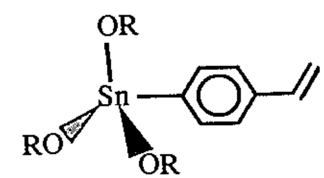
- $CH_3-(CH_2)_3-Sn(OPr^i)_3$: BSP



- $CH_3-(CH_2)_3-Sn(OAm^t)_3$: BSA
- $CH_2=CH-(CH_2)_2-Sn(OAm^t)_3$: BySA

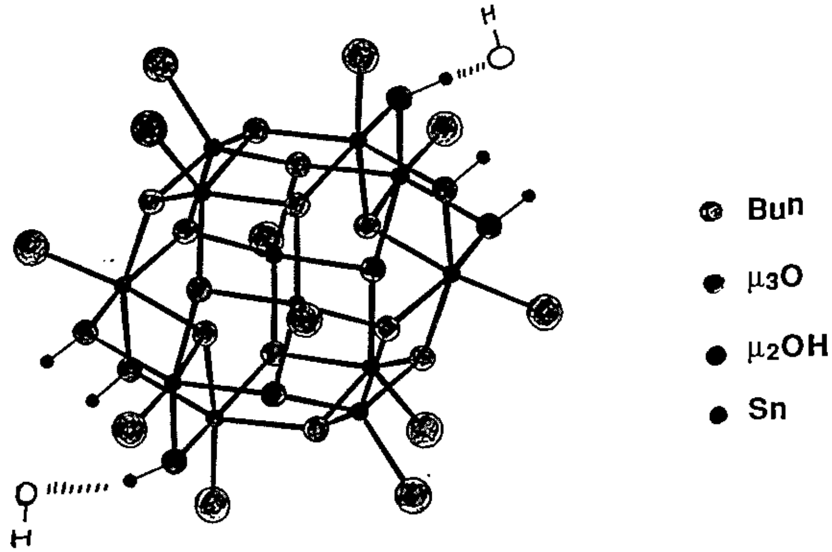


- $CH_2=CH-C_6H_4-Sn(OAm^t)_3$: SySA



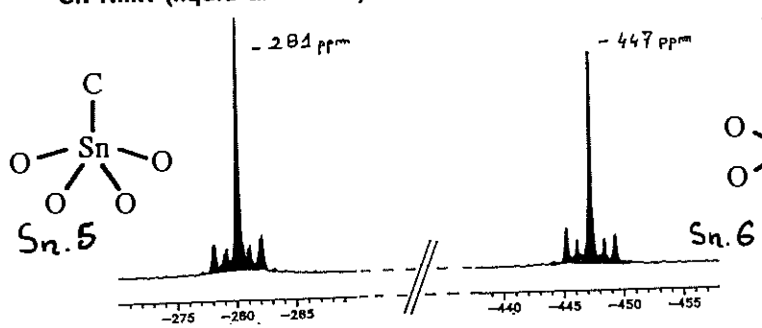
HYBRID NETWORKS FROM FUNCTIONALIZED TIN OXO NANO BUILDING BLOCK

Butyl-Sn(OR)$_3$ + 4 H_2O



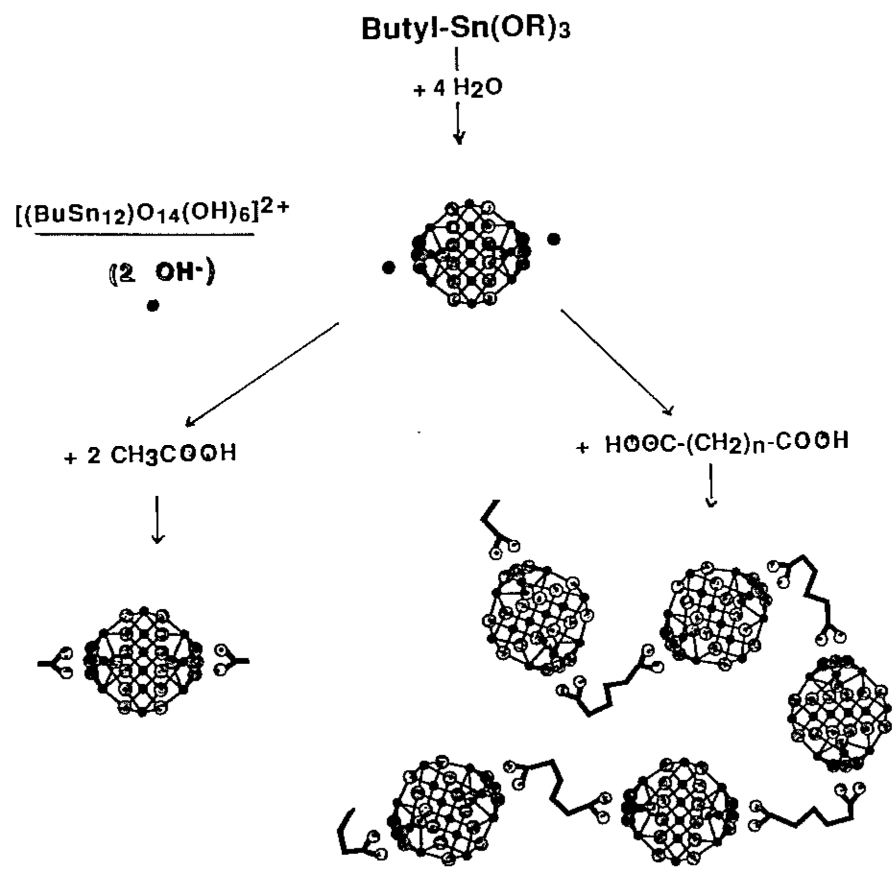
TIN OXO HYDROXO CORE = $[(BuSn_{12})O_{14}(OH)_6]^{2+}$, 2 OH^-

→ ^{119}Sn NMR (liquid and solid): The cluster structure is preserved



F.BANSE, F.RIBOT, C.SANCHEZ, MRS Proceedings, 271, 45, 1992.
F.BANSE, F.RIBOT, J.MAQUET, P.TOLEDANO, C.SANCHEZ, Inorg Chem.

SUPRAMOLECULAR HYBRID ASSEMBLIES FROM TIN OXO NANO BUILDING BLOCK



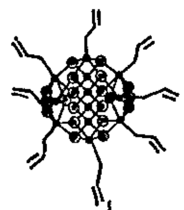
119 NMR (liquid and solid): The cluster structure is preserved
FTIR: ionic carboxylates

F. RIBOT, F . BANSE, F. DITER, C.SANCHEZ, New Journal of chemistry. 1995

HYBRID NETWORKS FROM FUNCTIONALIZED TIN OXO NANO BUILDING BLOCK

Butenyl-Sn(OR)$_3$ + 4 H_2O (butenyl = CH_2=CH-CH_2-CH_2-)

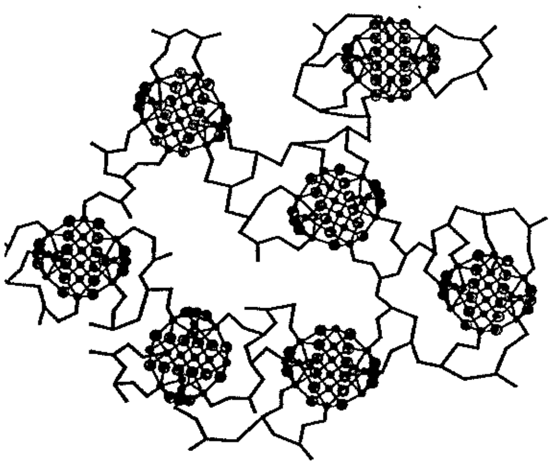
^{119}Sn NMR



Functionalized "Sn_{12}" CLUSTERS

AIBN 80°C

QELS: Φ_{hydro}= 80Å



"Sn_{12}" clusters crosslinked

by Polymeric Chains

^{119}Sn NMR (liquid and solid): The cluster structure is preserved

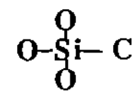
F.RIBOT, F.BANSE, C.SANCHEZ, MRS Proceedings, 346, 121, 1994

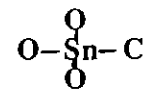
F.BANSE, F.RIBOT, C.SANCHEZ, M.LAHCINI, B.JOUSSEAUME, Advanced Materials

J. Sol. Gel Sci Techn. 1995

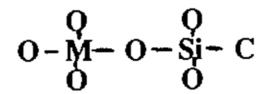
CLASS II HYBRIDS: ORGANIC-INORGANIC COMPONENTS ARE CHEMICALLY BONDED

1- Silanes et stananes

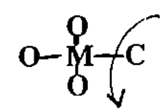




2- Transition metals: bonding via silicium



3- Transition metals (M= Ti^{IV}, Zr^{IV}, Ce^{IV}, V^{V}, W^{VI}..)

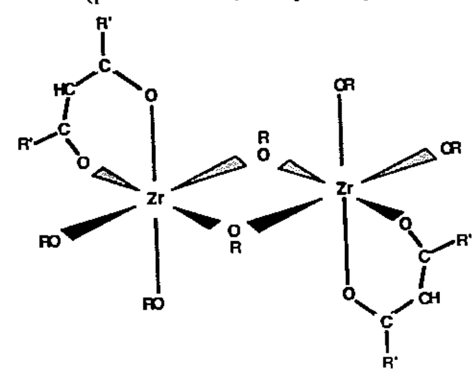


CHEMICAL MODIFICATION OF THE TRANSITION METAL ALKOXIDE

M - OR + H-OX ———> M - OX + ROH

M-OX is a new molecular precursor

OX = Strong complexing ligands
(β-dicétones, α-hydroxy acids and derivatives)



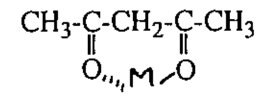
3- Transition metal oxide based organic-inorganic hybrids (class II)

→ - **Complexing ligands as particle size controllers**
(Complexing ligands as network modifiers)

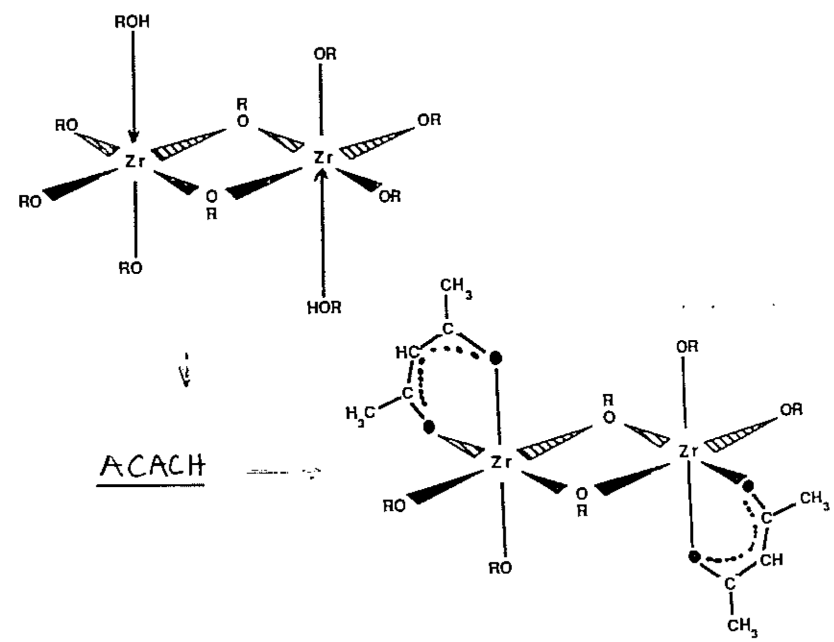
- **Copolymers zirconium oxo-PMMA**
(Organically polymerizable Complexing ligands as network formers)

Complexation of metal alkoxides with β- diketones or allied derivatives

β-diketones are chelating ligands often used to control the reactivity of metal alkoxide



M(OR)4 + AcaH------> M(OR)3Acac +ROH



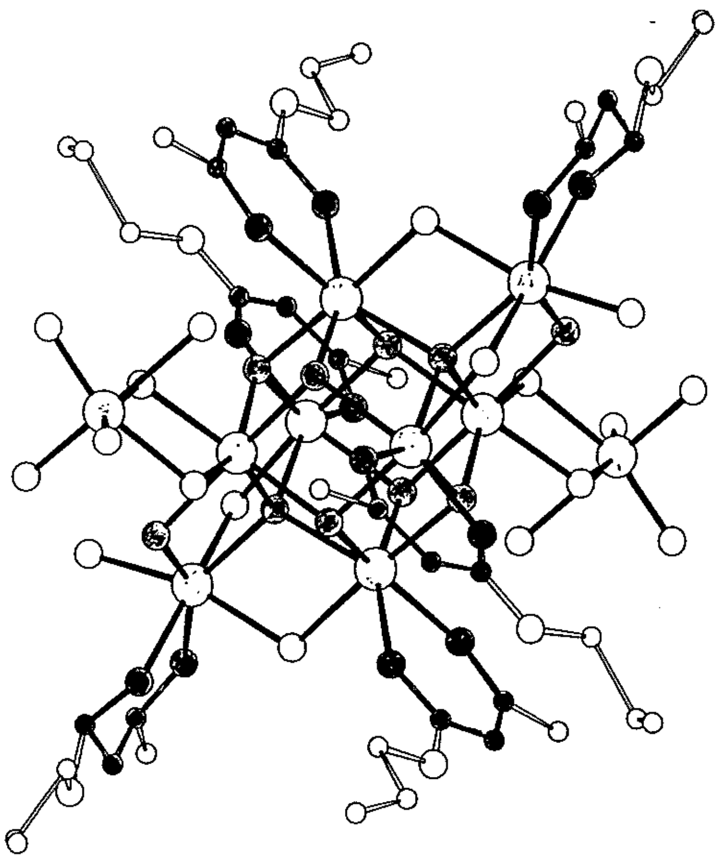
NMR, IR, XANES, EXAFS, X-Ray Diffraction

Ti (A. Leaustic, F. Babonneau , J.Livage, Chem Mat, 1,240,1989)
Ti (C.Sanchez , F. Babonneau, S.Doeuff, A. Leaustic, Mat.Res. Soc. Proc, 121,137, 1988)
Ce (F.Ribot, P.Toledano, C.Sanchez,Chem Mat, 1991)
Zr (M.In, P.Toledano, C.Sanchez,C. R. Acad SCi, Paris,1990)
Sn (D.C.Chandler,G.D.Fallon,A.J.Koplick, B.O.West , Aust. J. Chem.,40,1427,1987)

β-DIKETONES AND ALLIED DERIVATIVES AS COMPLEXING LIGANDS

Modification of the complexation ratio

[Allylacetoacetate(AA)/Zirconium] ratio= 0.6



$Zr_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OPr^n)_{10}(OPr^n)_{10})_4(AA)_6$

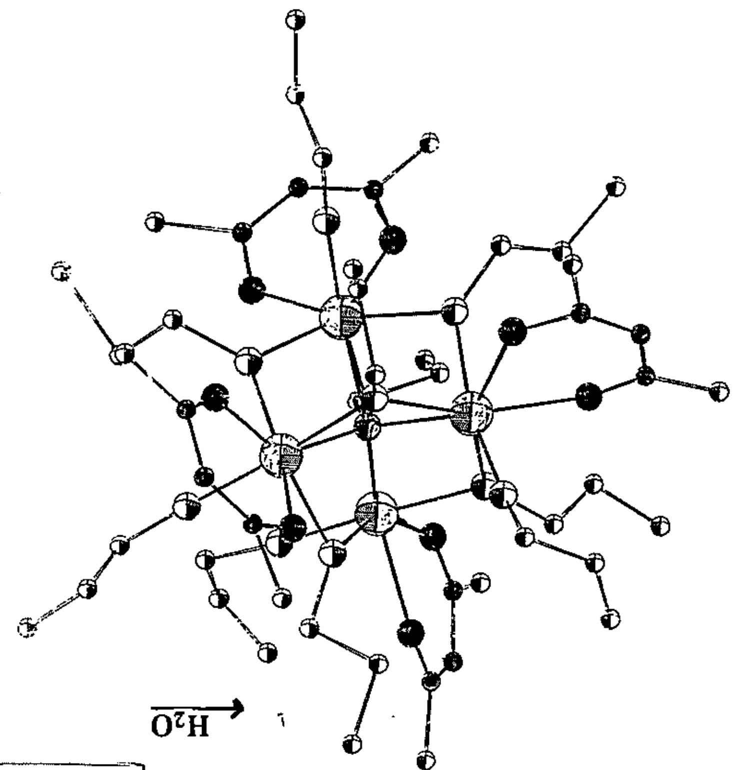
[illegible]

β-DIKETONES AND ALLIED DERIVATIVES AS COMPLEXING LIGANDS

$Zr(OPr^n)_4$ + acacH ------> $Zr(OPr^n)_3$ (acac) + $HOPr^n$

acac/Zr = 1

H_2O



$Zr_4O(OPr^n)_{10}(acac)_4$

acac/zr= 1

P.Toledano, M.In, C.Sanchez, (C.R.Acad.Sci. Paris, 311,1161,1990)

HYDROLYSIS OF β- DIKETONE MODIFIED TRANSITION METAL ALKOXIDES

$M(OR)_{4-x}(acac)_x$ M= Ti, Zr, Ce

↓ H_2O

Metal oxo-polymers

Size depends on the complexing ratio

X= Acac/ Metal

$M(OPr^i)_{4-x}(acac)_x$ Acac/M	QELS H. diameter in Å
0.15	450
0.25	170
0.50	30
0.75	15

F. Ribot, P.Toledano, C. Sanchez (Chem. Mat., 3, 759, 1991)
M. In, P.Toledano, C. Sanchez (C.R.Acad.Sci.Paris, 1991)

TRANSPARENT T.M.O GELS

→ **Hydrolysis of $M(OR)_4$ in presence of acac**

(M= Ti, Zr, Ce, Sn..)

Metal oxo particles surrounded by Acetylacetone

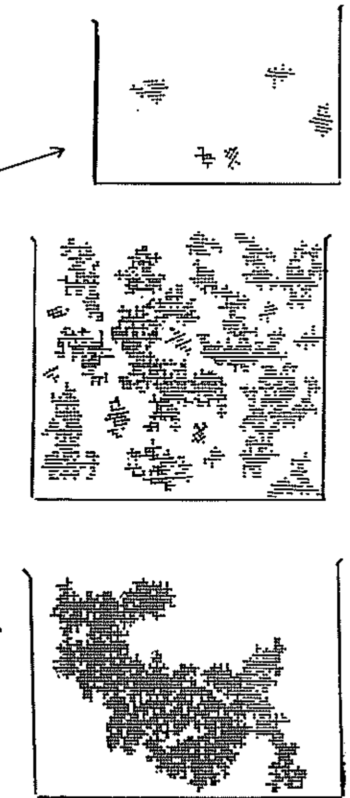
Acac inhibits surface sites

Acac/M is the key parameter

0.6 <Acac/Zr — CLUSTERS SOLS

0.2 <Acac/Zr< 0.6 — GELS

Acac/Zr< 0.2 — PRECIPITATES



(F.Ribot, P. Toledano, C. Sanchez, Chem. Mater.,2,759 1991)
(C.Sanchez, M. In, P. Toledano, P. Griesmar, Mat. Res. Soc. Proc., 271,669,1992)

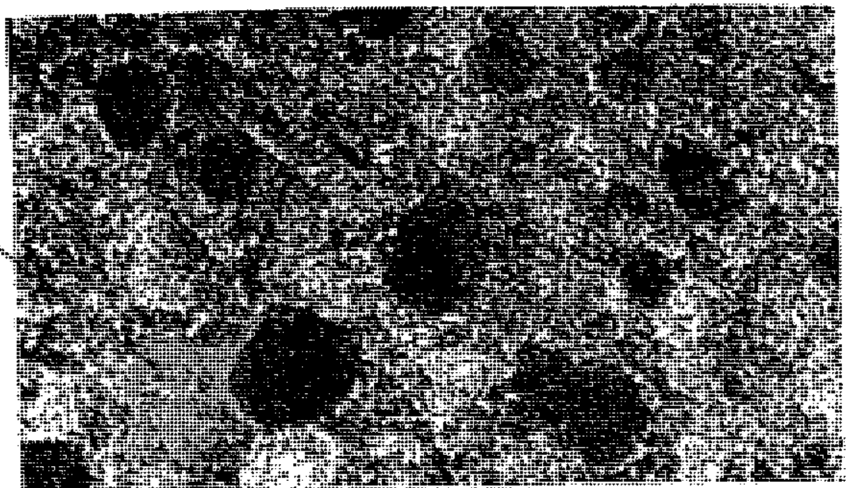
Stable sols containing ZrO_2 particles

→ $Zr(OPr^n)_4$ + x AcacH

$10\ H_2O\ (H^+)$

(T= 80°C)

- nanometric particles (3O-5OÅ)



Characterization by QELS, TEM, IR, DTA-GTA

nanometric particles of hexagonal ZrO2 surface caped by acac

1) (M. Chatry, M. In, M.Henry, C.Sanchez) patent N° 11623 (1991)
2) M. CHATRY et al J. Sol Gel Sci Techno. 1, 733, (1994).

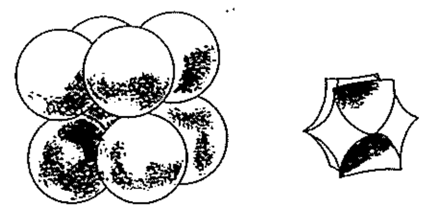
Nanoporous Zirconia Membranes

C. Guizard *et al.*, J. Sol-Gel Science and Technology, 2 (1994) 483

The preparation of nanoporous membranes requires

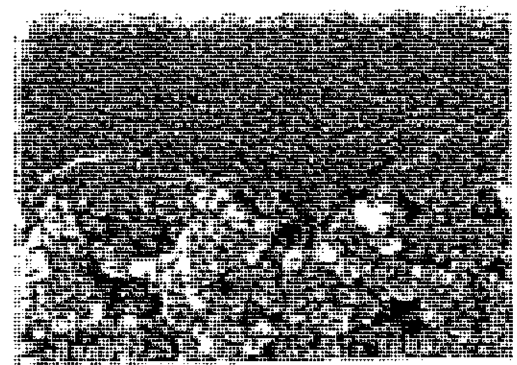
- particles smaller than 100 Å
- no aggregation in the sol state

particle size ⇔ pore size



pore size after heating at 600°C

x	0	1	2	3
d(Å)	84	72	68	32



3- Transition metal oxide based organic-inorganic hybrids (class II)

- Complexing ligands as particle size controllers
  (Complexing ligands as network modifiers)

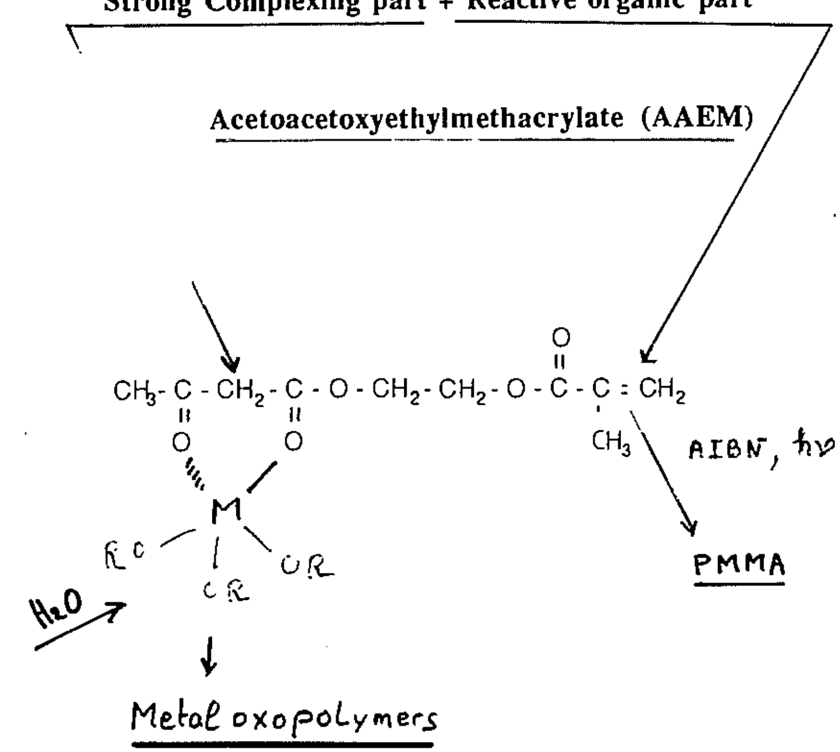
→ - Copolymers zirconium oxo-PMMA
  (Organically polymerizable Complexing ligands as network formers)

DESIGN OF LIGANDS FOR THE SYNTHESIS OF ORGANIC INORGANIC COPOLYMERS WITH TRANSITION METAL ALKOXIDES

Hybrid ligands

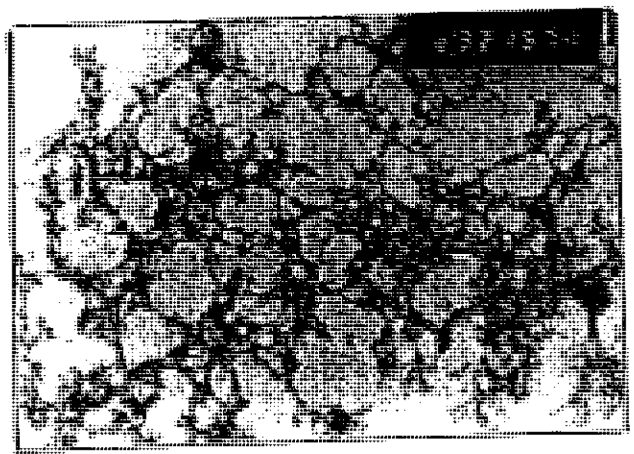
Strong Complexing part + Reactive organic part

Acetoacetoxyethylmethacrylate (AAEM)



HYBRID ORGANIC-INORGANIC COPOLYMERS
ZIRCONIUM-OXO- Poly AAEM

INFRARED	PAAEM bonded to Zr; Zr-O-Zr network
^{13}C CP MAS NMR	AAEM polymerization, PAAEM bonded to Zr
Light Scattering	Size of inorganic network depends on x=AAEM/ Zr Inorganic and organic growths are interdependent
DTA-GTA	% ZrO2/ PAAEM depends on x=AAEM/ Zr ratio (between 60% and 40% for x= 0.25to 0.75)
XANES	Zr is likely sevenfold coordinated
EXAFS	Zr-O (1.9Å, 2.1Å, 2.2Å) and Zr-Zr (3.53Å)distan
SAXS	Slope Ln (Scattered intensity) versus Ln (Q) =2.7 (bushy scatterers)
TEM	Bushy polymers

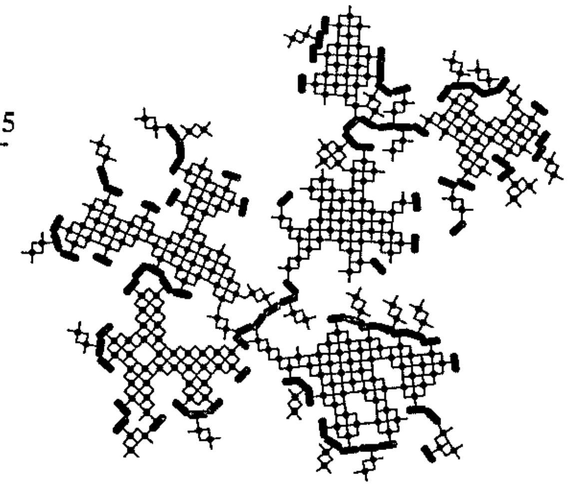


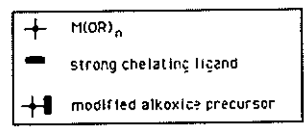
(C. Sanchez, M. In, JNCS, 1992)
147.141 0 1 (1992)

HYBRID ORGANIC INORGANIC COPOLYMERS
Zirconium-oxo-PAAEM Nanocomposites

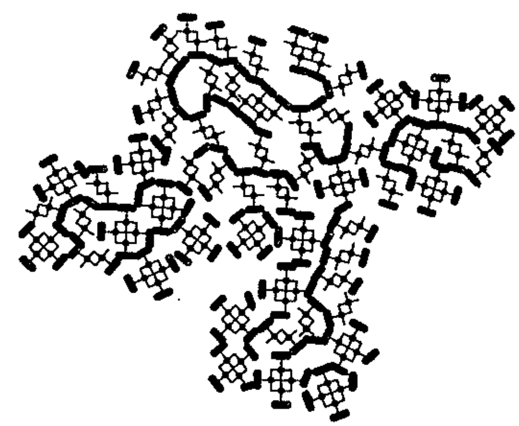
CARTOON

AAEM/ Zr= 0.25





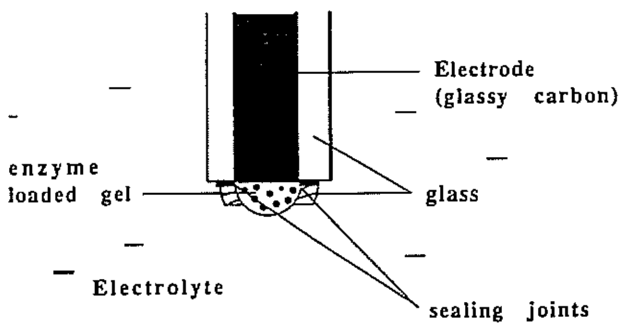
AAEM/Zr= 0.75



ENCAPSULATION OF THE GLUCOZE OXYDAZE IN SILICA GELS

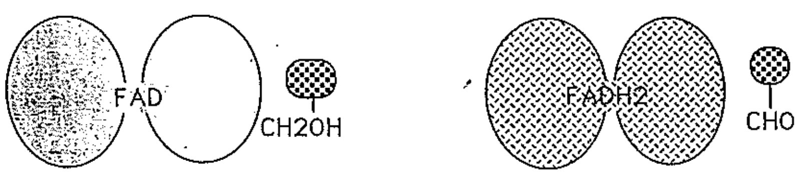
(P. Audebert, C. Demaille, C. Sanchez , Chem Mat, 1993) 5, 911
(P Audebert, C. Sanchez, J. Sol-Gel Sci Techno, 1994, 2 (1,2,3) p 809

Glucoze (GluCH2OH) —(GOD)→ Gluconolactone (GluCHO)
Oxygen ---> H_2O_2



Electrochemical detection: redox site of GOD = Flavine (FAD)

FAD + GluOH --> (FAD-GluOH)*---> FADH2+ GluCOH



FAD + 2 Ferrocens + 2 H+ <-----FADH2 + 2 ferrocinium

CONCLUSION

APPLIED INTEREST:

SYNTHESIS CONDITIONS: ---→
- Room temperature
- Métallo-organic precursors
- Organic solvents

The compatibility between organic and inorganic chemistrys opens a land of opportunities for the processing of new multifunctional materials

MATERIALS LOCATED AT A MULTIPLE INTERFACE

(Optical, electrical, sensors, membranes, catalysis, etc..)

FUNDAMENTAL INTEREST:

→ Understand the chemistry and growth of these systems
Organisation (weak and strong bonds and intercations)
Bypass or control the degree of phase separation(nanocomposites)

- Mechanical properties
- Transparency
- Hydrophilic/hydrophobic balance
- Porosity
- Stability and Photostability?

ACKNOWLEDGEMENTS

Permanent Researchers

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PHD students

Sol-gel chemistry of metal alkoxides and hybrids

Martin In
Frédéric Banse
Juliette Blanchard
Nathalie Steunou
Bruno Alonso

Optical properties of hybrids

Bénédicte Lebeau
Céline Guermeur
Pascal Griesmar

Collaborations and discussions

B. Viana, J. Maquet (URA 1466)
P. Toledano, F. Babonneau (URA 1466)

E . Toussaere and J. Zyss (CNET)
M. Lahcini and B. Jousseaume(U. Bordeaux)
P. Audebert (U. Besançon)

CNRS, MRT, Rhône-Poulenc, and DRET for their interest in this research and for their financial support

OPTICAL APPLICATIONS OF ORGANIC/INORGANIC HYBRID MATERIALS

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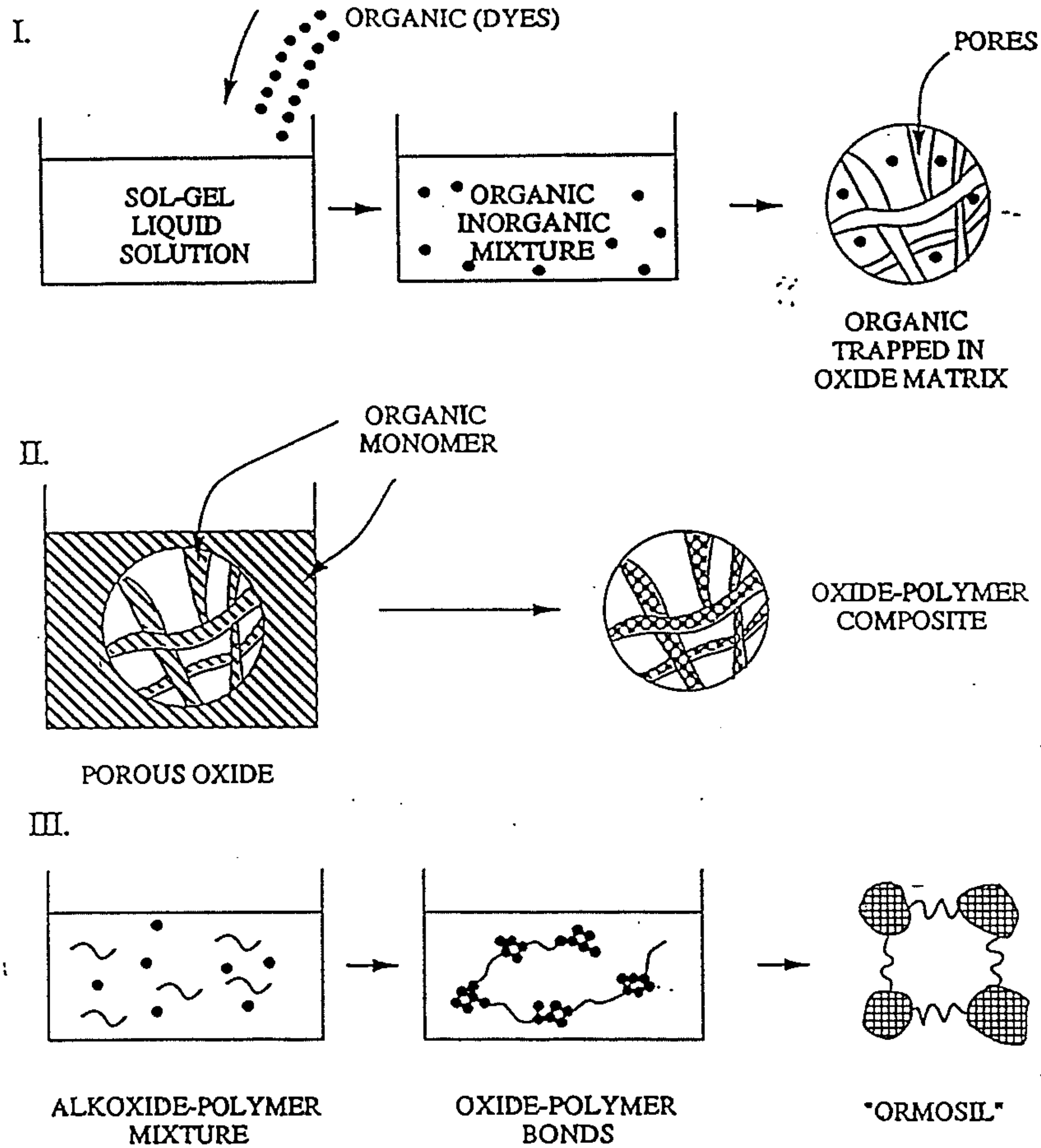
Co-Workers
T. Allik, J. Altman, K.E. Chung, B.C. Dave, L. Ellerby, T. Faltens,
P. Fuqua, A. Hutchinson, E. Knobbe, E. Lan, J. McKiernan, J. Miller,
F. Nishida, R. Toda, S. Yamanaka

OUTLINE

- Materials Synthesis
- Sol-Gel Dye Lasers
- Luminescent Probes of Sol-Gel Chemistry
- Biomolecules as Dopants in Sol-Gel Matrices


I.
ORGANIC (DYES)
PORES
SOL-GEL
LIQUID
SOLUTION
ORGANIC
INORGANIC
MIXTURE
ORGANIC
TRAPPED IN
OXIDE MATRIX
II.
ORGANIC
MONOMER
OXIDE-POLYMER
COMPOSITE
POROUS OXIDE
III.
ALKOXIDE-POLYMER
MIXTURE
OXIDE-POLYMER
BONDS
"ORMOSIL"

ORGANIC DOPED SOL-GEL MATRICES

AS SOLID-STATE OPTICAL MATERIALS

- Numerous organics possess interesting optical properties
  - optical gain and laser action
  - photochromism
  - nonlinear optical effects

- Organic polymers lack the necessary thermal and mechanical properties, photostability, chemical stability, optical uniformity

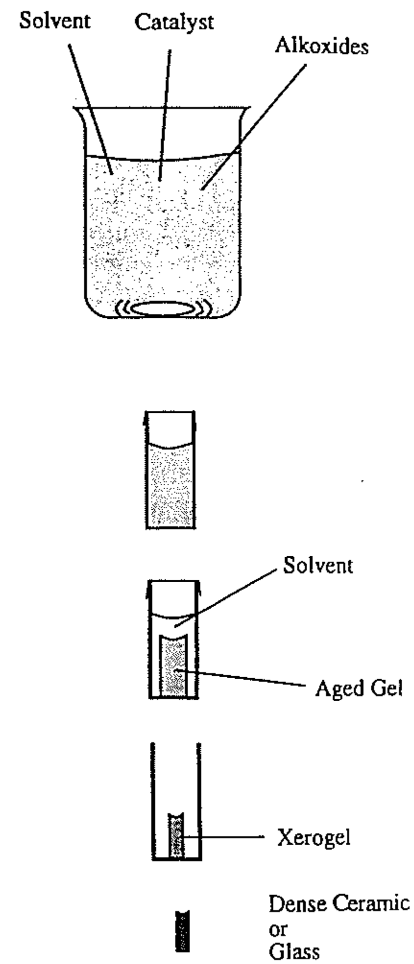
- Inorganic glasses offer superior properties; the organics cannot withstand the thermal conditions of conventional glasses

- Sol-gel techniques are room temperature methods for synthesizing amorphous materials which are essentially inorganic

- Sol-gel approaches for ORMOSILS (organically modified silicates) produce molecular level composites

Stages of the Sol-Gel Process

1. Sol Formation
2. Gelation
3. Aging
4. Drying
5. Firing



OPTICAL MATERIALS BASED ON ORGANIC-DOPED SOL-GEL GLASSES

• Tunable lasers	rhodamines, pyrromethenes
• Nonlinear optics (optical limiting)	phthalocyanines
• Photochromics	spiropyrans
• Chemiluminescence	luminol
• Phosphorescence	4-biphenyl carboxylic acid

The development of non-porous materials is generally important for applications

Oxide Polymer Network Formation

1) Hydrolysis:

$$\equiv MOR + H_2O \Leftrightarrow \equiv MOH + ROH$$

2) Condensation:

$$\equiv MOH + \equiv MOH \Leftrightarrow \equiv M\,O\,M\equiv + H_2O$$

$$\equiv MOH + \equiv MOR \Leftrightarrow \equiv M\,O\,M\equiv + ROH$$

3) Drying:

Solvent-filled Gel $\Leftrightarrow$ Desiccated Xerogel

(4) (Densification:)

Xerogel $\Leftrightarrow$ Dense Glass

ORMOSILS (Organically Modified Silicates)

- Molecular level composites of silica and polymer

- Attractive features for optical applications
  1. Processing techniques of sol-gel method maintained
  2. Optical transparency in the visible region; low loss
  3. Thermal and UV stability expected to be intermediate to that of silica and polymer
  4. Mechanical properties enhanced compared to silica xerogel; polishable
  5. Wide range of systems available; compositions can be tailored to dyes and applications

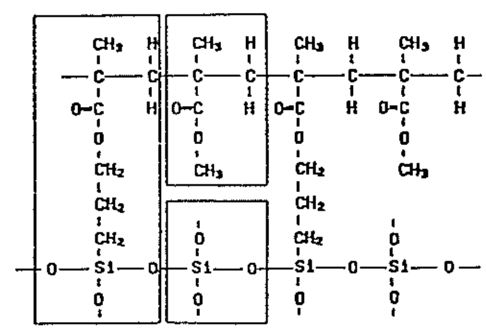
ORMOSIL MATRIX FOR DYE-DOPED SOLID STATE LASERS

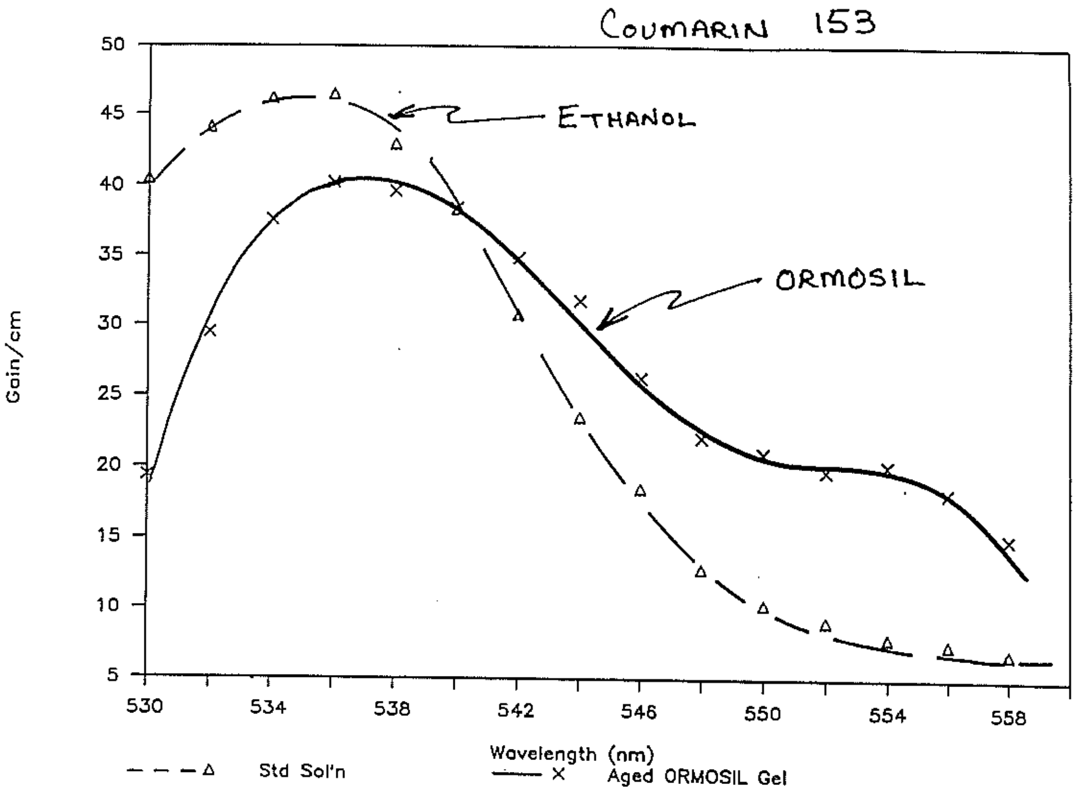
- TMOS -- $Si(OCH_3)_4$
- TMSPM -- $Si(OCH_3)_3(CH_2)_3OCOCCH_2CH_3$
- MMA -- $CH_2CCH_3COOCH_3$

- TMSPM ties onto Si — O backbone and MMA attaches to it

- Dense molecular level composite

  Pore - free
  Excellent laser damage threshold
  Polishable





Properties of ORMOSIL

OPTICAL:

- low absorption;
- [illegible]
- [illegible] figure;
- [illegible]

THERMAL:

- [illegible]
- [illegible]

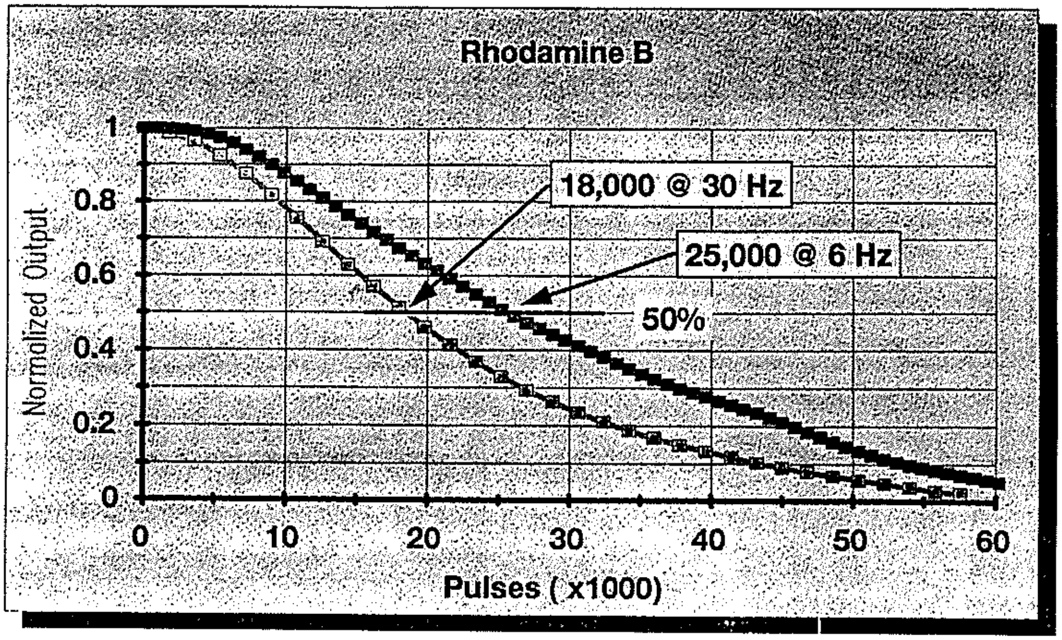
MECHANICAL:

- good physical strength;
- [illegible]
- [illegible]

CHEMICAL:

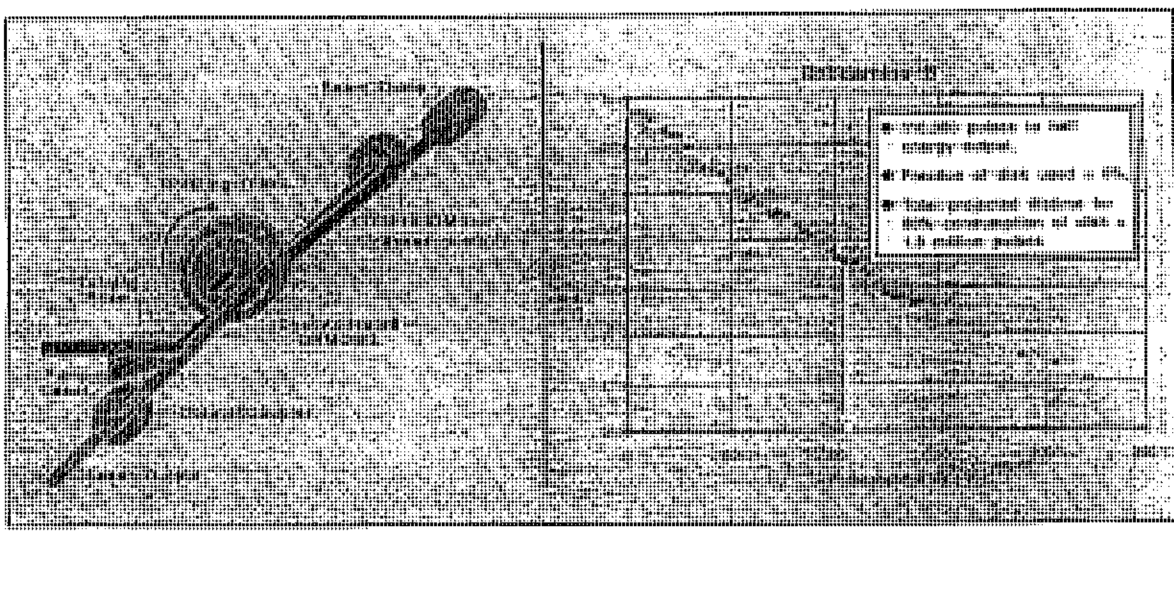
- [illegible] solvents;
- [illegible]

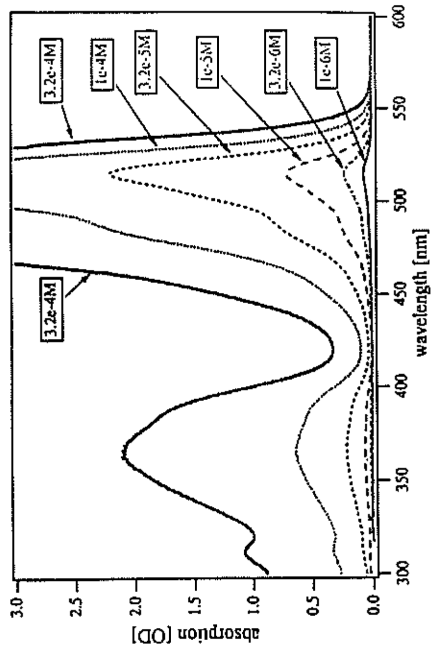
Slab Laser Lifetimes

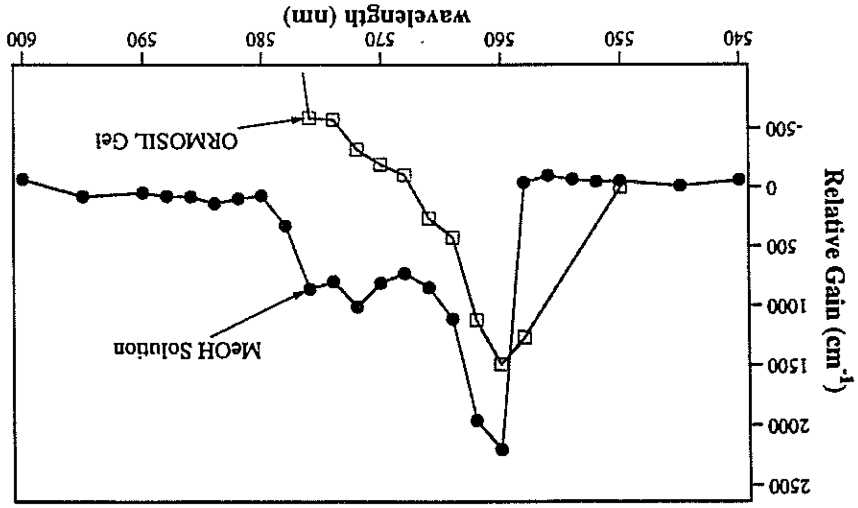


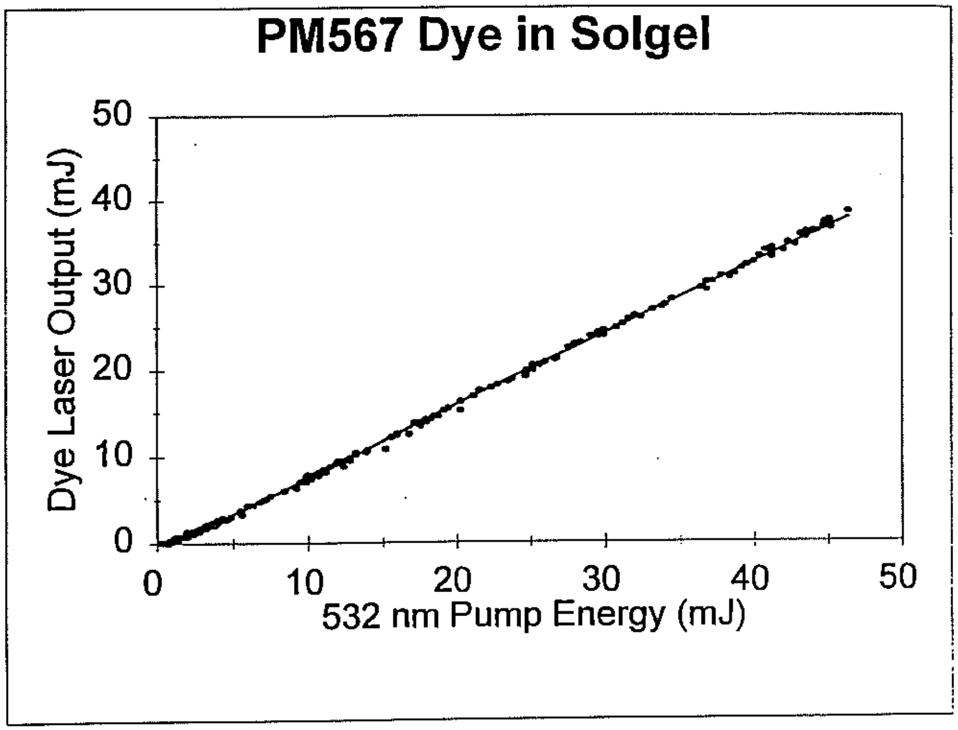
Long Life Laser Employing a Rotating Disk

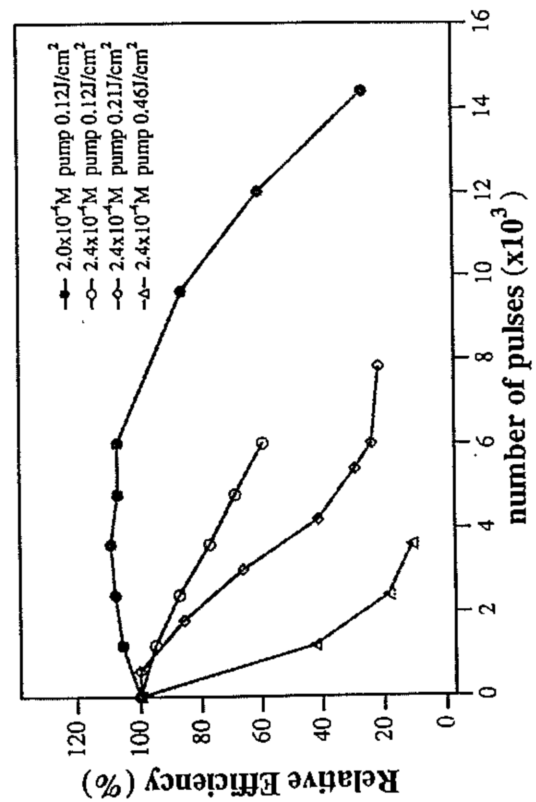
- Rotating disk design permits larger volume of dye to be consumed in the laser cavity thereby increasing the effective lifetime,
- Disks could be quickly swapped permitting easy replacement of gain elements and rapid dye changes.

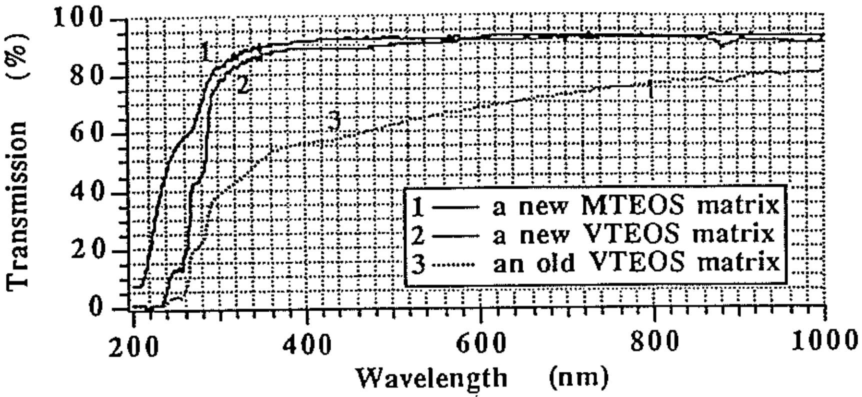



absorption [OD]
wavelength [nm]
3.2e-4M
1e-4M
3.2e-5M
1e-5M
3.2e-6M
1e-6M
3.2e-4M


Relative Gain (cm-1)
wavelength (nm)
MeOH Solution
ORMOSIL Gel


PM567 Dye in Solgel
Dye Laser Output (mJ)
532 nm Pump Energy (mJ)

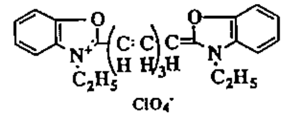

2.0x10⁻⁴M pump 0.12J/cm²
2.4x10⁻⁴M pump 0.12J/cm²
2.4x10⁻⁴M pump 0.21J/cm²
2.4x10⁻⁴M pump 0.46J/cm²
number of pulses (x10³)
Relative Efficiency (%)



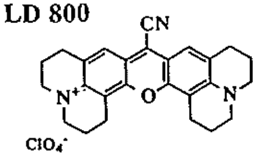
- New matrices have smaller pores
- Lifetimes (50% of initial output)
  - 59,000 shots for Py 567
  - 80,000 shots for Perylene Red
  - pump fluence of 140 mJ/cm² at 1 Hz.
- 63% slope efficiency for Py 597

* M. Canva et. al., SPIE Symposium on Sol-Gel Optics San Diego, July, 1994.

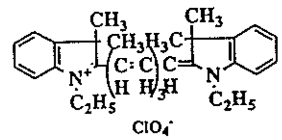
DOTC



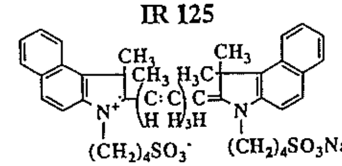
LD 800



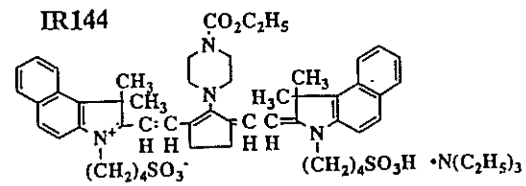
HITC

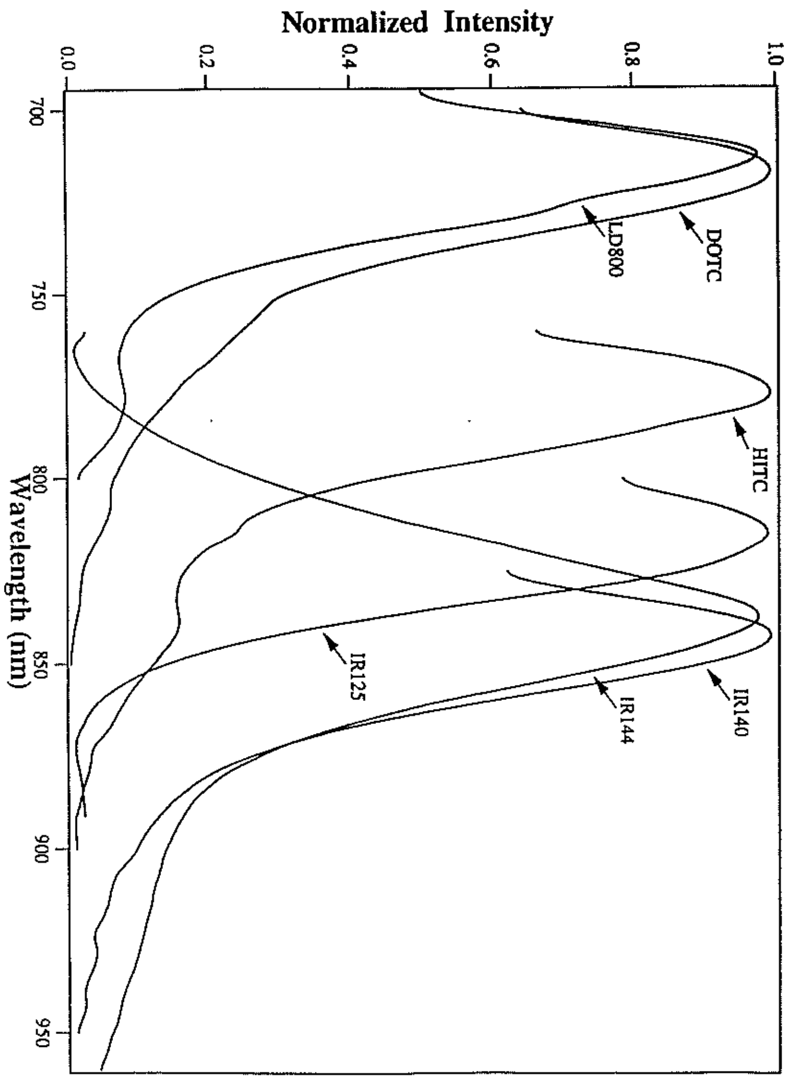


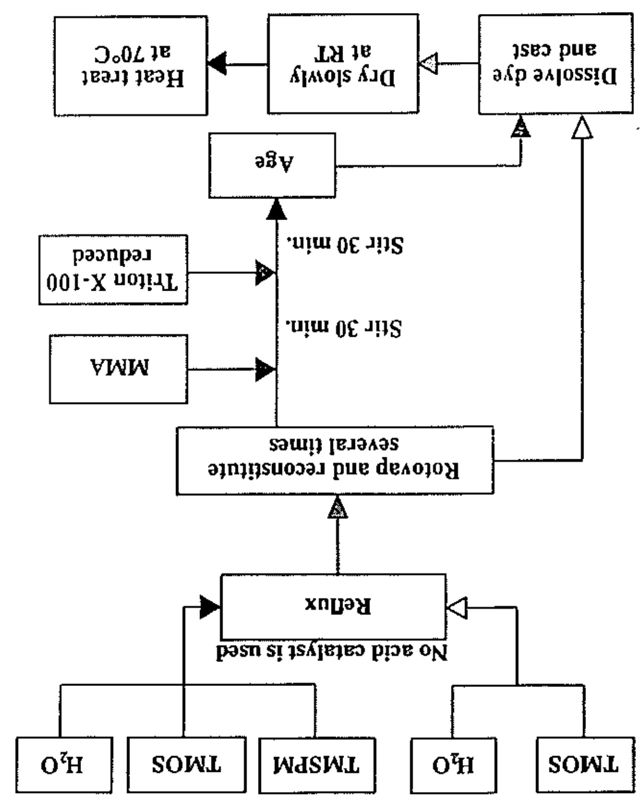
IR 125

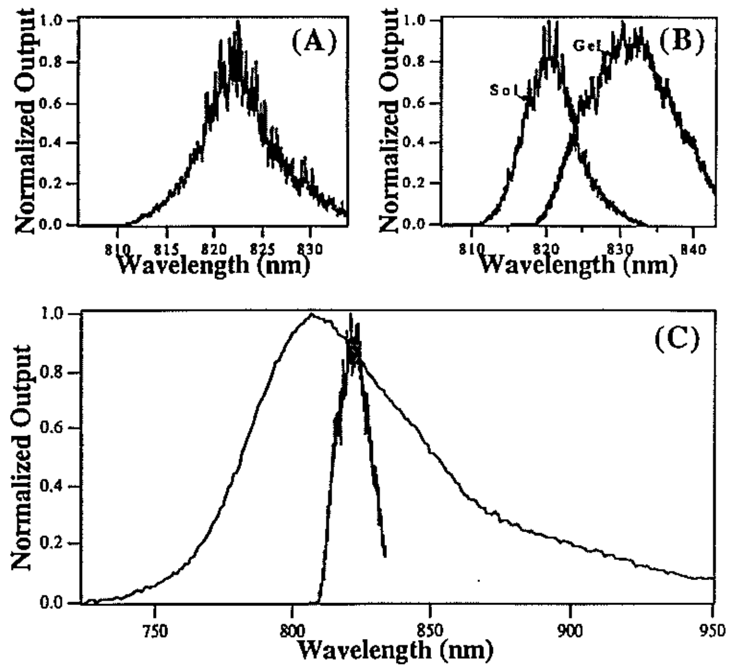


IR144




Normalized Intensity
0.0
0.2
0.4
0.6
0.8
1.0
700
750
800
850
900
950
Wavelength (nm)
DOTC
LD800
HITC
IR125
IR144
IR140


TMOS
H_2O
TMSPM
TMOS
H_2O
No acid catalyst is used
Reflux
Rotovap and reconstitute several times
MMA
Stir 30 min.
Triton X-100 reduced
Stir 30 min.
Age
Dissolve dye and cast
Dry slowly at RT
Heat treat at 70°C



SUMMARY

1. The sol-gel process has been used to encapsulate a variety of laser dyes in different sol-gel matrices

2. The dyes exhibit their characteristic luminescence, optical gain and laser behavior in the solid state matrix

3. The ability to tailor the synthesis conditions enables the chemical environment to be compatible with dopants; even 'delicate' dyes can be incorporated. Sol-gel lasers extended into the near IR.

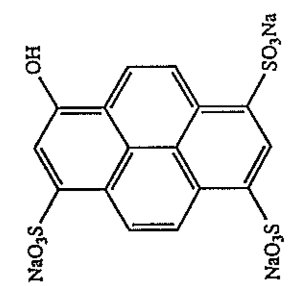
4. Pyrromethene (567) in ORMOSIL exhibits extremely high slope efficiency and output energy for sol-gel lasers. Photostability/laser longevity is still a major concern; need to achieve better process control and to customize the matrix.

ORGANIC DOPED SOL-GEL MATRICES -

OPTICAL PROBES OF THE SOL-GEL PROCESS

- Solution chemistry serves as a reference to interpret spectroscopic response
- Information obtained on local chemical and structural changes during sol-gel process
- Examples:
  1) Water/alcohol variations during gelation, aging, drying
  2) Water consumption/generation to map hydrolysis/condensation reactions
  3) Local pH changes during processing
  4) Local polarity changes during processing
  5) Rigidochromic effect to determine local rigidity
  6) Fluorescence depolarization to measure local viscosity

Pyranine (trisodiumtrisulfonatehydroxypyrene)

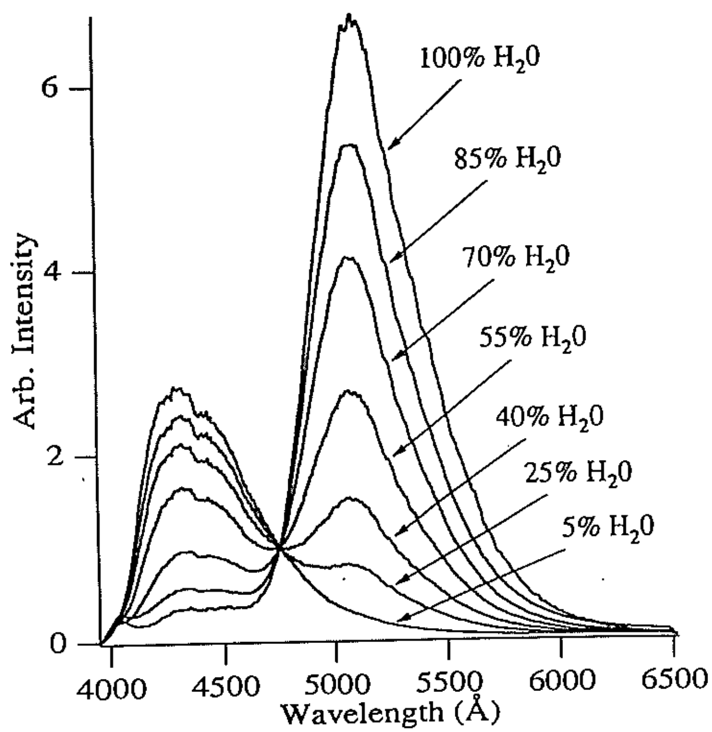


Emission depend on protonation/deprotonation

Deprotonated in water ⇒ Green emission (515 nm)

Protonated in alcohol ⇒ Blue emission (430 nm)

PYRANINE EMISSION IN WATER/ETHANOL SOLUTIONS



IN-SITU FLUORESCENCE IMAGING OF SOL-GEL THIN FILM DEPOSITION

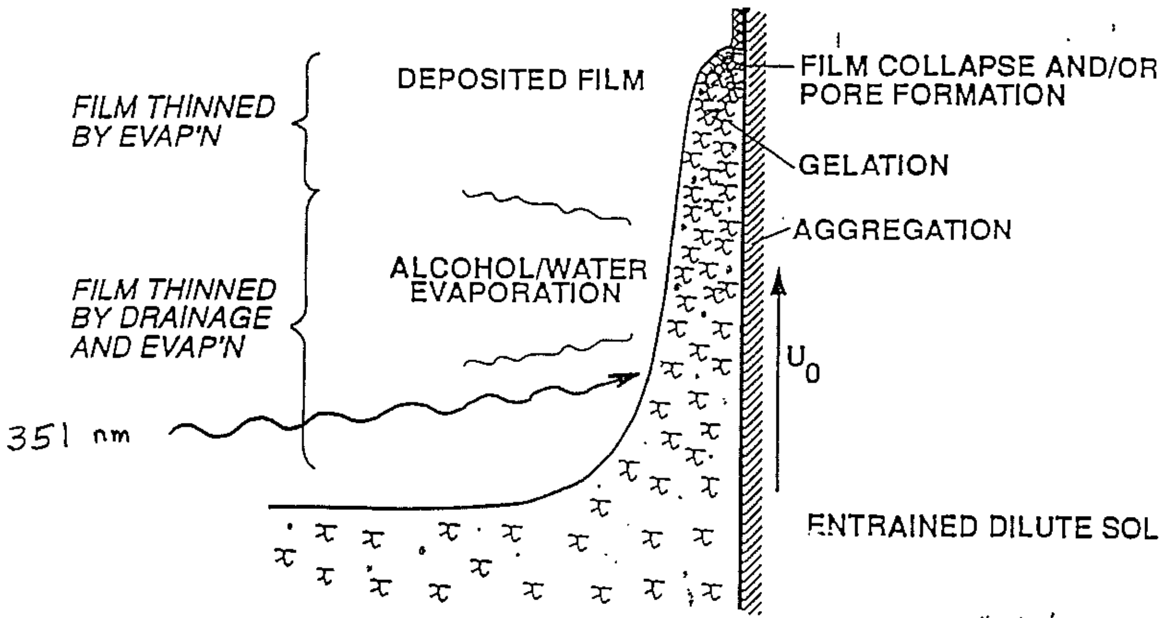
F. Nishida*, J.M. McKiernan§, B. Dunn*, J.I. Zink§, C.J. Brinker† and A.J. Hurd†

* Department of Materials Science and Engineering, UCLA, Los Angeles, CA
§ Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA
† Sandia National Laboratories, Albuquerque, NM

Can optical probe techniques be applied to thin films?

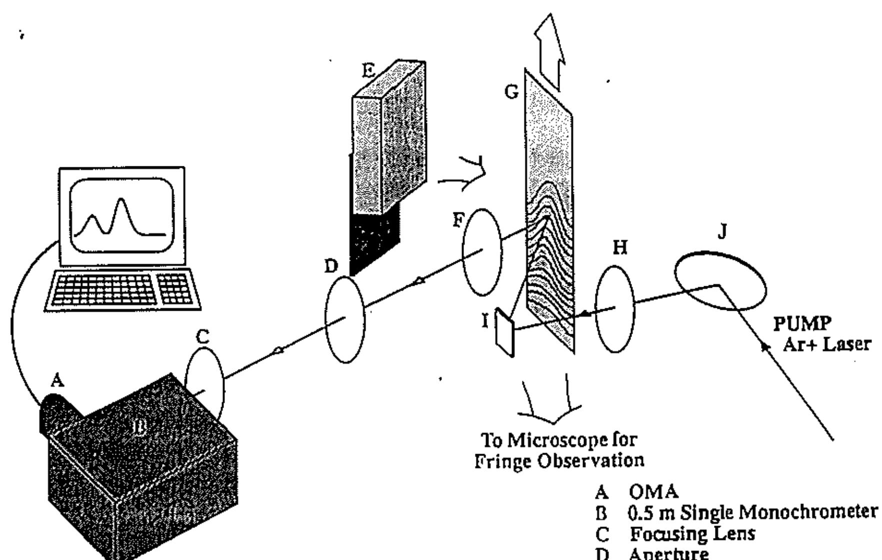
Potential Advantages:

- In-situ monitoring of chemical/structural changes
- Better control of film properties and microstructure
- Real time observations amenable to automated control

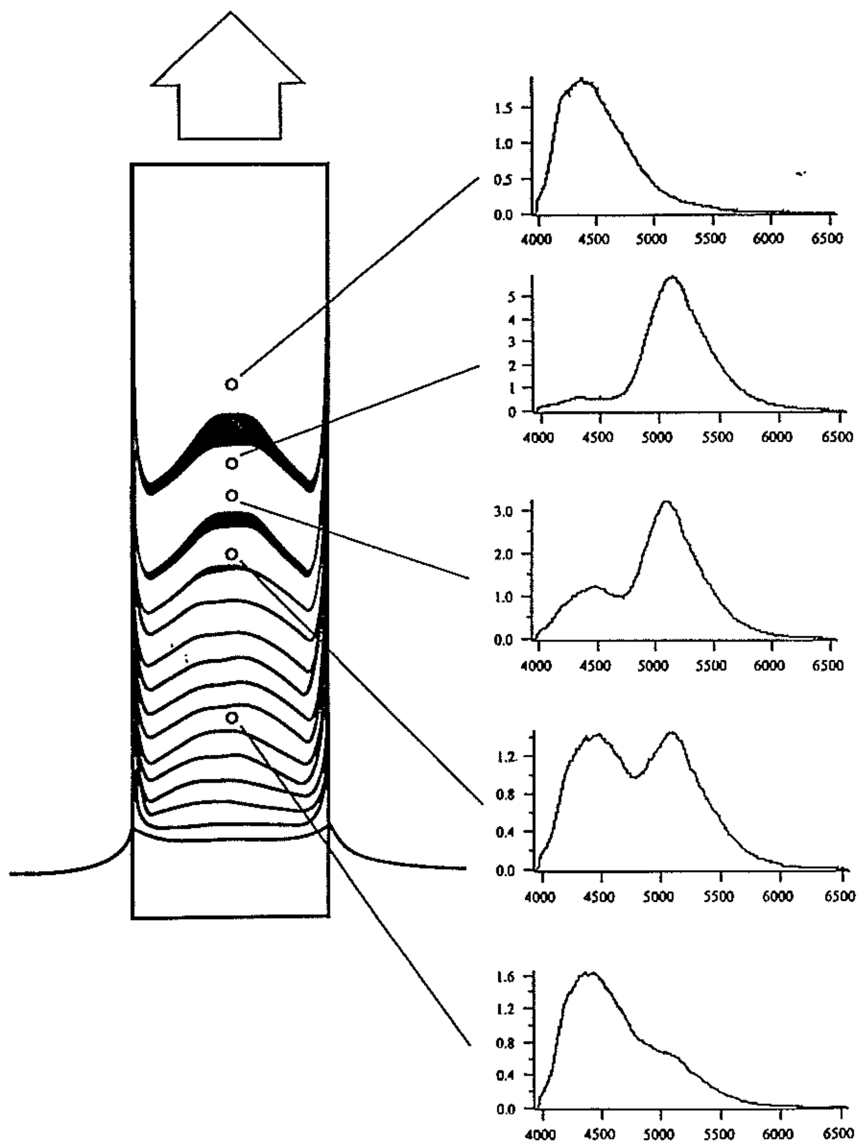


· Pyranine (2×10^{-4} M)

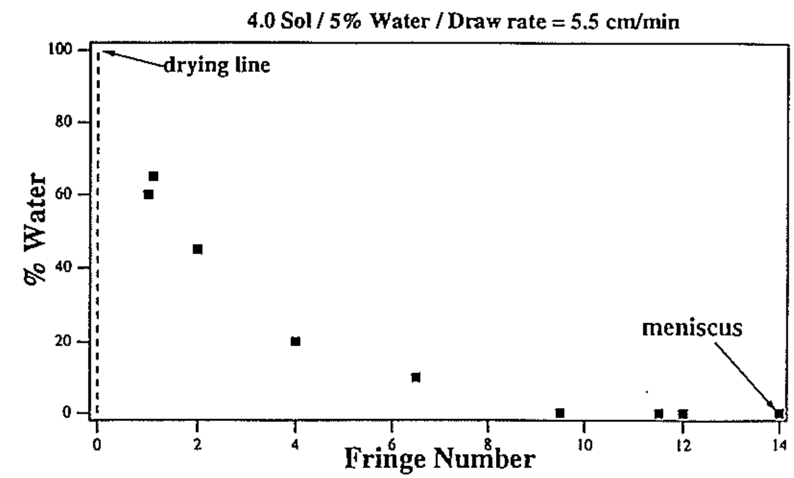
EXPERIMENTAL ARRANGEMENT



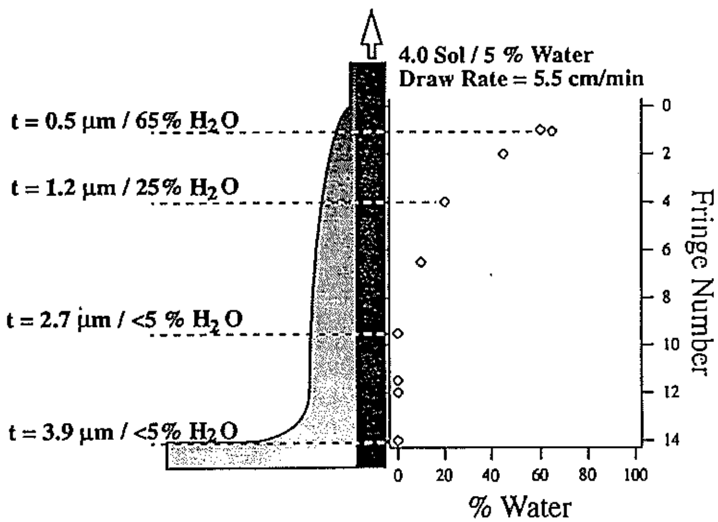
A OMA
B 0.5 m Single Monochrometer
C Focusing Lens
D Aperture
E Hg Lamp (546 nm)
F Objective Lens
G Substrate (Si Wafer)
H Focusing Lens
I,J Mirrors

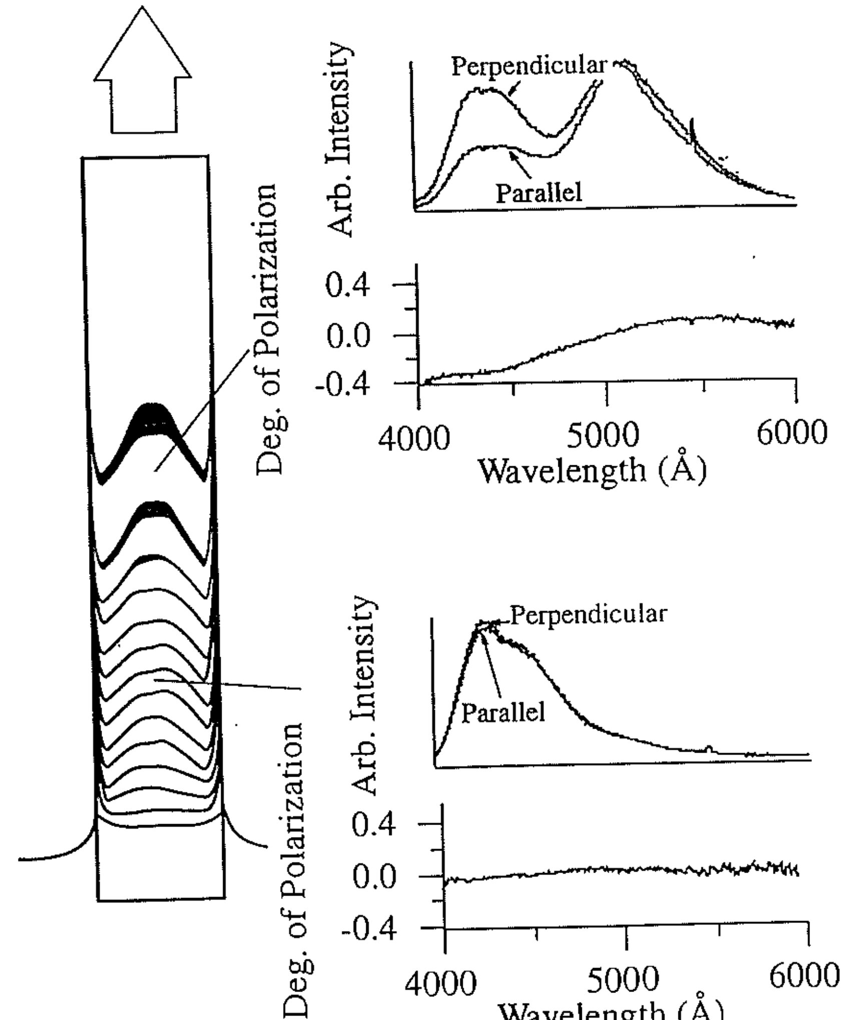


SOLVENT COMPOSITION DURING FILM DEPOSITION



SOLVENT COMPOSITION PROFILE





Sol-Gel Materials Doped with Enzymes and Other Proteins

- Extension of previous studies where organic molecules are encapsulated in sol-gel matrix
- Intrinsic Problem ;

  Sol-gel synthesis conditions are generally too harsh for enzymes and proteins

  High acidity and high alcohol concentration destabilizes protein structure

UNIQUE FEATURES OF SOL-GEL MATERIALS CONTAINING DOPANT MOLECULES

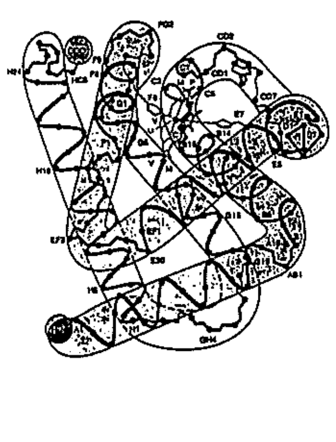
1. Physical encapsulation of molecules in porous matrices
   - Molecules including proteins retain their characteristic reactivities and spectroscopic properties
   - Inorganic matrix offers stable host environment
   - Controlled porosity allows transport of small molecules into and out of the glass
   - Room temperature synthesis
   - Films, fibers, monoliths
2. Optical Transparency
   - Near UV to near IR
   - Absorption, luminescence and Raman spectroscopies
   - Photochemical reactions in the pores

ENCAPSULATION OF BIOMOLECULES IN SOL-GEL MATRICES

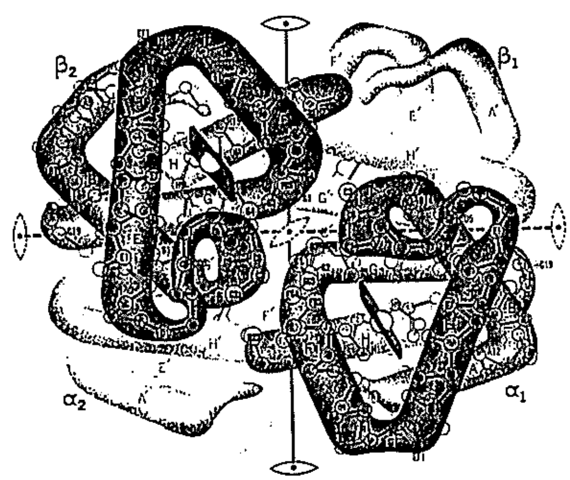
Glucose Oxidase	Catalase	Oxalate Oxidase
Alcohol Dehydrogenase	Peroxidase	Acid Phosphatase
Alkaline Phosphatase	Aspartase	Nitrate Reductase
Cytochrome C	Urease	Cu-Zn Superoxide Dismutase
Myoglobin	Trypsin	Hemoglobin
Bacteriorhodopsin	Ferritin	

❑ **Hb and Mb are heme proteins:** **Mb with molecular weight of 16,900**
Hb with molecular weight of 64,500

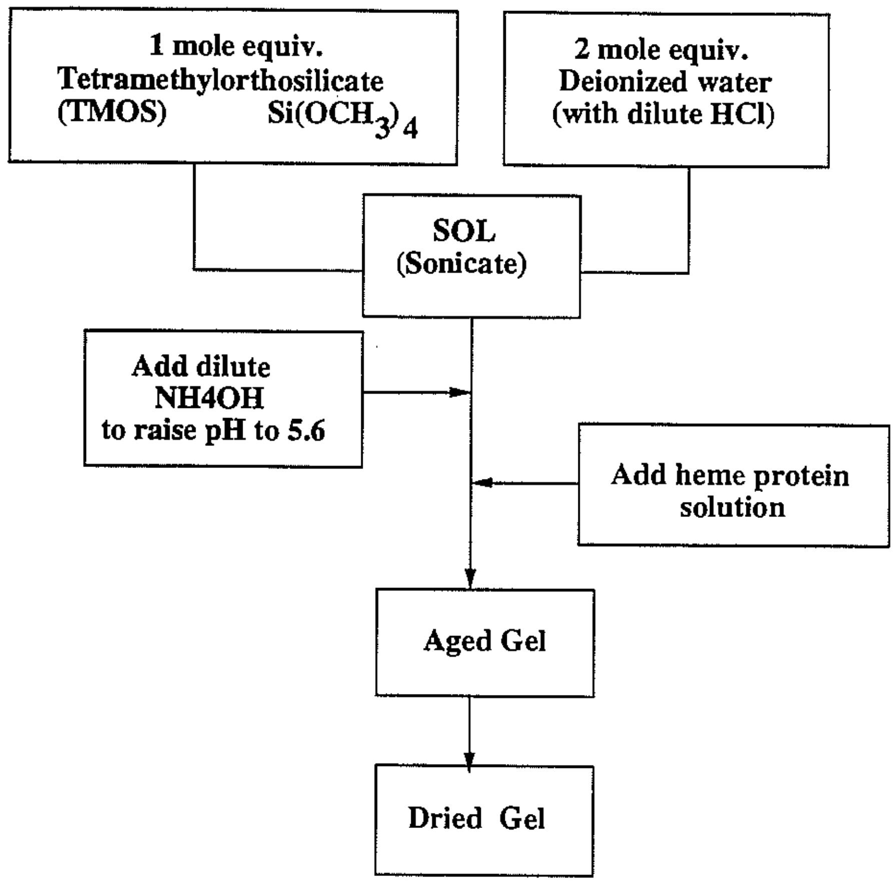
(Reference: G. Zubay, Biochemistry, Addison-Wesley, Reading, 1983)



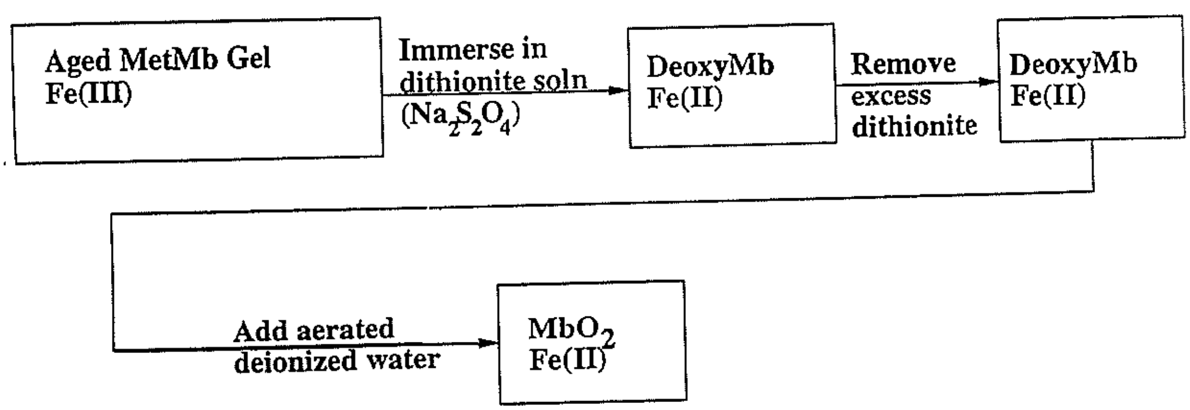
Mb: 44Å x 35Å x 25Å
(Reference: L. Stryer, Biochemistry, W. H. Freeman, San Francisco, 1981)

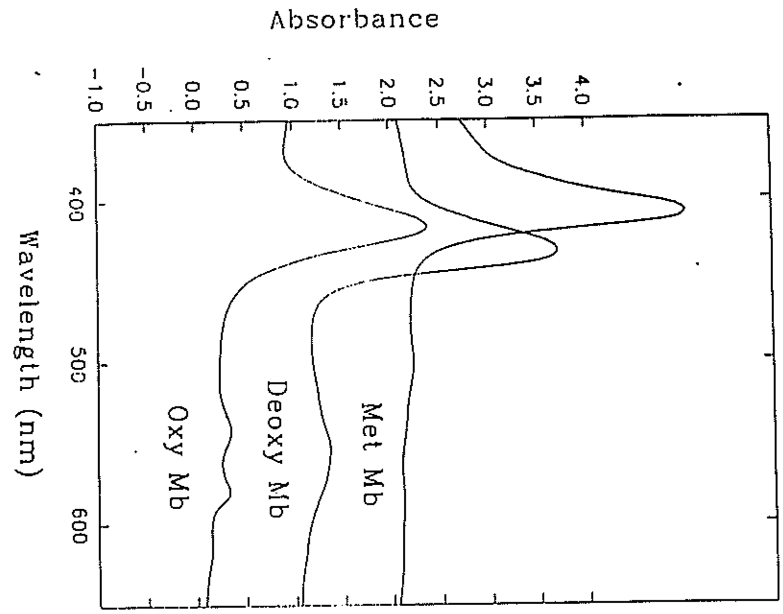


Hb: 65Å x 55Å x 50Å
(Reference: C. Branden & J. Tooze, Introduction to Protein Structure, Garland Publishing, NY 1991)

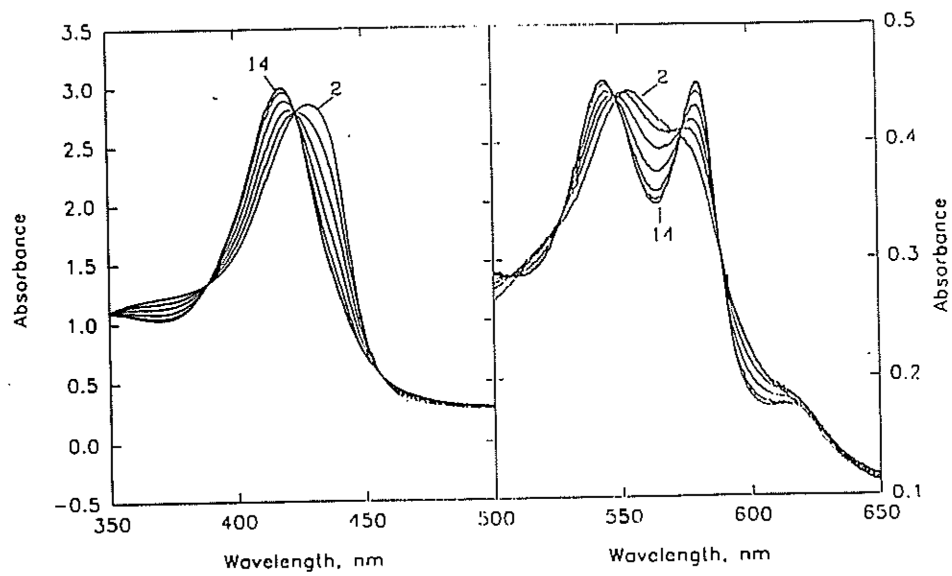


Reaction with O_2:

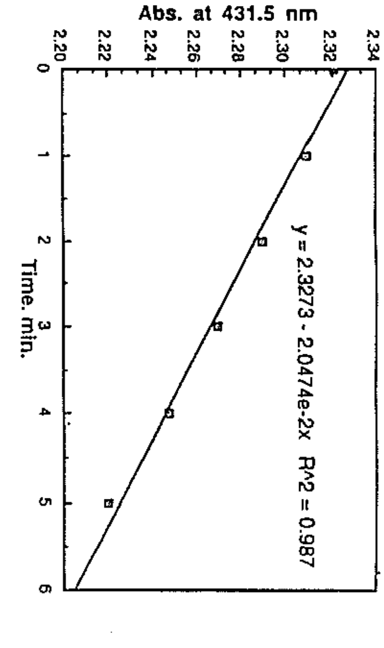




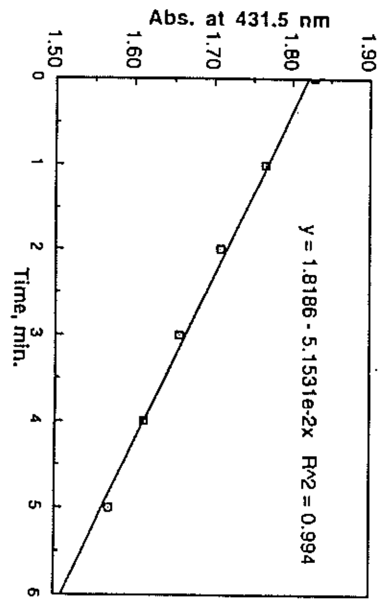
Visible Absorption Spectra of Different Forms of Encapsulated myoglobin



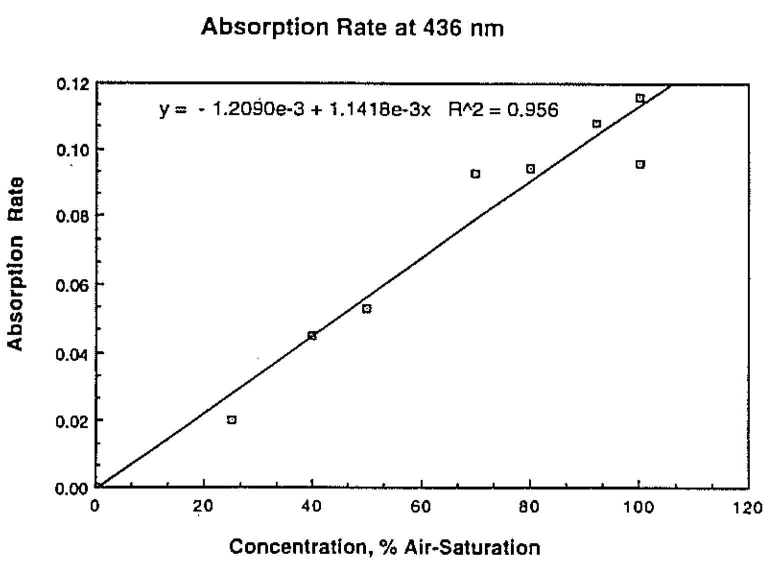
Absorbance Change with Time
After Exposing to Saturated Water



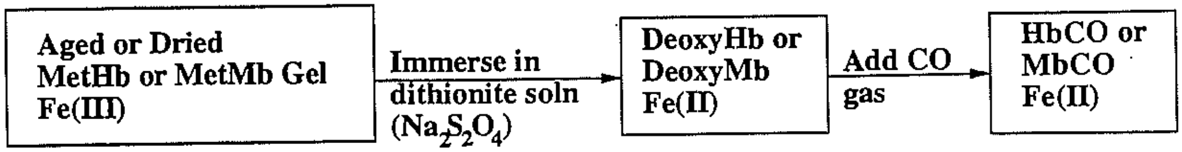
Absorbance Change in 5 minutes After Exposing to 40% Saturated Water



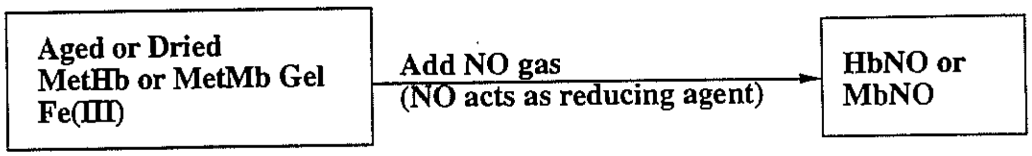
Absorbance Change in 5 Minutes After Exposing to 80% Saturated Water



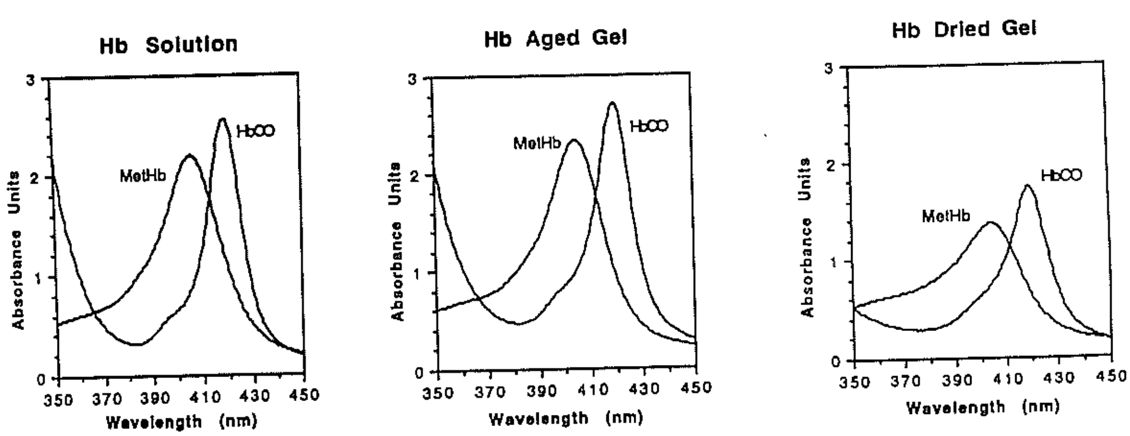
Reaction with CO:



Reaction with NO:



❑ Absorption spectra of HbCO in silica gels vs. in liquid buffer



- Excellent correlation between absorption spectra observed

GLUCOSE OXIDASE and PEROXIDASE

- No visible absorption
- Glucose oxidase and peroxidase are enzymes

Reactions*:

<u>Glucose Oxidase</u> Oxidation of β–D-Glucose to Gluconic Acid

$$\text{Glucose} + H_2O + O_2 \xrightarrow{\text{Glucose Oxidase}} \text{Gluconic Acid} + H_2O_2$$

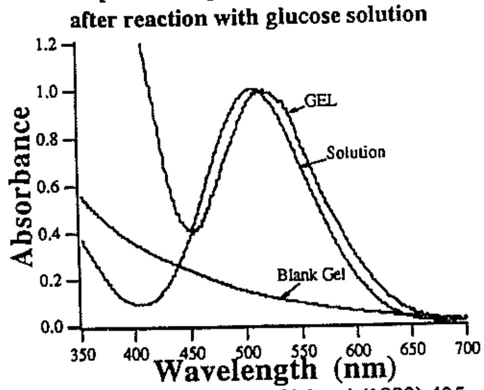
<u>Peroxidase</u> Reaction of Dye

$$H_2O_2 + \text{4-Aminoantipyrine} + \text{p-Hydroxybenzene Sulfonate} \xrightarrow{\text{Peroxidase}} \underset{\text{(Red)}}{\text{Quinoneimine Dye}} + H_2O$$

* Sigma Diagnostics, Glucose (Trinder)

Results: Glucose Oxidase and Peroxidase*

Spectral response of GO-PO gel after reaction with glucose solution



	K_m (M)	K_{cat} (s^{-1})
Aged Gel	0.075 ± 0.025	250 ± 80
Solution	0.028 ± 0.003	251 ± 25
Literature†	0.026	293

K_m: binding constant (dissociation constant of enzyme-product complex)

K_{cat}: turnover number (number of substrate turned into product by an enzyme)

* Yamanaka et al., Chem. of Mat. 4 (1992) 495.

† Bright et al., J. Biol. Chem. 242 (1967) 994.

GELS CONTAINING ENCAPSULATED PROTEINS AND ENZYMES

- Modification of sol-gel chemistry to provide friendly environment for biomolecules
- Biomolecules retain characteristic reactivities and spectroscopic properties
- Porosity allows transport of small molecules into and out of the glass
- Chemical reactions monitored by means of changes in optical spectra

OPTICAL APPLICATIONS OF ORGANIC/INORGANIC HYBRID MATERIALS

- Hybrid materials consisting of a wide range of dopant molecules (organic, organometallic, biological) encapsulated in sol-gel derived matrices have been prepared
- The molecules retain their optical properties and chemical functions in the solid state
- The ability to tailor the synthesis conditions enables the chemical environment to be compatible with dopant molecules
- Optical materials are prepared by the deliberate doping of specific molecules
- Results:

  Solid state optical materials

  Luminescent probes of sol-gel chemistry and processing

  Optically based chemical sensors which exploit the sensitivity/selectivity of enzyme and protein chemistry

ORGANIC/INORGANIC AEROGELS: CONTROLLING STRUCTURE AT THE NANOMETER SCALE

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Aerogel compositions and properties

Composition

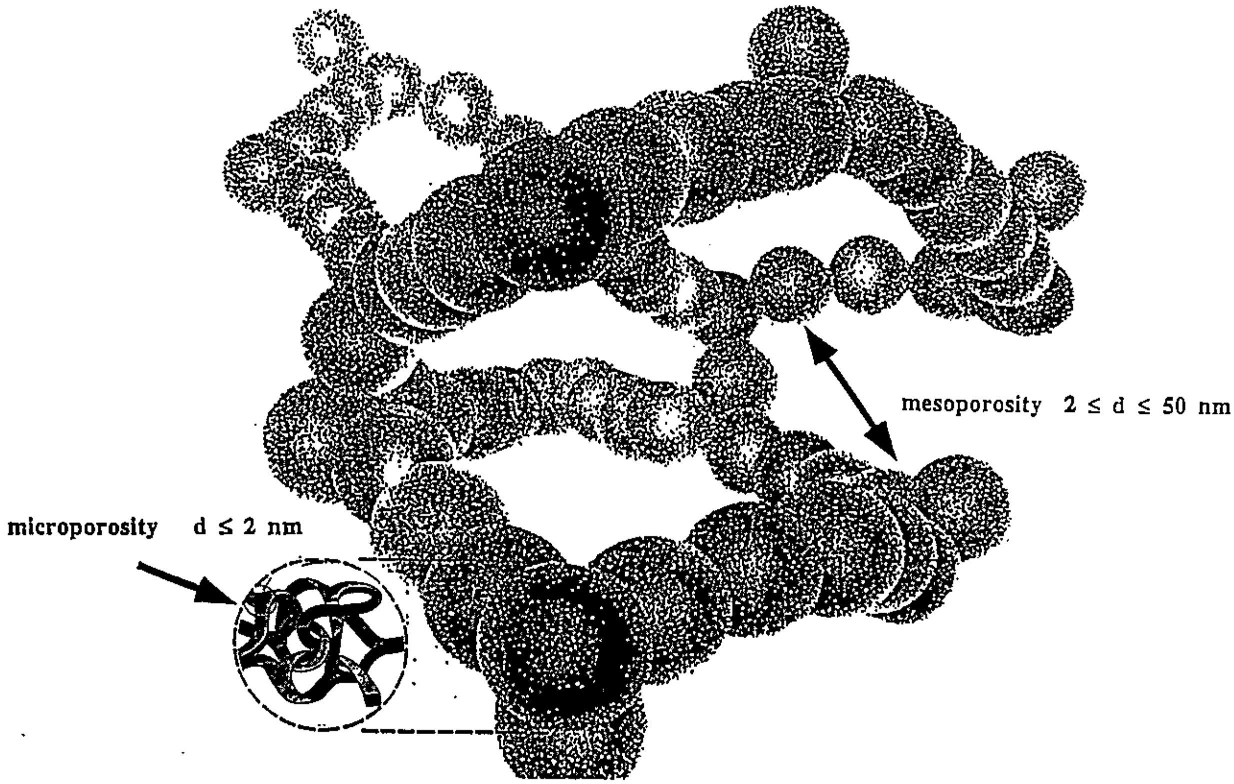
Inorganic
- silica
- titania
- tantala
- zirconia
- mixed metal oxides

Organic
- resorcinol-formaldehyde
- melamine-formaldehyde
- phenolic-furfural
- carbon

Properties

- high surface area (> 400 sq.m./g)
- ultrafine cell/pore size (< 50 nm)
- low thermal conductivity (~ 0.015 W/m-K)
- low sound velocities (20-300 m/s)
- mechanical properties depend on bulk density ($E \sim \rho^n$ where n= 2.8-3.8)
- low dielectric constant ($\varepsilon < 2$)

Structural model



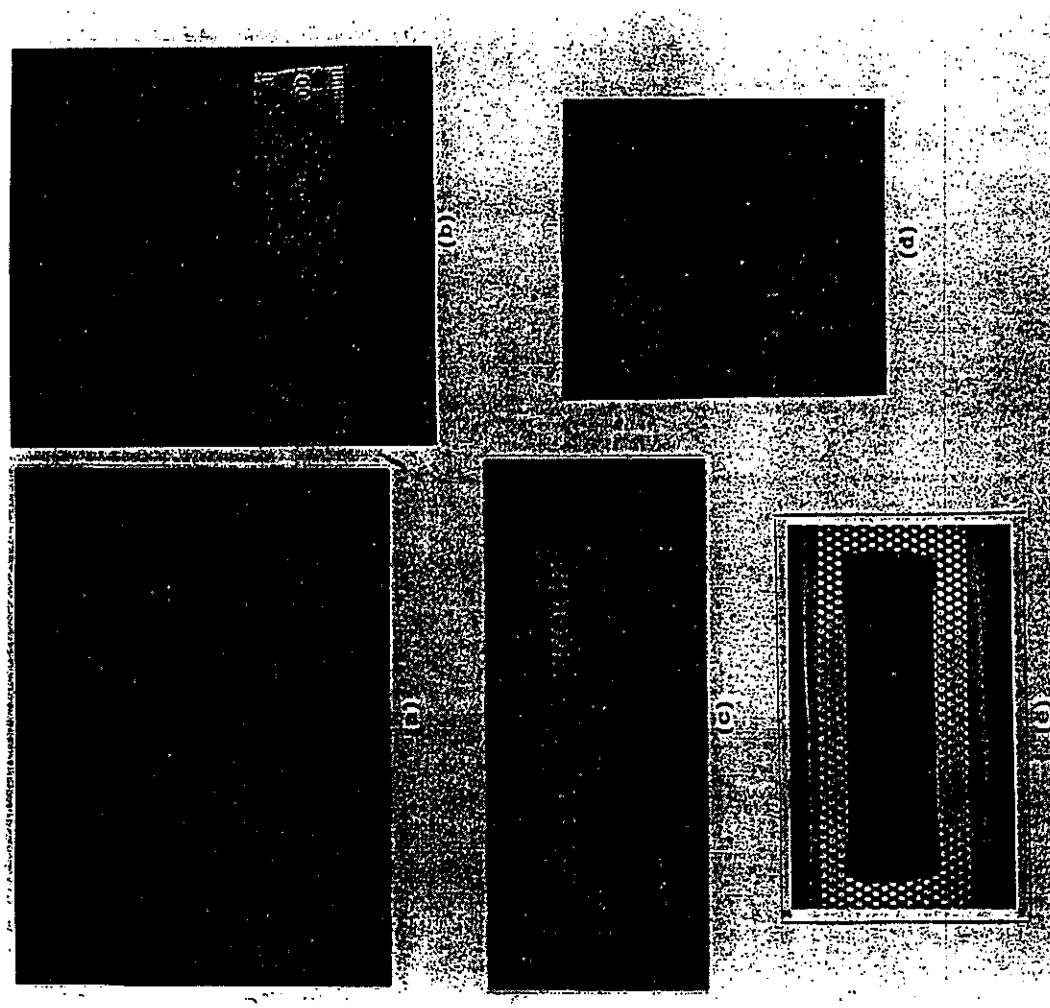
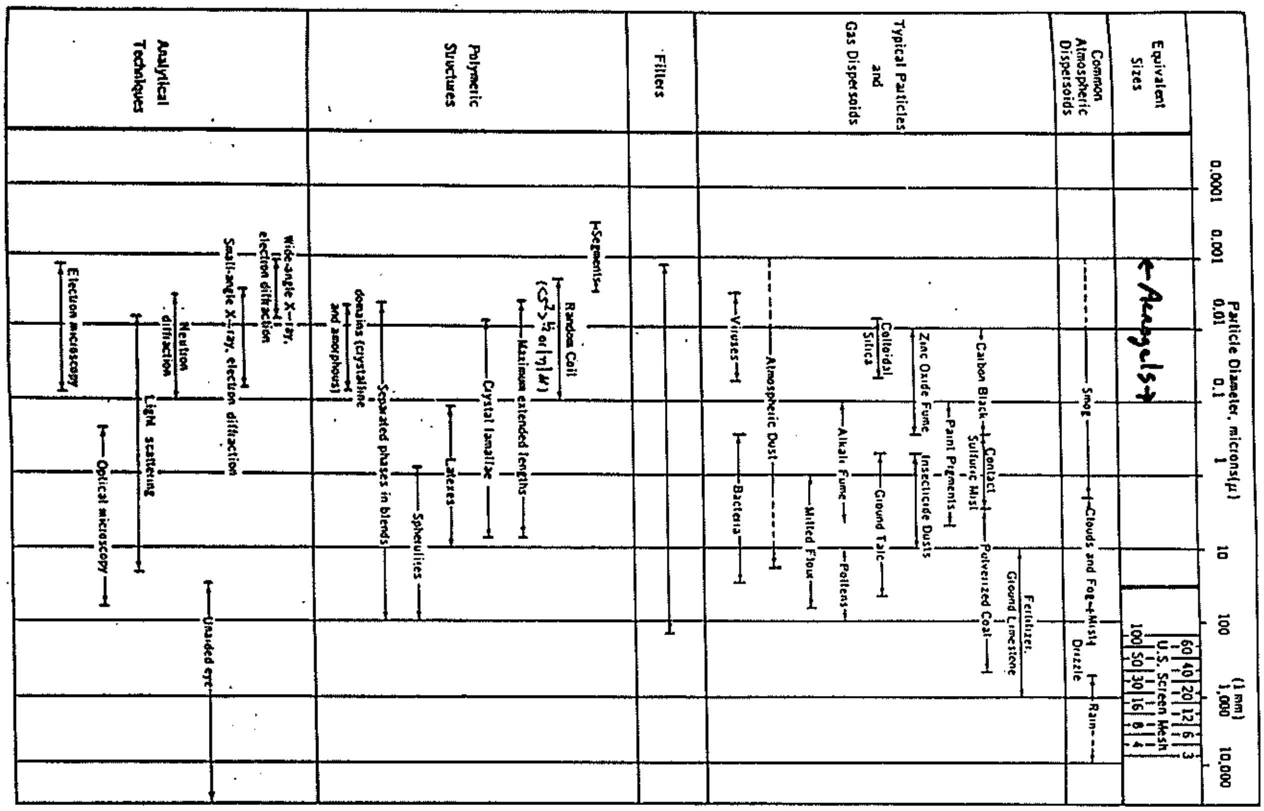


Figure [illegible]. Photographs of various aerogels: (a) ultra-low density silica (0.01 g/cc); (b) base catalyzed silica (0.10 g/cc); (c) melamine-formaldehyde (0.15 g/cc); (d) carbon (0.05 g/cc); and (e) resorcinol-formaldehyde (0.06 g/cc).



Silica chemistry

$$n\,Si(OCH_3)_4 + 4n\,H_2O \rightleftharpoons n\,Si(OH)_4 + 4n\,CH_3OH \qquad \text{Hydrolysis}$$

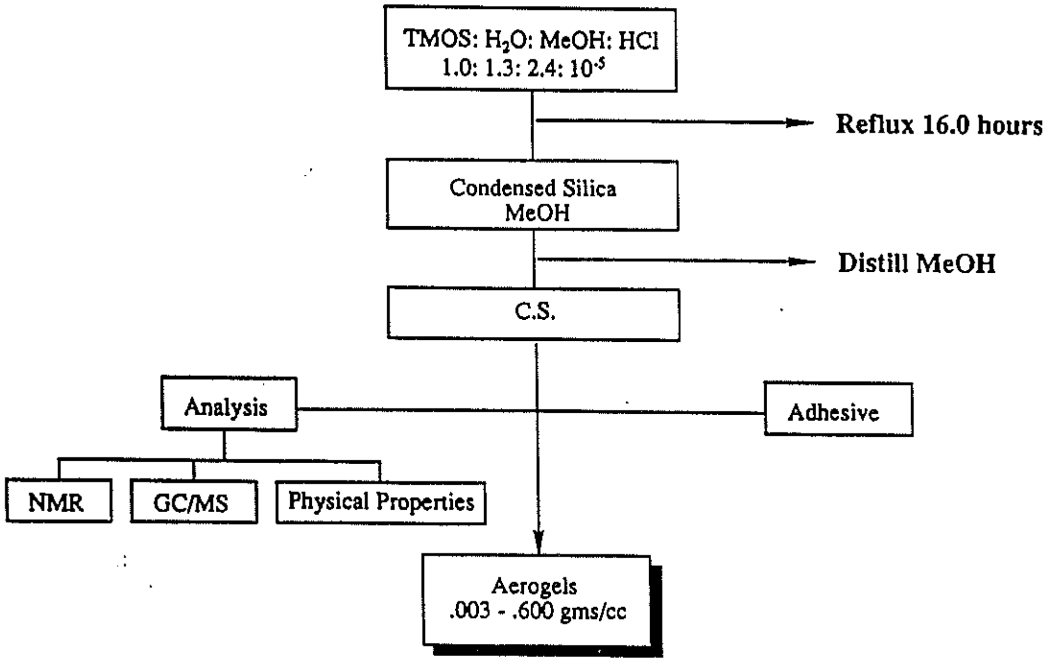
$$n\,Si(OH)_4 \rightleftharpoons n\,SiO_2 + 2n\,H_2O \qquad \text{Condensation}$$

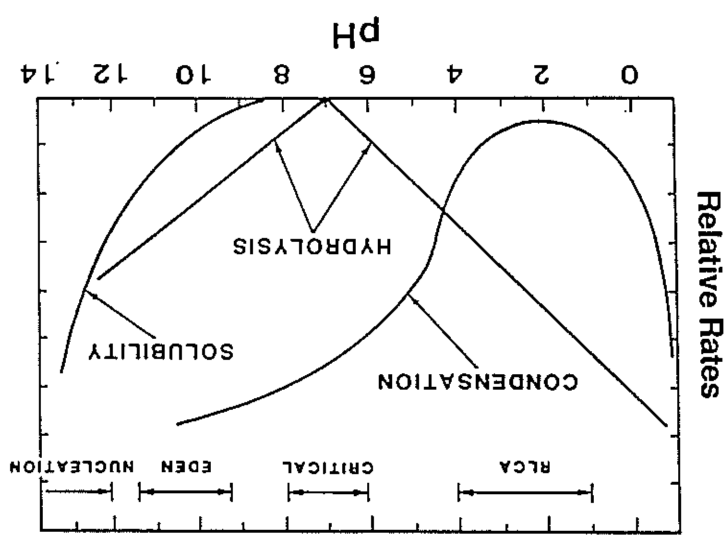
$$n\,Si(OCH_3)_4 + 2n\,H_2O \rightleftharpoons n\,SiO_2 + 4n\,CH_3OH \qquad \text{Net Reaction}$$

Factors influencing reaction:

- Catalyst -- Acid vs. Base
- Temperature
- [Water]/[TMOS] ratio
- One step vs. two step polymerization

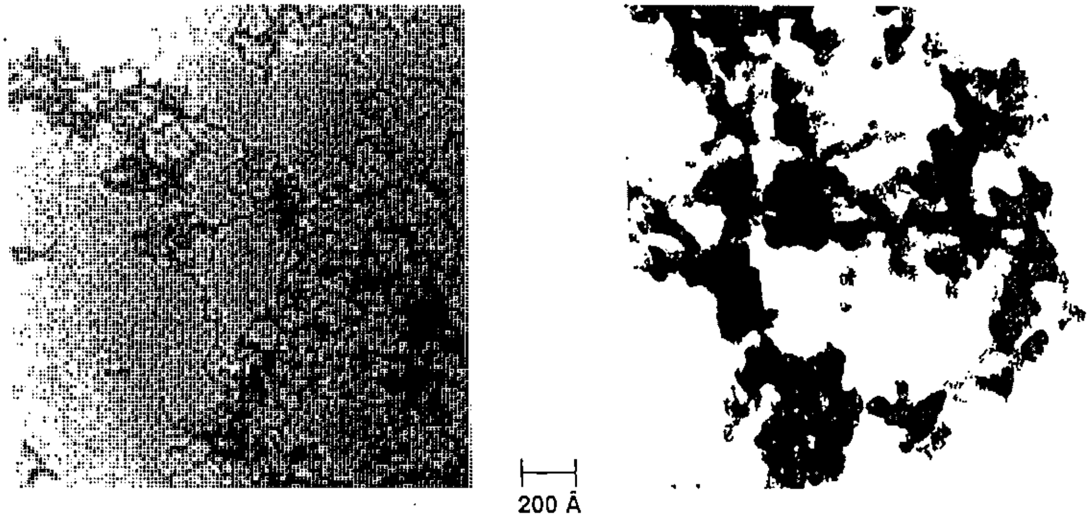
Schematic Flowchart of the C.S. Method





Growth mechanism depends upon polymerization conditions

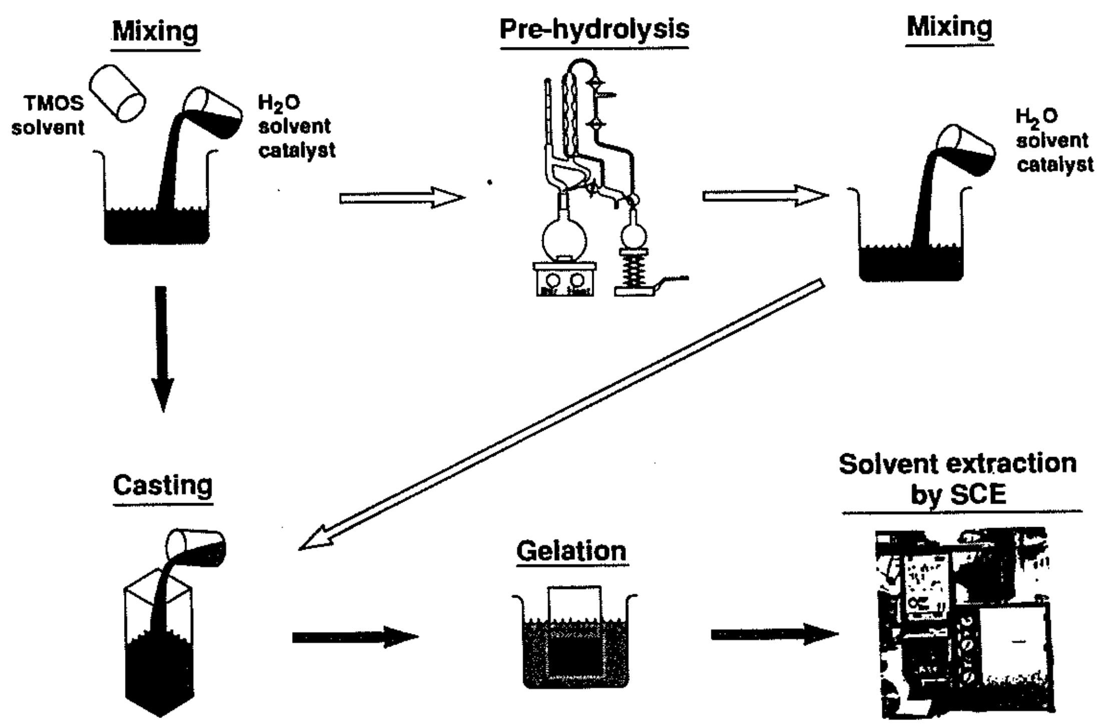
Comparison of TEMs Shows Chain-like vs. Colloidal Microstructures



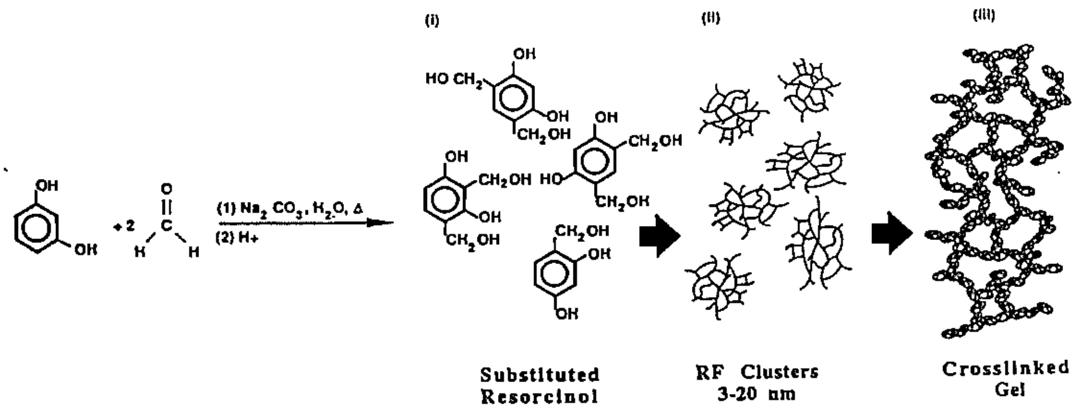
TEM of two-step aerogel (0.008 g/cm^3)

TEM of conventional aerogel (0.04 g/cm^3)

Two Sol-Gel Routes for Producing Aerogels



A synthetic route for the production of organic aerogels has been developed

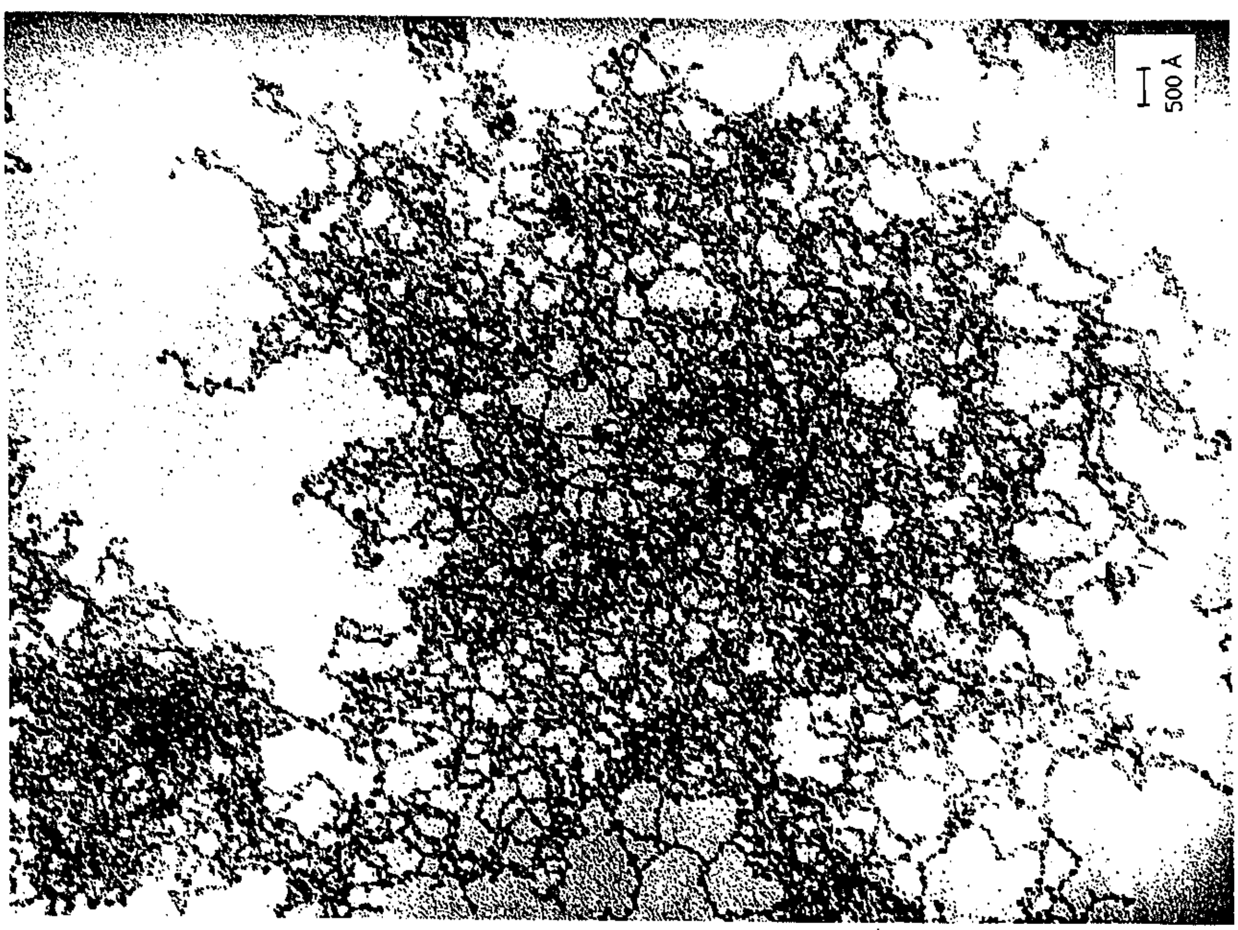


Requirements for organic sol-gel polymerizations

- Multifunctional monomers
- High degree of crosslinking
- Surface functional groups
- Particle stabilization
  - electrostatic
  - polymer / solvent interactions

Solution chemistry dictates the structure and properties of RF aerogels

High Catalyst Conditions R/C=50	Low Catalyst Conditions R/C=300
• small particle size ~ 30 Å • high surface area ~ 900 sq.m./g • more shrinkage upon drying • polymeric; interconnected fibers • higher compressive modulus	• large particle size ~200 Å • low surface area ~ 350 sq.m./g • less shrinkage upon drying • colloidal; interconnected particles • lower compressive modulus



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High Catalyst Conditions R/C=50	Low Catalyst Conditions R/C=300
• small particle size ~ 30 Å	• large particle size ~200 Å
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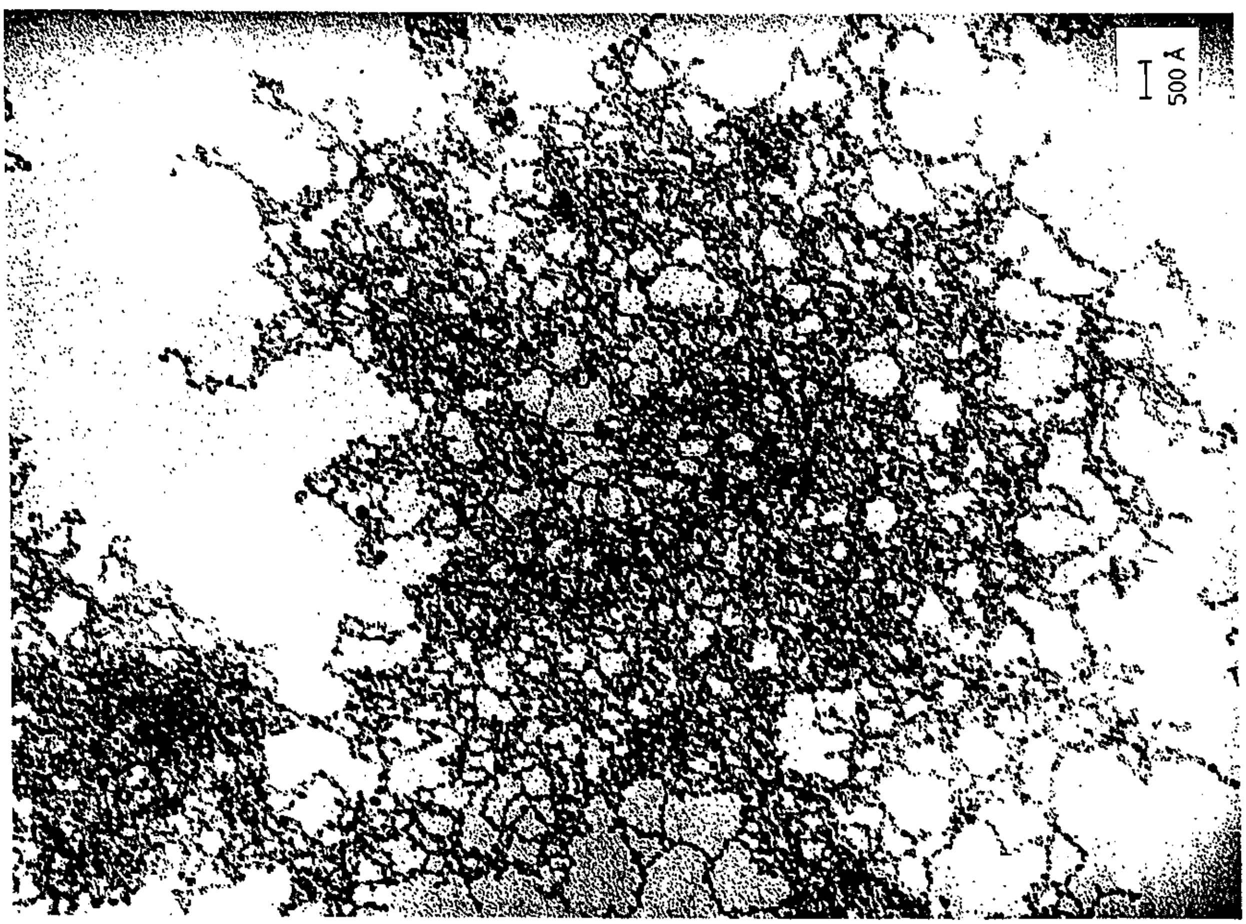
• more shrinkage upon drying	• less shrinkage upon drying
• polymeric; interconnected fibers	• colloidal; interconnected particles
• higher compressive modulus	• lower compressive modulus

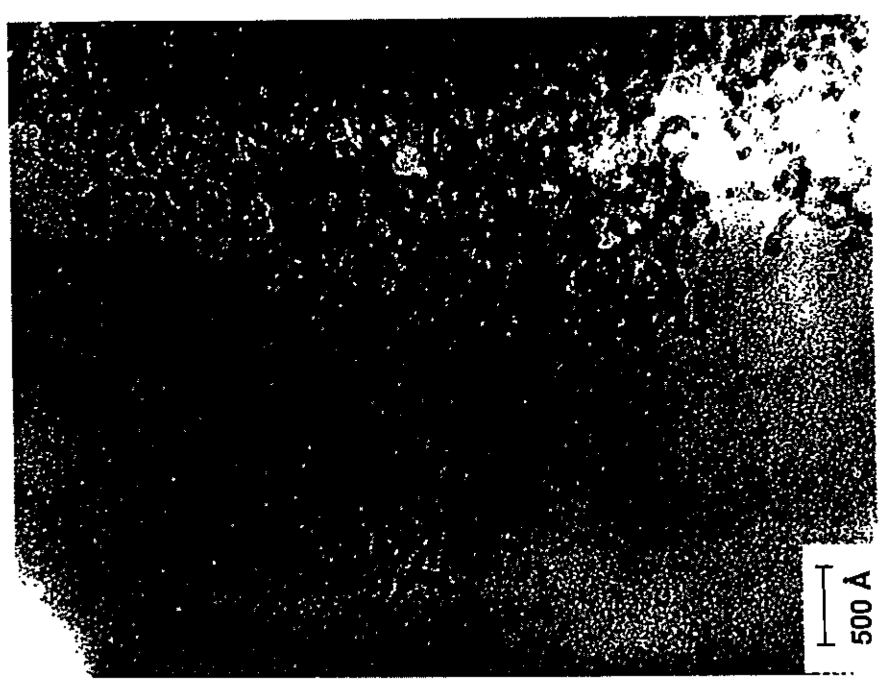


Organic modifications of the traditional sol-gel approach

- Reaction of hydroxy terminated polymers with metal alkoxides
  - Ormosils
  - Ormocers
  - Ceramers

- Formation of a crosslinked inorganic gel followed by free radical polymerization of an organic monomer in the pores

- Swelling of a crosslinked rubber with a metal alkoxide followed by a sol-gel polymerization



TEM reveals the interconnected bead morphology of a carbonized aerogel

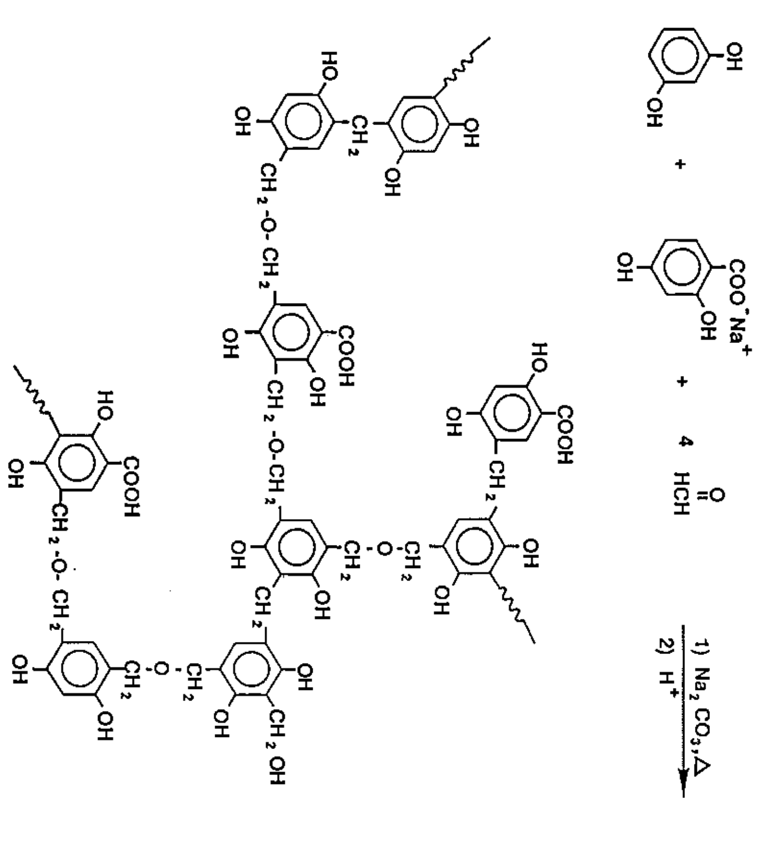
Our approach

- Sol-gel polymerization of multifunctional organic monomers having ion exchange capacity
    - resorcinol + 2,4 dihydroxy benzoic acid + formaldehyde

- Copolymerization of metal alkoxides with an organic sol
    - tetramethoxysilane + resorcinol-formaldehyde
    - tetramethoxysilane + melamine-formaldehyde

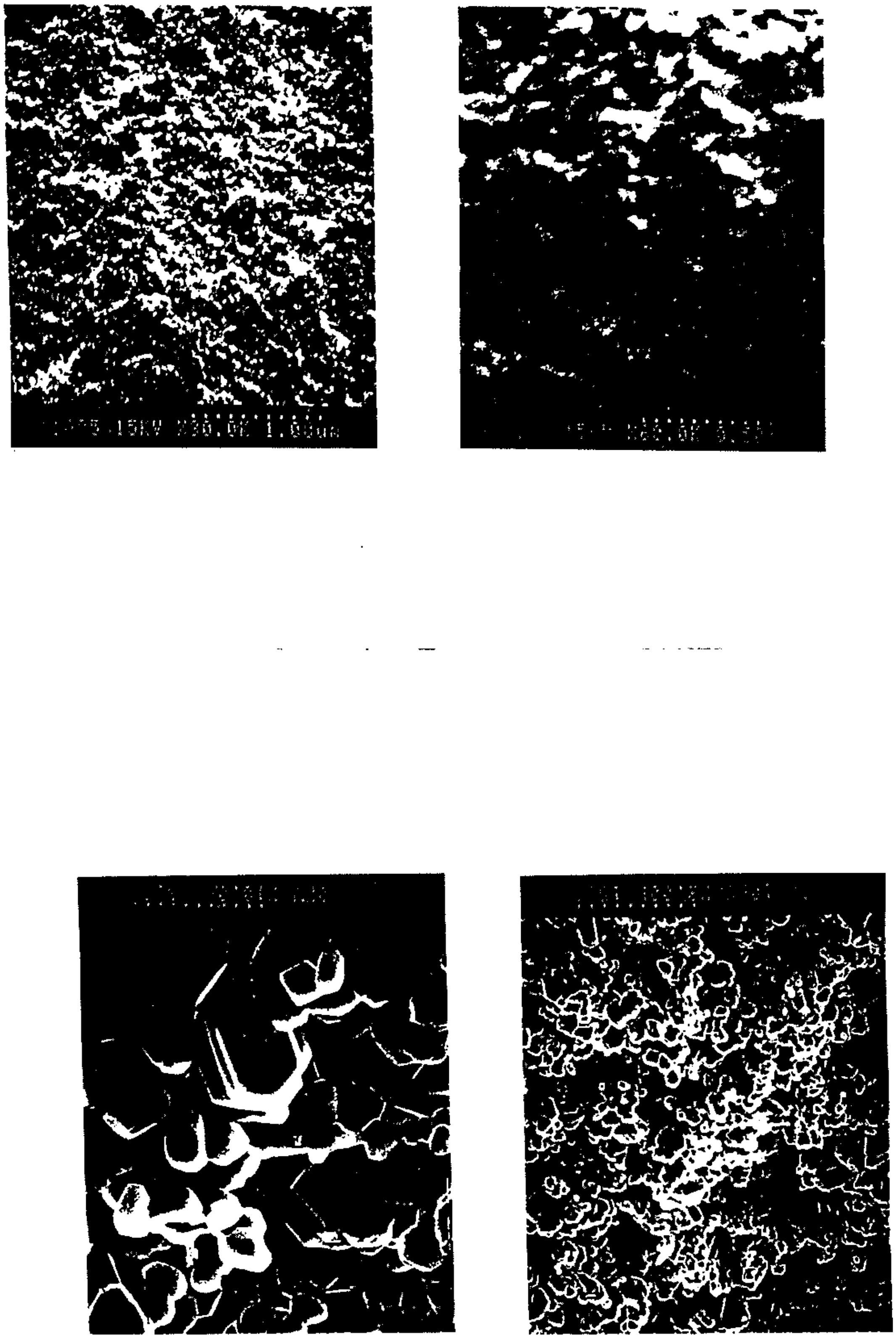
- Copolymerization of an inorganic colloid with an organic sol
    - silica + resorcinol-formaldehyde
    - gold + melamine-formaldehyde
    - titania + carbon

RF chemistry can be modified to provide carboxyl groups for ion-exchange



Crosslinked ion-exchange resin

SEM of a resorcinol-formaldehyde / silica aerogel



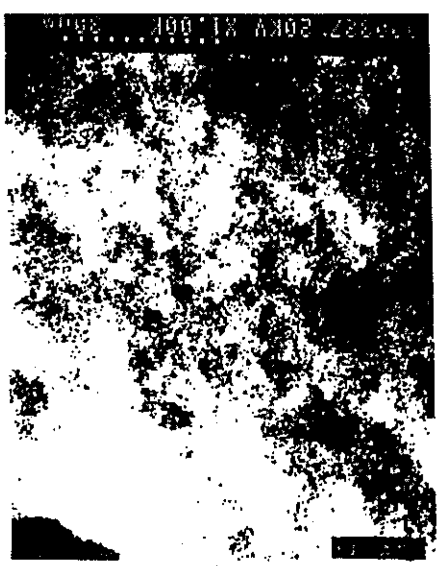
Processing issues

Aerogel Forms

- monoliths
- microspheres
- thin films
- composites

Synthesis

- improved gel strength
- elimination of solvent exchange step
- improved drying times



SEM of a Carbon/Titania Aerogel

Ambient pressure drying

Approach

- induce additional crosslinking in gel through aging or chemistry (i.e., improve gel matrix strength)
- modify surface chemistry to change contact angle of pore fluid with respect to the skeleton
- solvent evaporation from appropriate fluid

> ***UNM and SNLA have demostrated the feasibility of ambient pressure drying for silica aerogels; however, the approach still suffers from multiple solvent exchanges. In addition, the density must be lowered to achieve the lowest thermal conductivity.***

Keys to successful drying

Lawrence Livermore National Lab

- Surface chemistry (control contact angle)
  - capillary pressure: $\Delta P = -\gamma \cos(\theta) / r$
- Pore morphology (size & uniformity)
  - capillary pressure: $\Delta P = -\gamma \cos(\theta) / r$
  - permeability: $K = K' (1 + \alpha r/P)$
- Gel strength (to withstand drying forces)
  - stress to crack: $\sigma \approx [10\, \alpha^2/1+4\pi\alpha]$; $\alpha = [(2/k)(P/\tau)(\Pi/D')\eta\, r^2]$
- Selection of solvent (low surface tension; low viscosity)
  - e.g., carbon dioxide
- Geometry (reduce differential stress)
  - $\sigma_{sphere} < \sigma_{cylinder} < \sigma_{plate}$

Use chemistry to control four of the five above

Motivation

Although aerogels were first developed in the 1930s, only limited commercial applications exist for this fascinating material. Monolithic aerogels have very low thermal conductivities (i.e., 0.012-0.016 W/m-K), yet these materials are not as cost-competitive or user-friendly as standard foam insulation. A potential solution to the above problems is the synthesis of aerogels in a granular form. While BASF (Ludwigshafen, Germany) has demonstrated the production of silica aerogel granules, our research is focused on new methods for the production of *organic aerogel* microspheres or powders.

Potential Advantages

- decreased diffusion times since microspheres are only 10-200 μm in diameter
- faster processing, semi-continuous operation
- lower cost
- minimized material handling

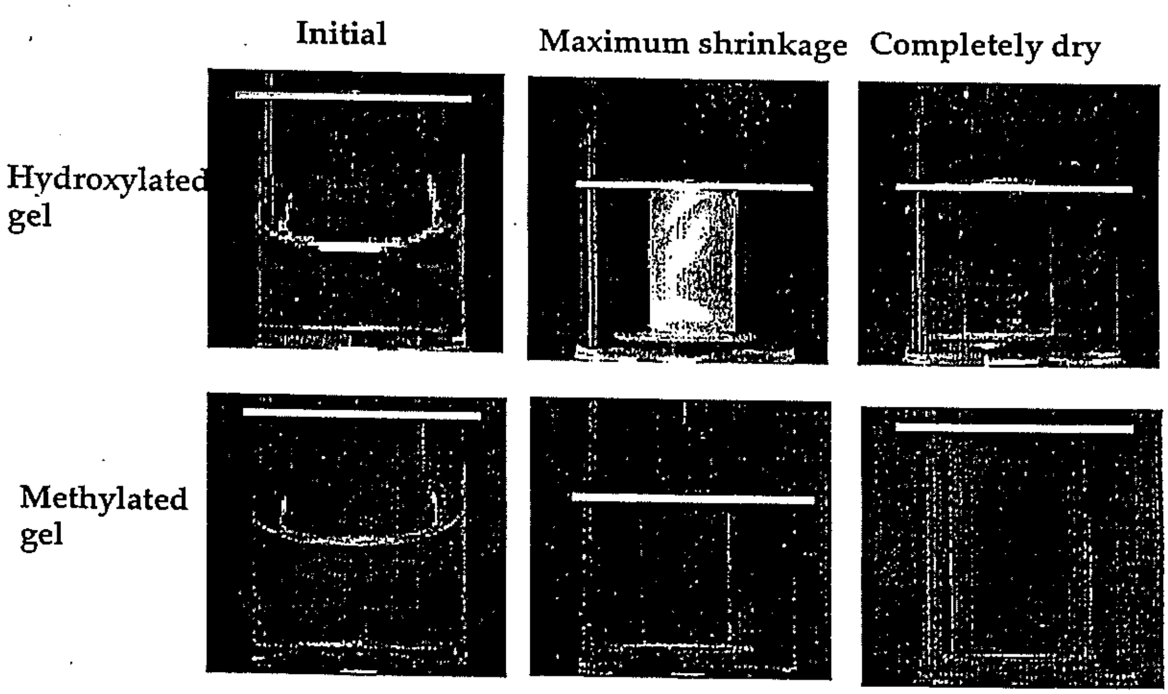
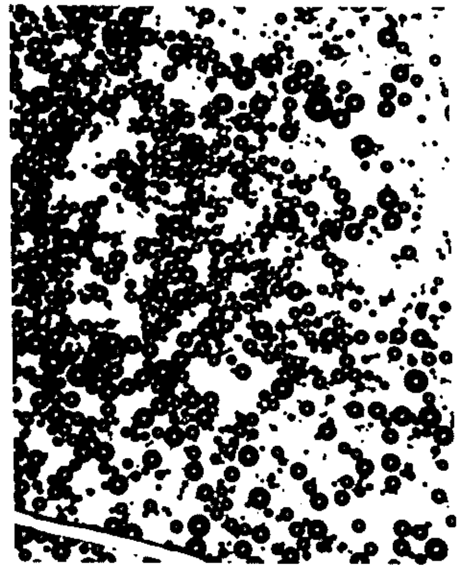


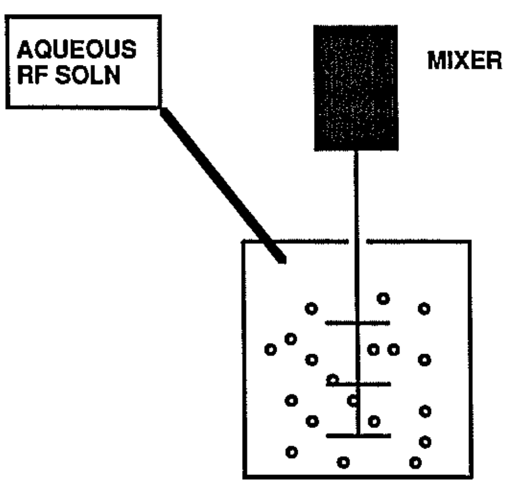
Figure 10 In-situ video images of silica gel with either a hydroxylated or methylated surface at various stages of drying.

Resorcinol-formaldehyde



Carbon

Inverse emulsion polymerization can be used to form organic aerogel microspheres

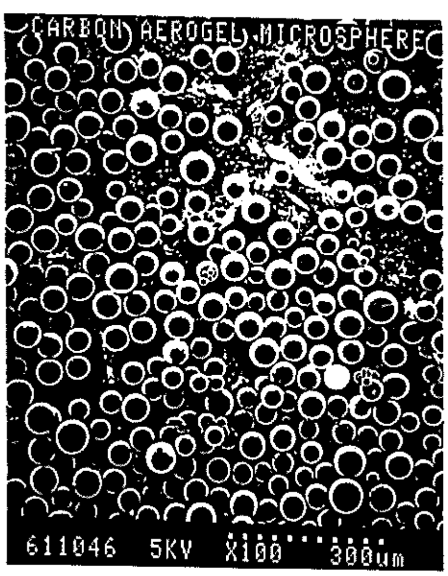


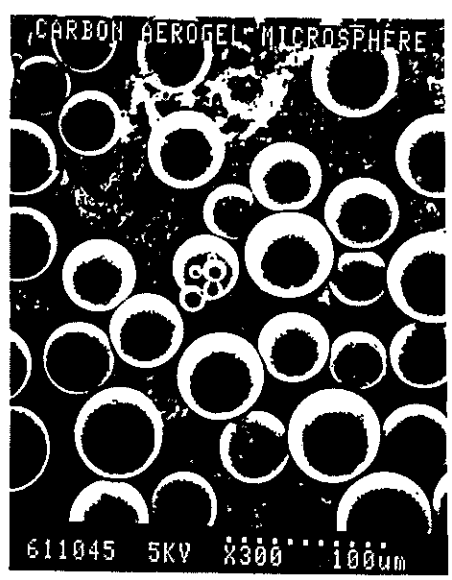
1) add RF solution to immiscible solvent (e.g. cyclohexane)
2) agitate and heat
3) filter crosslinked gel spheres
4) dry
5) pyrolyze at 1050 °C

Aerogel structure-property relationships

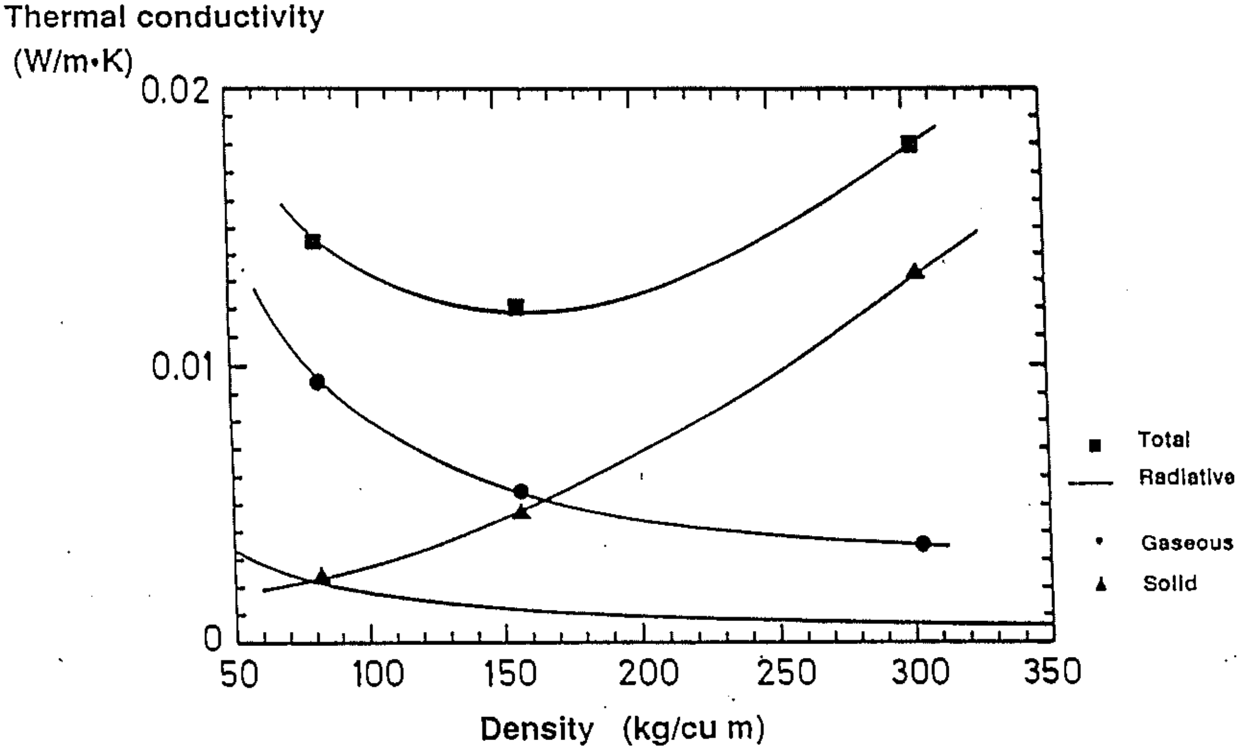
- Optical
- Thermal
- Acoustic
- Electrical
- Mechanical

Controlling structure at the nanometer scale has
a dramatic effect upon the properties of porous materials





Total thermal conductivity of RF aerogel monoliths as a function of density



Minimum conductivity occurs at an optimum aerogel density

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The total thermal conductivity of aerogel is the sum of the contributions:

$$\lambda t' = \lambda s' + \lambda g' + \lambda r'$$

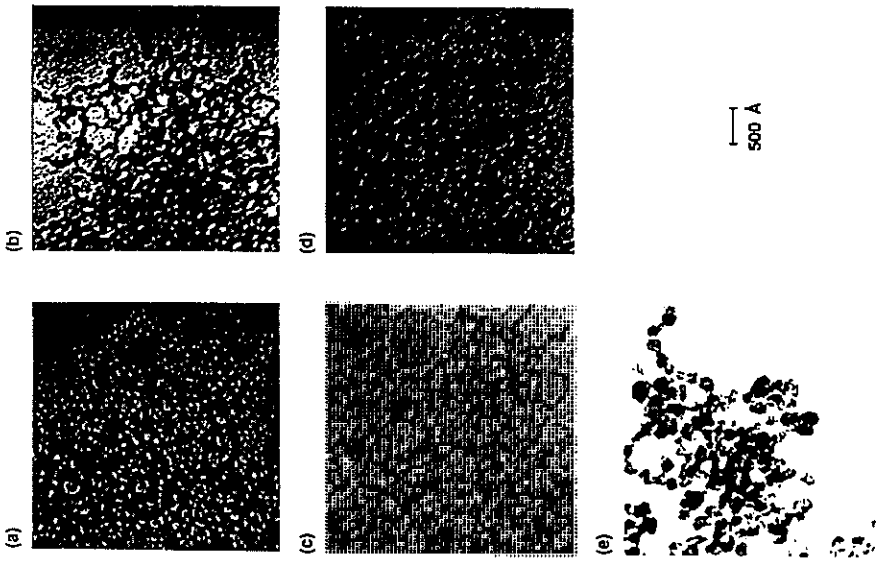
All contributions are density dependent.

The optimum density for minimum thermal conductivity can be calculated from:

$$\rho'_{opt} = 10^{x}$$

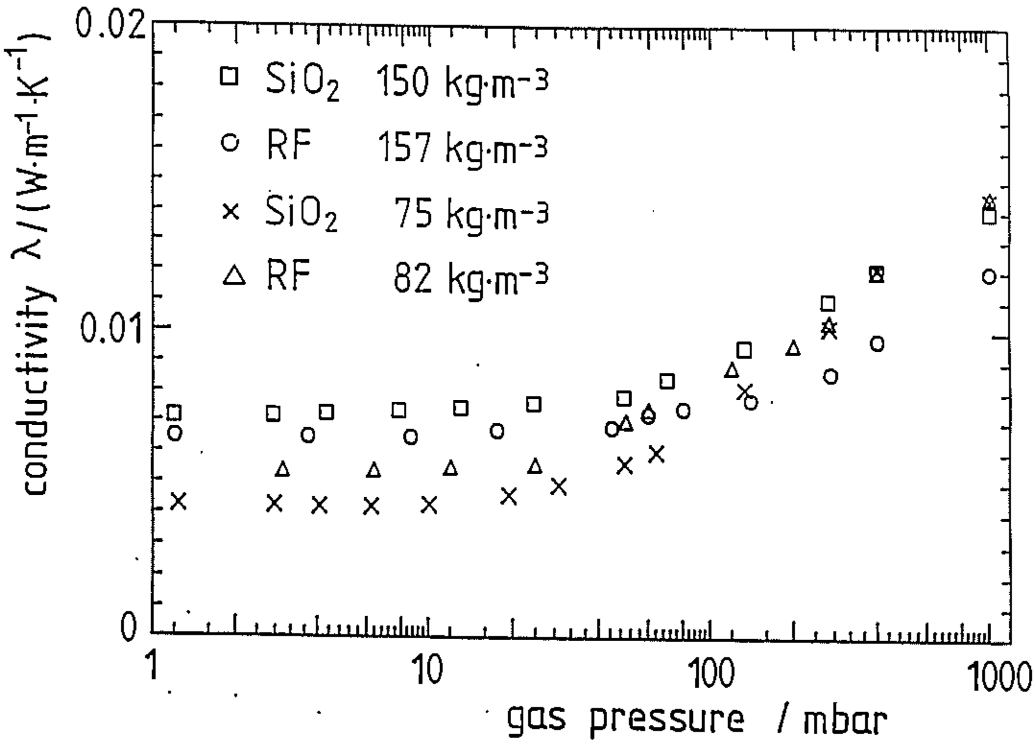
where

$$x = (0.347)\{\log(0.025 + 882/K_s) - \log(91.4 \cdot \lambda_s)\} + \log \rho_s$$

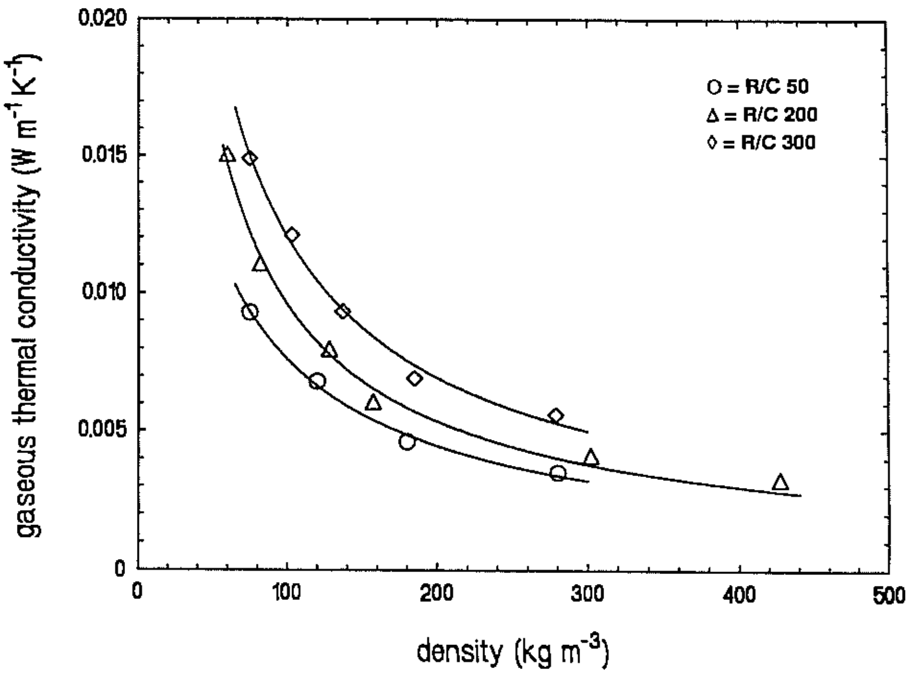


Transmission electron micrographs of RF aerogels synthesized at different catalyst concentrations. [Resorcinol] / [catalyst] equals (a) 50 (b) 100 (c) 150 (d) 200 and (e) 300.

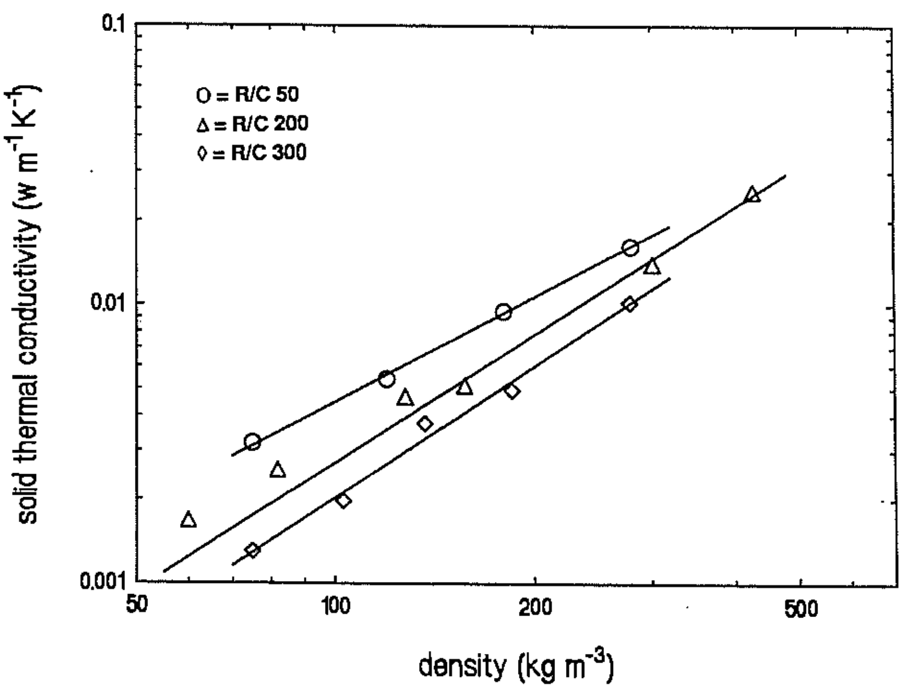
Thermal conductivity of evacuated aerogels



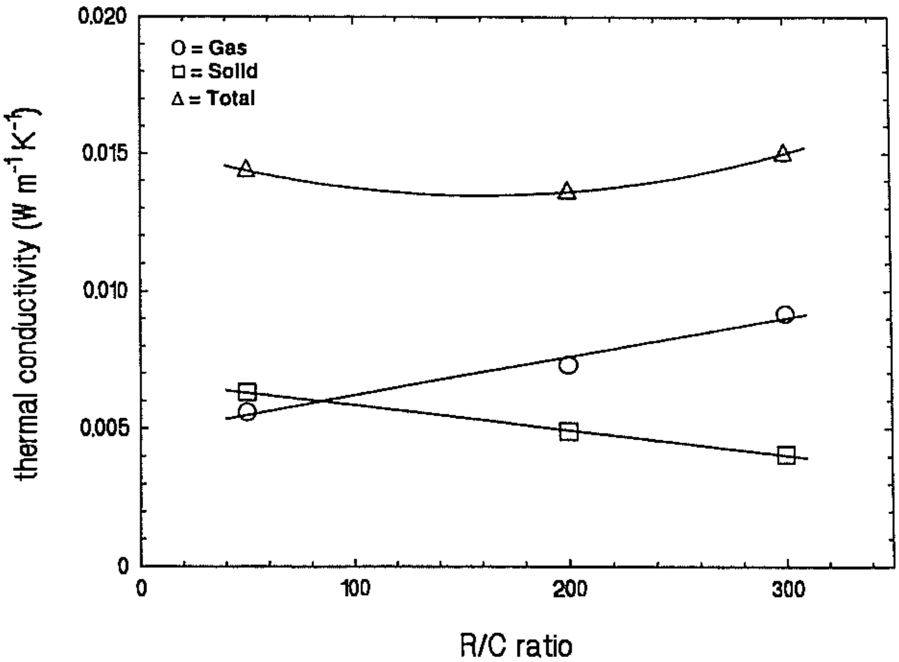
Gaseous conductivity vs. density for RF aerogels having different nanostructures



Double log plot of solid conductivity vs. density for RF aerogels having different nanostructures

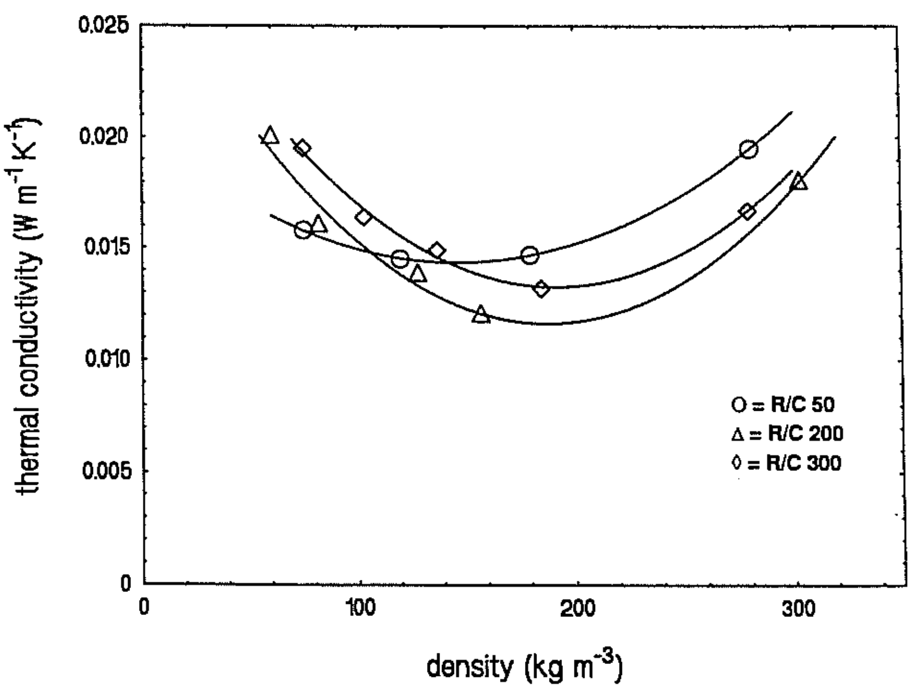


Variation in gaseous, solid, and total thermal conductivity as a function of the R/C ratio



* Aerogel bulk density equals 137 kg/m³ for all samples

Total th:rmal conductivity vs. density for RF aerogels having different nanostructures



Foam structure-property relationships

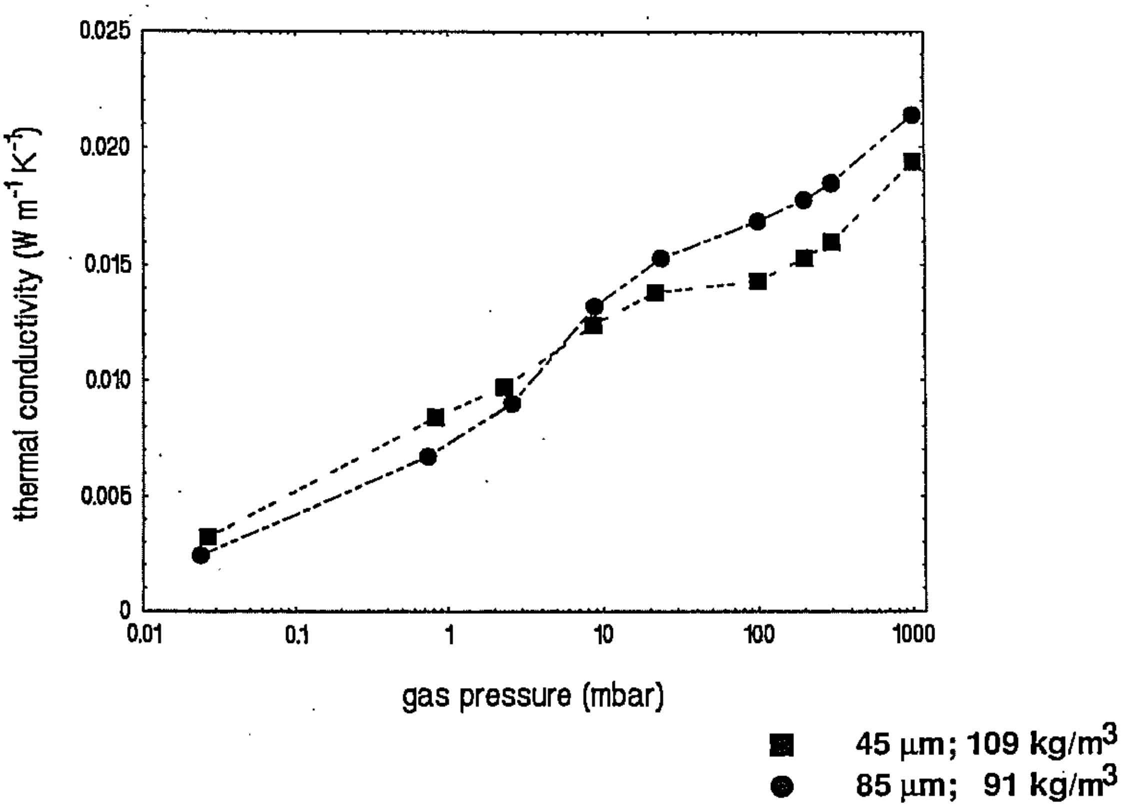
- Typical observation...

$$E \propto \rho^n$$

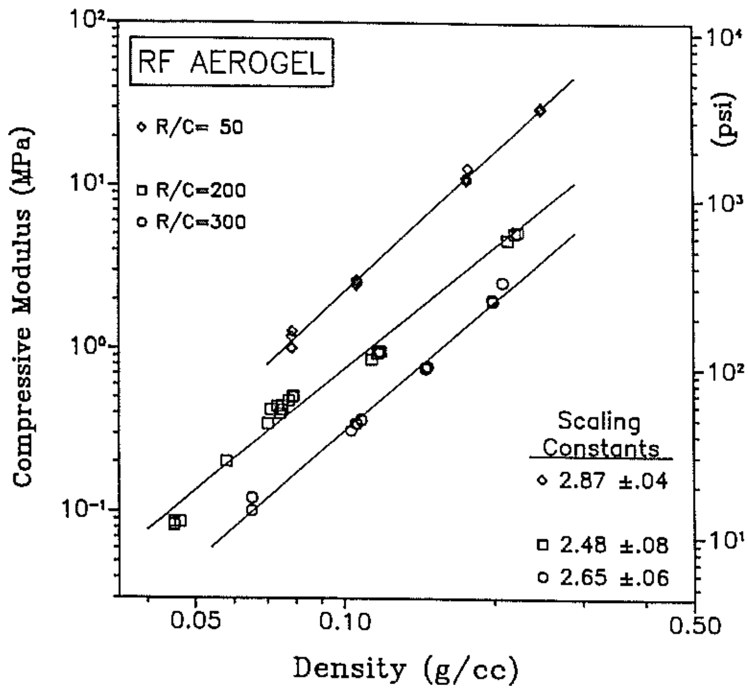
where E = Young's Modulus
ρ = foam density
n = scaling exponent

- Comments...
  - For most foams $2 \leq n \leq 4$
  - For silica aerogels $n \simeq 3.7 \pm 0.5$
  - The empirical relationship is predicted by a variety of structural models at the limit of low density.
  - The empirical relationship does not account for variations in foam structure.

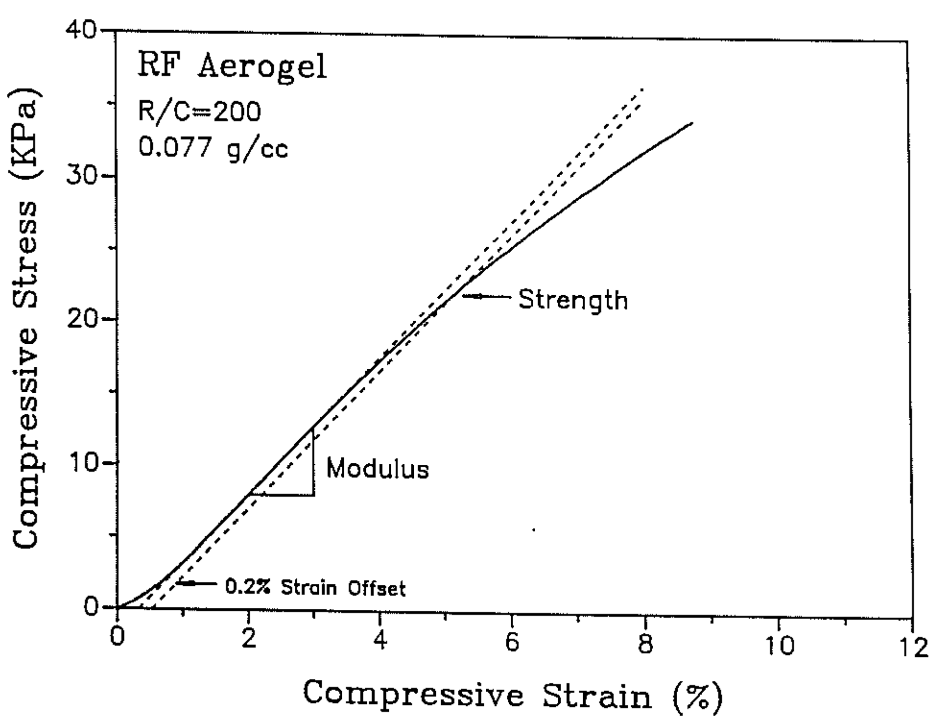
Thermal conductivity of loosely packed RF microspheres as a function of gas pressure



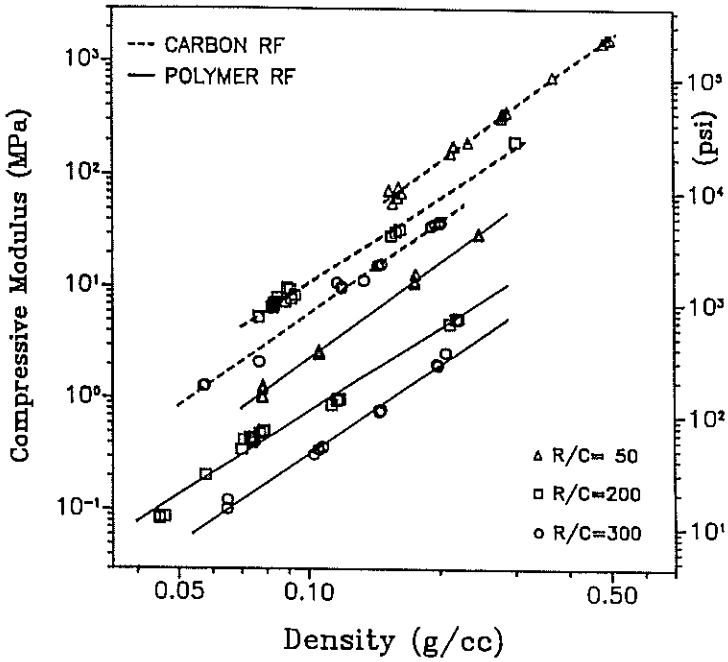
The mechanical properties of RF aerogels depend upon synthetic conditions



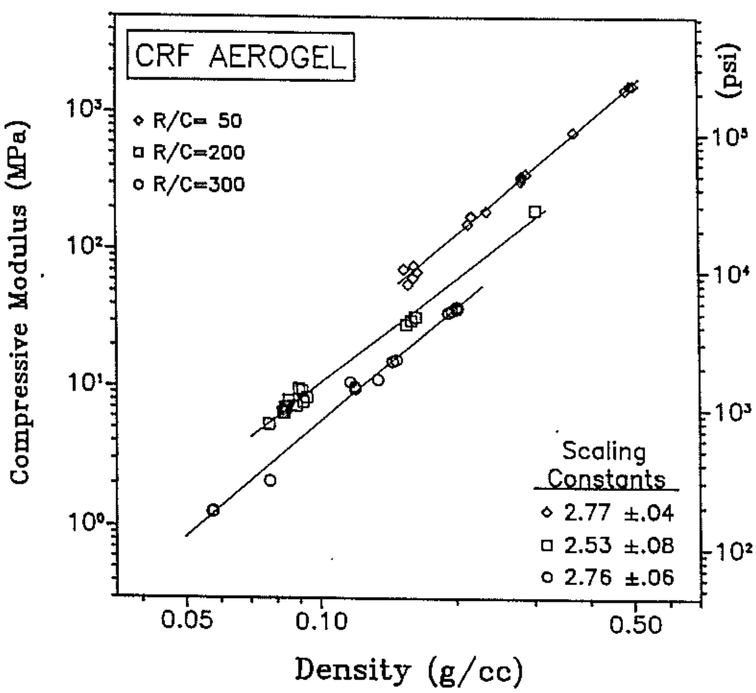
Stress-strain curve for an RF aerogel



Compressive modulus data for RF and carbon aerogels



The mechanical properties of carbon aerogels depend upon synthetic conditions

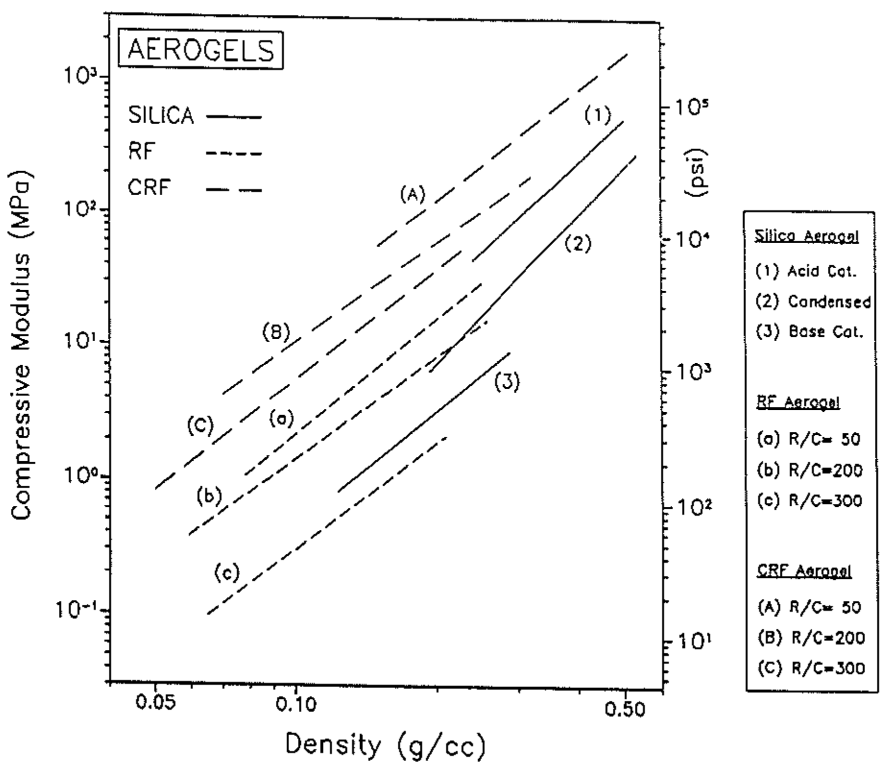


Aerogel applications and research opportunities

- **Potential applications**
  - superinsulators
  - Cerenkov detectors
  - battery electrodes
  - supercapacitors
  - permselective membranes
  - thin film dielectrics
  - acoustic impedance matching devices
  - chemical sensors
  - cosmic dust collection
  - lightweight mirrors
  - catalyst supports
  - gas storage
  - capacitive deionization

The aerogel nanostructure is responsible for the unique optical, thermal, acoustic, mechanical, and electrical properties of these porous materials

Mechanical property comparison for RF, carbon, and silica aerogels

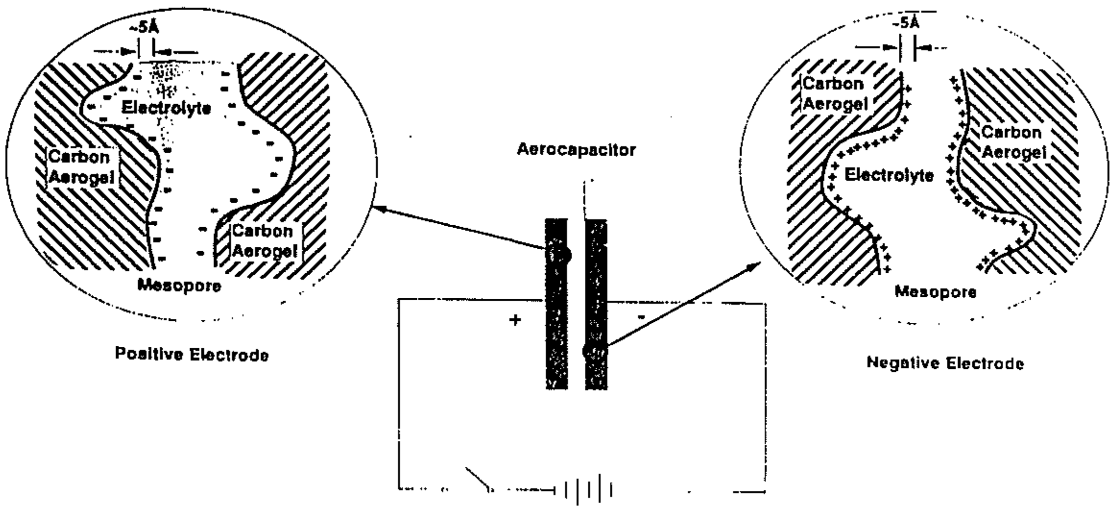


What is an Aerocapacitor?

• A high power and energy capacitor based on the voltage induced separation of charge (double layer) at an electrolyte/solid interface

• The amount of double-layer space-charge effect (capacity) scales directly with the amount of usable electrode surface area

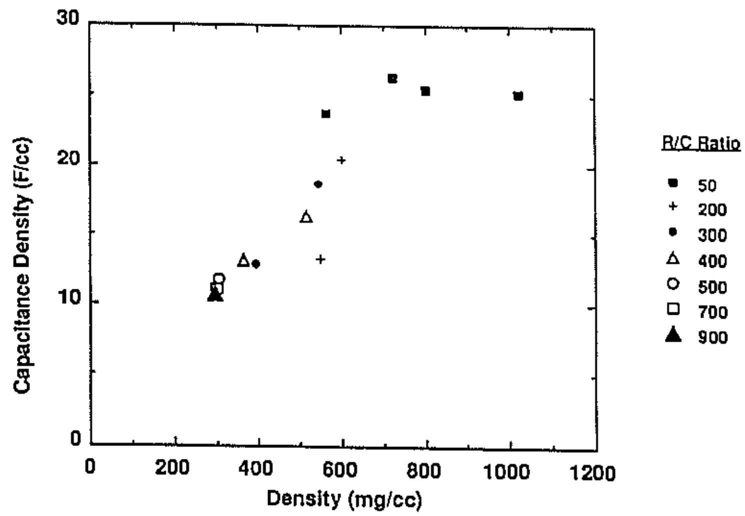
• The Aerocapacitor uses LLNL high surface area carbon Aerogels as both the positive and negative electrodes



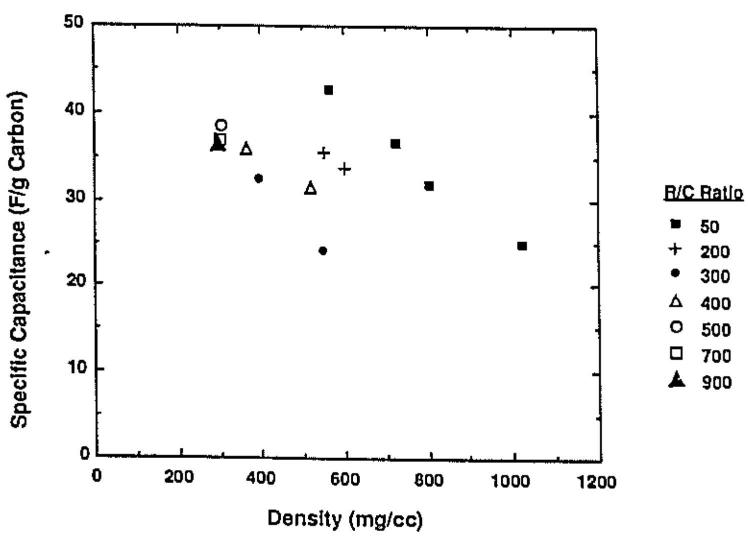
Carbon aerogels are being tailored for supercapacitor applications

- pore size distribution
- surface area
- surface groups (e.g. -COOH, -OH)
- carbon structure (amorphous vs graphitic)
- electrical conductivity
- incorporation of selected dopants

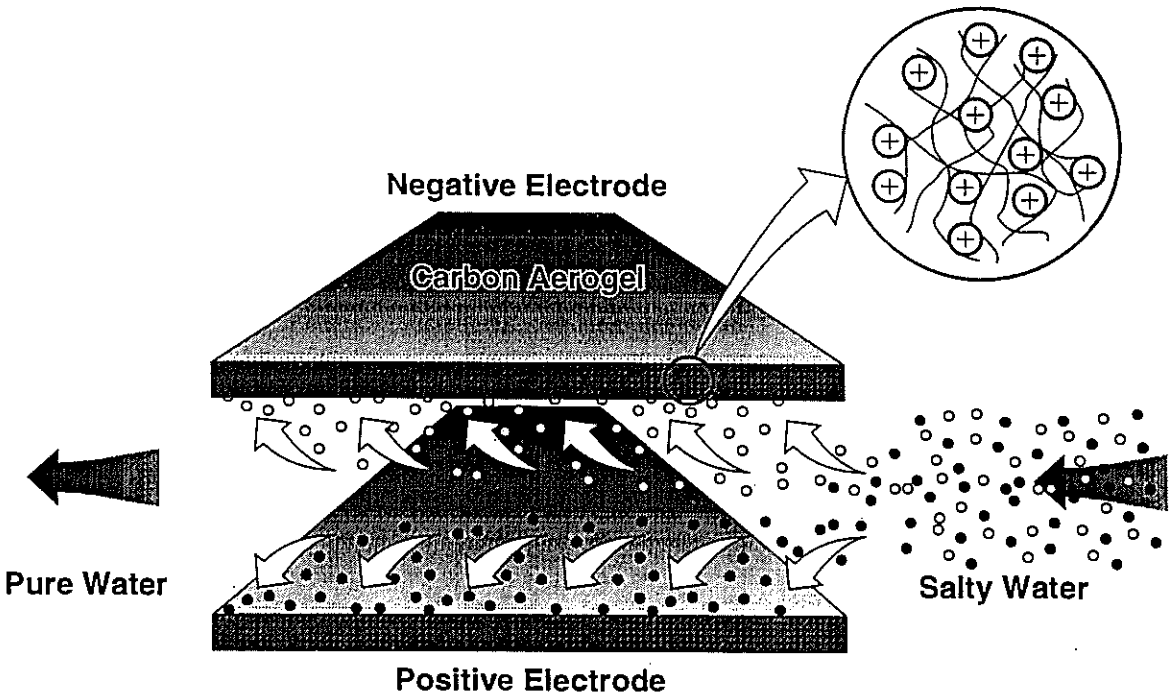
Capacitance Density vs. Density



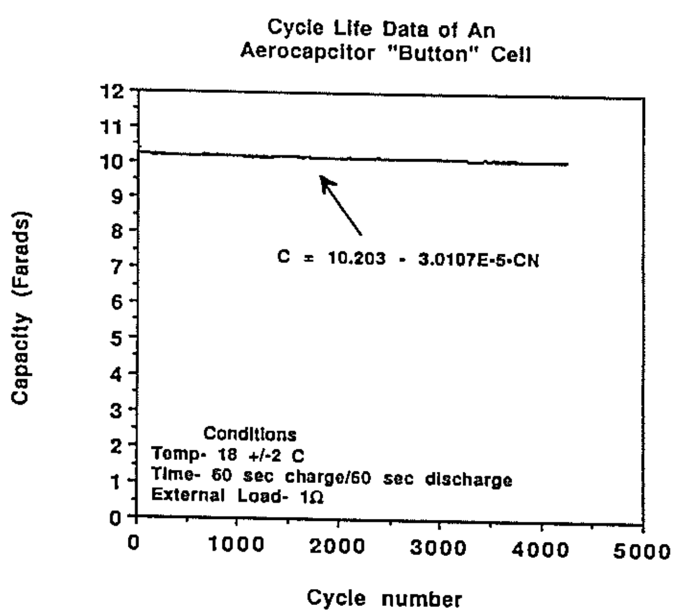
Specific Capacitance (Dry) vs. Density

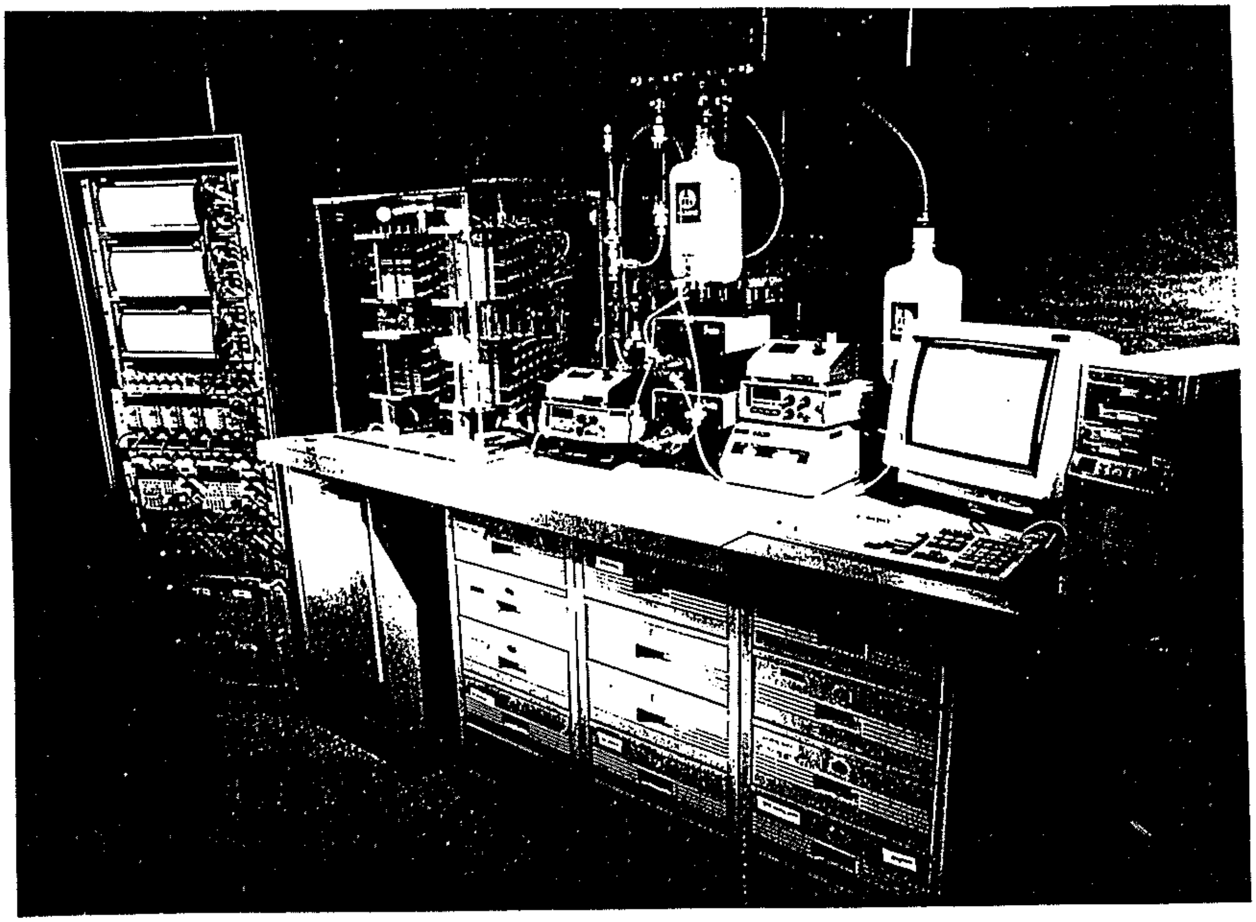


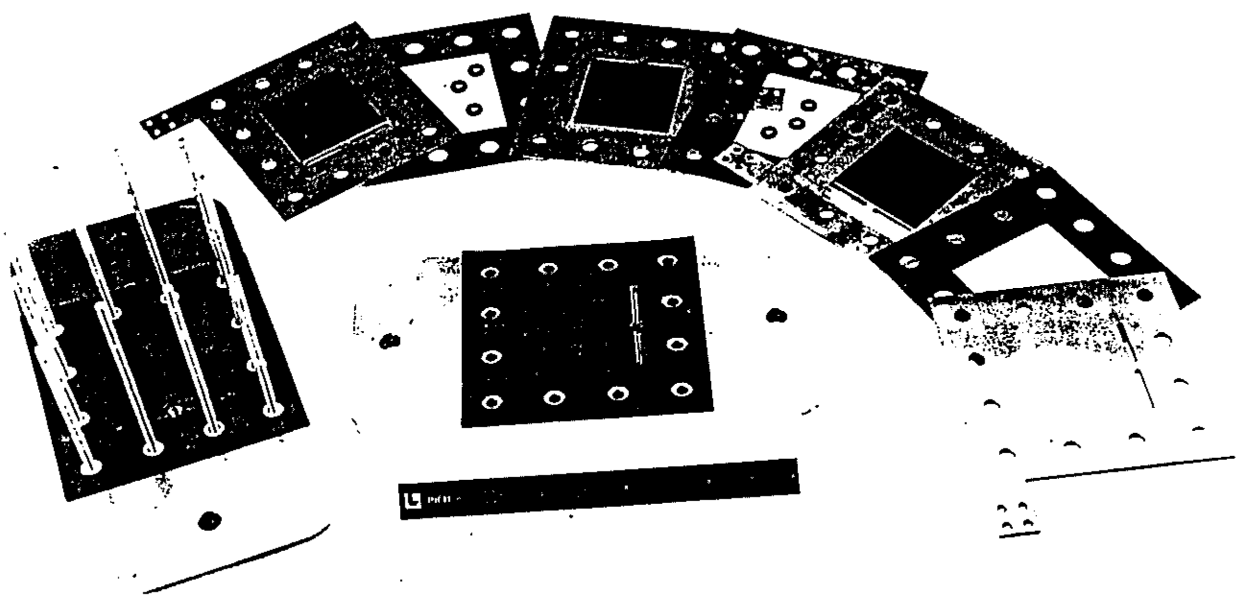
Capacitive Deionization



The aerocapacitor is projected to have 85% of its original capacity after 100 K cycles



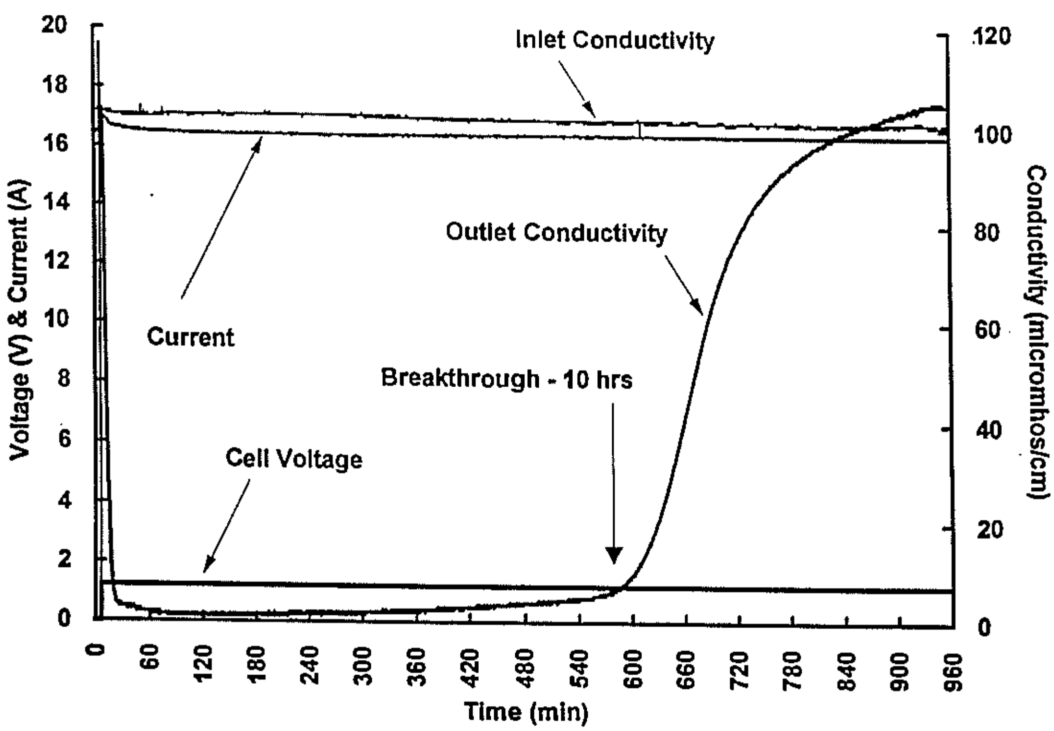




Summary

- Aerogels are a special class of open-cell foams that have unique optical, thermal, acoustic, mechanical, and electrical properties.
- Sol-gel chemistry can be used to tailor the structure and properties of aerogels at the nanometer scale.
- Alternative processing methods have been demonstrated to produce both inorganic and organic aerogels as microspheres, powders, thin films, and composites
- New inorganic/organic hybrid aerogels have been synthesized and show promise as ceramic precursors.
- Commonalities between inorganic and organic aerogels suggest that a universal model might be developed for the sol-gel polymerization of multifunctional monomers in dilute solution.

Single pass experiment with NaCl solution



Acknowledgment

Personnel

- C.T. Alviso
- T. M. Tillotson
- Dr. J. Farmer
- Dr. X. Lu

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- OBES - Division of Advanced Energy Projects
- ARPA - Technology Reinvestment Program

Organic/Inorganic Hybrid Polymers

Michael Michalczyk	Star Gels: New Single Component Organic/Inorganic Network Materials
Barry Arkles	Commercial Production of Inorganic/Organometallic Hybrids
Frank J. Feher	Rational Synthesis of Si/O and Si/O/M Frameworks
Helmut Schmidt	Inorganic/Organometallic Hybrid Polymers: Routes to Industrial Applications

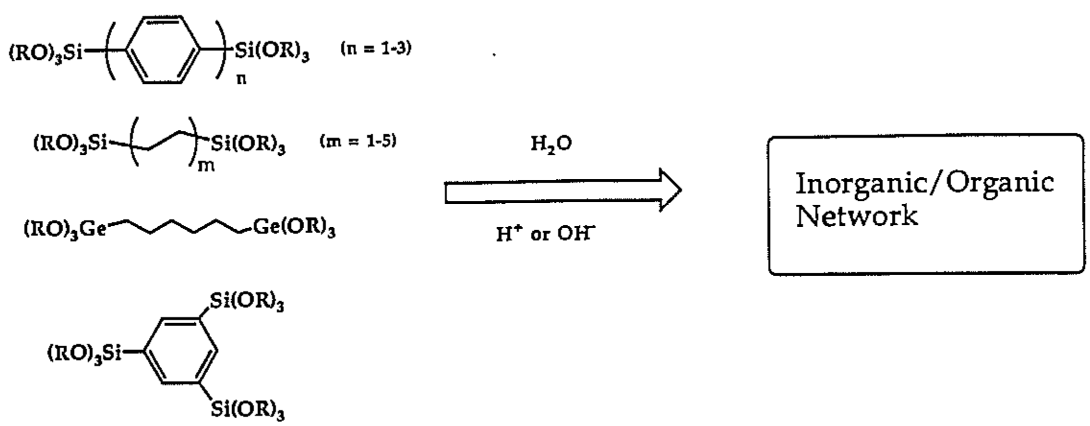
Star Gels: New Single Component Organic/Inorganic Network Materials

Mike Michalczyk
Ken Sharp

DuPont Central Research

February 13, 1995

Single Component Inorganic/Organic Hybrid Materials



K. Shea, D. Loy, O. Webster, Chem. Mater., (1989), *1*, 572
R. Corriu, J. Moreau, P. Thepot and M. Man, Chem. Mater., (1992), *4*, 1217
H. Oviatt, K. Shea, J. Small, Chem. Mater., (1993), *5*, 943
G. Jamison, D. Loy, K. Shea, Chem. Mater., (1993), *4*, 1193
B. Tamami, C. Betrabet, G. Wilkes, Polymer Bulletin, (1993), *30*, 39

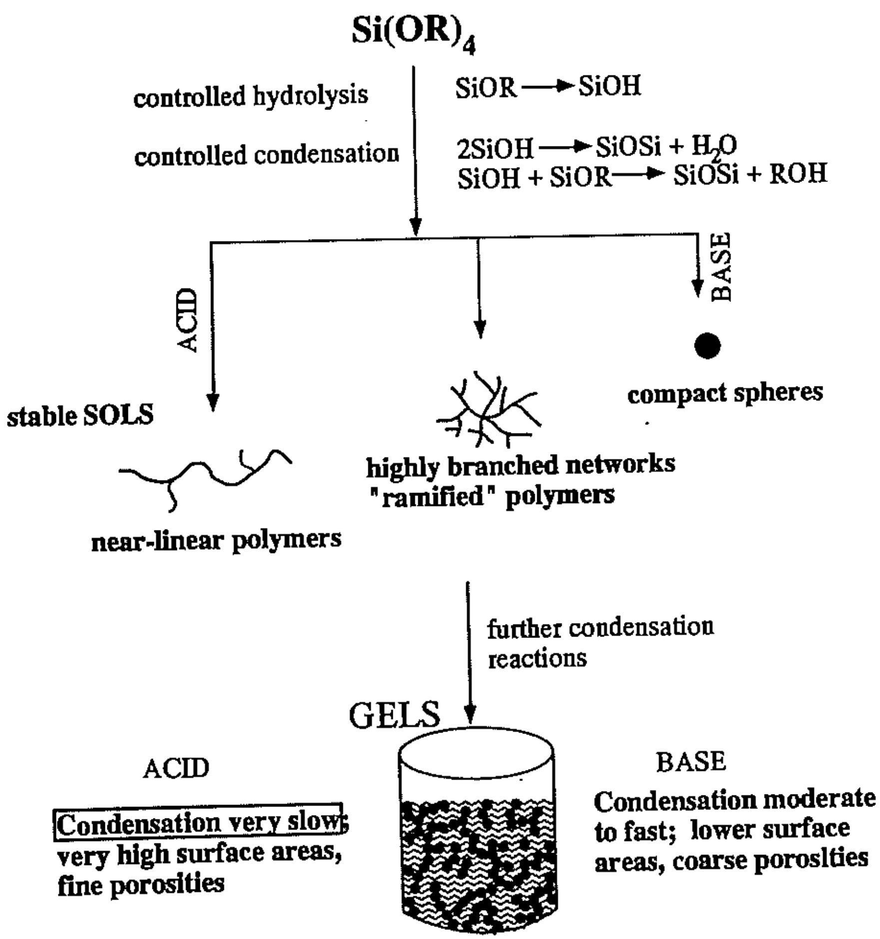
Inorganic/Organic Hybrid Materials

- Interpenetrating networks (IPN's) (polymers + silica)
- Organically modified silicates (Ormosils, Ceramers)
- Single component inorganic/organic hybrids (Star-gels, aryl and alkyl silsesquioxanes)

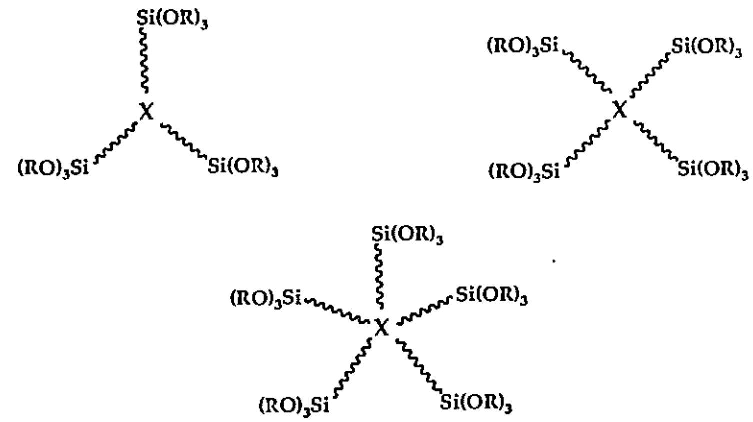
Why? To obtain new, unique materials and properties that can not be obtained by either the inorganic or organic phases alone, or by just mixing.

Review: B. M. Novak, Adv. Mater., (1993), **5**, 422
C. Sanchez, F. Ribot, New J. Chem., (1994), **18**, 1007

ACID AND BASE-CATALYZED SOL/GEL



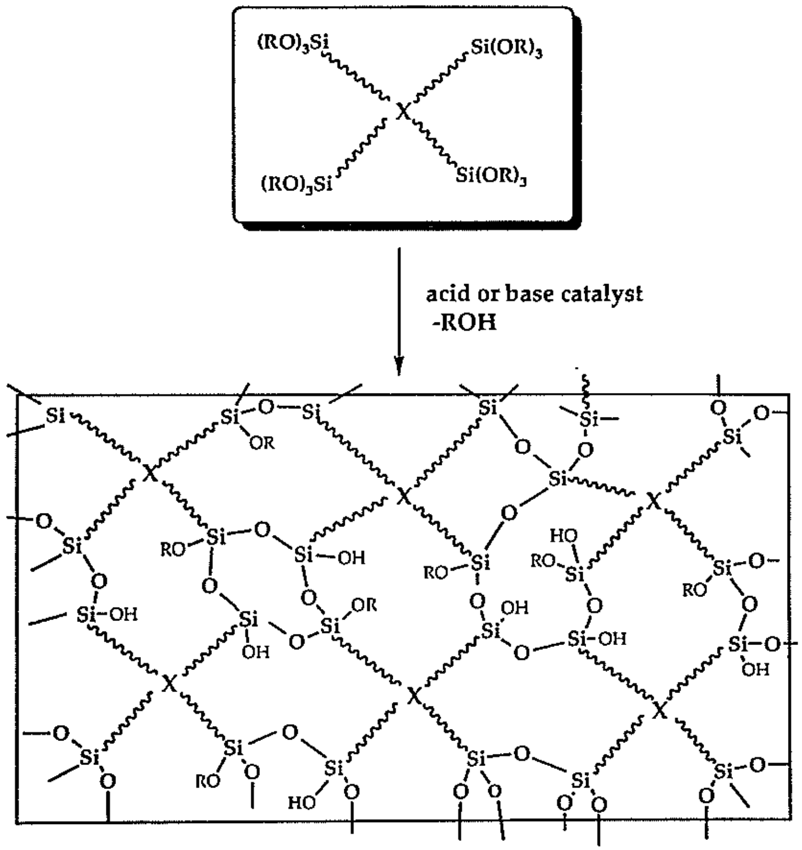
Star Sol-Gel Precursors
(Star Gels)



where: X = star core (atomic •, linear ⌃ or cyclic ⬡ cores)

~~~~~ = flexible arm (-CH_2CH_2- or -$CH_2CH_2CH_2$-)
~~~~~

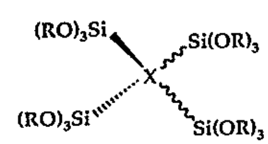
Formation of a Star-Gel Network



X = star core

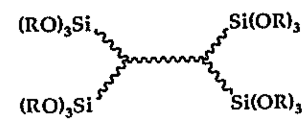

= flexible arm connecting star core to polysilicate (molecular shock absorbers)

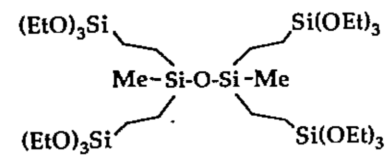
Synthesized Star-Gel Precursors

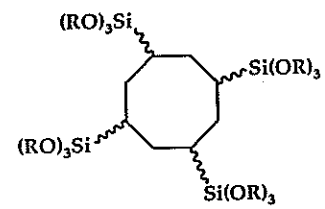


$Si(CH_2CH_2Si(OEt)_3)_4$
$Si(CH_2CH_2CH_2Si(OEt)_3)_4$
$Si(CH_2CH_2CH_2CH_2Si(OEt)_3)_4$

$Si(OSiMe_2CH_2CH_2Si(OEt)_3)_4$
$Si(OSiMe_2CH_2CH_2CH_2Si(OEt)_3)_4$



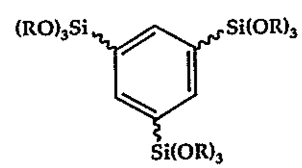




$((EtO)_3SiCH_2CH_2)MeSiO)_4$
$((EtO)_3SiCH_2CH_2CH_2)MeSiO)_4$

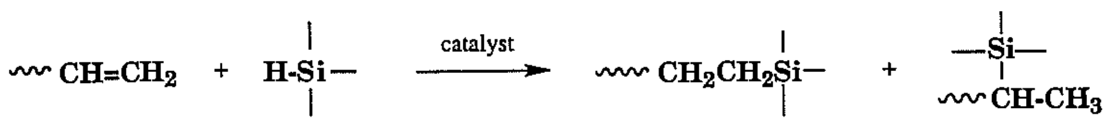
$((EtO)_3SiCH_2CH_2)MeSiO)_5$
$((EtO)_3SiCH_2CH_2CH_2)MeSiO)_5$

1,2,4-$((EtO)_3SiCH_2CH_2)_3C_6H_9$



1,3,5-$((EtO)_3SiCH_2CH_2Me_2Si)_3C_6H_3$

Hydrosilylation

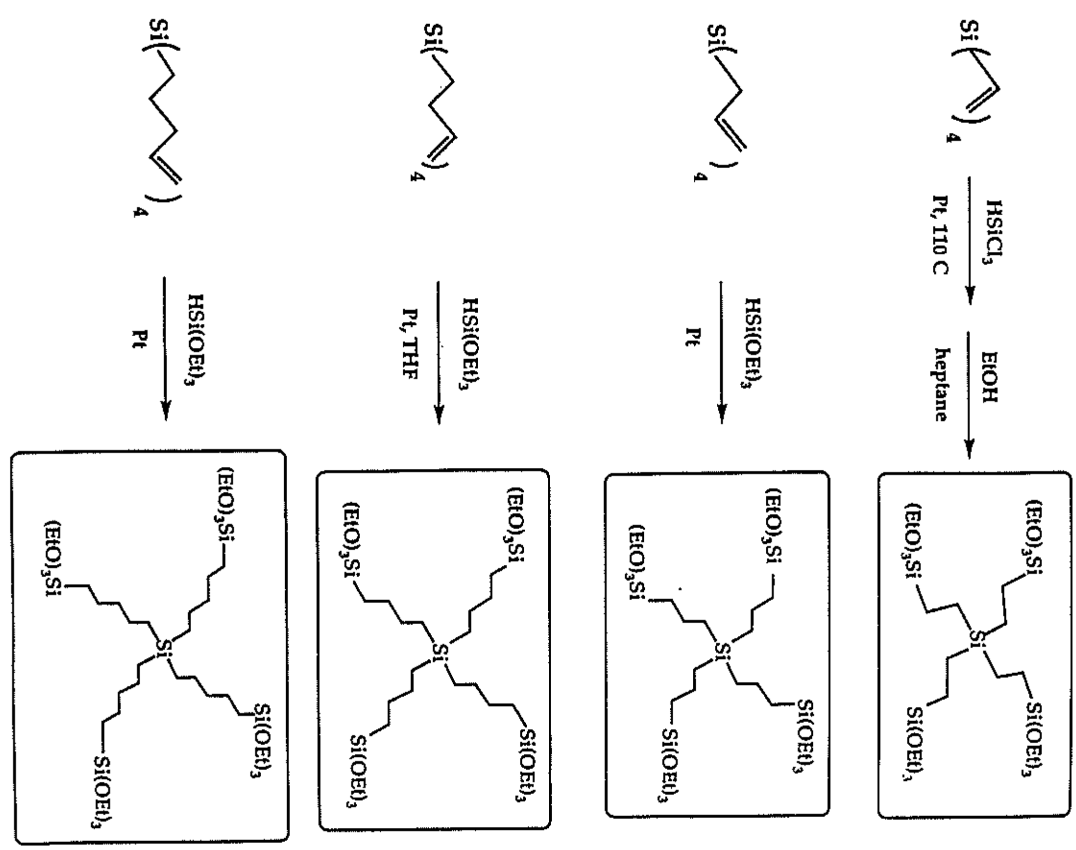


ß-adduct (Markovnikov)

α-adduct (Anti-Markovnikov)

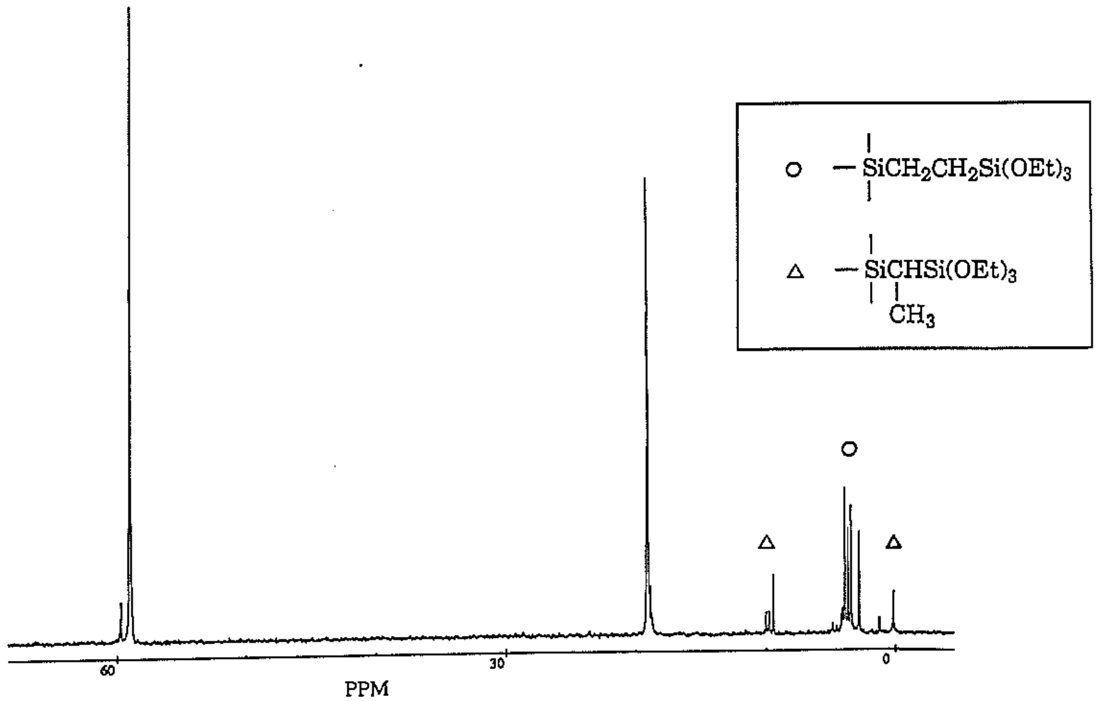
- Platinum is the catalyst of choice
- α-adduct is not wanted and minimized by the use of $HSiCl_3$/THF. Works best with vinyl ($CH=CH_2$) groups

Tetra-Functional Stars

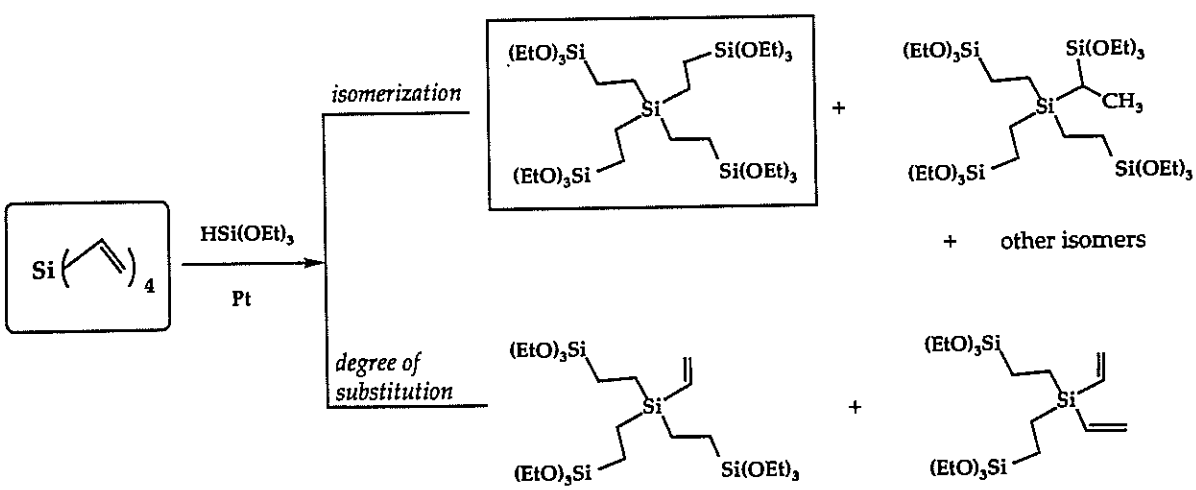


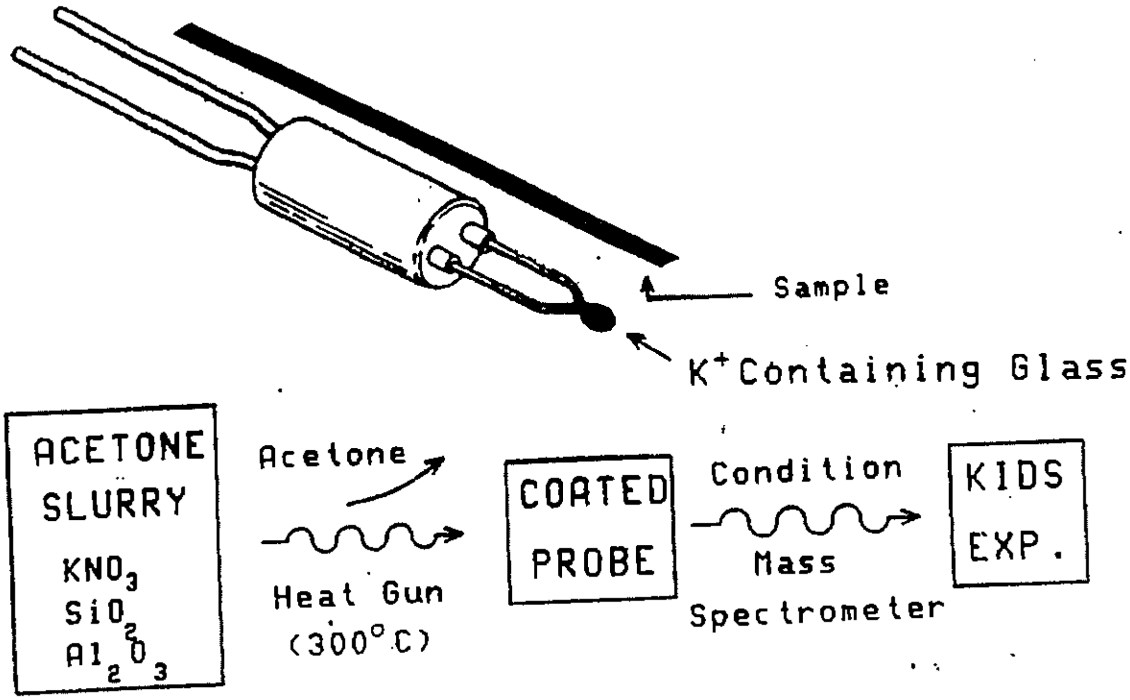
^{13}C NMR Spectrum of $Si(CH_2CH_2Si(OEt)_3)_4$

(from HSi(OEt)3)



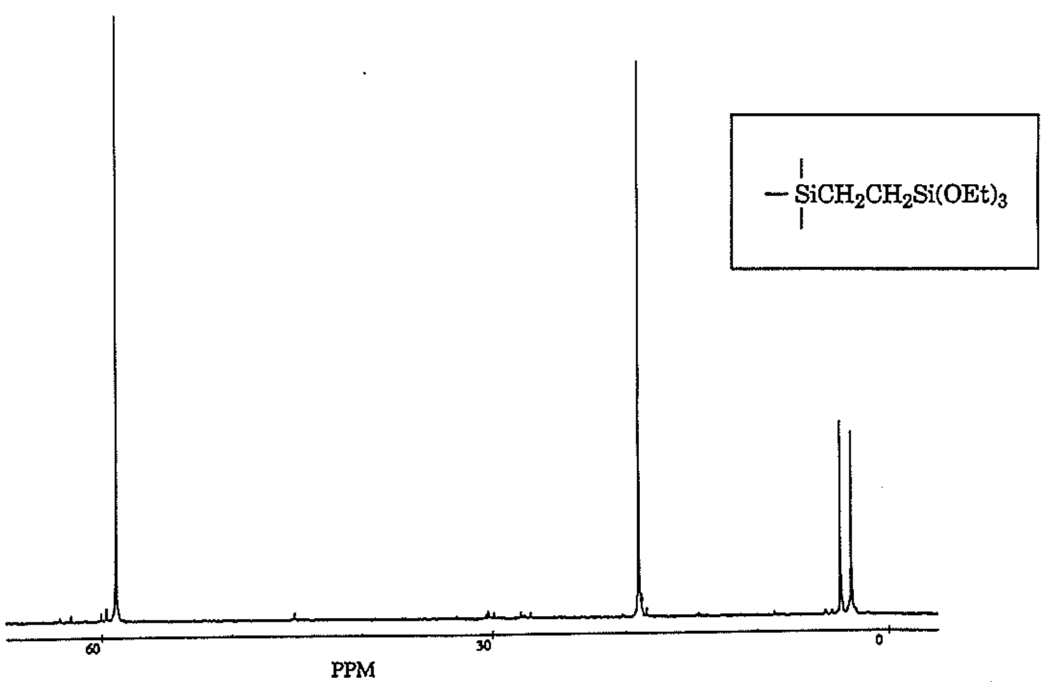
Synthetic Problems





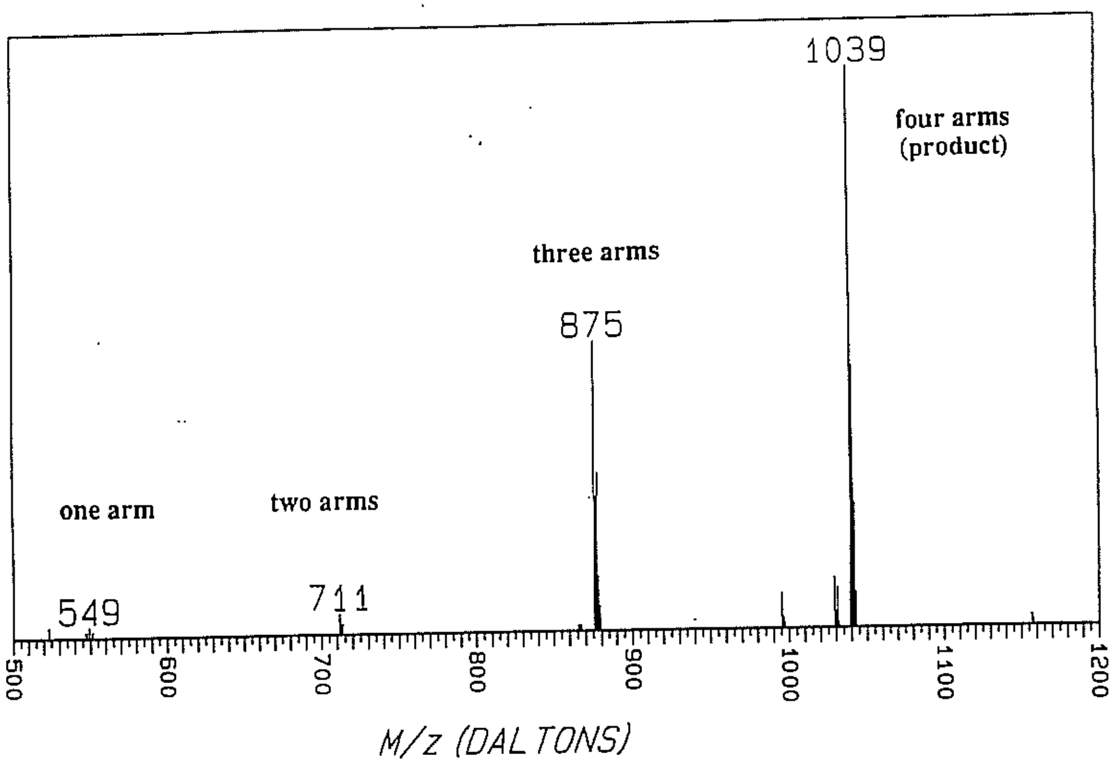
^{13}C NMR Spectrum of $Si(CH_2CH_2Si(OEt)_3)_4$

(from HSiCl3/THF)



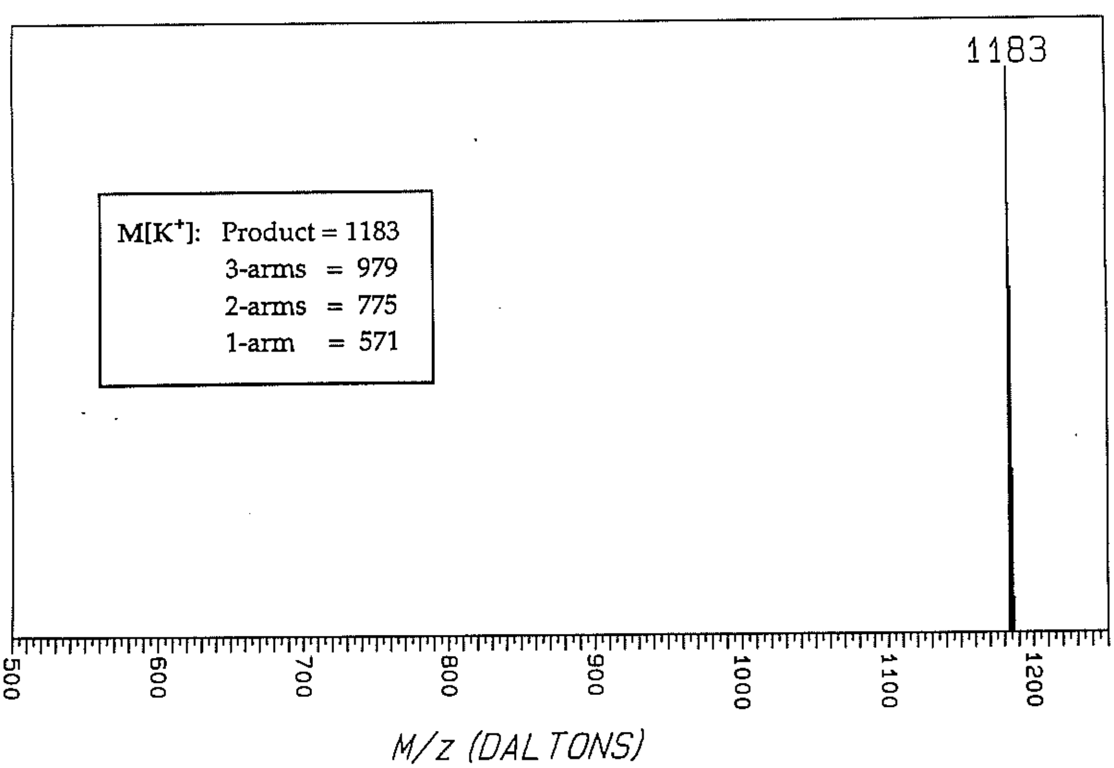
K+IDS MASS SPECTRUM

cyclo-(MeSiO(CH=CH_2))$_4$ + HSi(OEt)$_3$ -----------> (cyclo-(MeSiO(CH_2CH_2Si(OEt)$_3$)$_4$



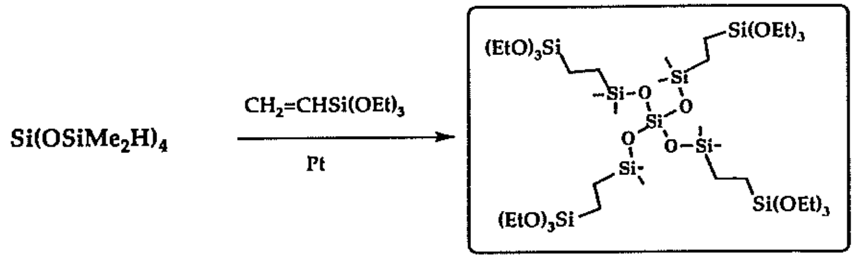
K+IDS MASS SPECTRUM

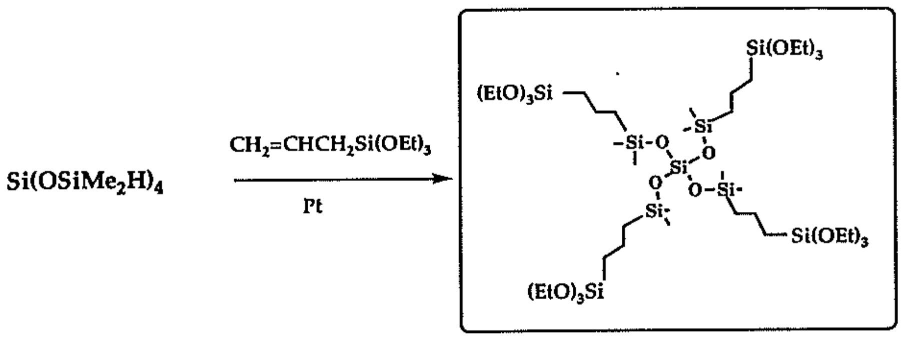
Si(OSiMe$_2$H)$_4$ + 4 CH_2=CHCH$_2$Si(OEt)$_3$ ---------> Si(OSiMe$_2CH_2CH_2CH_2$Si(OEt)$_3$)$_4$

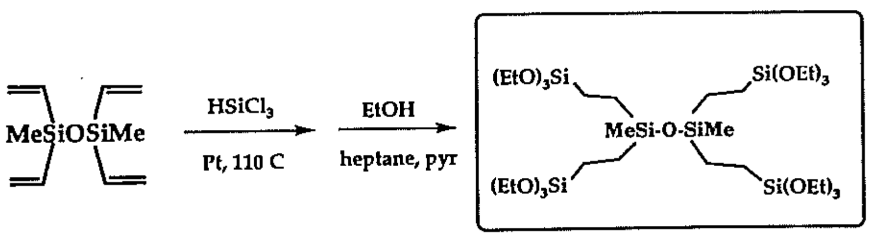


K+IDS MS: W. J. Simonsick, J. Appl. Poly. Sci. (Appl. Poly. Symp.), (1989), 43, 257

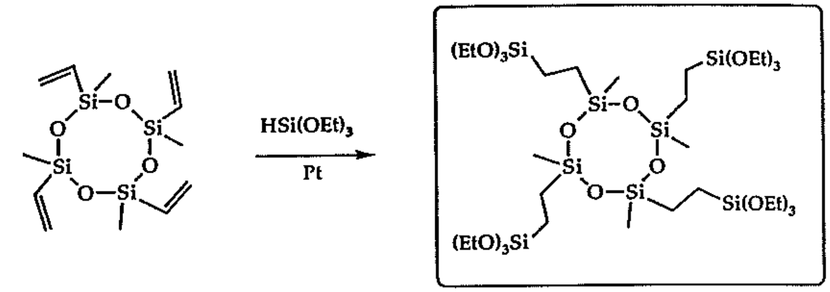
Tetra-Functional Stars

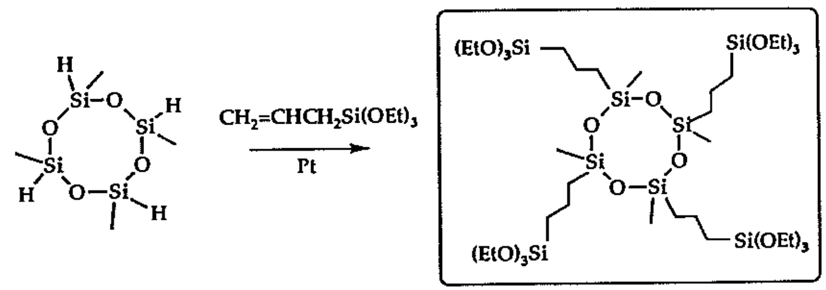






Cyclic Stars

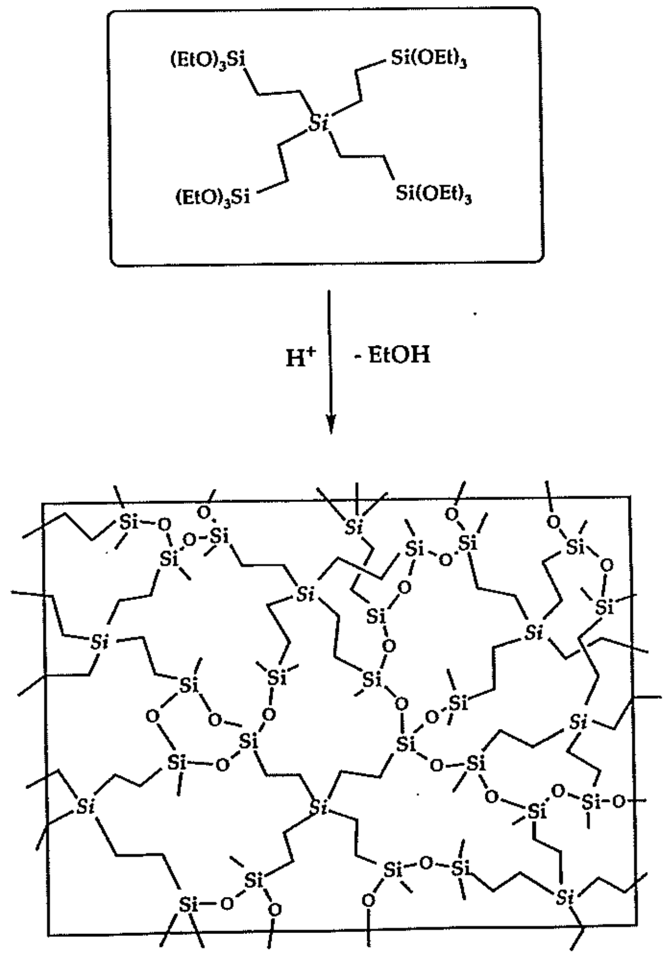




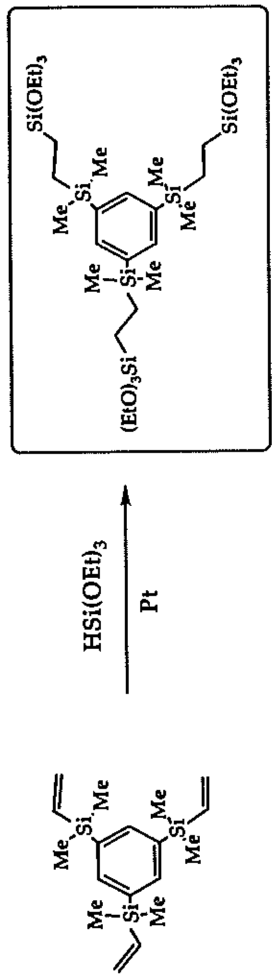
- Cyclopentasiloxane systems have also been synthesized

References: R. P. Supernant, US Patent 4,461,867 (7/24/84)
E. P. Plueddemann, US Patent 4,698,085 (8/25/87)
I. Ona, et. al., Euro Patent Appl 0,183,533 (11/27/85)

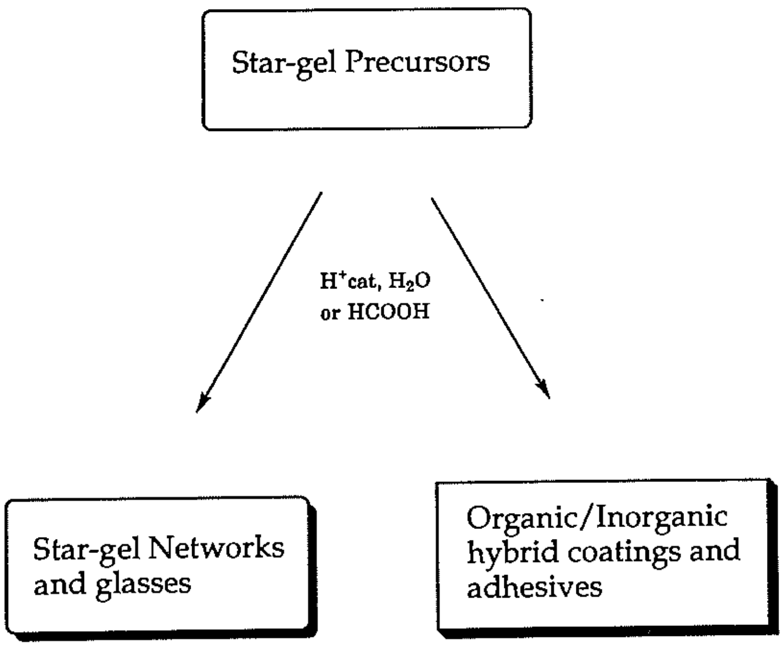
Formation of Star-Gel Network

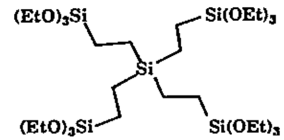


Aryl Stars

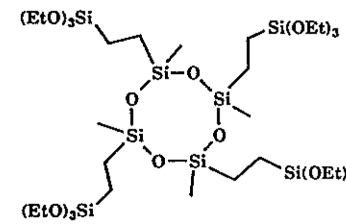


Formation of Star-Gel Materials

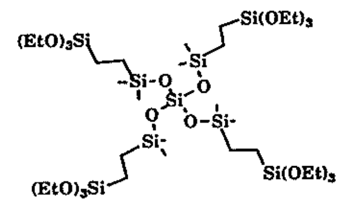




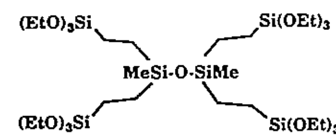
Star 1



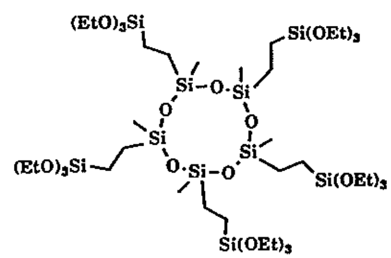
Star 2



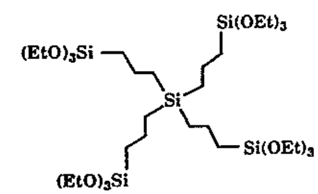
Star 3



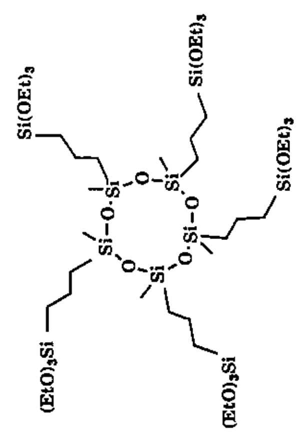
Star 5



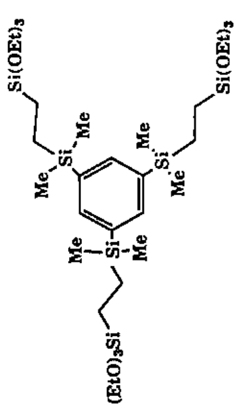
Star 10



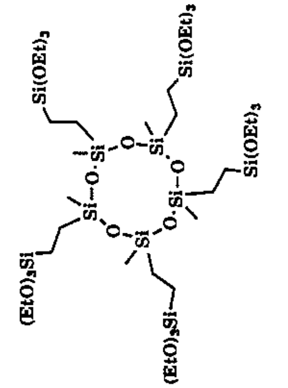
Star 11



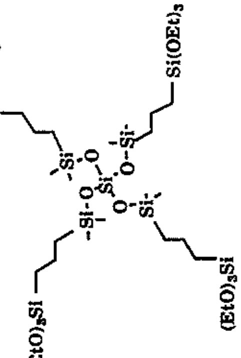
Star 13



Star 19



Star 12



Star 14

TWO COMPONENT, NON-AQUEOUS ROUTE TO SILICA GEL

Via formic or other strong carboxylic acids

$Si(OR)_4$ + HCOOH (or CF_3COOH)

leads to rapid hydrolysis and gelation of silane

without additional water or catalyst

- Form transparent gels in as little as 25 min. at 25° -- 100-500x faster than "normal" acid catalysis
- System creates its own water for hydrolysis
- Acid serves as solvent, water source and catalyst for both hydrolysis and condensation
- Limiting reaction

2 HCOOH + $Si(OEt)_4$ = SiO_2 + 2 EtOH + 2 EtOOCH

STAR GELATION PHENOMENOLOGY

$Si[CH_2CH_2Si(OEt)_3]_4$

+ HCOOH
"Immiscible" -- nearly instant gelation!
Attenuate reaction with THF cosolvent

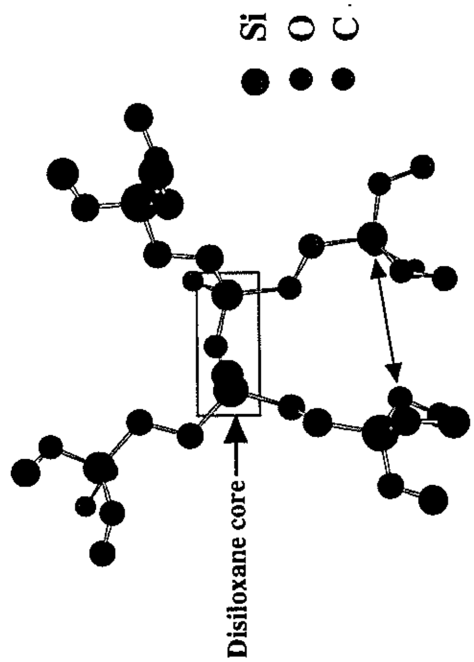
+ water/EtOH/H^+
Clear gels over entire pH range
Rapid gel at pH 7!

+ water/EtOH/NH4OH
Some problems with miscibility

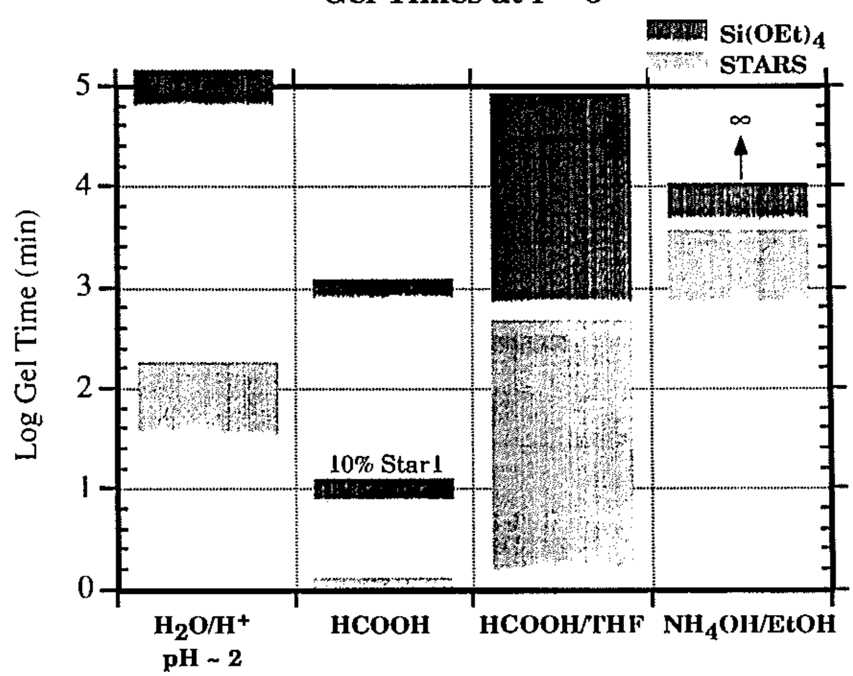
+ water/EtOH/F^-
Only small increase in gel rate rel. to OH^-

NETWORK-FORMING (CONDENSATION) CHEMISTRY

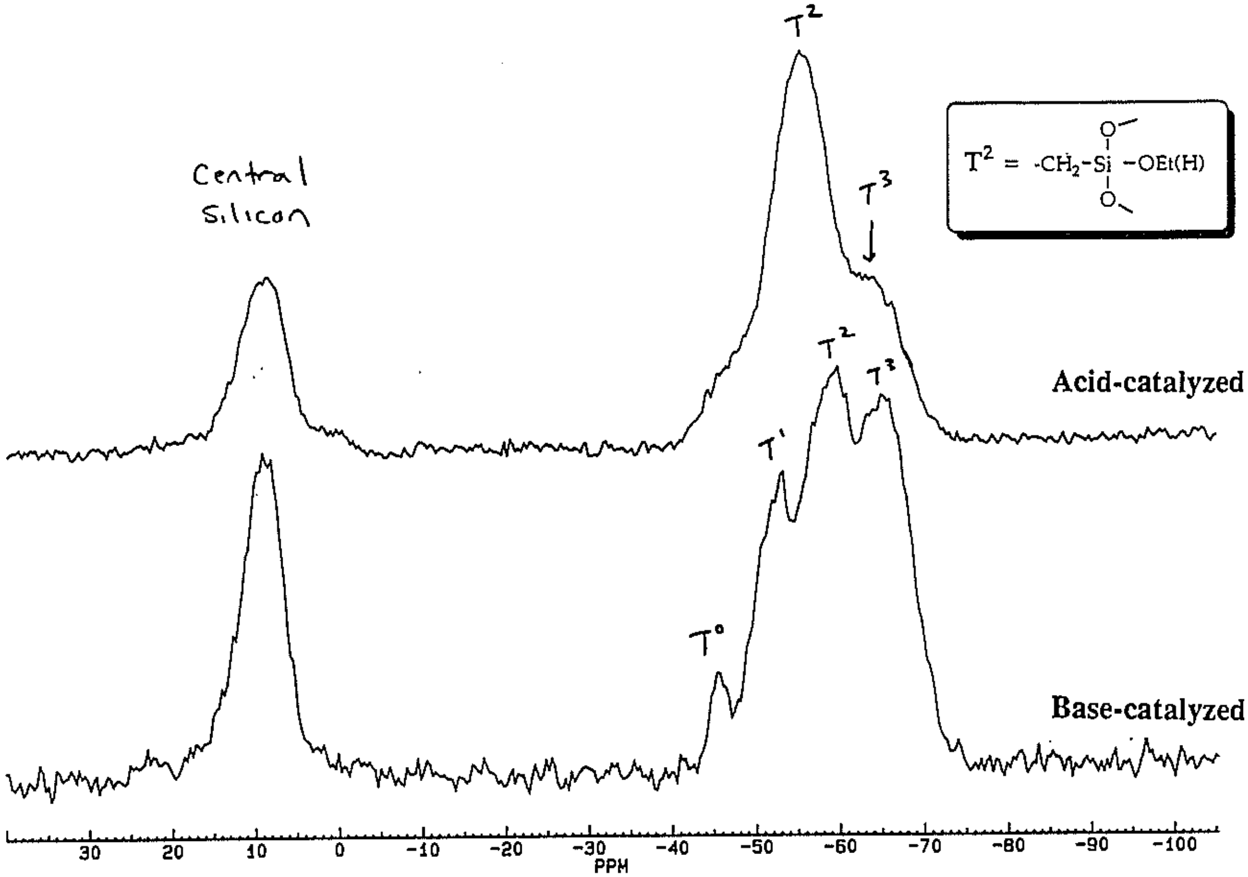
For Stars with long, flexible arms, will *intra*molecular condensation be a major factor?



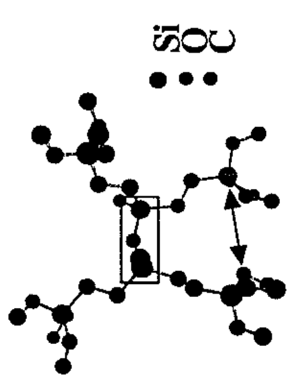
Gel Times at r ~ 3



^{29}Si CP/MAS NMR of Dry Gels from $Si(CH_2CH_2Si(OEt)_3)_4$



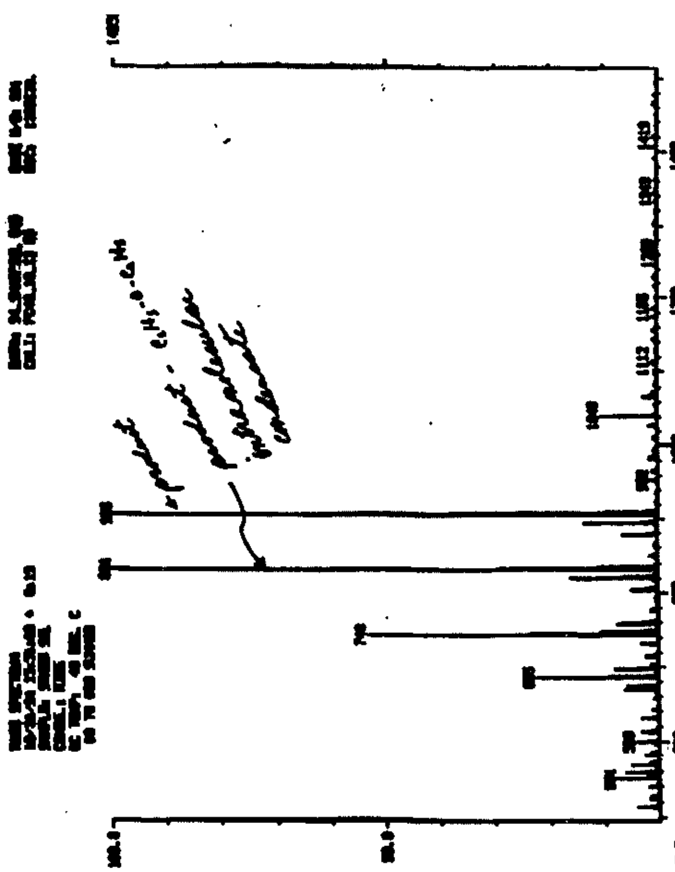
INTRAMOLECULAR CONDENSATION



Si NMR isn't much help -- insufficient chem. shift distinction

Use KIDS mass spec on partially reacted sol

Shows appreciable amount in intramol. "dimer"



HETEROGENEOUS GELS

Stars can be combined with $Si(OR)_4$ in (apparently) any proportion to give mixed T/Q Gels

Properties are far from rule-of-mixtures predictions

TEOS + 10% Star 1
- **Porosity *increases* 10%**
- **Gel time decreases 100x!**
- **Toughness - ?**

Si NMR best used to verify network incorporation efficiency. Should not use CP for Q^4 structures

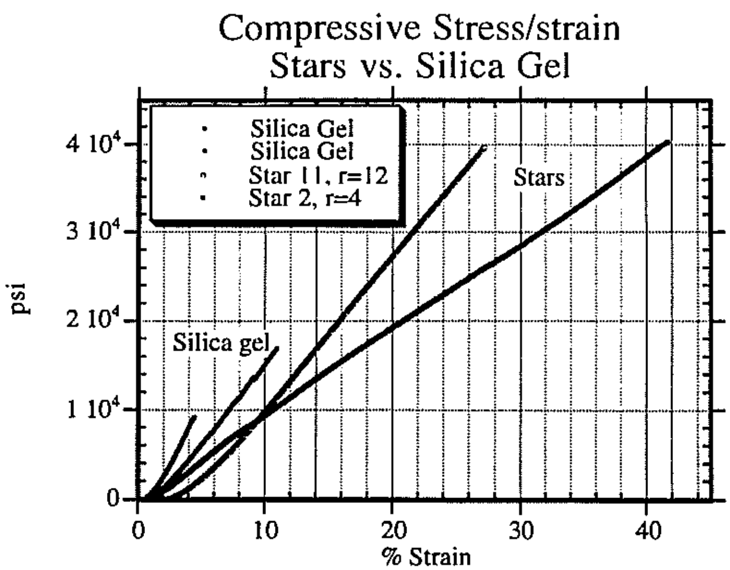
POROSITY OF DRY GELS

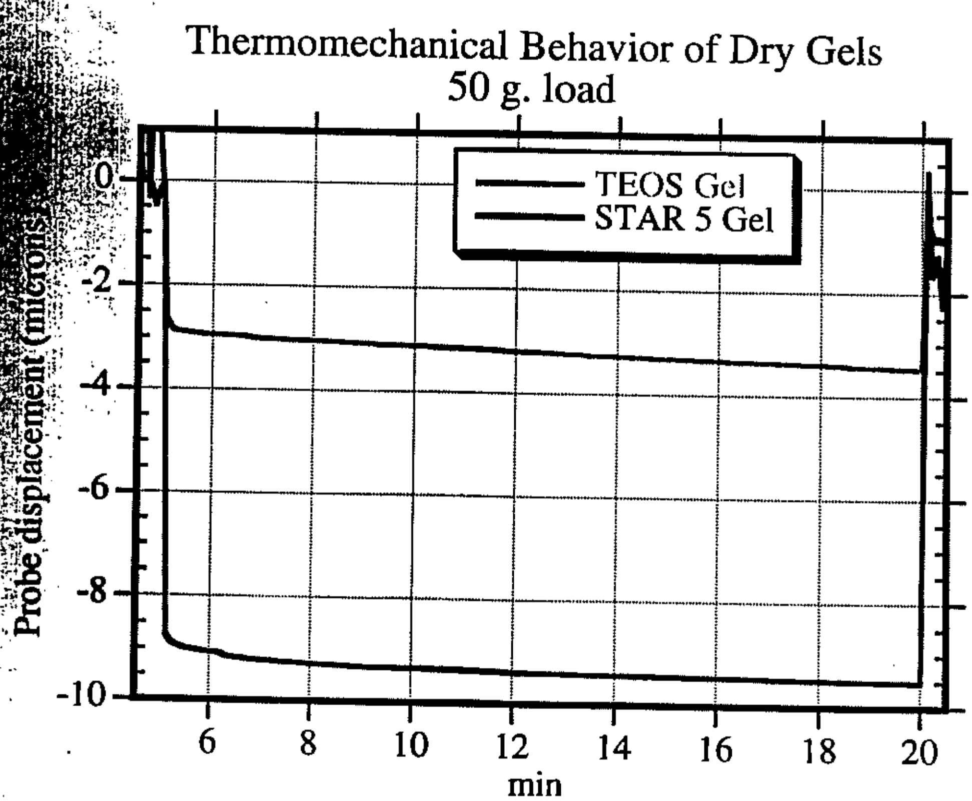
Three techniques used to look for open porosity

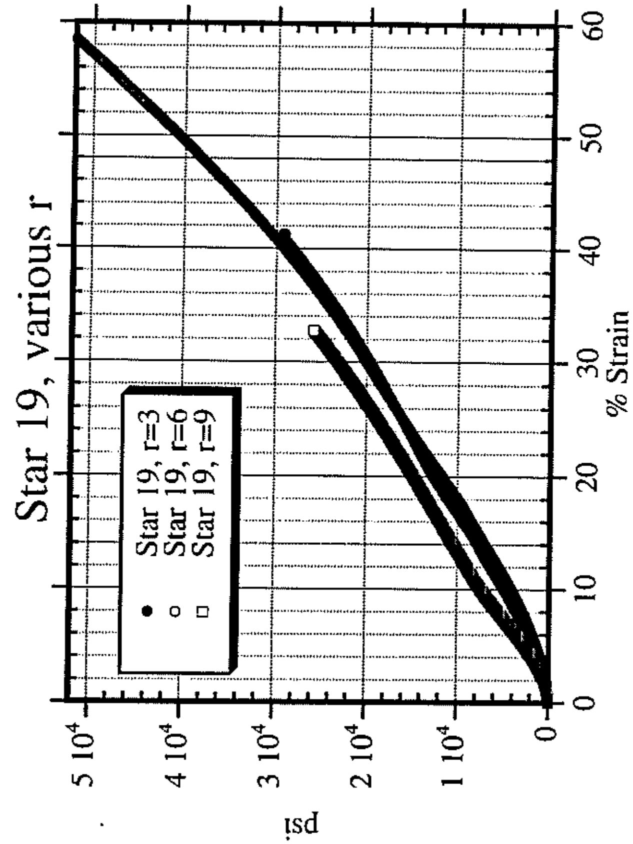
- **Nitrogen adsorption isotherms (77 °K)**
- **Bulk vs skeletal density (He pycnometry)**
- **Behavior on water immersion**

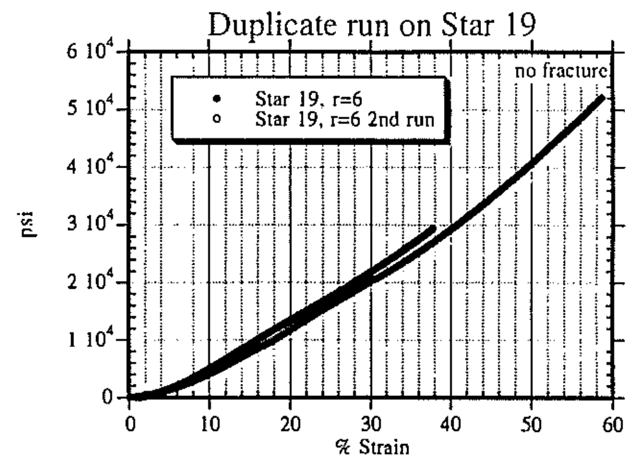
All have shown dried Star gels to be non-porous

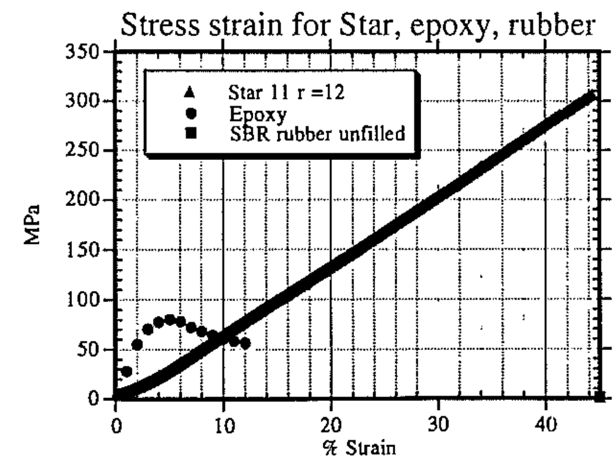
but base-catalyzed gels not yet explored. . .

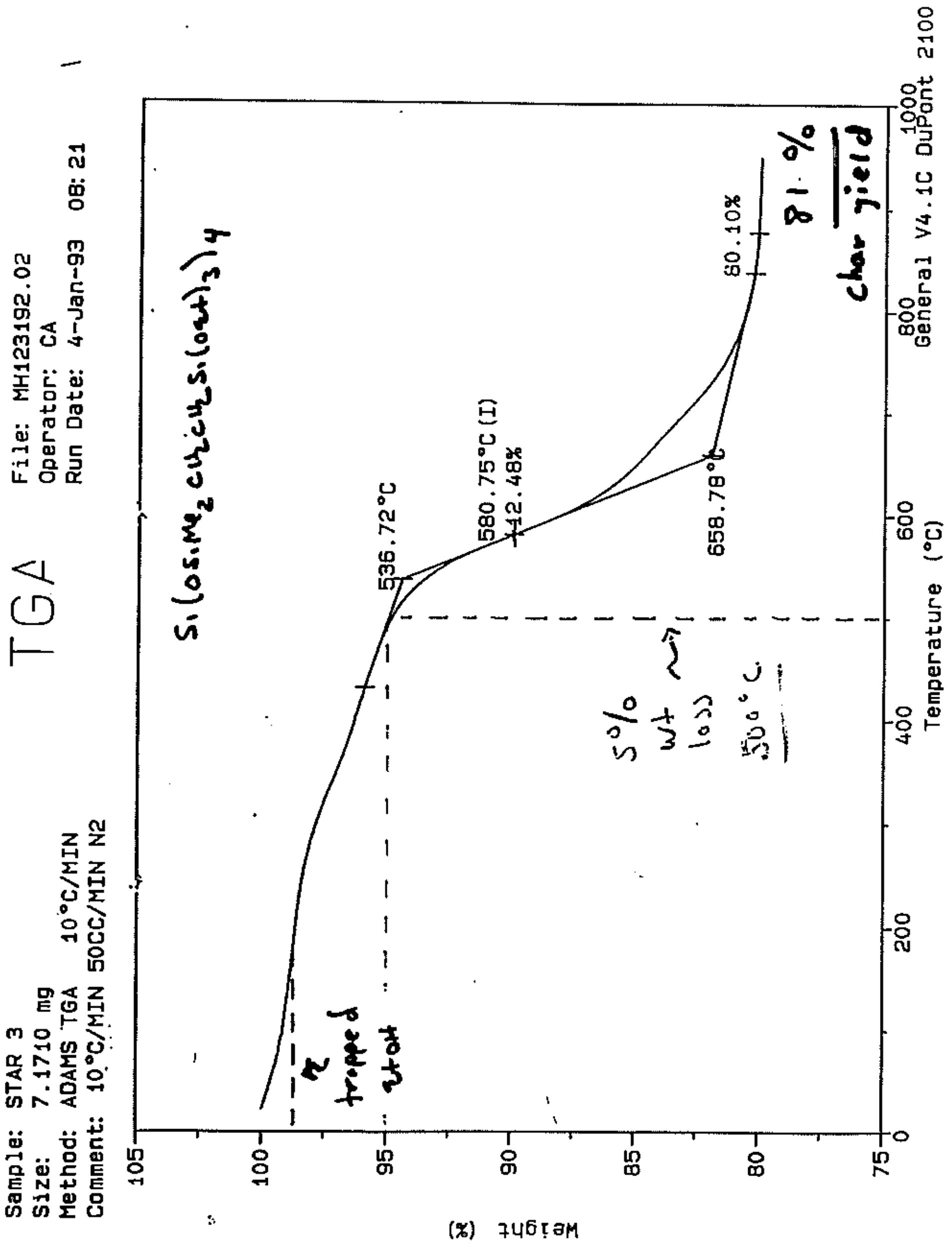

Compressive Stress/strain
Stars vs. Silica Gel
Silica Gel
Silica Gel
Star 11, r=12
Star 2, r=4
Stars
Silica gel
psi
4 10⁴
3 10⁴
2 10⁴
1 10⁴
0
0
10
20
30
40
% Strain


Thermomechanical Behavior of Dry Gels
50 g. load
TEOS Gel
STAR 5 Gel
Probe displacement (microns)
0
-2
-4
-6
-8
-10
6
8
10
12
14
16
18
20
min


Star 19, various r
Star 19, r=3
Star 19, r=6
Star 19, r=9
psi
% Strain


Duplicate run on Star 19
Star 19, r=6
Star 19, r=6 2nd run
no fracture
psi
% Strain


Stress strain for Star, epoxy, rubber
Star 11 r =12
Epoxy
SBR rubber unfilled
MPa
% Strain



SWELLING BEHAVIOR

For fully dried Star glasses:

No significant swelling observed in either THF or methylene chloride

IMPACT RESISTANCE

Measured crudely by dropping weight from various heights onto disks of silica gel or Stars

Stars definitely show enhanced impact resistance

ABRASION RESISTANCE

When combined with silane-functional polymers, Stars show superior abrasion resistance to simple alkyl(trialkoxy) silanes

A Taber abrader was used to assess abrasion resistance

AEROGELS

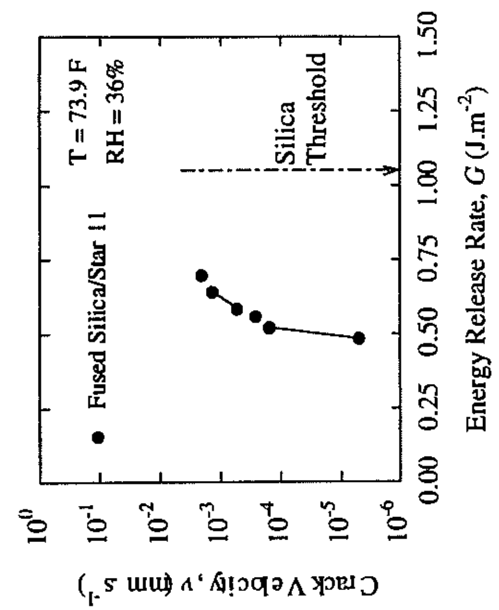
Aerogels are very low density porous solids generated by supercritical fluid drying

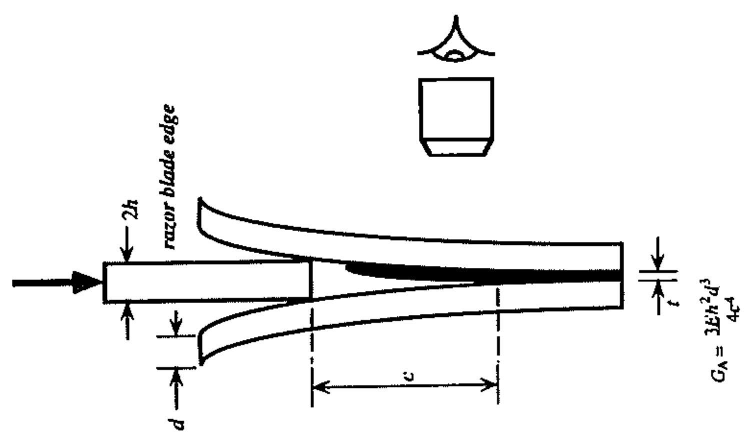
They are extraordinarily good acoustic and thermal insulators, but are very fragile

Stars could be useful precursors to tough low-density solids

Preliminary experiments using supercritical CO_2 show good compatibility, although some shrinkage occurred during drying.

Glass Adhesion via Double Cantilever Beam Test





SUMMARY

- Star Gel precursors with flexible cores and arms and up to 15 reactive alkoxy groups have been synthesized in high yields
- Cores can be atomic, linear segments or cyclics
- Gelation rates can be extremely high, but can be attenuated with solvent
- Star Gels show appreciable toughness in compression, impact and abrasion resistance
- Co-networks with tetraalkoxysilanes or silane-functional polymers are possible
- Stars offer prospect of tough aerogels

Commercial Hybrid Inorganic-Organic Polymers

Barry Arkles

Gelest, Inc.
612 William Leigh Drive
Tullytown, PA 19007
(215) 547-1015

Crosslinkable Polyethylene (XLPE) Through Siloxane Bond Formation

Applications:

- Wire & Cable Insulation - Telephone, Medium Voltage Power Cables
- Heat-Shrinkable Tubing
- Compression Resistant Foam

Crosslinkable Polyethylene - Graft

Sioplas® Process

H. Scott — US Pat. 3,646,155 — 1972

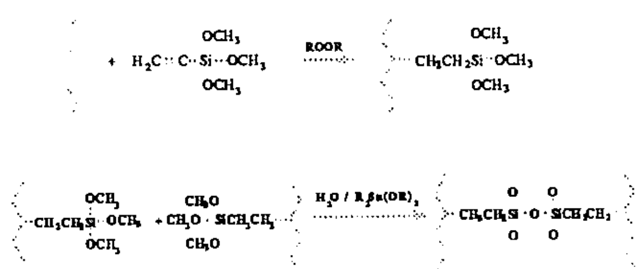
2-step Post-Polymerization

Monosil® Process

P. Swarbrick — US Pat. 4,117,195 — 1978

1-step Post-Polymerization

Crosslinkable Polyethylene

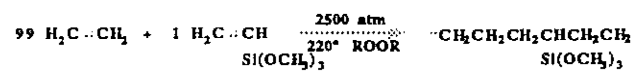


Crosslinkable Polyethylene - Graft

Manufacturers: Quantum

Cable Processors: BICC, Alcan, Okonite

Crosslinkable Polyethylene - Copolymer
Mitsubishi US Pat. 4,413,066 1983



Crosslinkable Polyethylene - Copolymer

Applications:

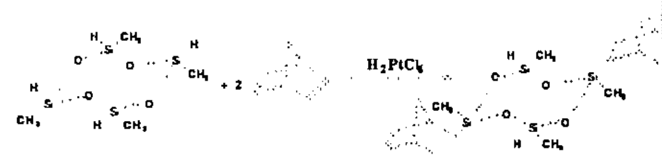
- Wire & Cable, Crosslinked Foam, Composites, Heat-Shrink Tubing

Manufacturers:

- Neste Polymers (Finland) - Visico®
- AT Polymers (Canada) - Aqua-Link®
- Union Carbide (US) - Si-Link®
- Allied-Signal (US) - LDPE/Methacryoxypropyltrimethoxysilane

Diene-Hydrosiloxane Resins

R. Liebfried US Pat. 4,900,779 1990



Diene-Hydrosiloxane Resins

Manufacturer:

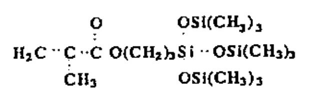
- Hercules - Sycar®

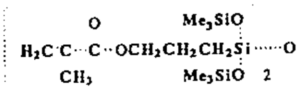
Applications:

- Printed Circuit Boards (PCBs)
- Liquid Encapsulants (Glob-Top) for Chips on Board (COB)
- Die-bonding Adhesive

Methacrylates with Silicon in Pendant Group

Contact Lens N. Gaylord US Pat. 3,808,178 1974





Typical Formulation:

- silane monomer - 10-40%
- silane cross-linker - 5%
- hydrophilic monomer - 2-5%
- methylmethacrylate - balance

Methacrylates with Silicon in Pendant Group

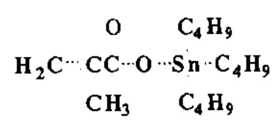
Pilkington Barnes-Hind - Polycon®, Paraperm®

Bausch & Lomb - Boston Lens®

Others: Wohlk (Germany), Menicon (Japan), Permeable Technologies (US)

Methacrylates with Tin in Pendant Group

A. Milne US Pat. 4,021,392 1977



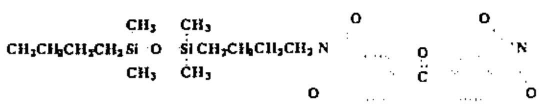
15-35% Tributyltinmethacrylate - 65-85% Methylmethacrylate Copolymer

Anti-Foulant Marine Coatings

Manufacturer: Atochem - Biomet® 300

Silicone Polyimides

Thermoset *A. Berger US Pat. 3,274,155 1966*



Applications: Planarization/Dielectric

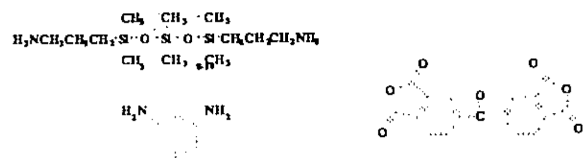
Die-bonding adhesive

Manufacturers: National Starch / Ablestick

Relyamid®, Tab-Coat®, Conductimer®

Silicone Polyimides

Thermoplastic J. Cella US Pat. 4,808,686 1989

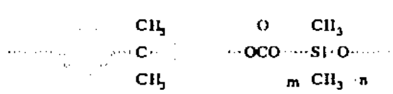


~ 40% Dimethylsiloxane

GE Siltem® Wire Insulation, Enamels

Silicone Polycarbonate

H. Vaughn US Pat. 3,189,662 1965

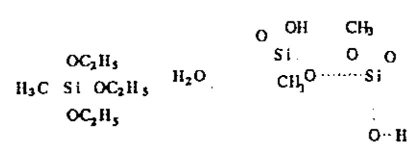


Manufacturer: GE Copel® LR Resin

Applications:

- Aerospace Canopies
- Bullet-Proof Glazing Interlayer
- Oxygen Enrichment Membranes

T-Resins (Silsesquioxanes) Un-Modified



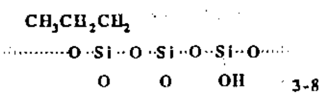
Applications:

Resistor Coatings

Planarizing Coatings for Microelectronics

Manufacturers: NEC (former O-I) Glassrock®

T- Resin (Silsesquioxane) Modified Alkyds & Polyesters

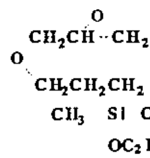


Typical High Solids Formulation

Pentaerythritol	9.7
Glycerol	1.8
Phthalic Anhydride	12.7
Soya Fatty Acid	34.3
Methyl Amyl Ketone	16.5
PhenylPropyl T-Siloxane	25.0

Coil Coating, High Temperature Finishes

Modified T-resins



Ormosils

Abrasion Resistant Coatings, Heat Resistant Resins

Dow-Corning, GE, Wacker, Shin-etsu

Scratch, High Refractive Index Coatings for Eyewear

Gentec, Essilor, American Optical

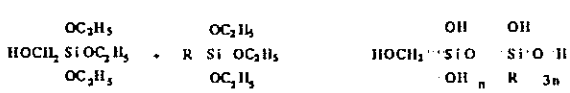
G. Phillip, H. Schmidt US Pat. 4,746,366 1988

K. Mori et al, US Pat. 4,895,767 1990

E. Yajima et al, US Pat. 5,165992 1992

T-Resins via Stabilized Silanol Solutions

B. Arkles US Pat. 5,371,262 1994

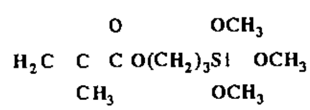


Architectural Water-repellents

Gelest / The Weather Company Weatherex®

Copolymers with Alkoxysilanes

I. Hazan US Pat. 5,162,426 1993



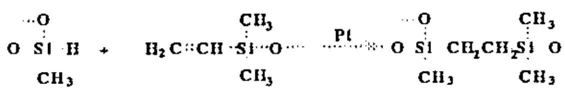
Clear Topcoats for Automotive

DuPont Generation 4®

PPG, Kaneka

Silicone Semi-Interpenetrating Networks

B. Arkles US Pat. 4,500,668 1985



Silicone Semi-Interpenetrating Networks

Injection Molded Applications

Precision Optics Transport

High Speed Paper, Tape Transport

Extrusion Applications

Medical Catheters

Manufacturers:

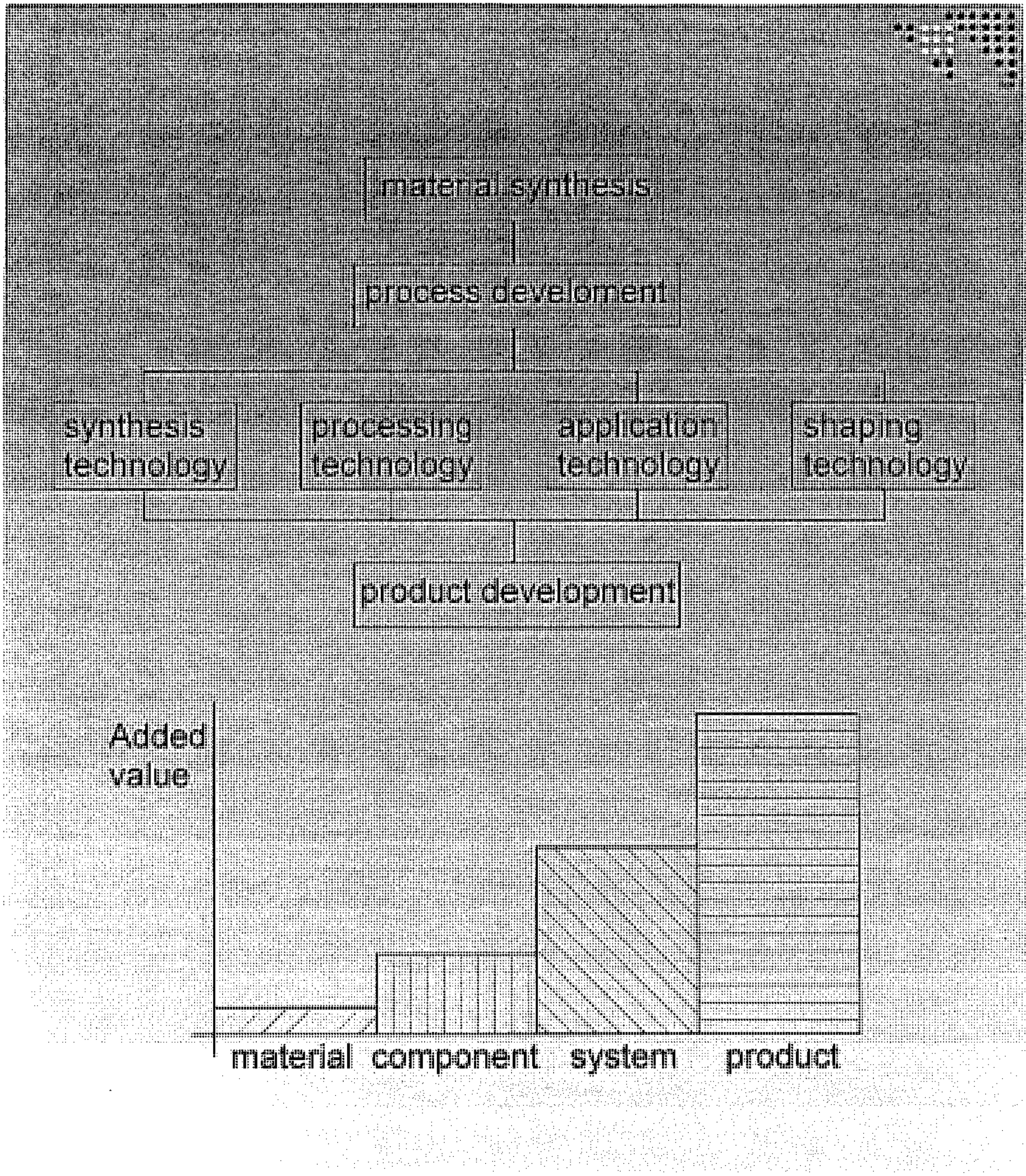
LNP Engineering Plastics / ICI Advanced Materials

Inorganic / Organic Hybrid Polymers: Routes to Industrial Applications

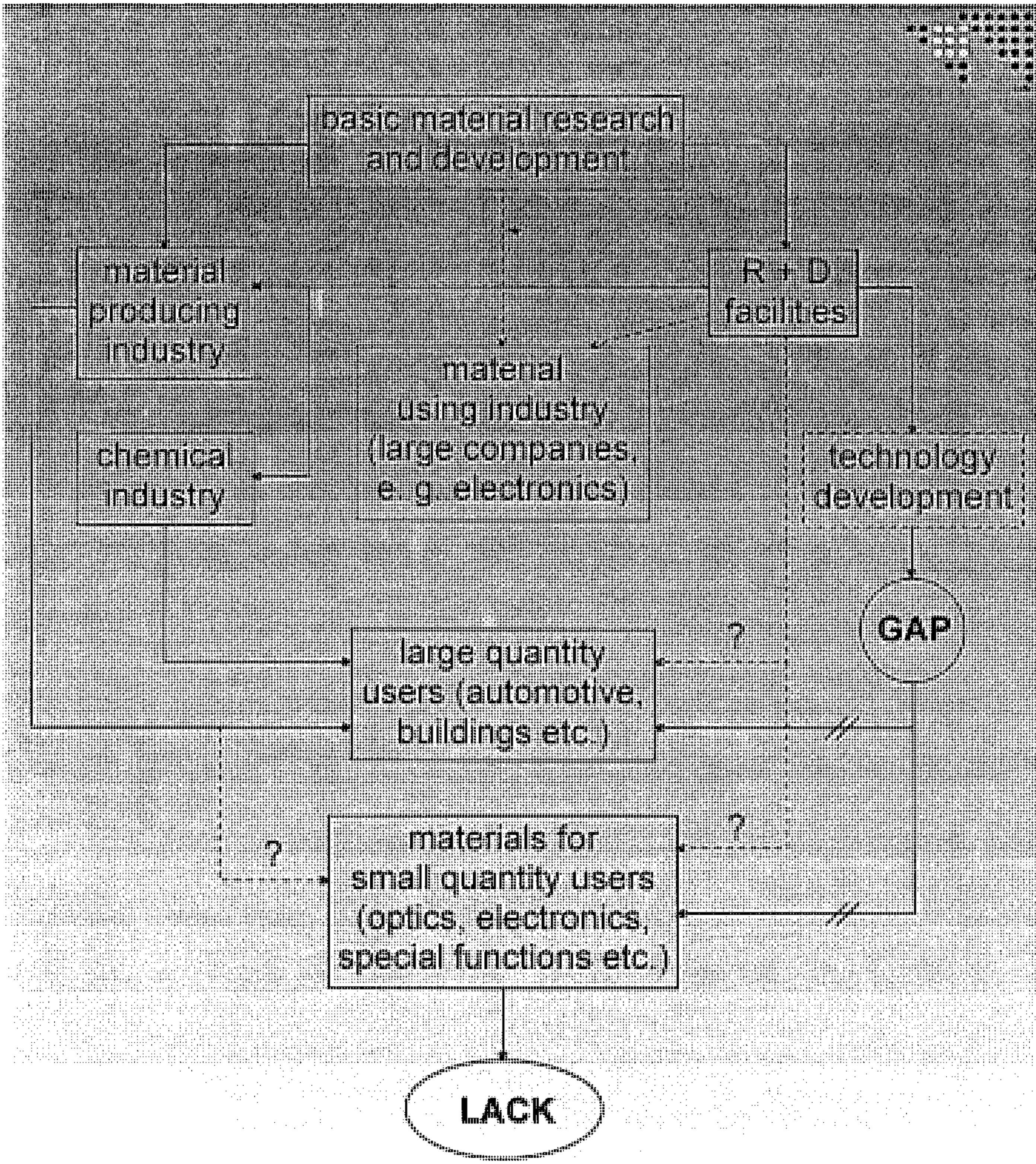
H. Schmidt

Institut für Neue Materialien gem. GmbH
Saarbrücken, FRG

002.939


material synthesis
process develoment
synthesis technology
processing technology
application technology
shaping technology
product development
Added value
material
component
system
product

002.932



* depending on type of company and
type of material technology

002.934

Chemistry as a key technology for innovative materials

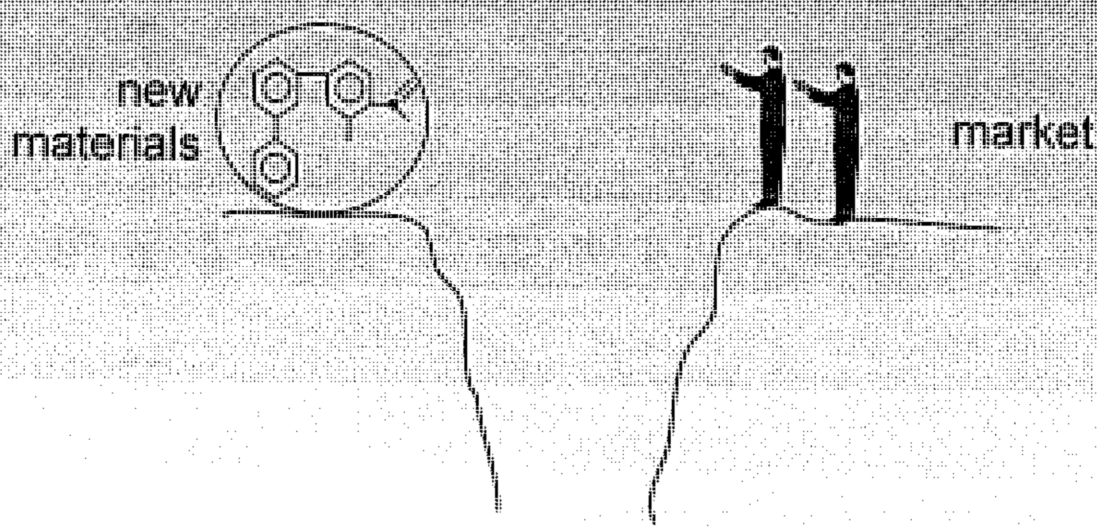
- extremely high "stock" of data, results
- even larger potential
- "new chemistry" is produced permanently
- use of this potential is close to zero

⇒ long return of investment times

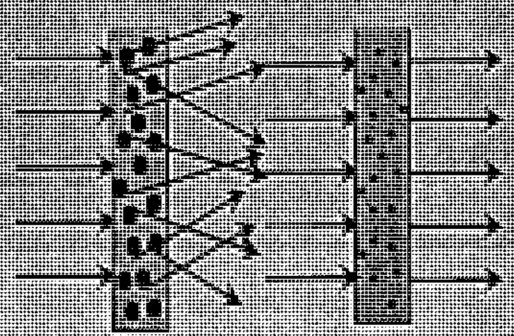
⇒ "separation" between material developers and users

⇒ lack of tailor made technologies for users

- overdominating technology drive
- market pull becomes not effective due to lack of bridges



Nano composites



$T = \exp[(-\gamma_{ext} + \gamma_a)d]$

$\gamma_{ext} = f(c_v, \Delta n, R^3 \lambda^{-4})$

c_v = filler volume fraction,

Δn = difference of refractive index,

R = particle diameter

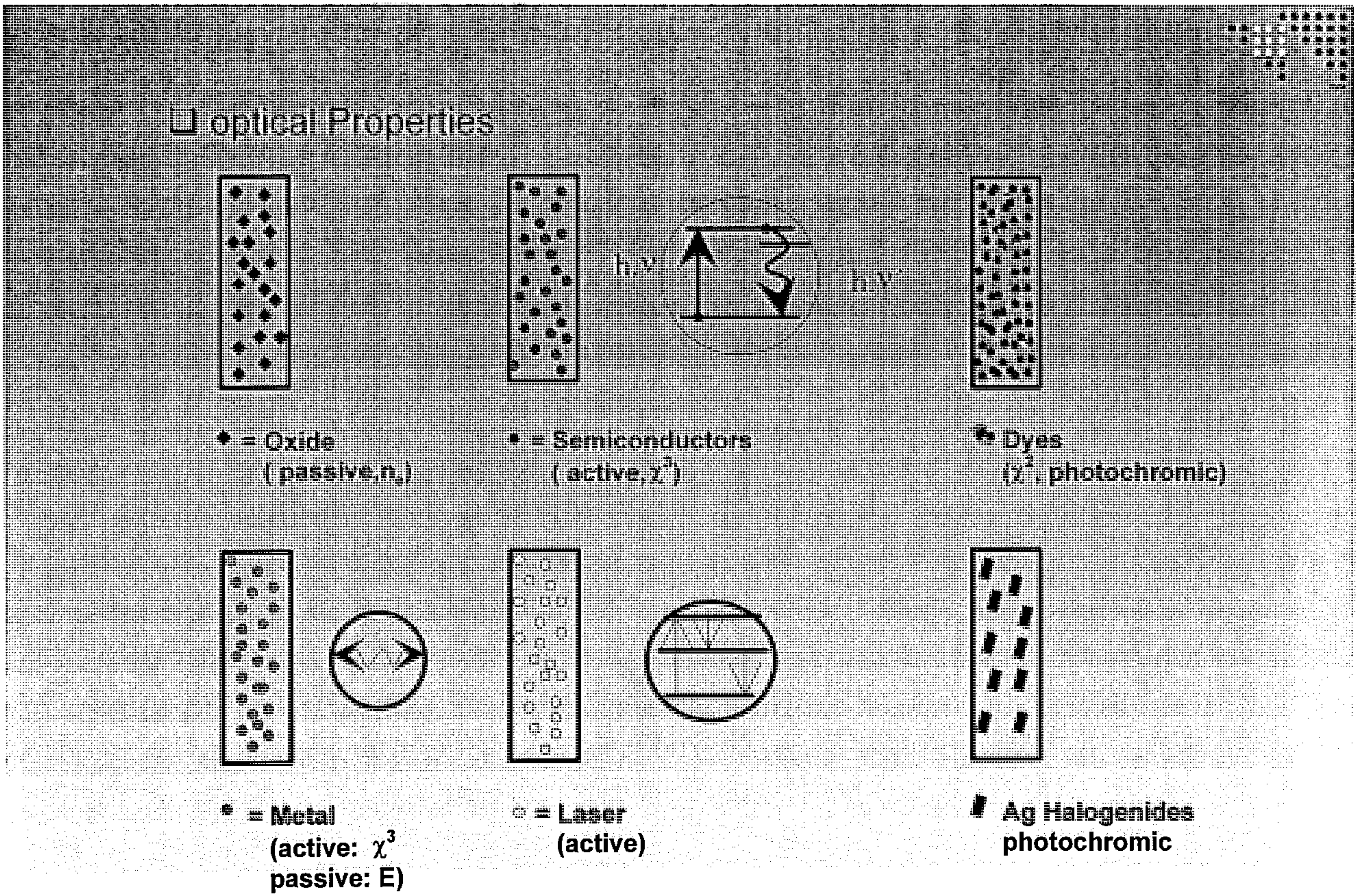
λ = wavelength

"small" particles ->
suitable for optics

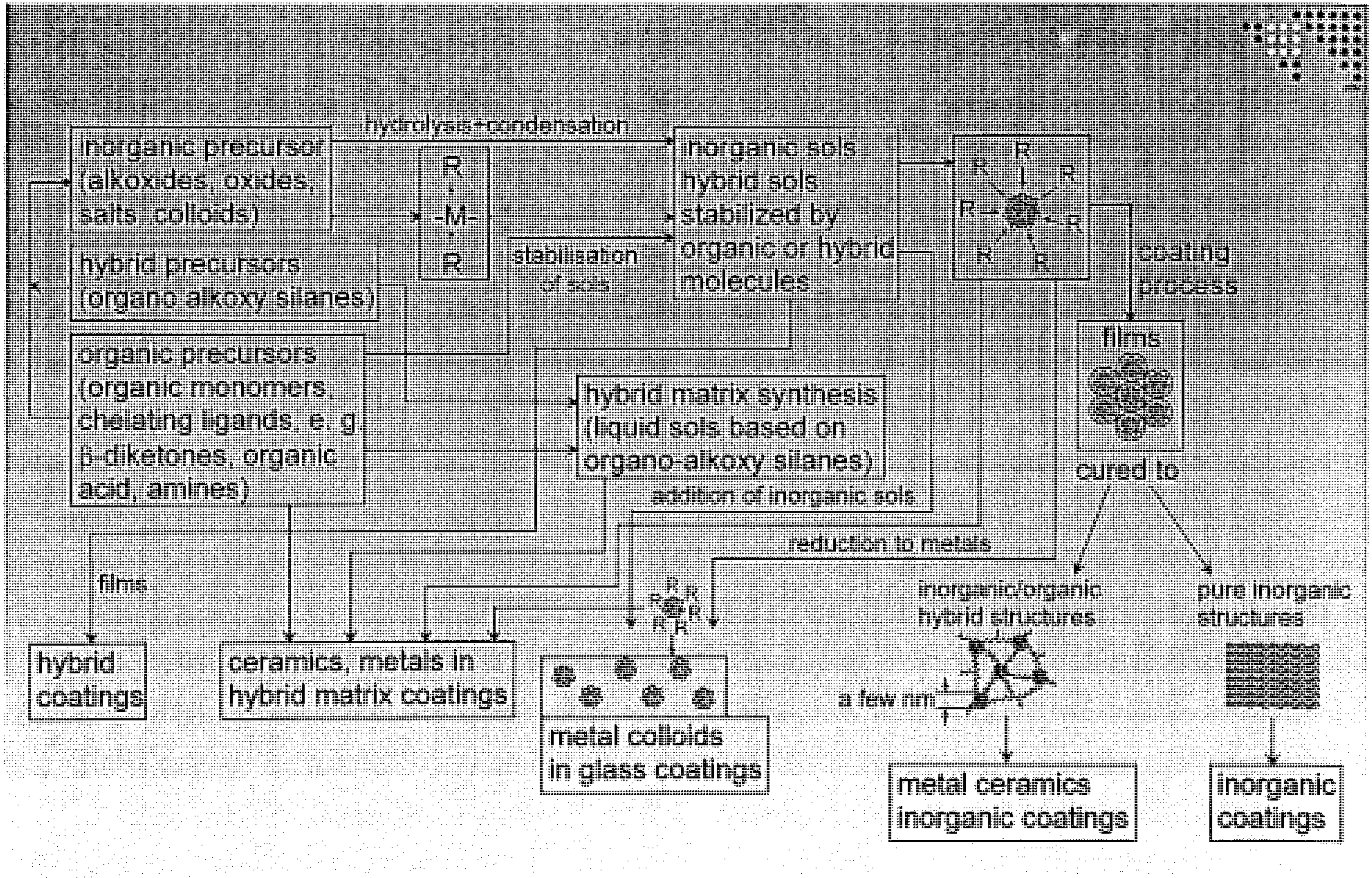
○ passive "functions": reactive index (n_E)
mechanical properties
interface properties
absorptive properties

○ active "functions": semiconductor properties
(band gap, intermediate electron location)
⇒ NLO
plasmon properties
photochromic, electrochromic properties

002.550

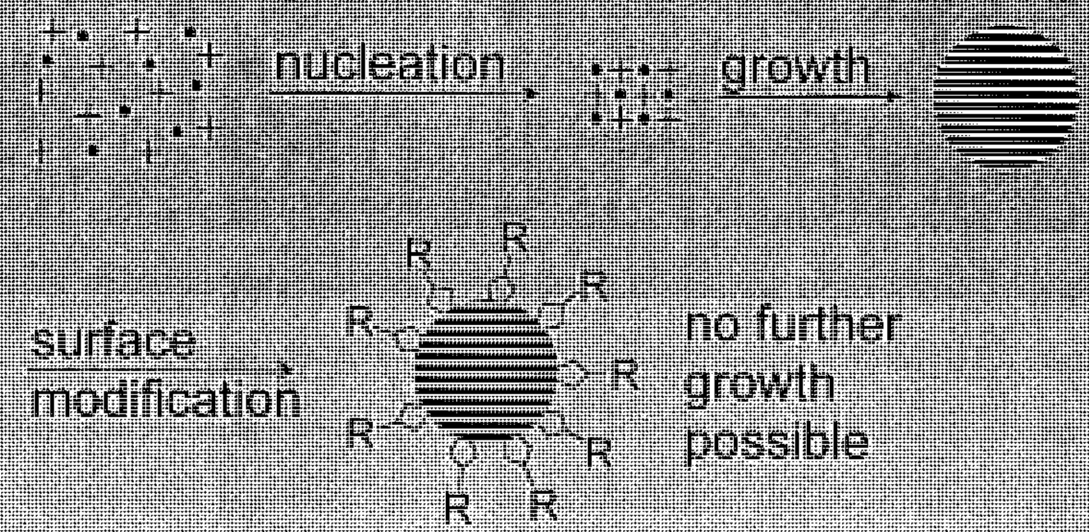


optical Properties
h.v
h.v'
= Oxide
(passive, n_s)
= Semiconductors
(active, χ^3)
Dyes
(χ^2, photochromic)
= Metal
(active: χ^3
passive: E)
= Laser
(active)
Ag Halogenides
photochromic



hydrolysis+condensation
inorganic precursor (alkoxides, oxides, salts, colloids)
hybrid precursors (organo alkoxy silanes)
organic precursors (organic monomers, chelating ligands, e. g. β-diketones, organic acid, amines)
R -M- R
stabilisation of sols
inorganic sols hybrid sols stabilized by organic or hybrid molecules
hybrid matrix synthesis (liquid sols based on organo-alkoxy silanes)
addition of inorganic sols
reduction to metals
coating process
films
cured to
films
inorganic/organic hybrid structures
pure inorganic structures
a few nm
hybrid coatings
ceramics, metals in hybrid matrix coatings
metal colloids in glass coatings
metal ceramics inorganic coatings
inorganic coatings

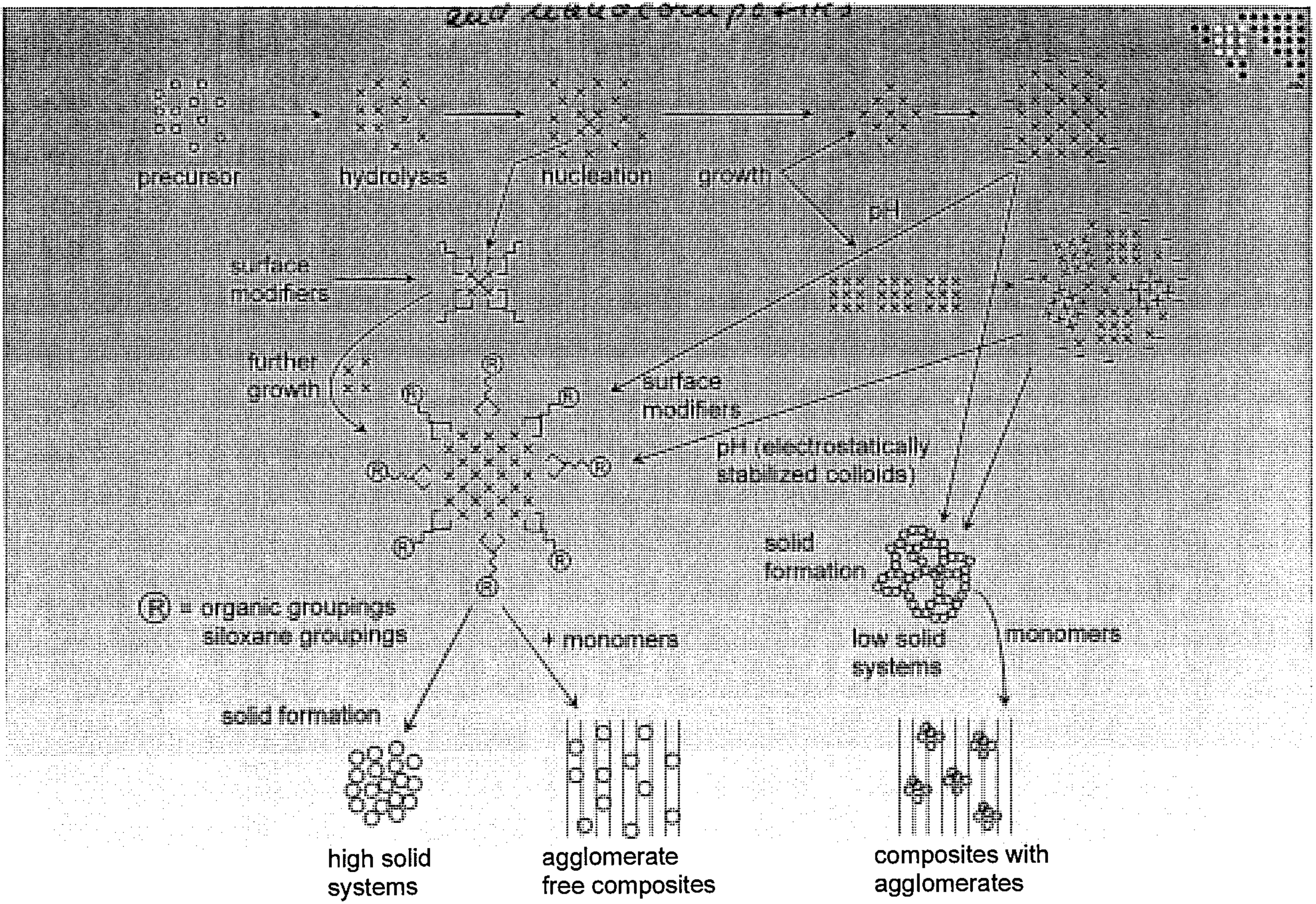
002.923



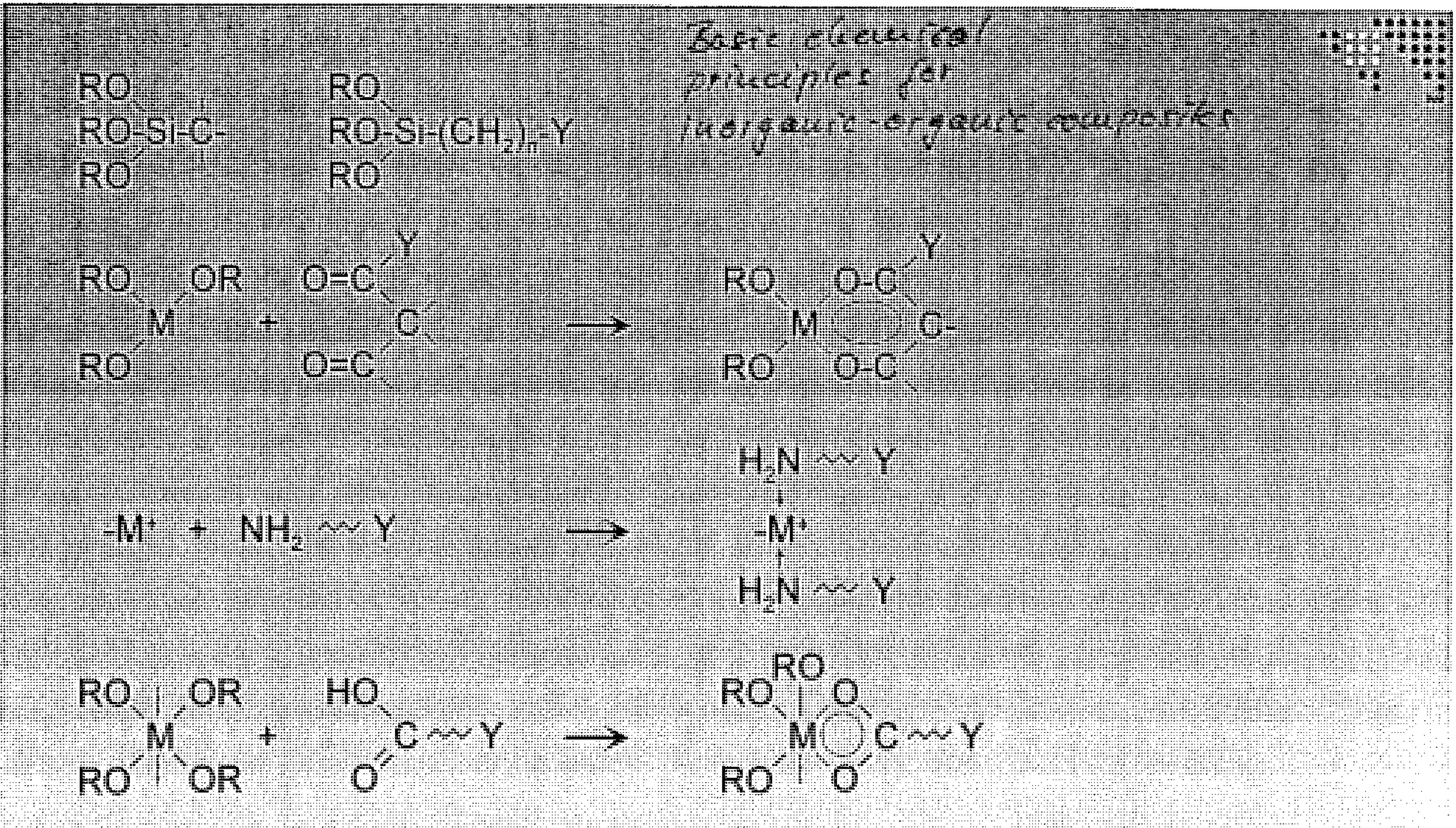
R:

a: inert grouping like alkyl or aryl
b: fuctional groupings like acids or bases
c: reactive groupings like polymerisable
or "sol-gel" groupings, e.g. ^^ $Si(OR)_3$

002.744


precursor
hydrolysis
nucleation
growth
pH
surface modifiers
further growth
surface modifiers
pH (electrostatically stabilized colloids)
solid formation
Ⓡ = organic groupings siloxane groupings
+ monomers
low solid systems
monomers
solid formation
high solid systems
agglomerate free composites
composites with agglomerates

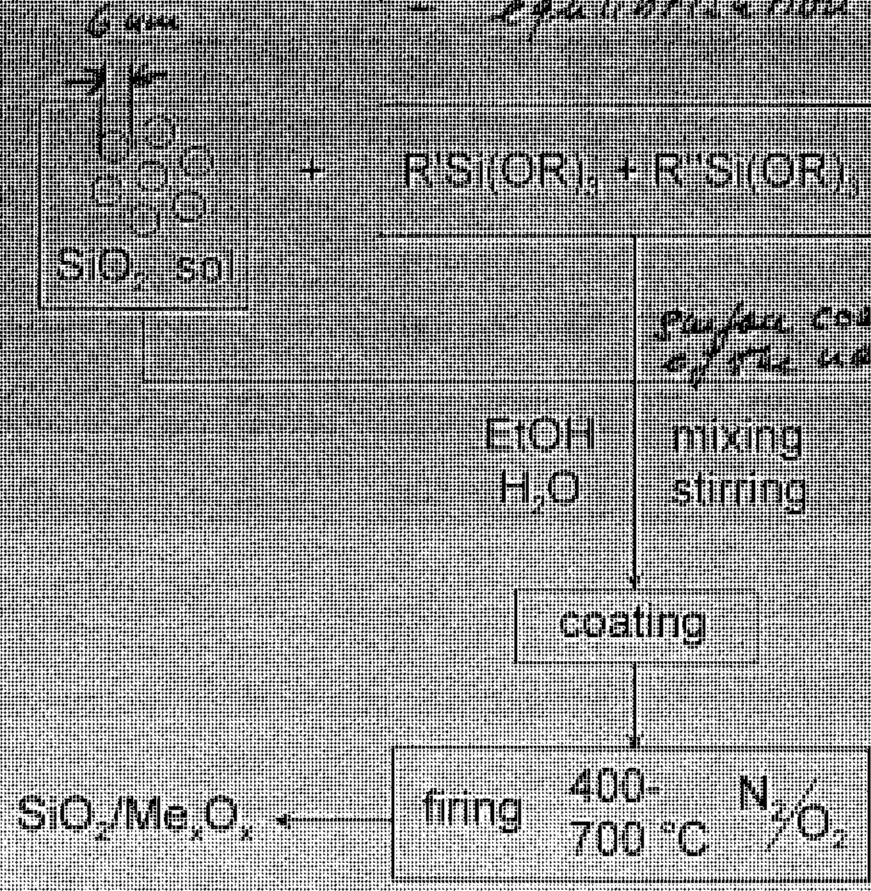
002.907



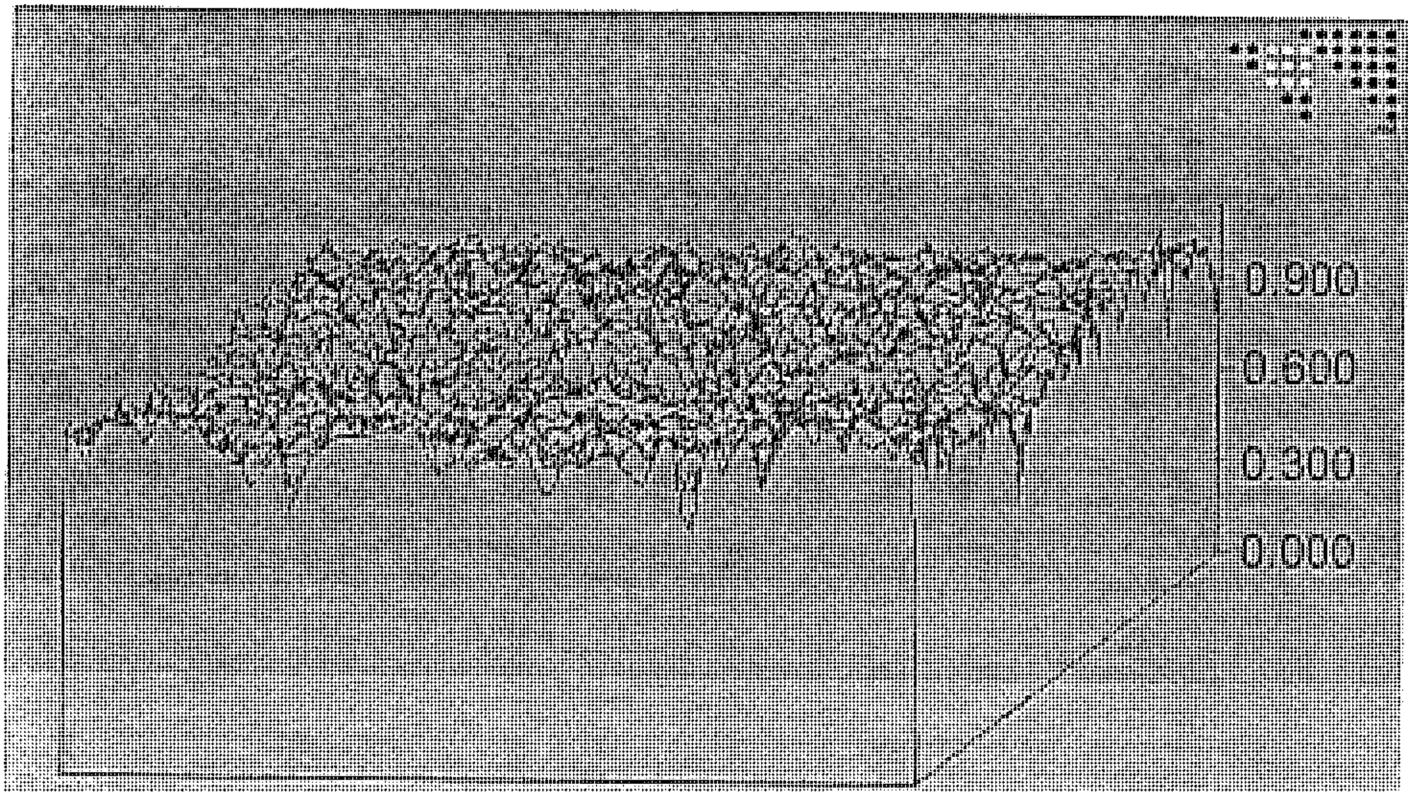
Y = base, acid, epoxides, vinyl, methacrylates and others
OR = alkoxy grouping to form inorganic networks by hydrolysis and condensation
M = metal ion

SiO_2 layers for

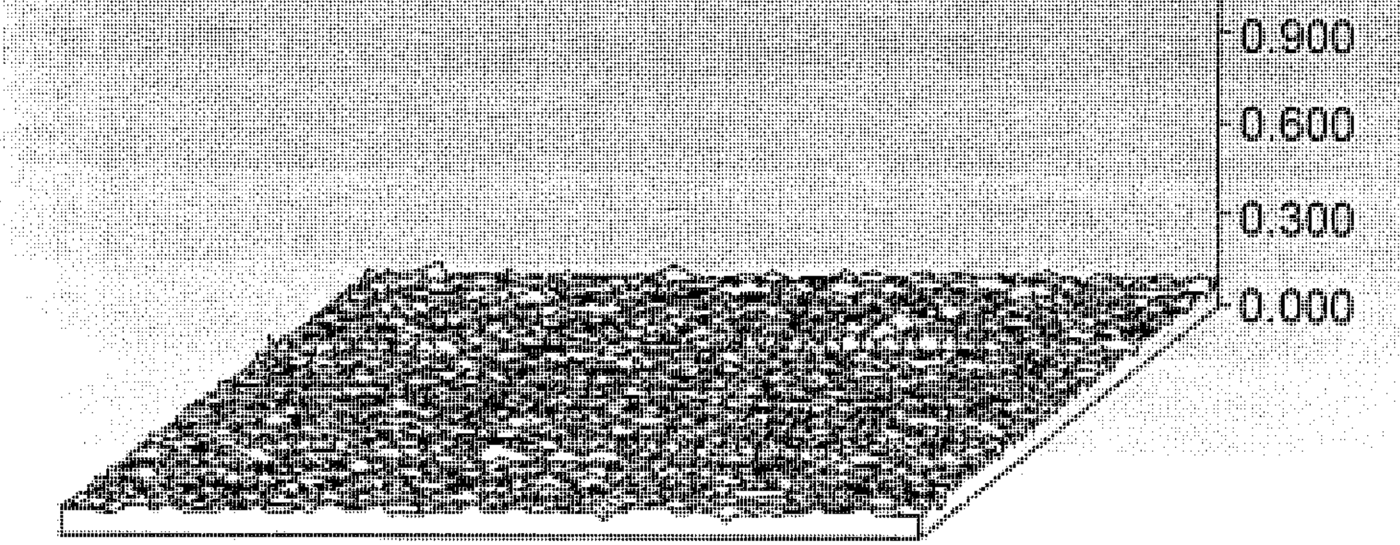
- scratch resistance on metals
- high temperature corrosion resistance
- equilibrisation of surface



→ dense layers
→ 3-5 mm thickness
→ transparent
→ equilibrizing 1,5 µm → 15 nm

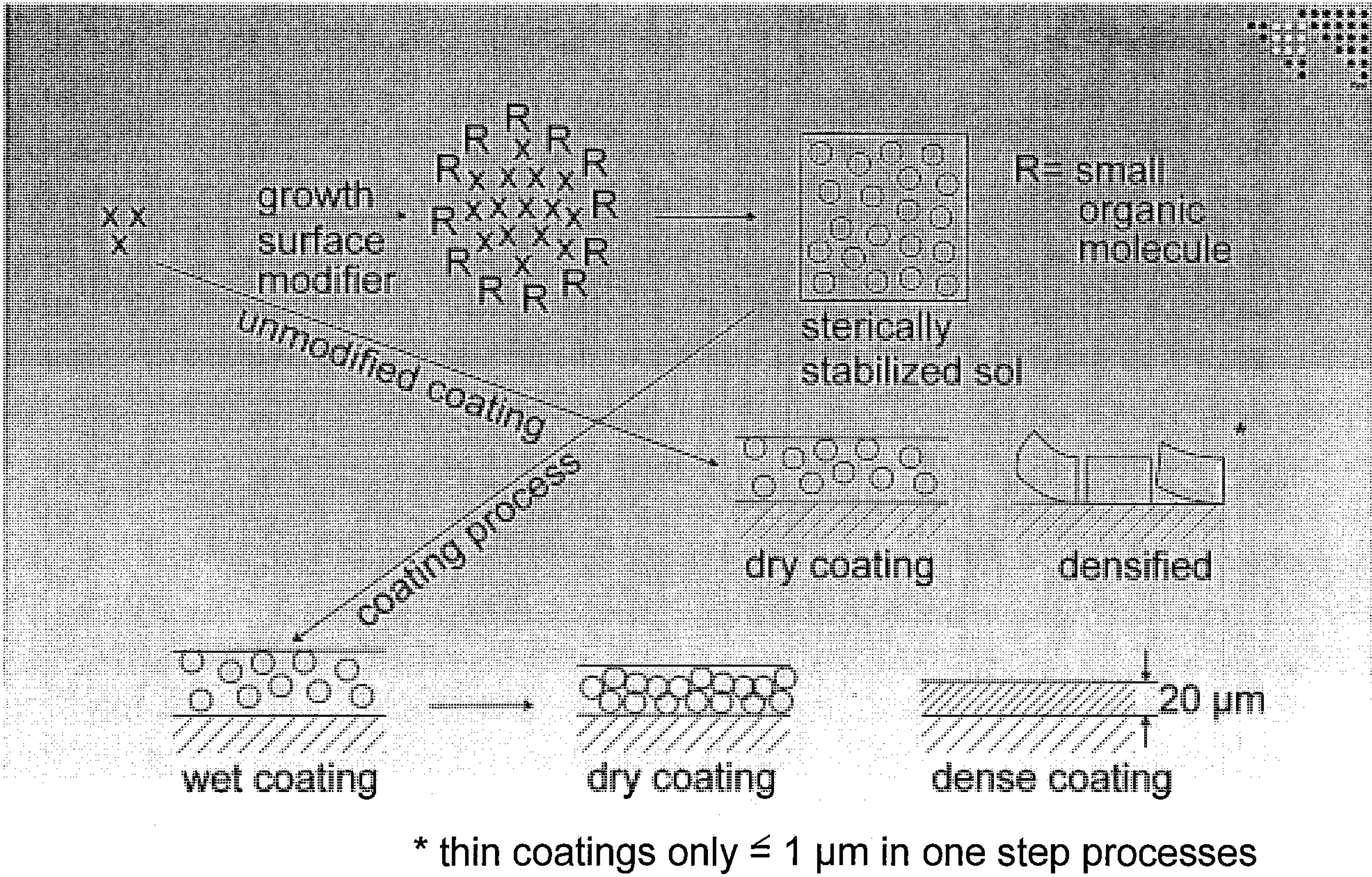


Stainless steel, uncoated (R_a = 35 nm)

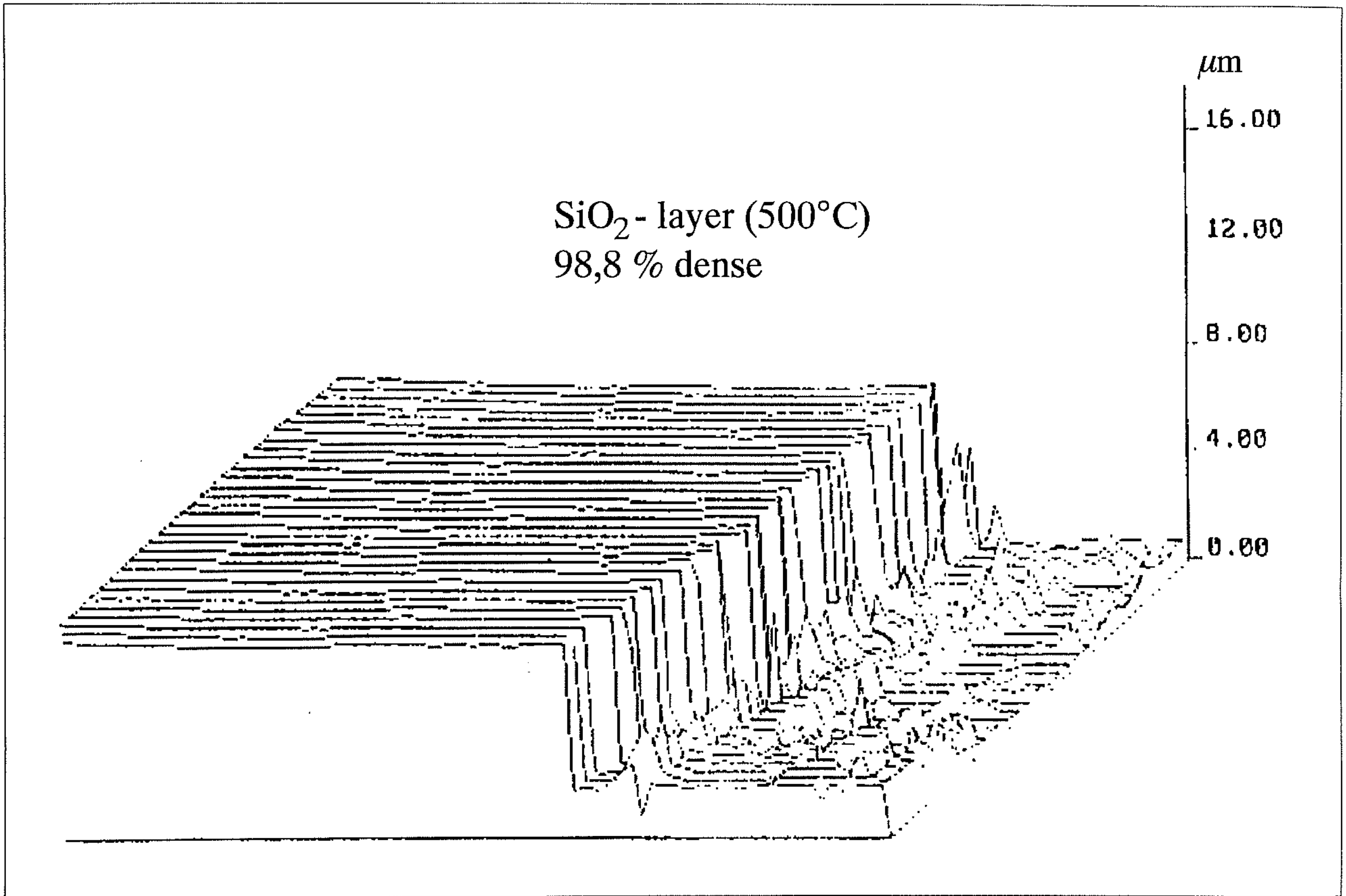


SiO_2 glass coating (700 °C) on stainless steel (R_a = 10 nm)

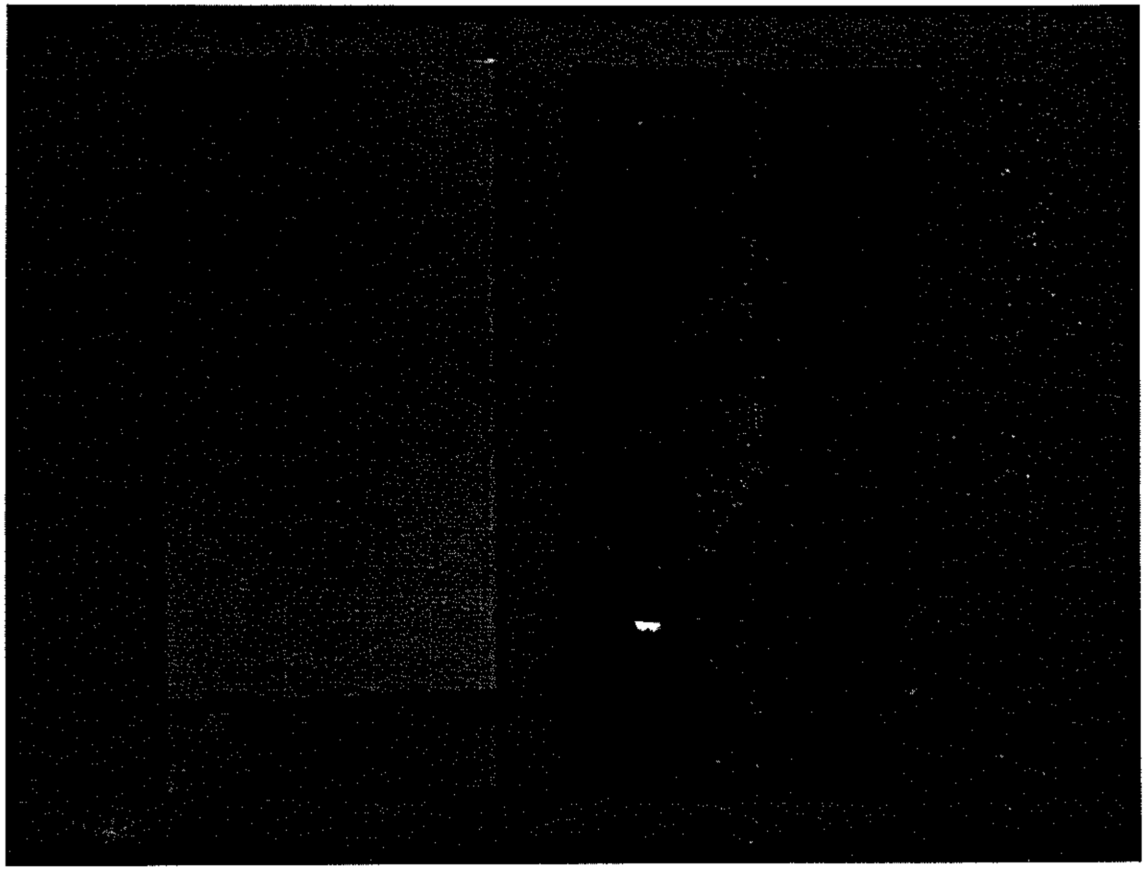
002.827


growth
surface
modifier
R= small
organic
molecule
sterically
stabilized sol
unmodified coating
coating process
dry coating
densified
wet coating
dry coating
dense coating
20 µm
* thin coatings only ≤ 1 µm in one step processes

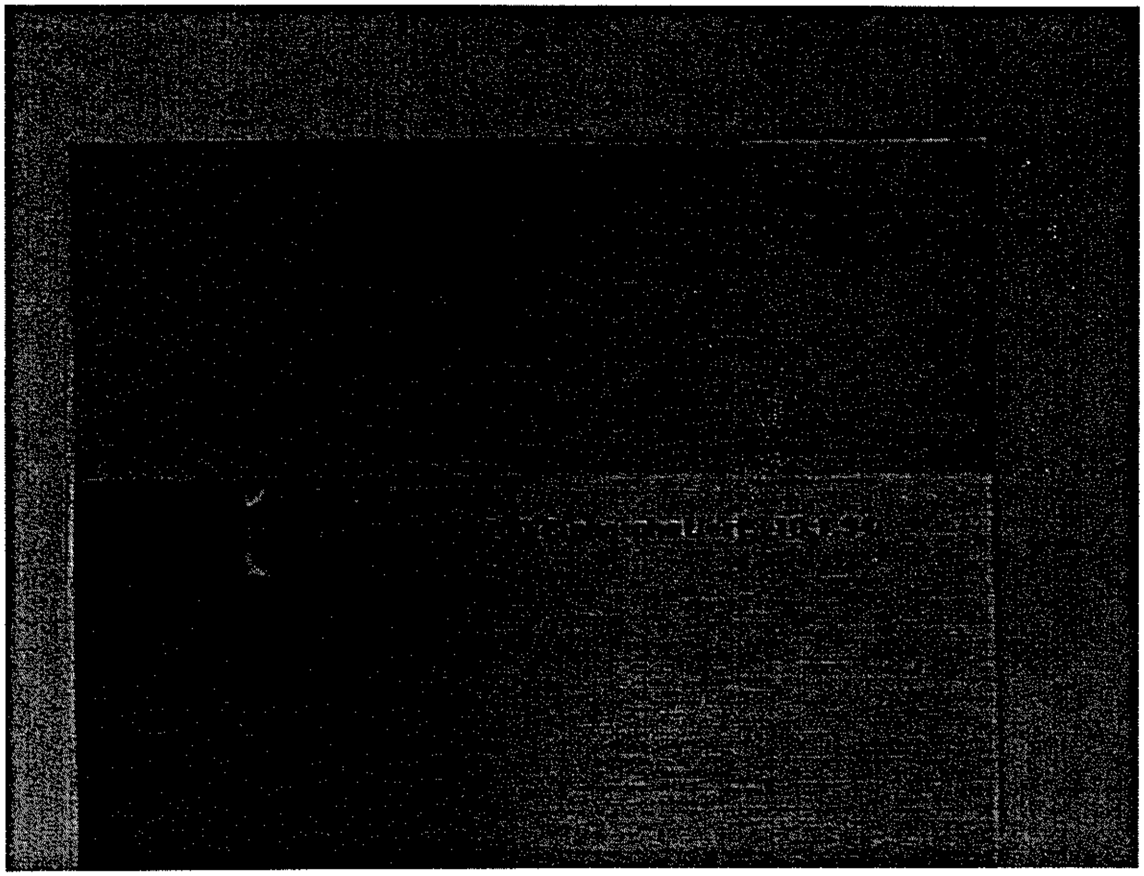
002.925



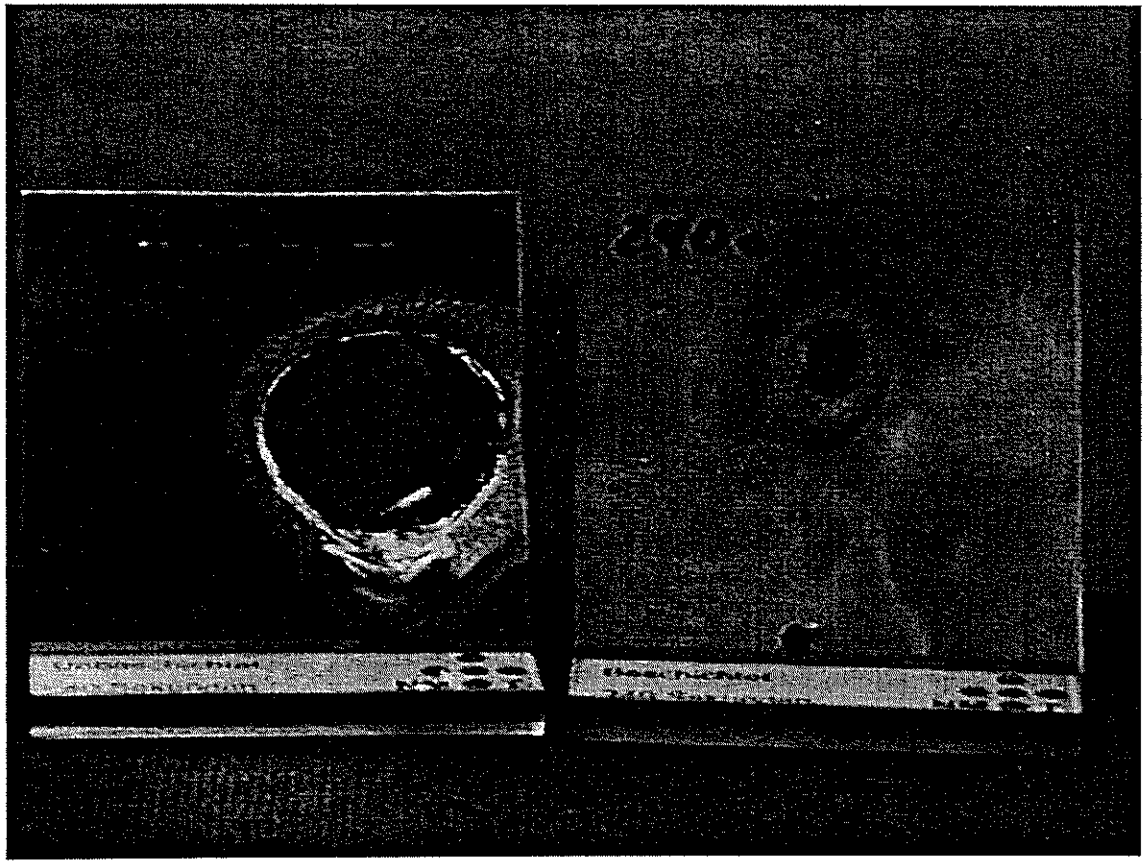
001.341



Copper with SiO_2 coating (left)
after high T treatment



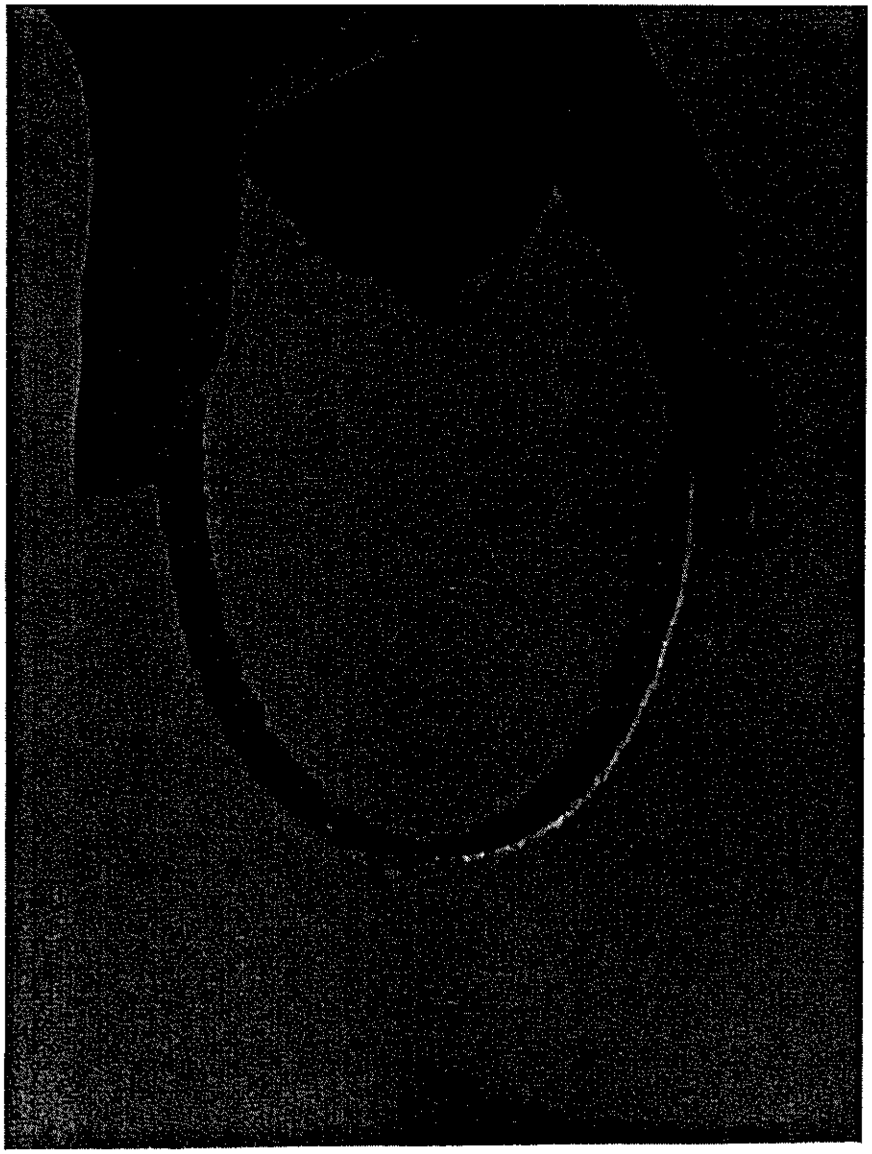
stainless steel with TiO_2
coating after 700 °C treatment
lower part: coated

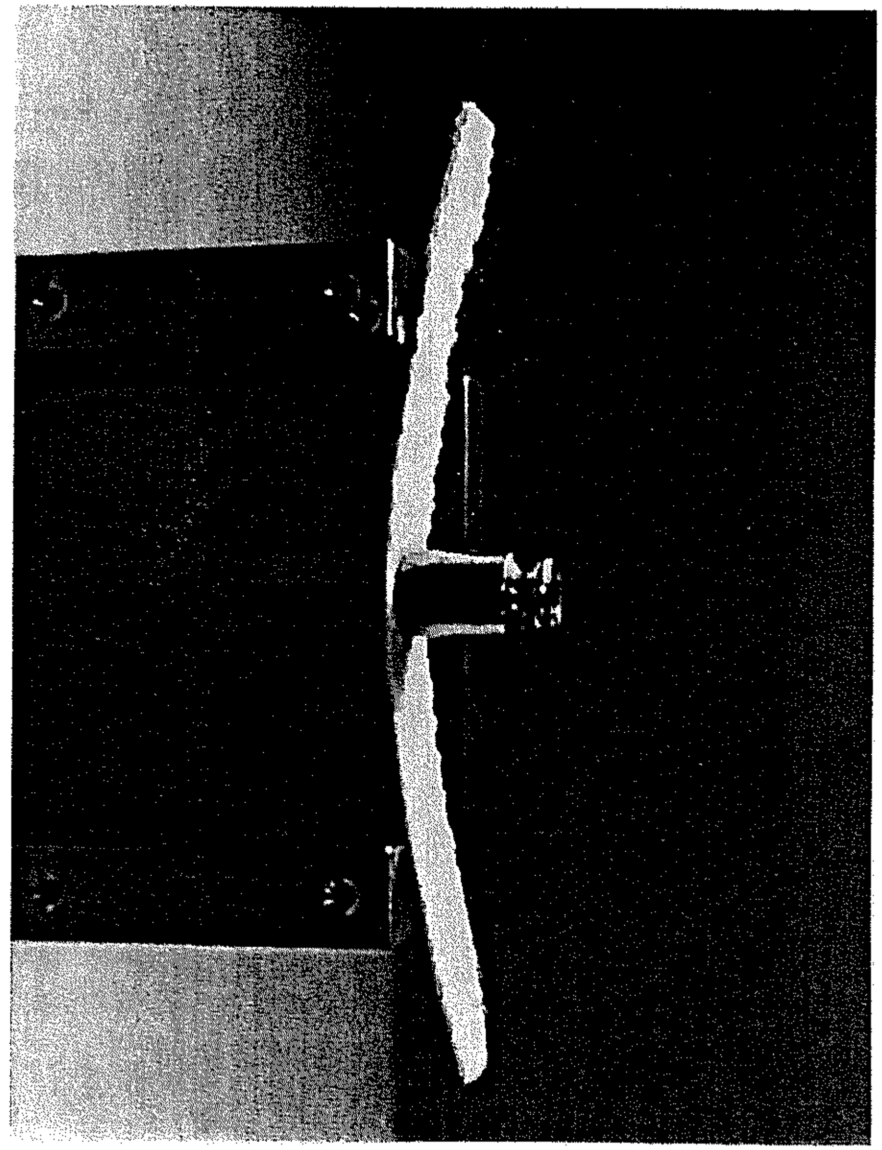


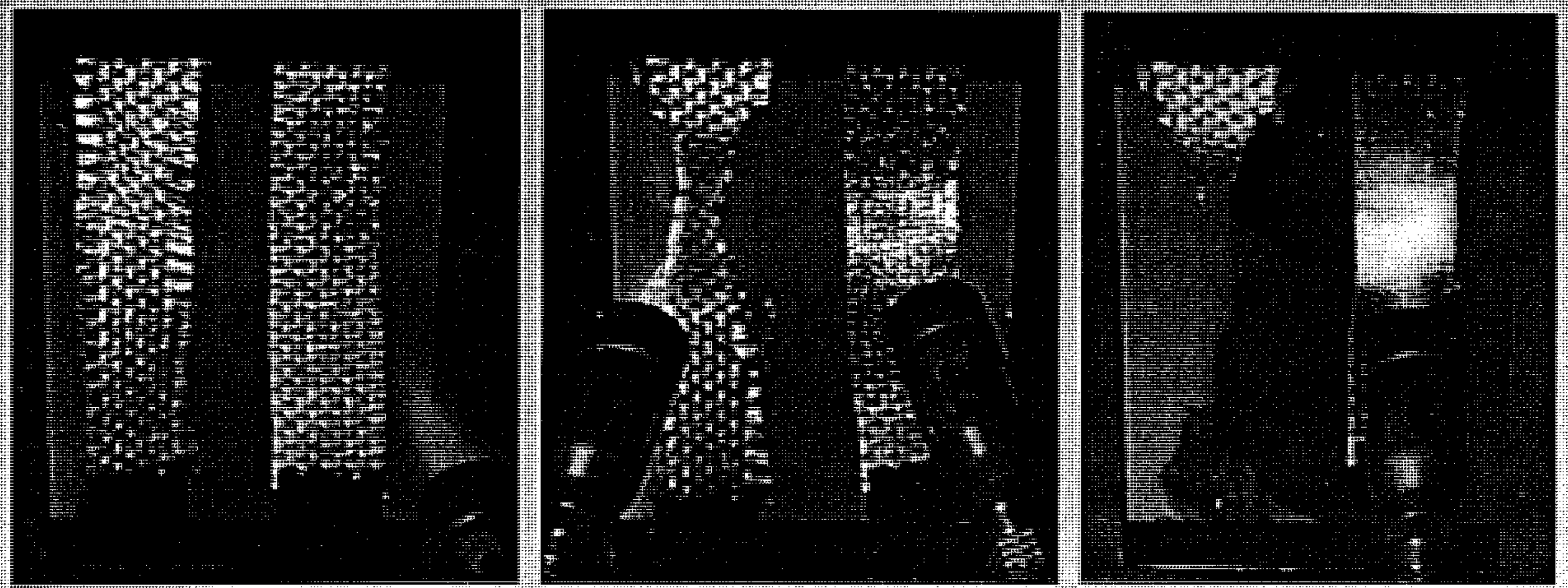
Al with glass coating;
gas burner test: left: uncoated, after 40 sec
right: coated, after 240 sec

Weavings:

- Flexibility of the coated weave



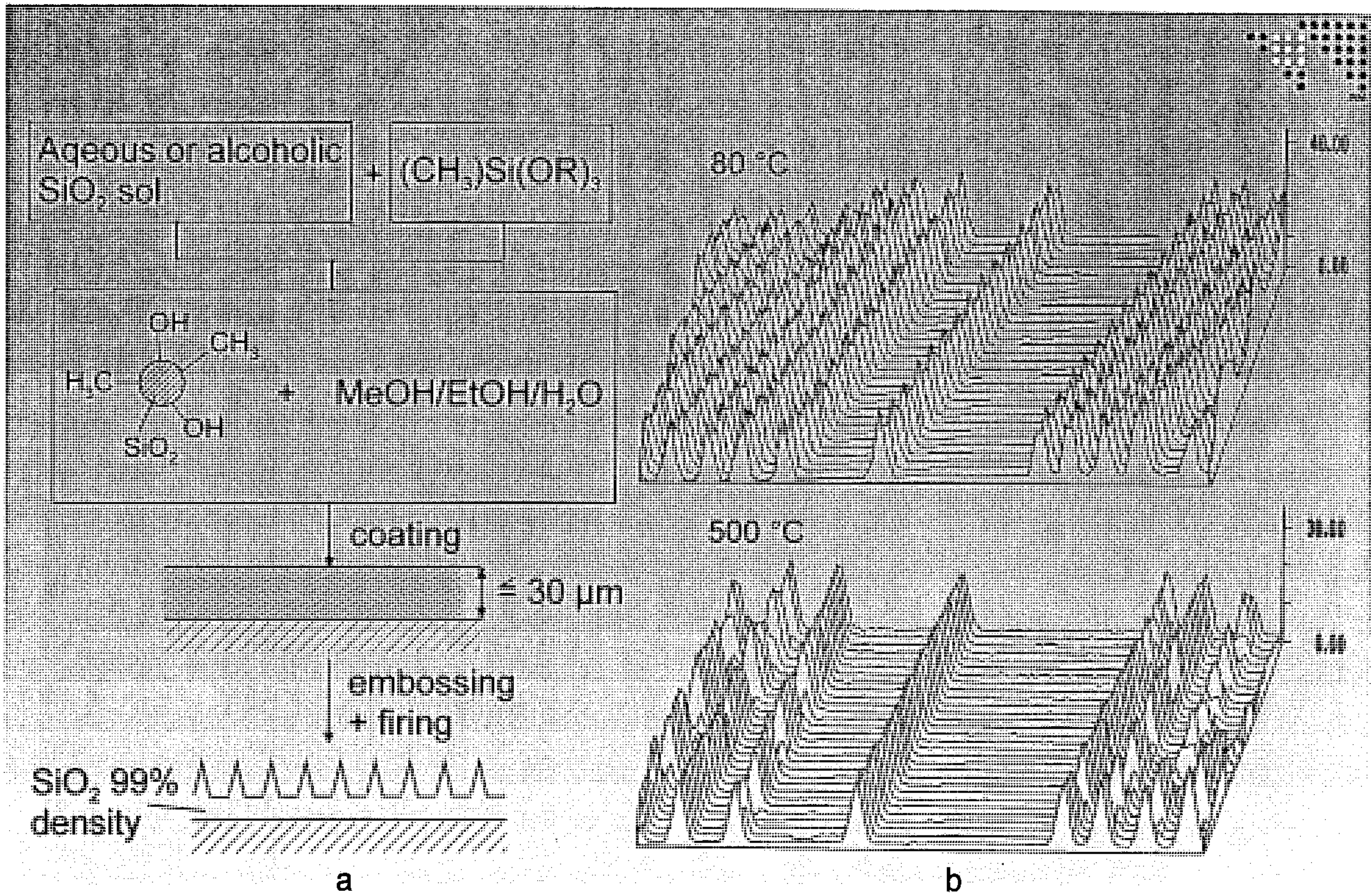




a b c

temperature resistance of glass fibre fabrics
left : uncoated
right : coated , 1050 °C

002.926

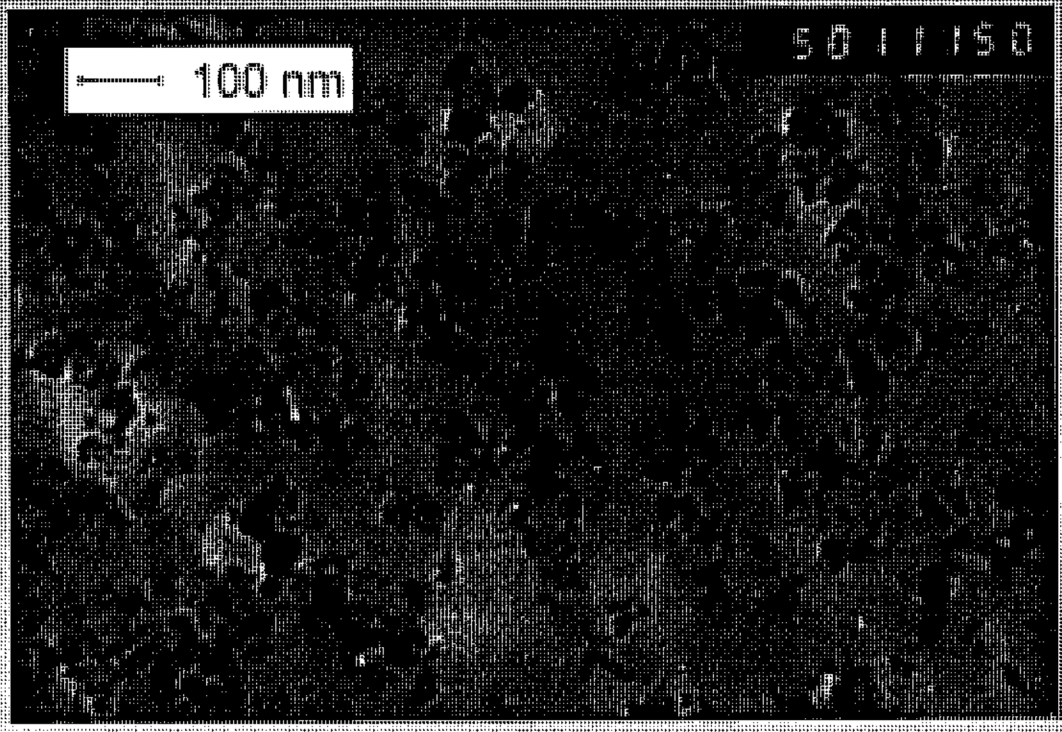


Aqeous or alcoholic SiO2 sol
+ (CH3)Si(OR)3
H3C
OH
CH3
OH
SiO2
+ MeOH/EtOH/H2O
coating
≤ 30 µm
embossing
+ firing
SiO2 99% density
a
80 °C
500 °C
b

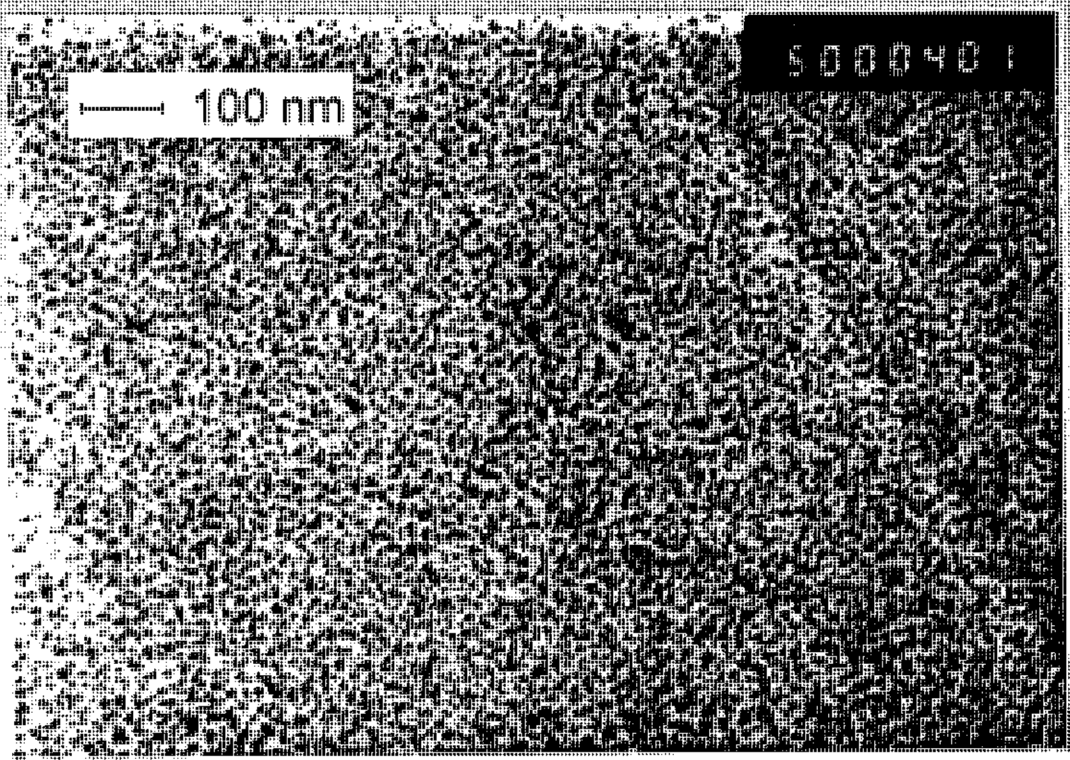
002.927

SiO_2 particles in an UV-cured, epoxy based adhesive for optical applications

a



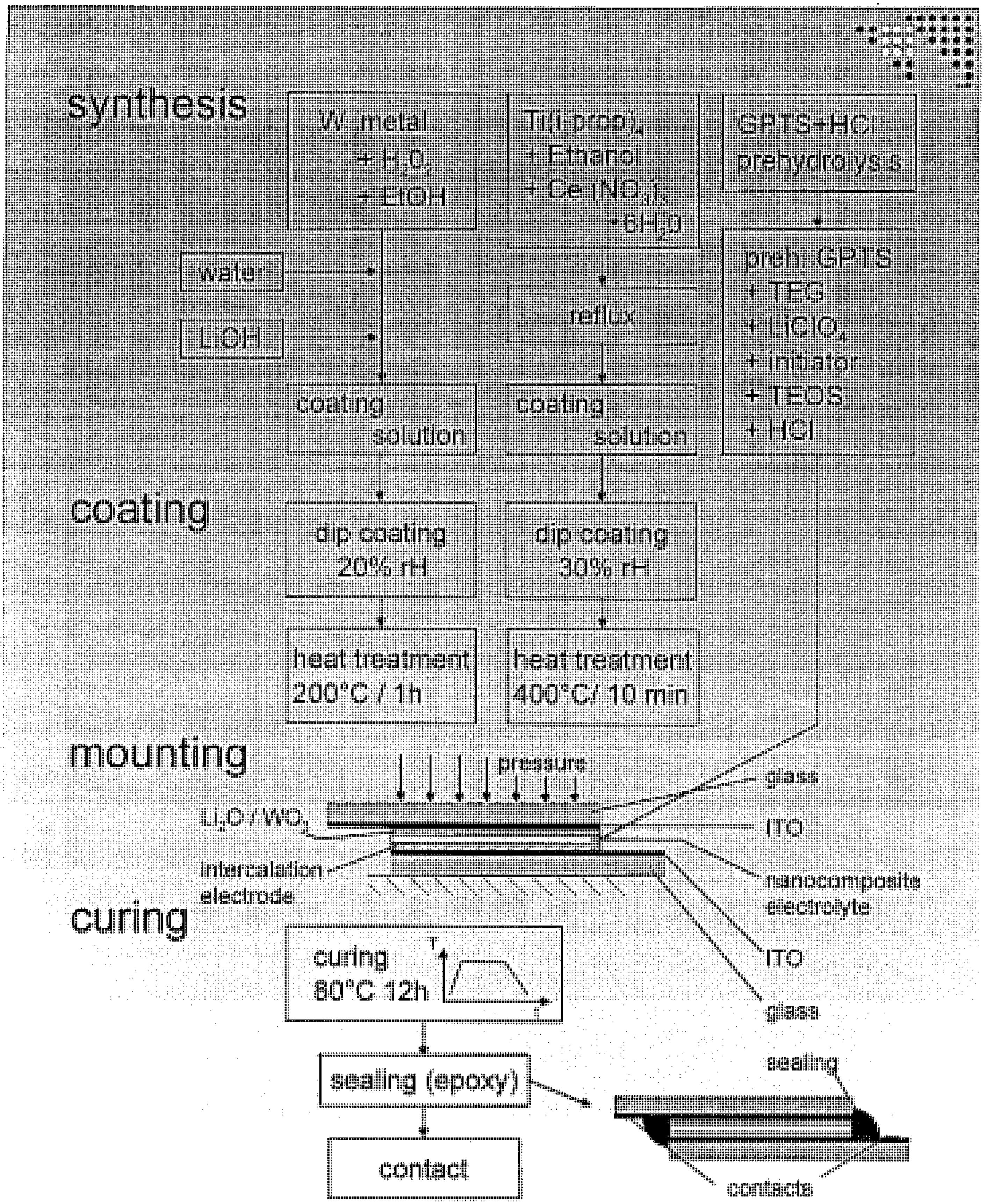
b



nano composite as low shrinkage low TEC adhesive

a) without appropriate surface treatment

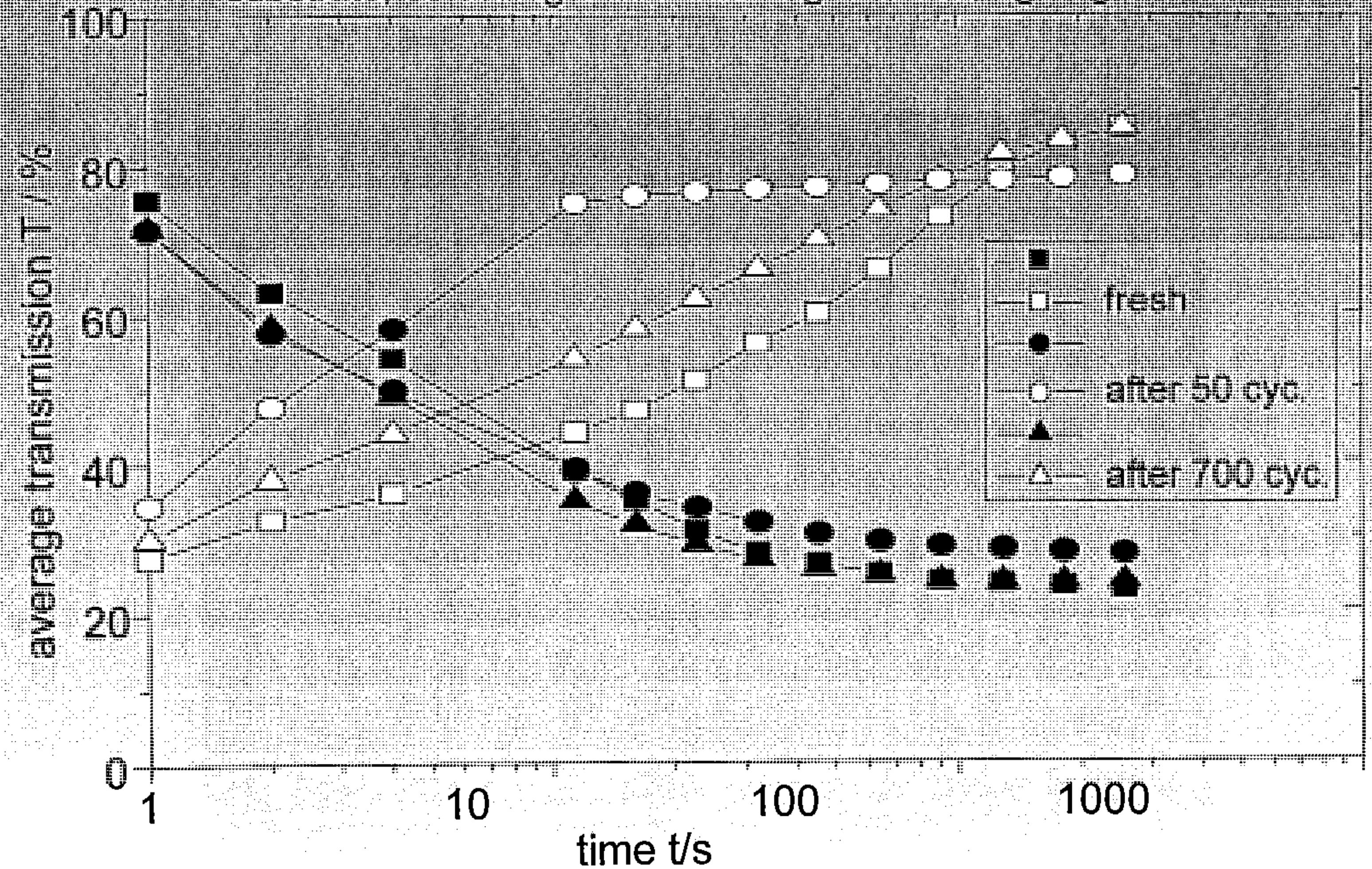
002.920



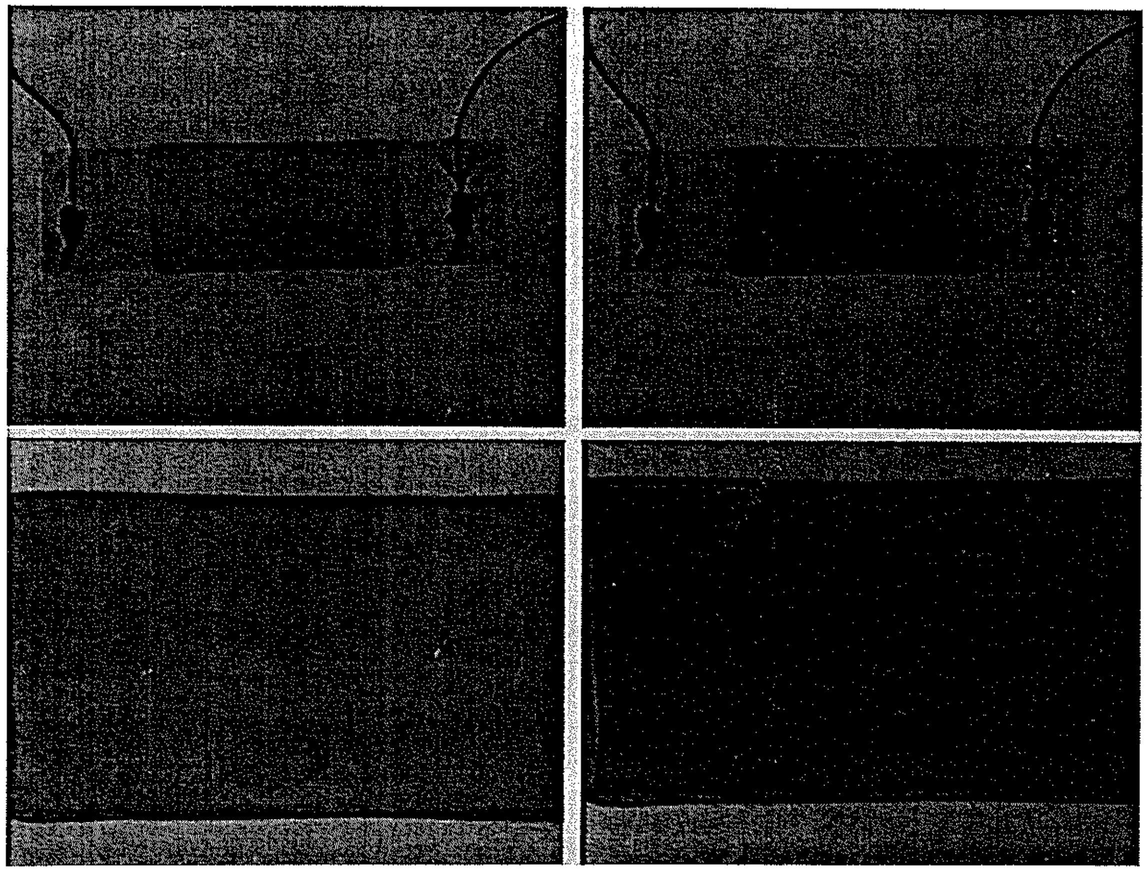
synthesis
W metal
+ H2O2
+ EtOH
Ti(i-prop)4
+ Ethanol
+ Ce (NO3)3
·6H2O
GPTS+HCl
prehydrolysis
water
LiOH
reflux
preh. GPTS
+ TEG
+ LiClO4
+ initiator
+ TEOS
+ HCl
coating
solution
coating
solution
coating
dip coating
20% rH
dip coating
30% rH
heat treatment
200°C / 1h
heat treatment
400°C/ 10 min
mounting
pressure
glass
Li2O / WO3
ITO
intercalation
electrode
nanocomposite
electrolyte
ITO
glass
curing
curing
80°C 12h
T
t
sealing (epoxy)
contact
sealing
contacts

002.930

Average transmission (380-750 nm) of a WO_3 layer on ITO substrate, colouring and bleaching kinetics, ageing effekts.

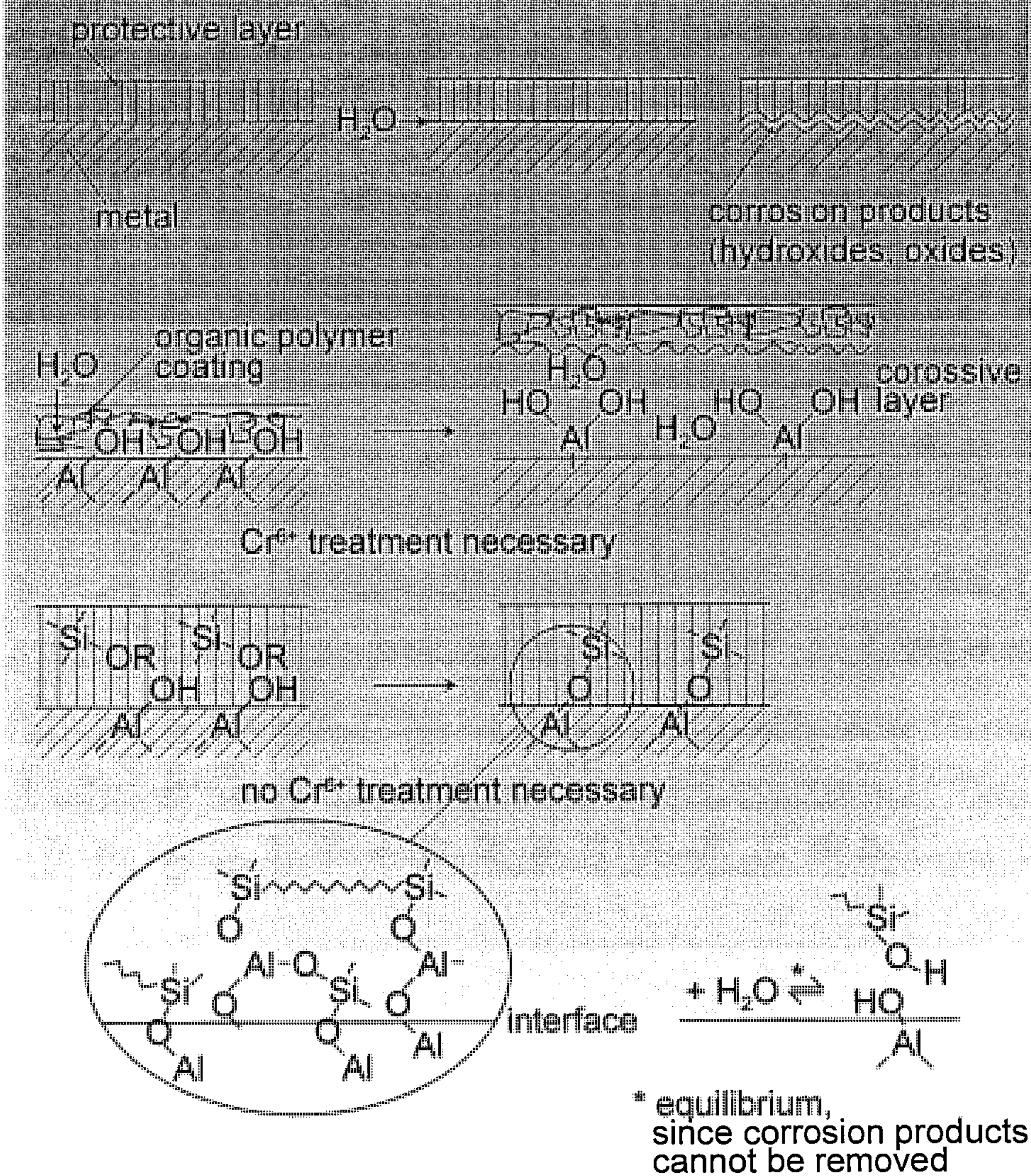


002.929



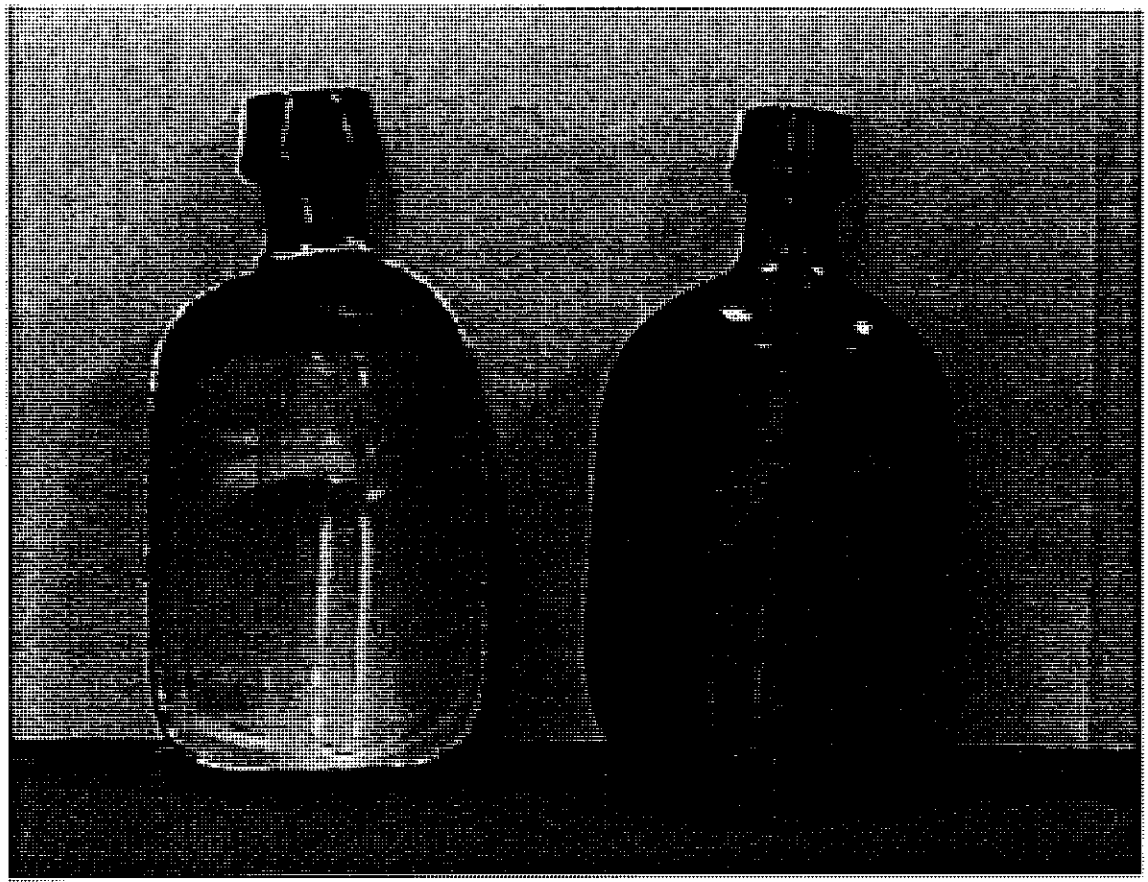
all sol-gel electrochromic system

Tailored interfaces for corrossion protection

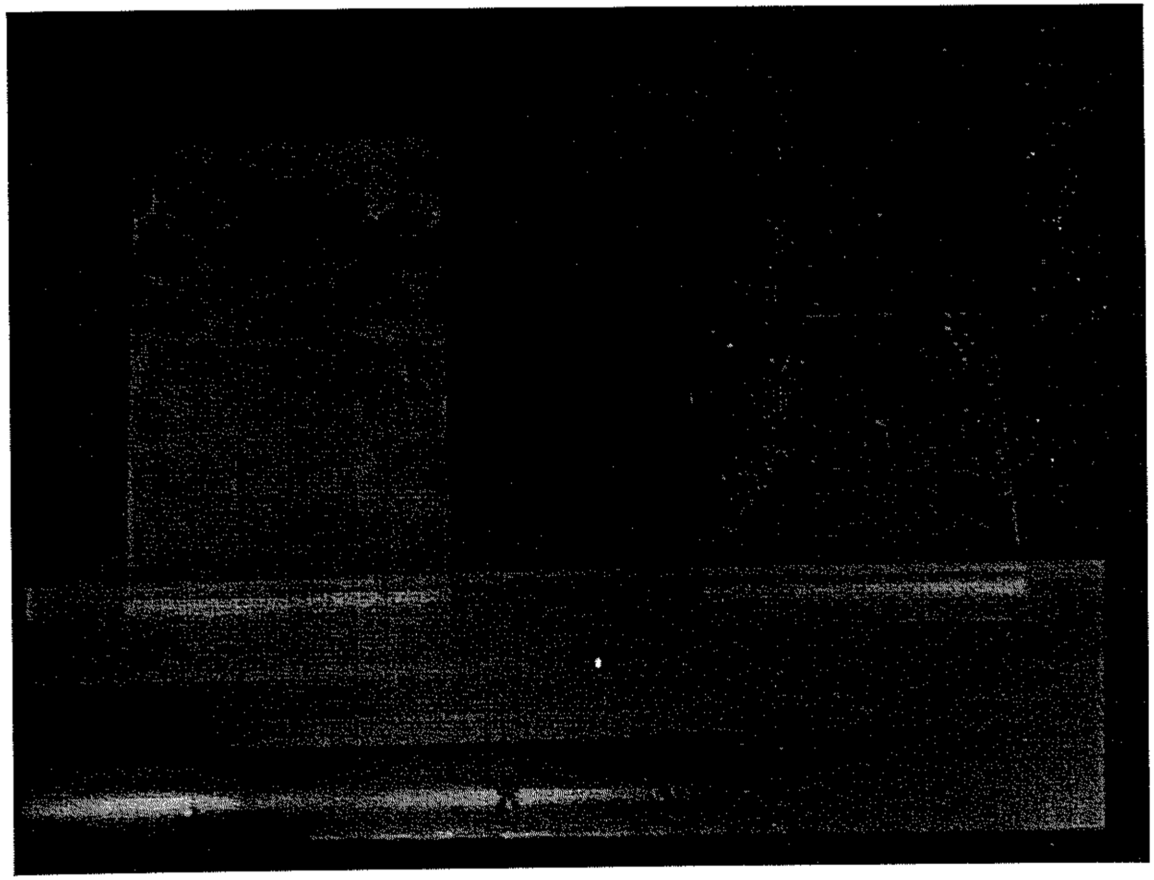


no pretreatment for Al necessary

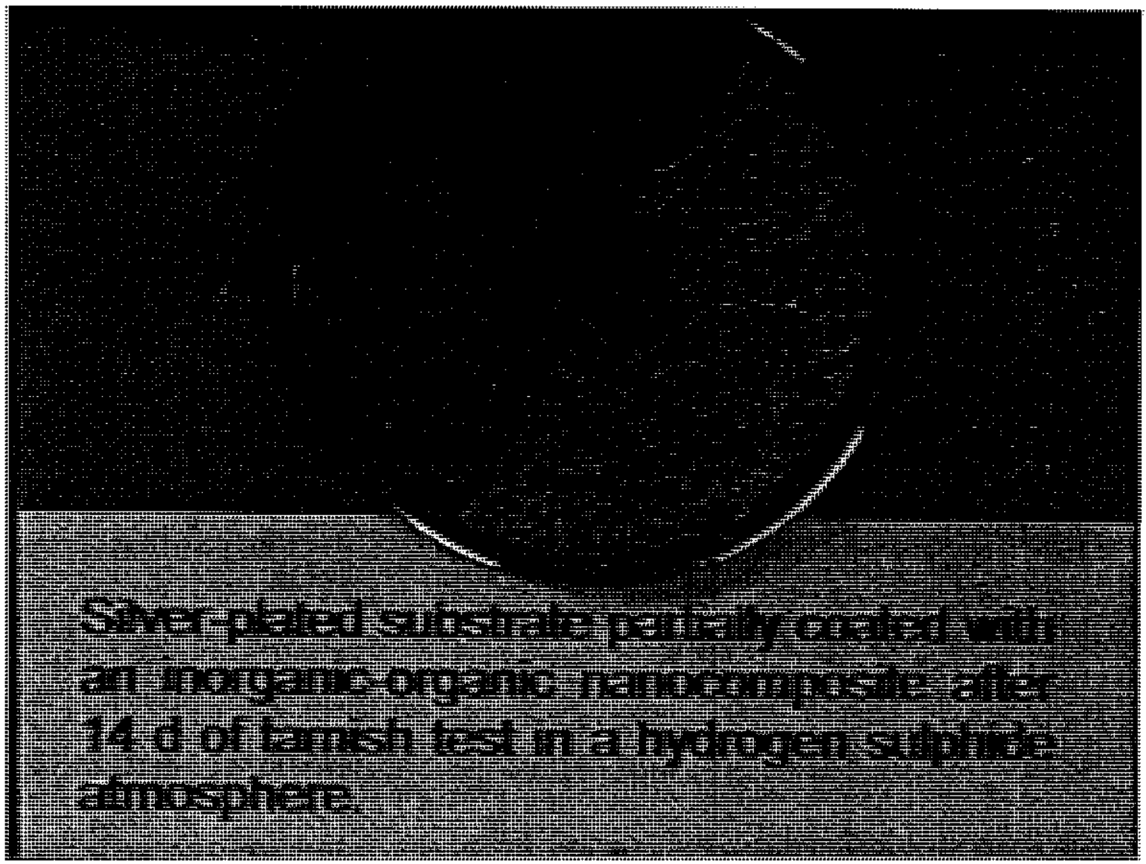
002.777

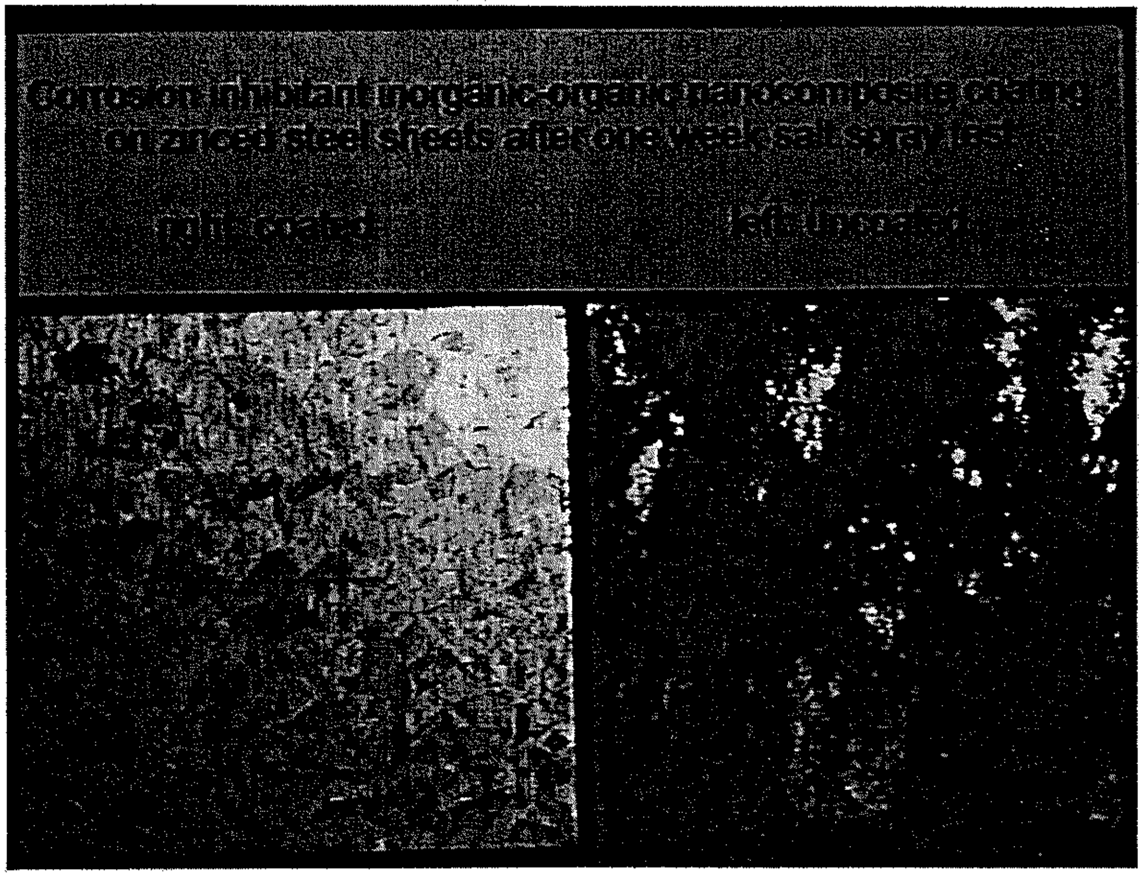


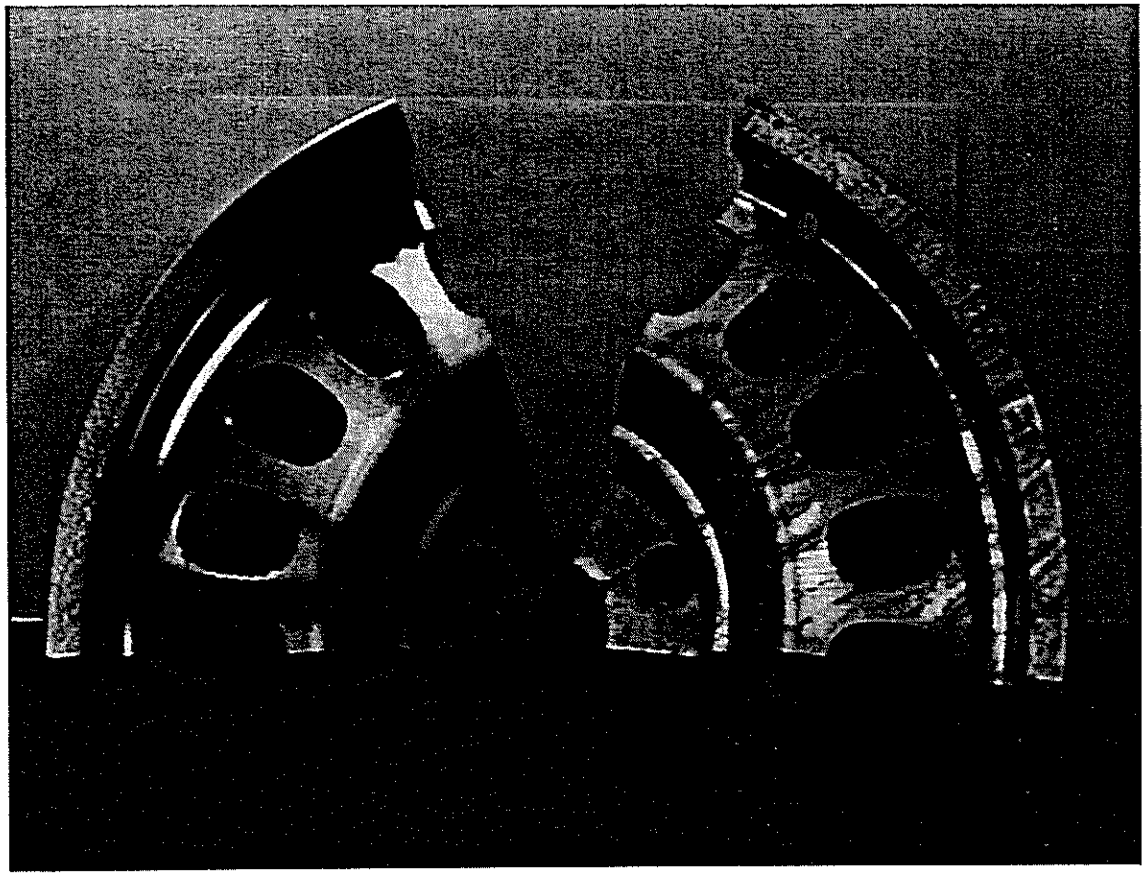
Al food containers with corrosion protection
anti soiling coating



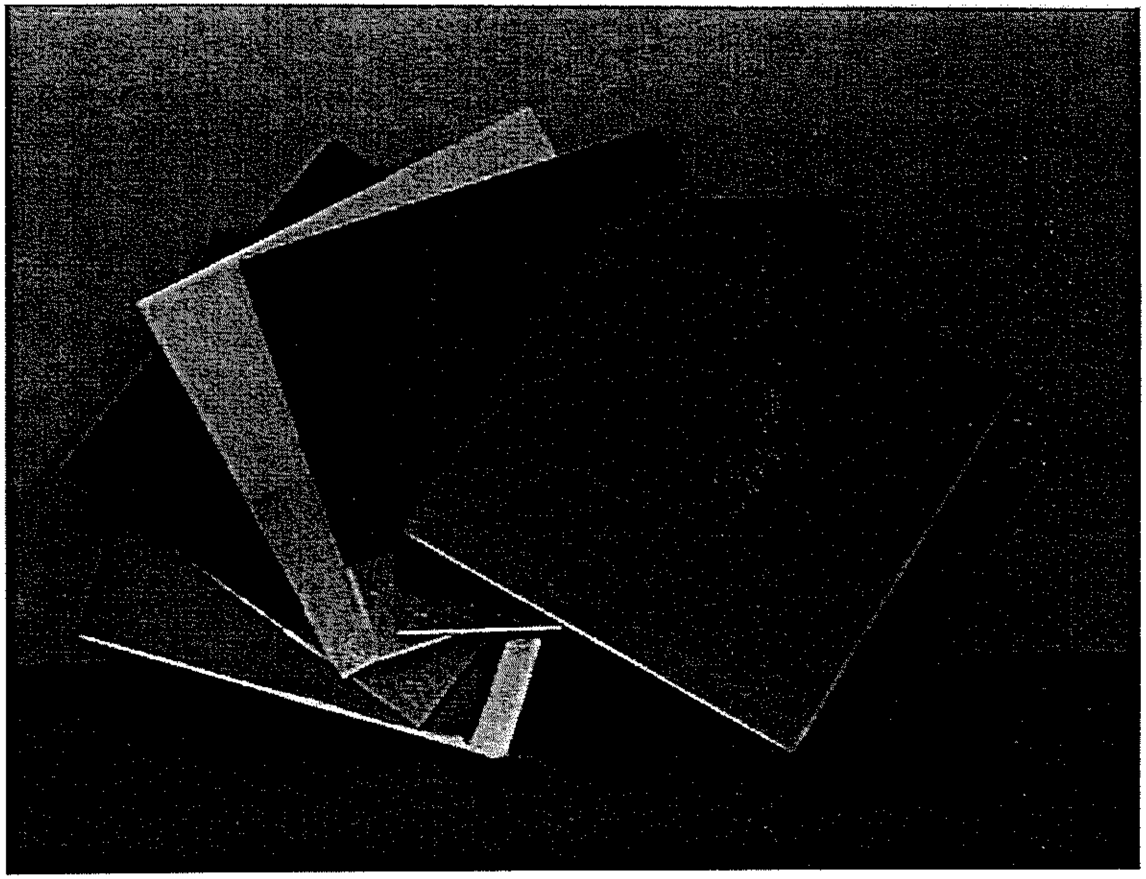
corrosion protection of Al in the salt spray chamber
left: uncoated
right: coated with cross cut before test


Silver-plated substrate partially coated with an inorganic-organic nanocomposite after 14 d of tarnish test in a hydrogen sulphide atmosphere.

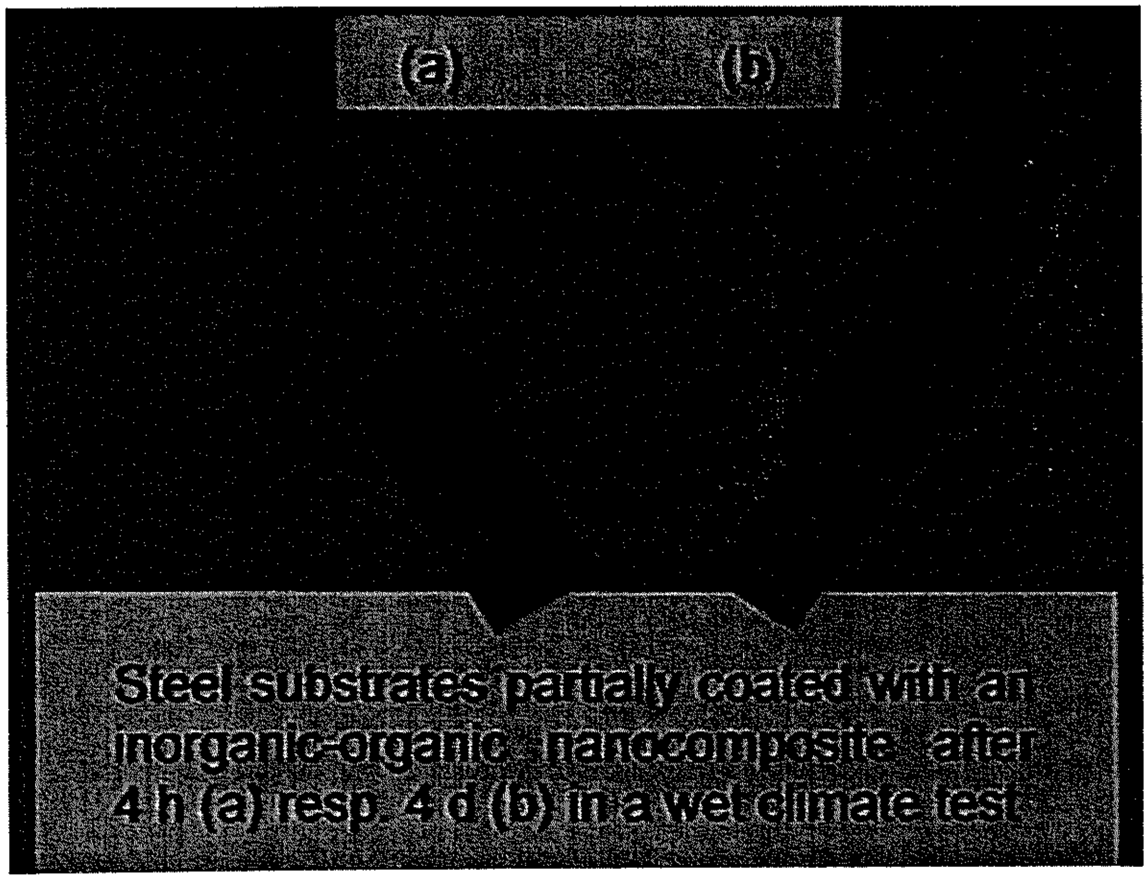

Corrosion inhibitant inorganic-organic nanocomposite coating on zinced steel sheets after one week salt spray test
right: coated
left: uncoated



Al car wheel after corrosion test
left : coated
right : uncoated

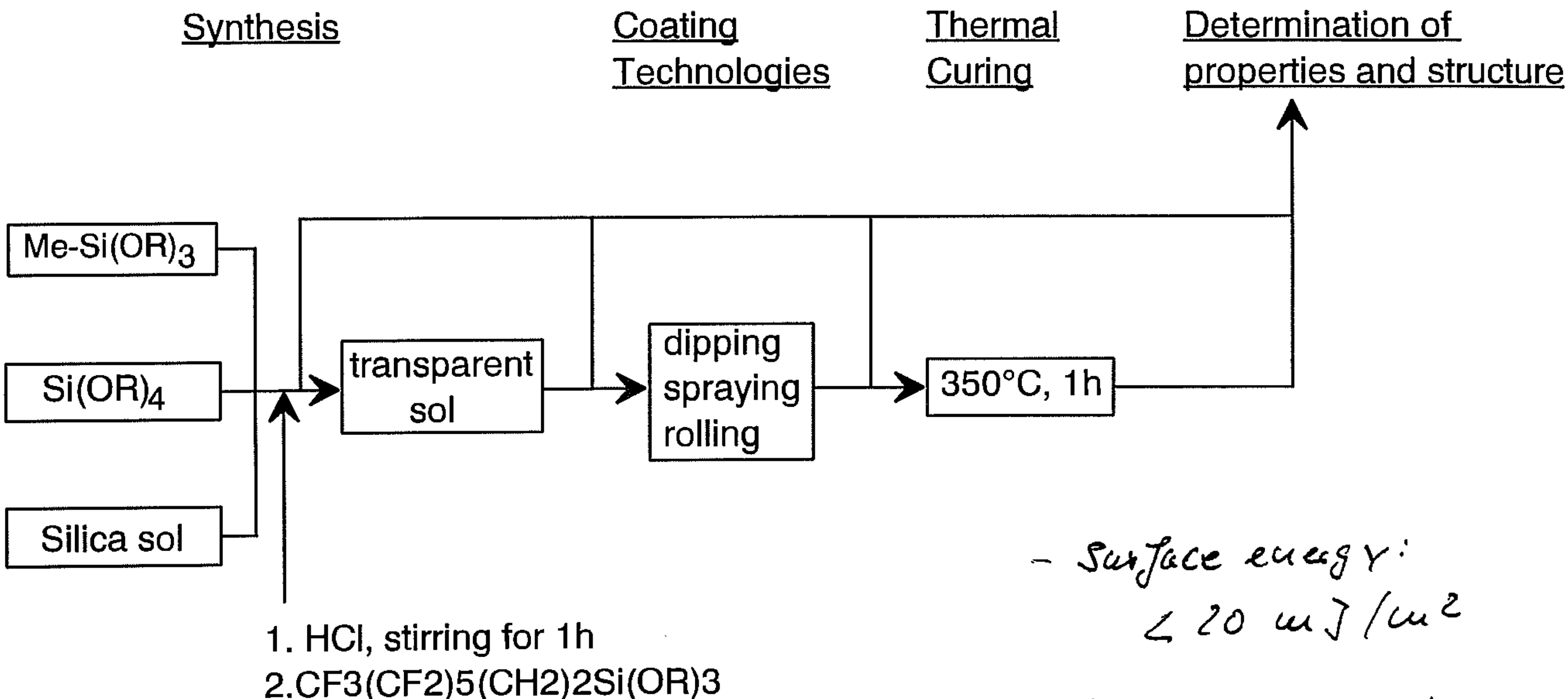


Al with various coloured anticorrosion coatings



dark part: uncoated

High temperature low surface free energy coatings on glass (dust repellent properties)



- surface energy: < 20 mJ/m²
- highly transparent
- high scratch resistance

002.026

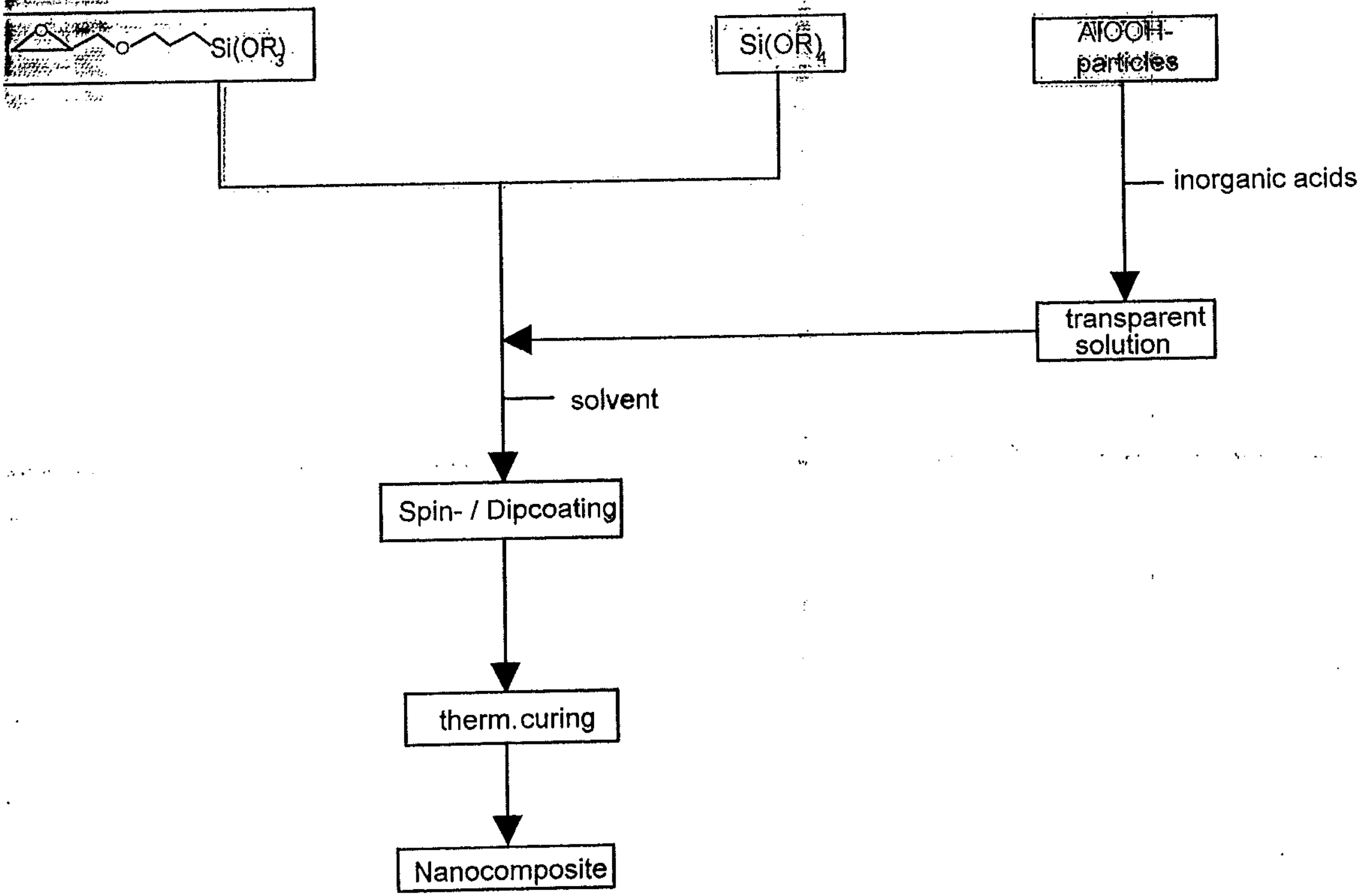
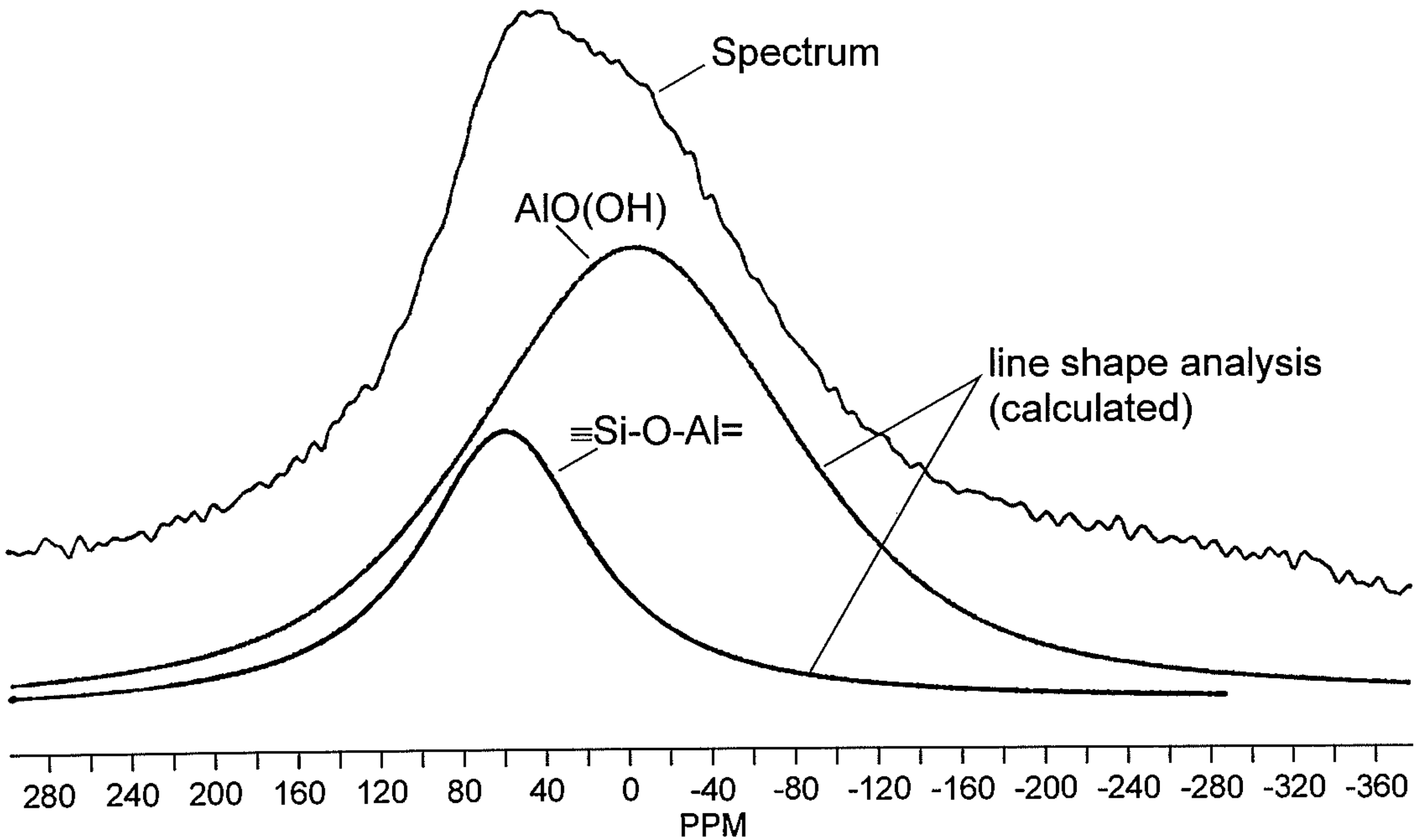
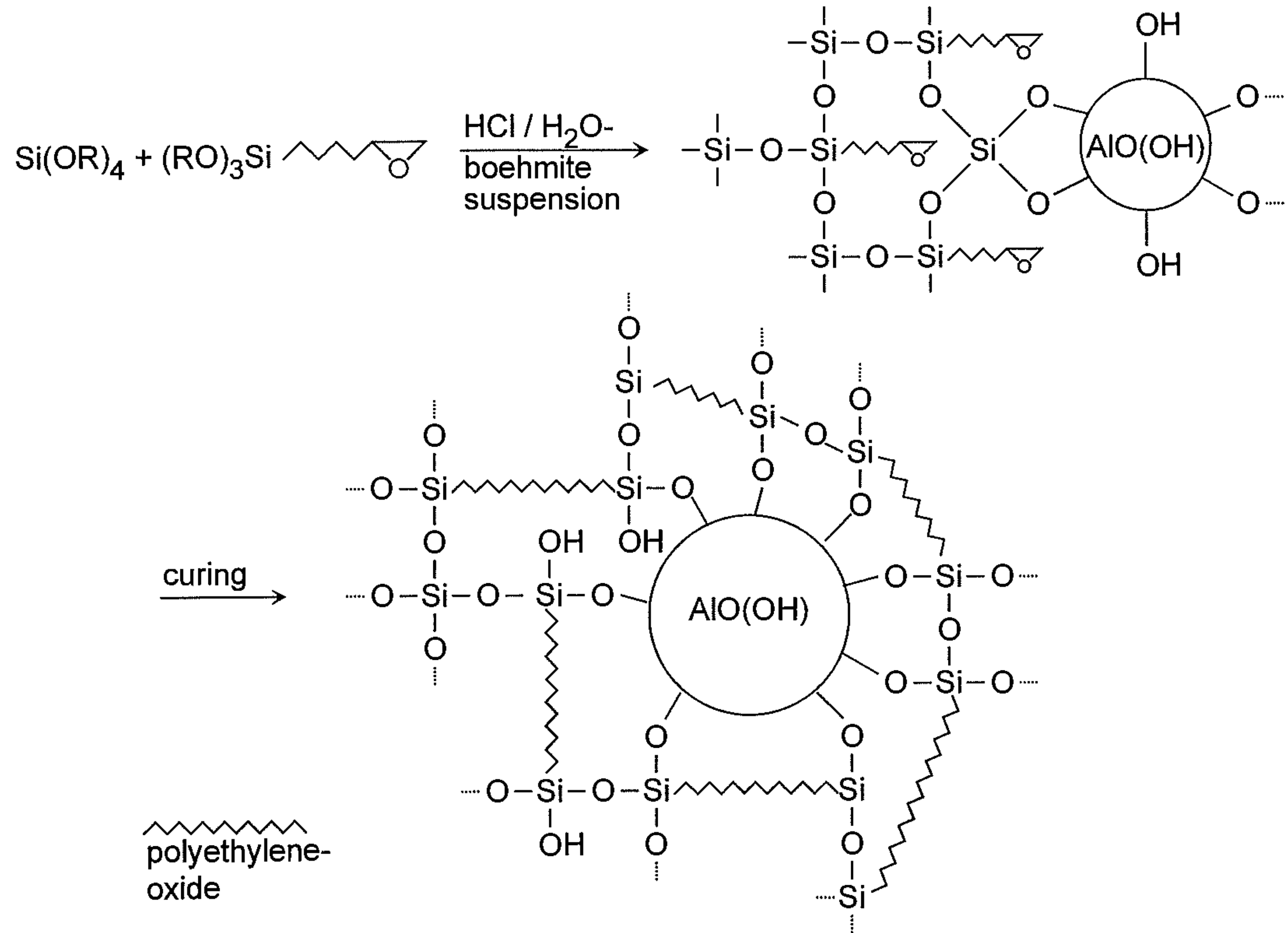


Figure 2: Synthesis of high scratch resistant Coatings



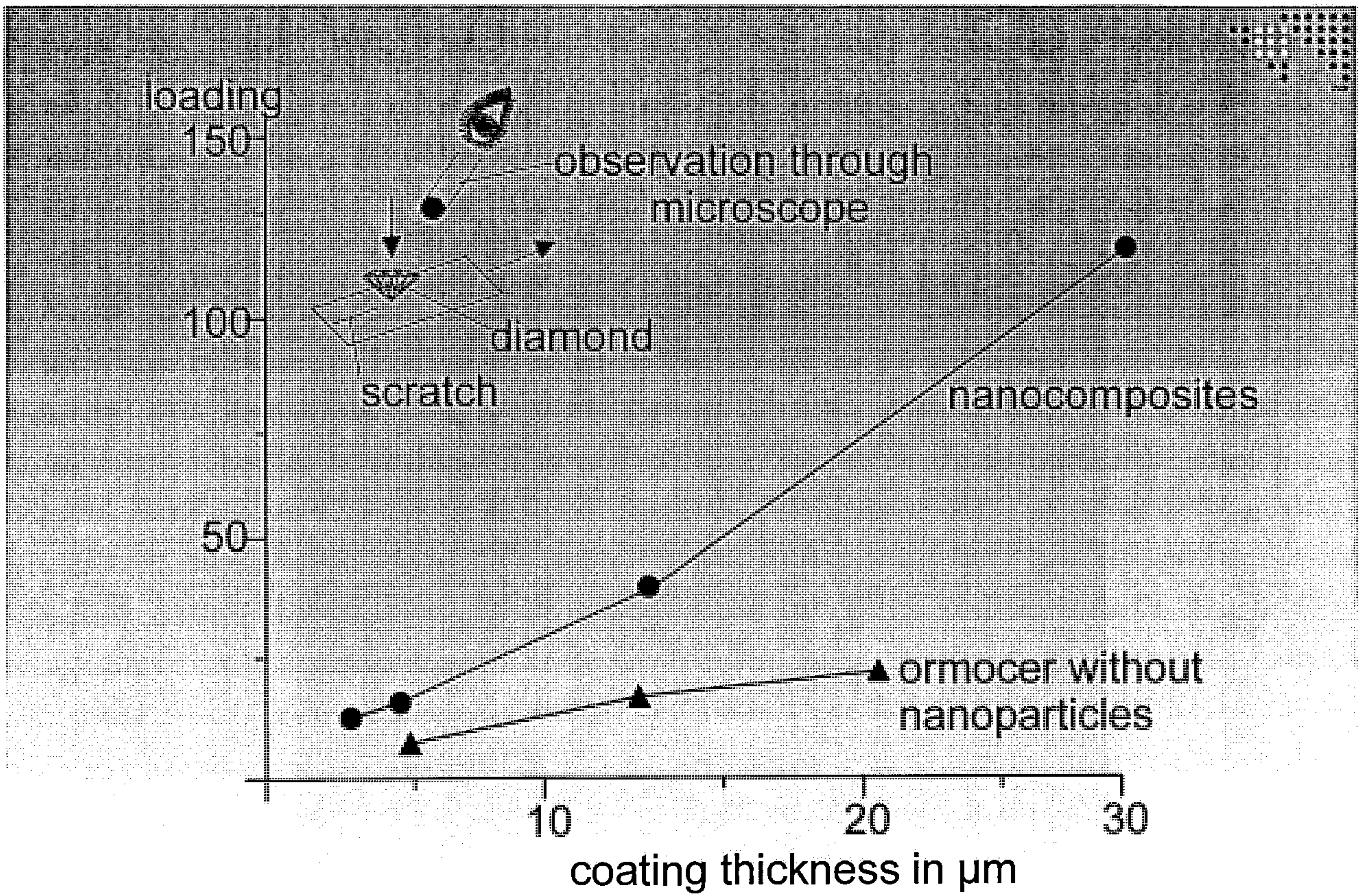
Formation of ≡Si-O-Al= bonds in

002.252



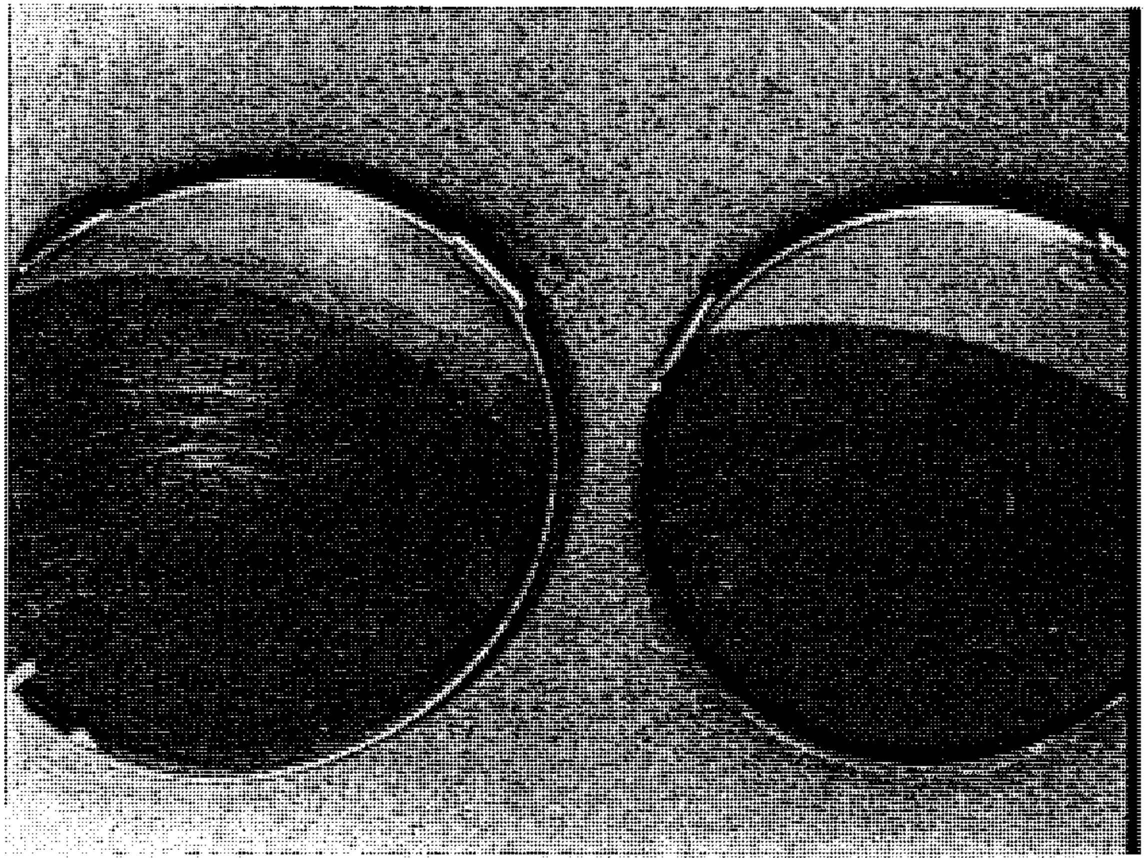
Reaction scheme and structural model of the GPTS/TEOS/boehmite-based material

002.404

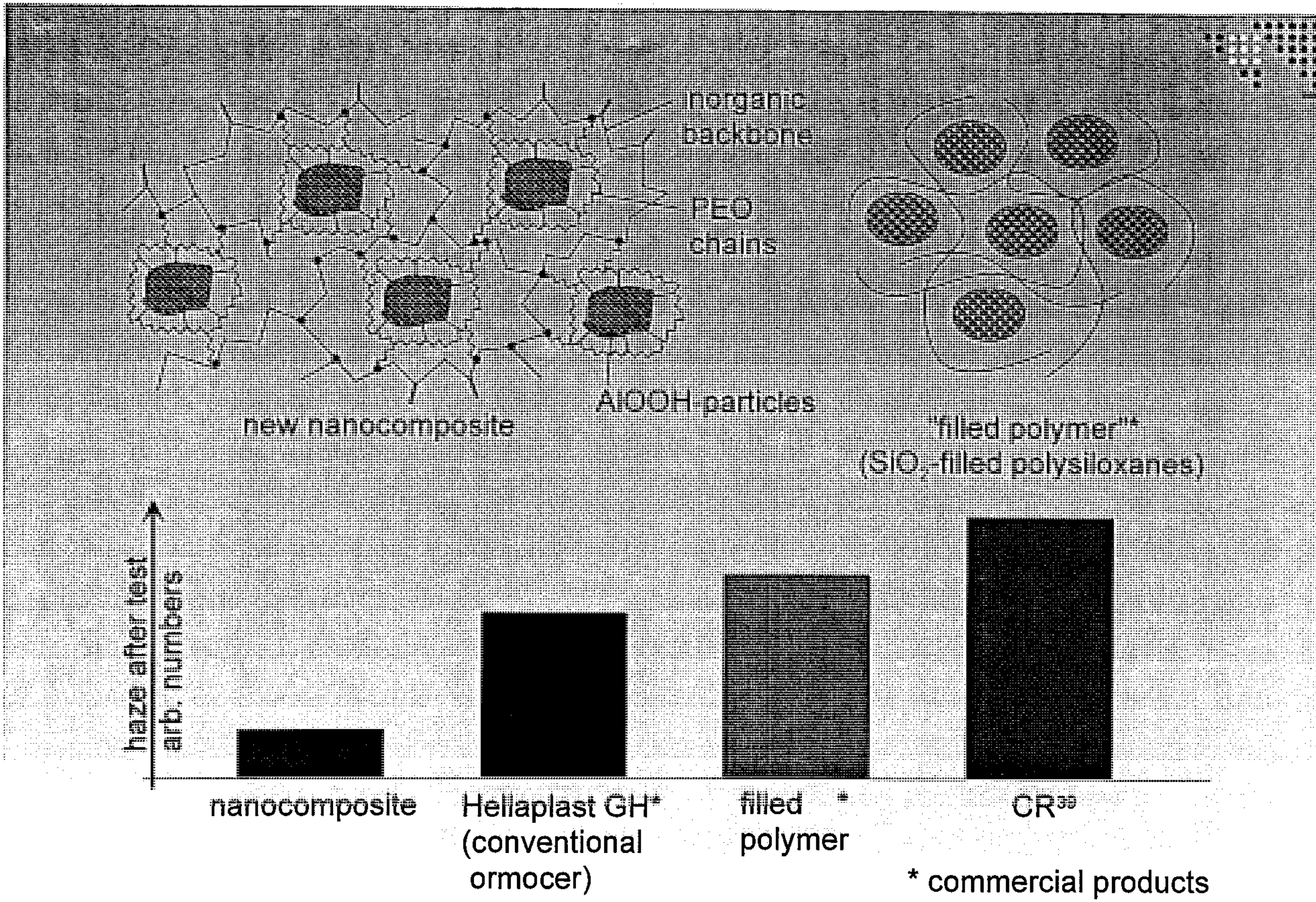


scratch resistance of nanocomposite coatings

002.778

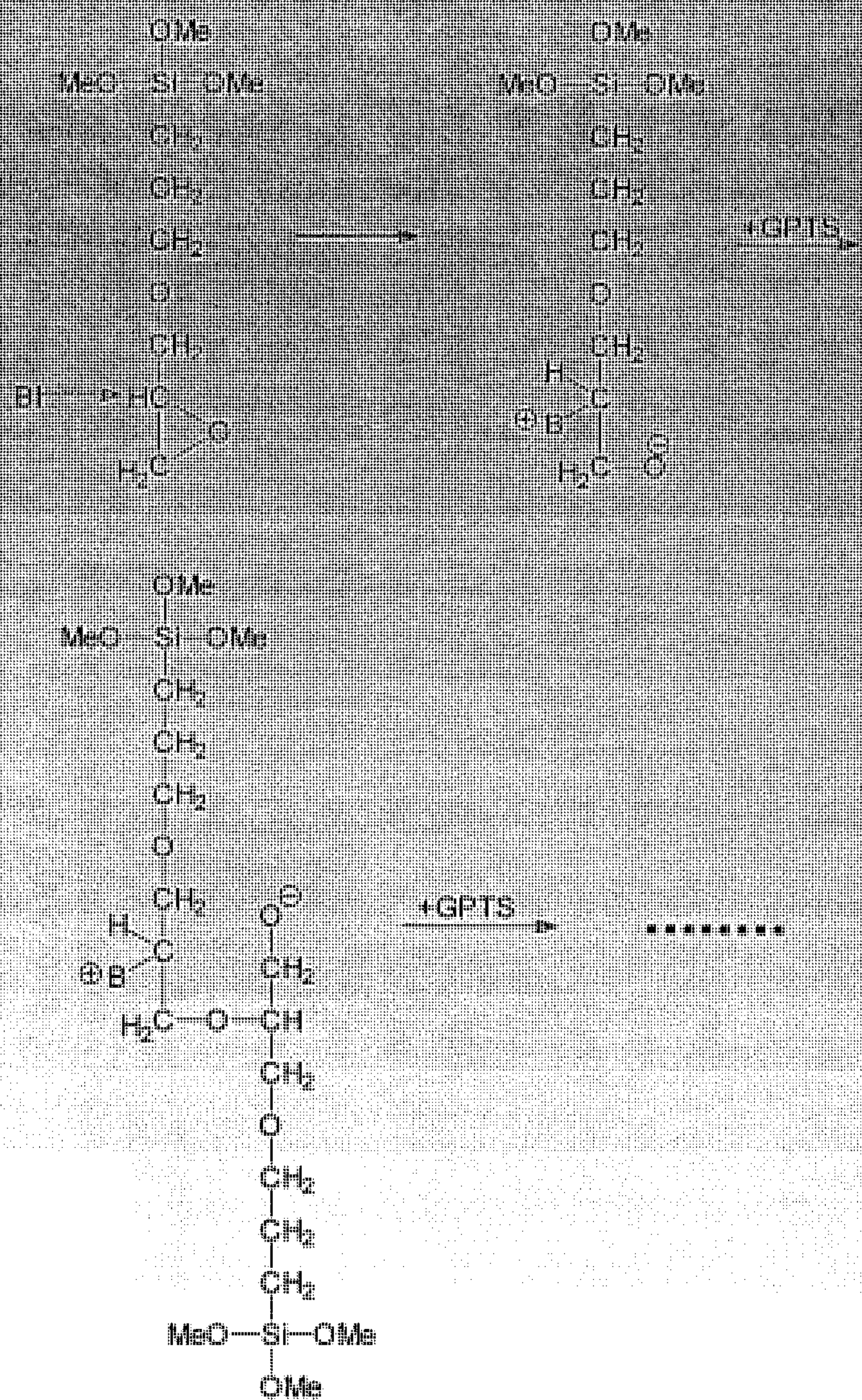


eye glass lenses after scearch test:
left: uncoated; right: coated

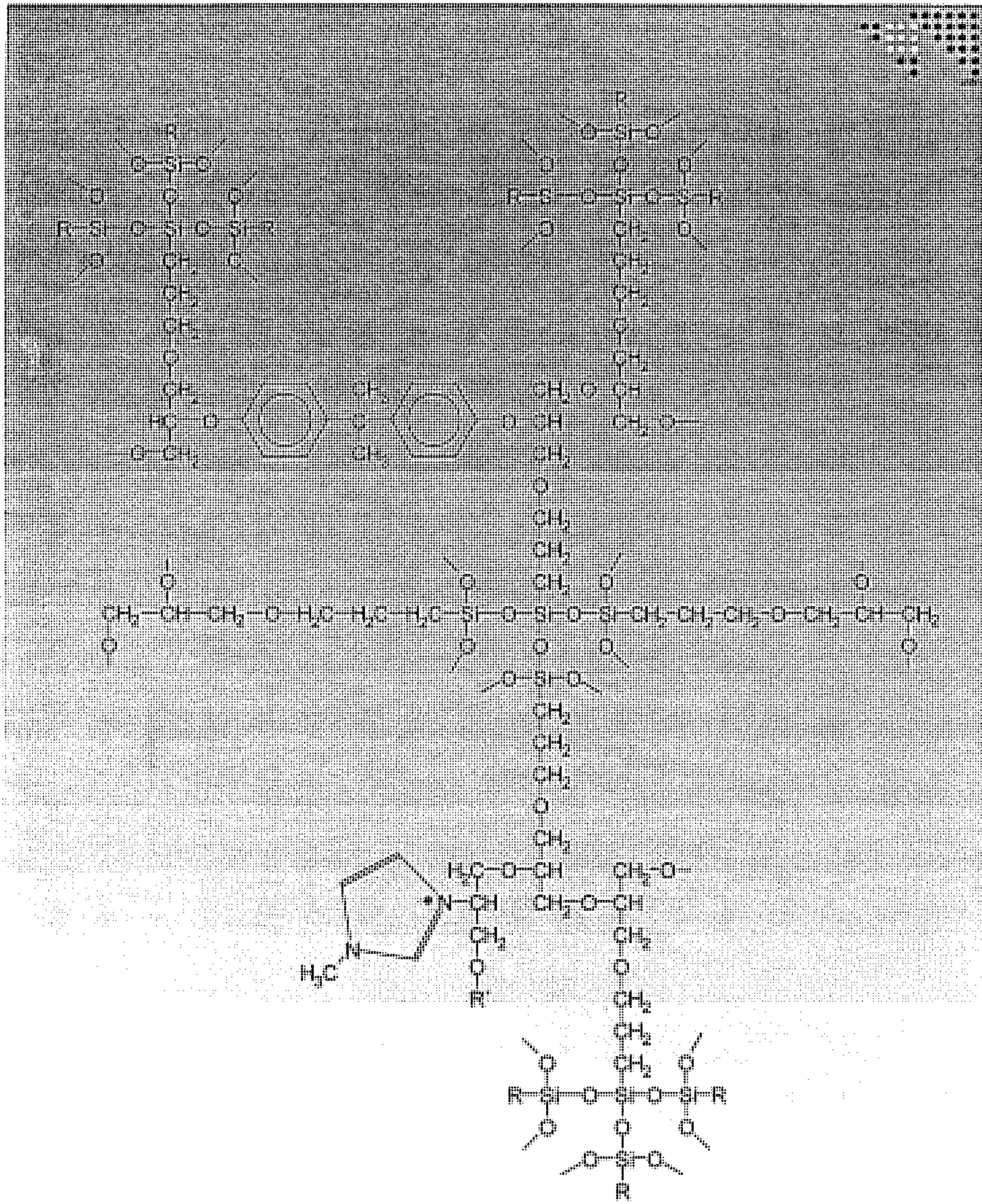

inorganic backbone
PEO chains
AlOOH particles
new nanocomposite
"filled polymer"*
(SiO_2-filled polysiloxanes)
haze after test
arb. numbers
nanocomposite
Hellaplast GH*
(conventional ormocer)
filled polymer *
CR39
* commercial products

002.909

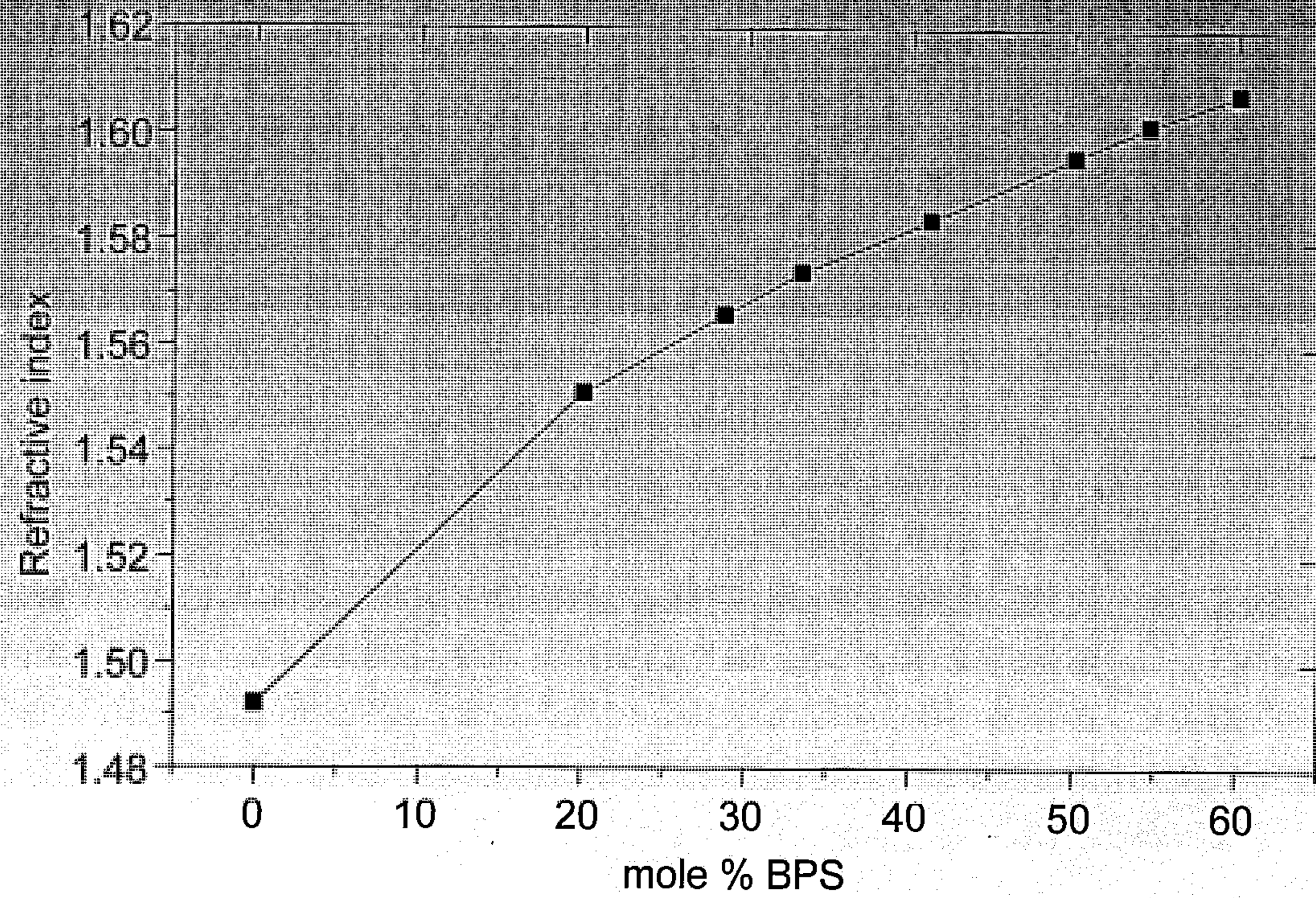
scratch resistant coatings for 1.6 n_D eyeglass lenses



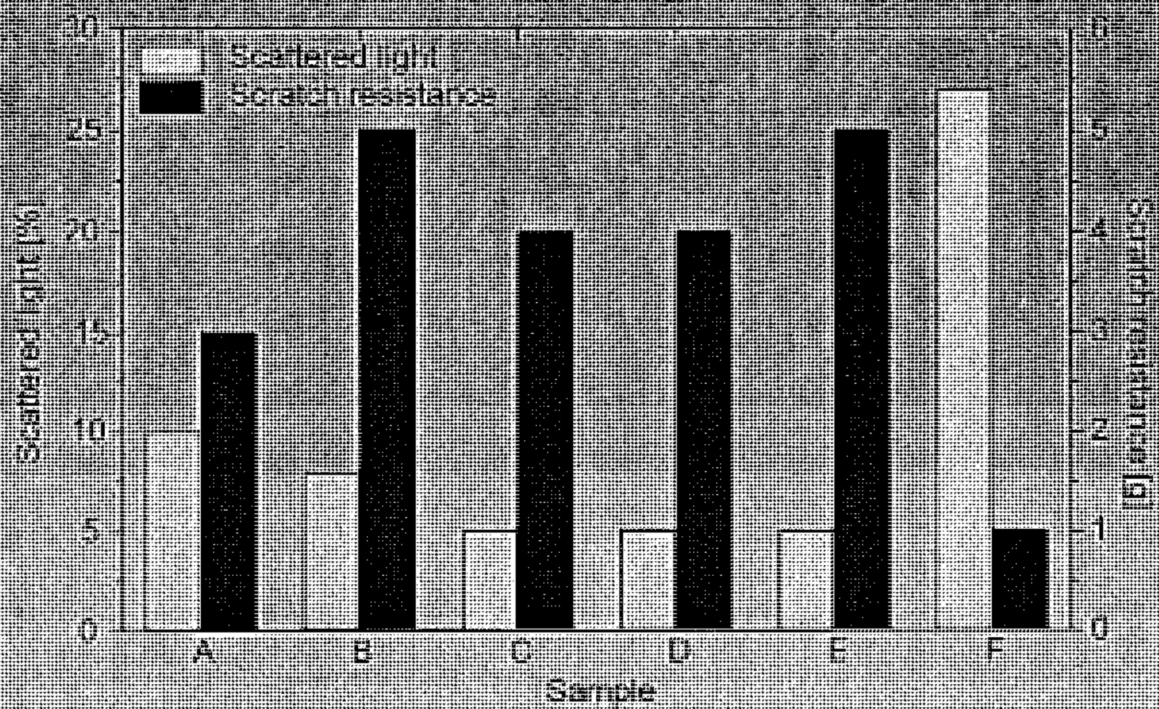
002.890



002.891


Refractive index
1.62
1.60
1.58
1.56
1.54
1.52
1.50
1.48
0
10
20
30
40
50
60
mole % BPS

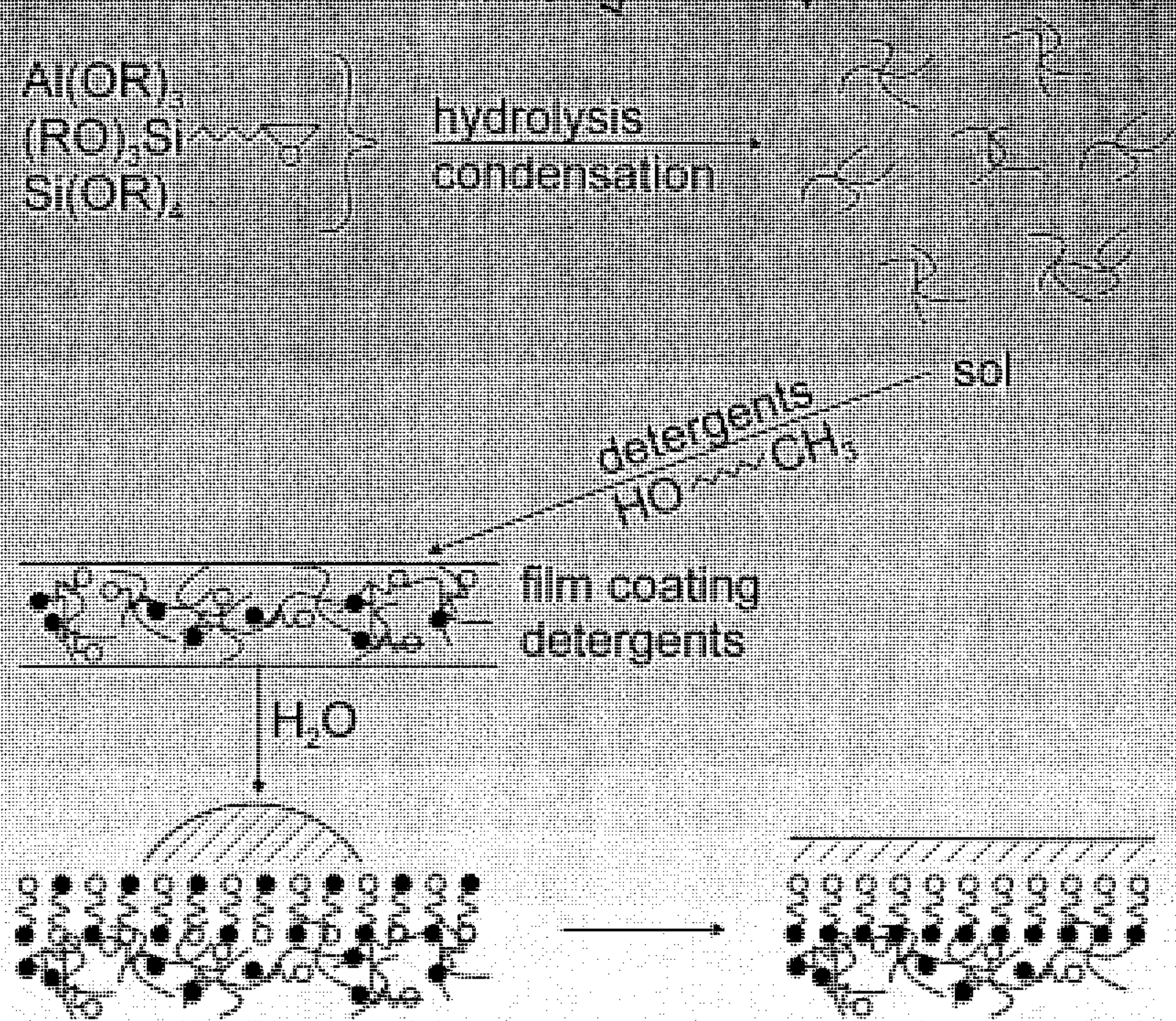
002.892



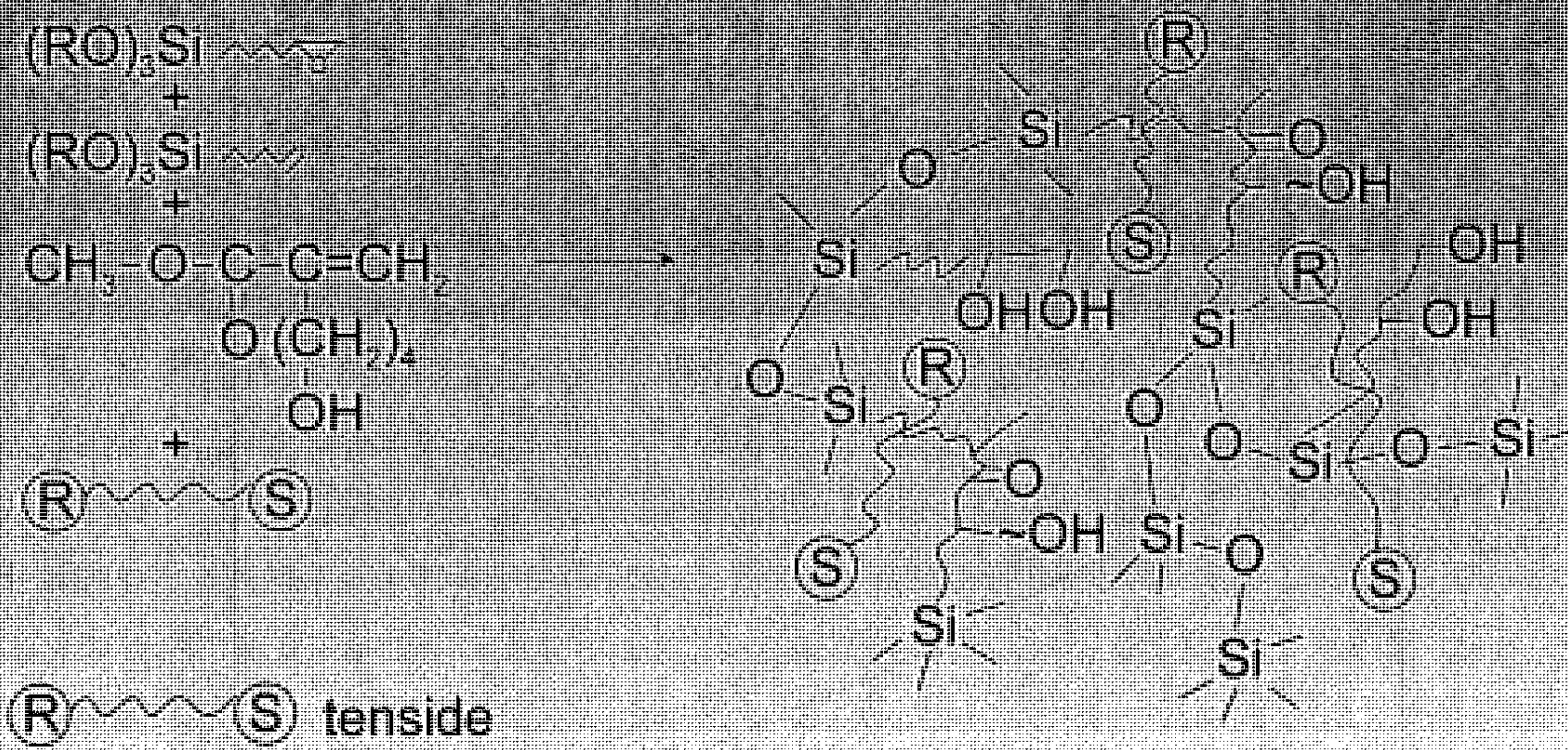
Sample	GPTS	BPS	TEOS	PTEOS
A	1	0.2	0	0
B	1	0.4	0	0
C	1	0.5	0	0
D	1	0.4	0.2	0
E	1	0.4	0	0.2
F	uncoated polycarbonate			

002.894

Controlled release systems as antifogging coatings



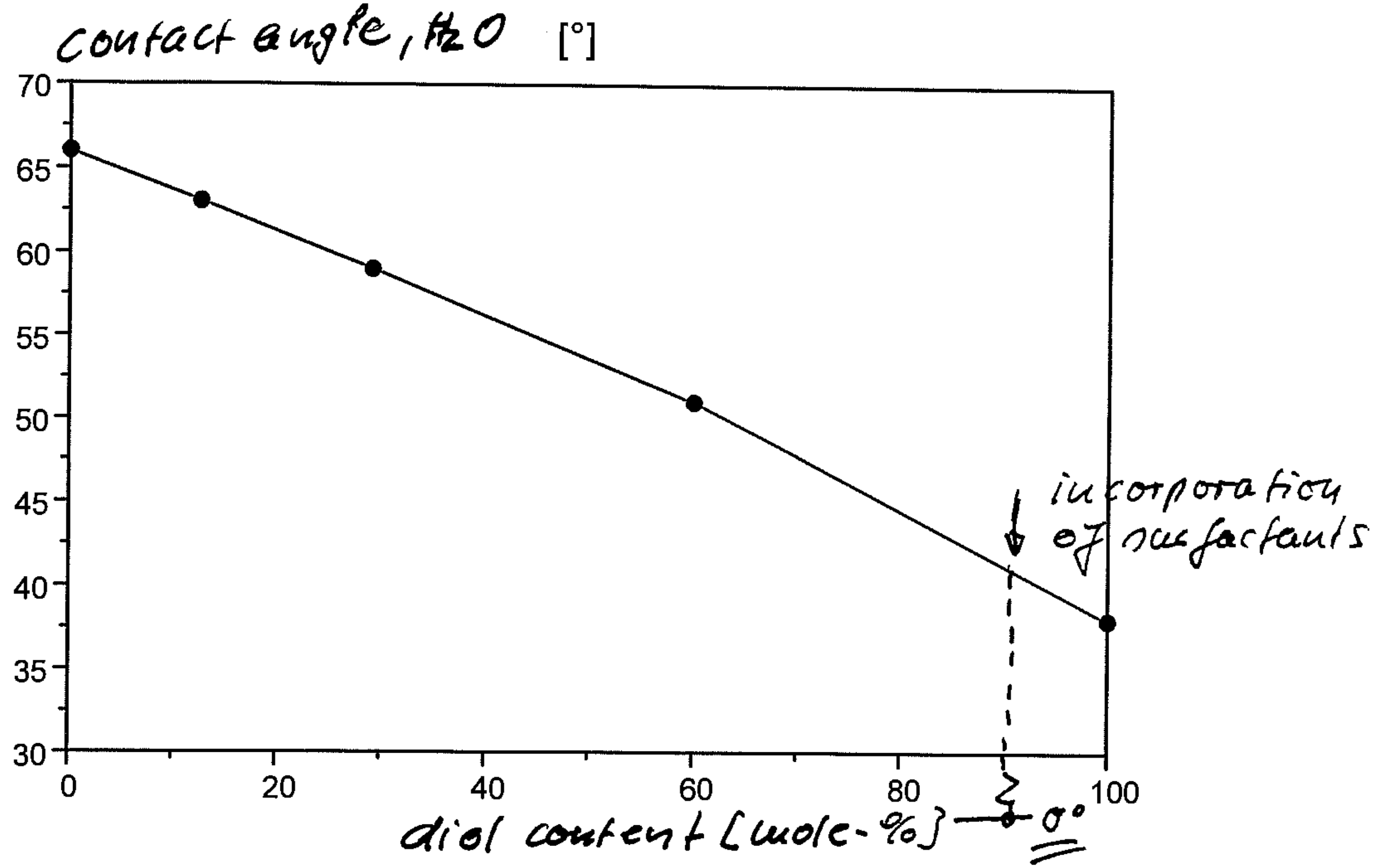
002.924



R = hydrophobic grouping
S = hydrophilic grouping

002.810

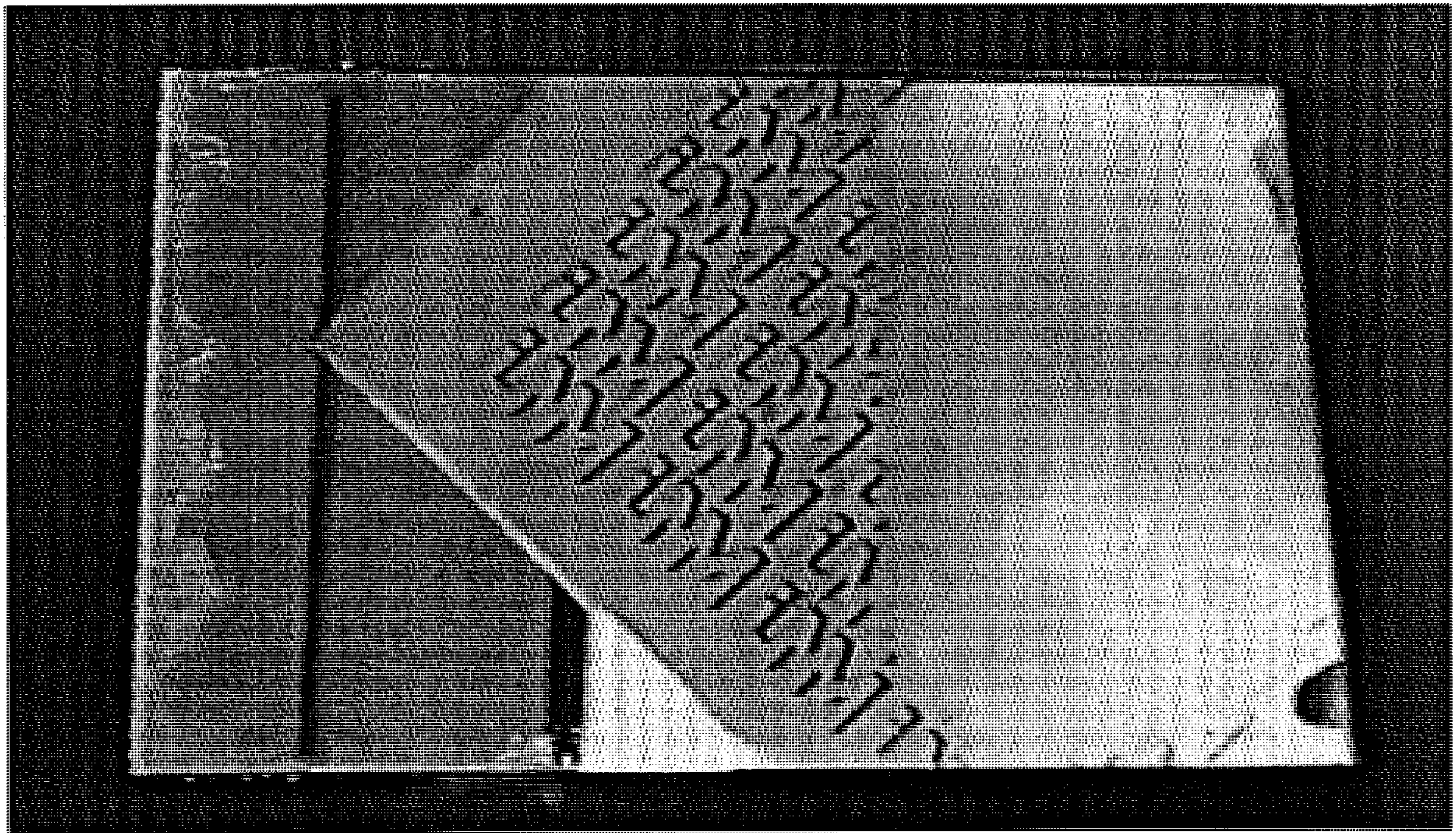
Effect of ring opening of the epoxysilane/AlOOH nanocomposite system



anti fogging effect

002.166

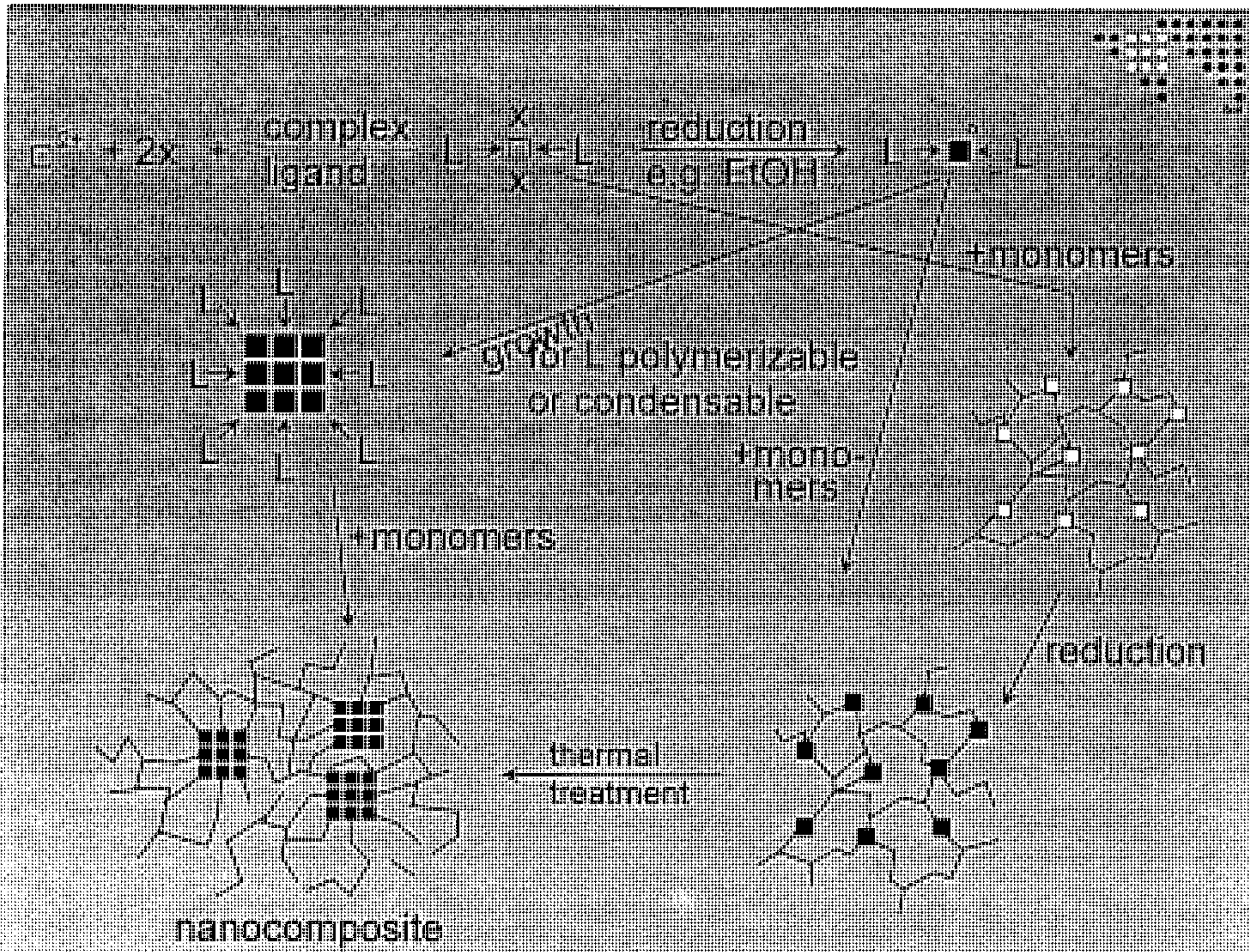
fogging experiment on glass



coated side uncoated

002.027

metal containing nanocomposites



monomers

a: for polymerisation : e. g. olefins, acrylates

b: for sol-gel processing : alkoxides

c: for inorganic-organic sol-gel processing : e. g. alkoxy silanes with epoxy or methacryloxy groupings

L= amines with functional groupings (e. g. double bonds or alkoxy silanes) ■: e. g. Au, Ag, Pd, Pt, Cu

examples

H_2N^^^$CH=CH_2$

... ^^^O-C(=O)-C(CH_3)=CH_2

H_2N^^^$Si(OR)_3$

002.747

NLO materials

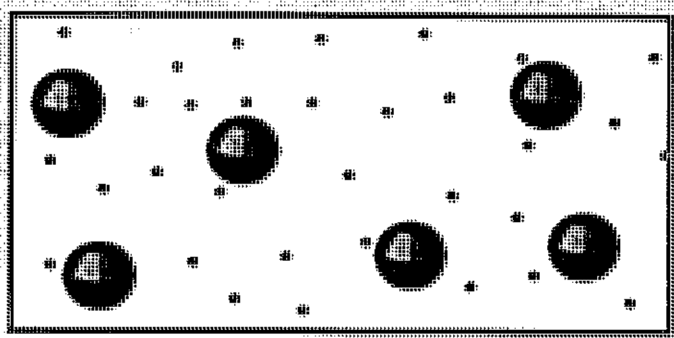
Local electric field factor

$$\chi^{(3)} = p\, f_1^2\, |f_1|^2\, \chi^{(3)}_m$$

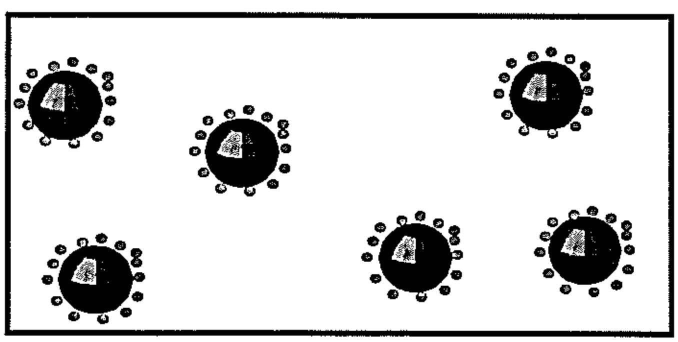
$\chi^{(3)}$ = third order nonlinear susceptibility of the composite
$\chi^{(3)}_m$ = third order nonlinear susceptibility of the colloid
p = volume fraction of colloids
f_1 = local electric field factor

$$f_1 = \frac{3\varepsilon_d}{2\varepsilon_d + \varepsilon_m}$$

ε_d = dielectric function of the matrix
ε_m = dielectric function of the metal



homogeneous matrix



tailored interface:
- shell with large ε
- ligands
  (e⁻ donor/acceptor)

002.820

Determination of nonlinear optical properties

$$\chi^{(3)} = \frac{8n^2c^2\varepsilon_0\alpha\sqrt{\eta}}{3\omega I_p(1-T)\sqrt{T}}$$

η = grating efficiency
c = speed of light
ω = frequency of I_p
T = transmission of I_p
n = refractive index
α = linear absorption
I_p = pump intensity

local field factor: $$\chi^{(3)} = p f_1^2 |f_1|^2 \chi_m^{(3)}$$

$$f_1 = f_1(\omega) = \frac{3\varepsilon_d}{\varepsilon_m(\omega) + 2\varepsilon_d}$$

$\varepsilon_m(\omega), \varepsilon_d$ = dielectric function of the metal and the matrix

Determination of ε''_m (Hache et al.) :

$$\frac{W}{W_\infty} = \frac{\varepsilon''_m}{\varepsilon''^{\infty}_m}$$

W_∞ = halfwidth, $\varepsilon_m''^{\infty}$ = dielectric function in large particle size limit

Determination of the volume fraction p:

$$\alpha = p\frac{\omega}{n_d c}|f_1|^2 \varepsilon''_m$$

Ormocer sol:

$CH_2=C(CH_3)$-COO-$(CH_2)_3$-$Si(OCH_3)_3$ (MPTS)
prehydrolysis with HCl

+

$Zr(OC_3H_7)_4$ + $CH_2=C(CH_3)$-COOH (1:1) (4 h, RT)

+

H_2O (10 h, RT)

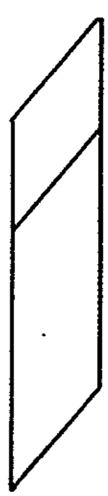
Au precursor:

$HAuCl_4 \cdot 3H_2O$ dissolved
ethanol + isopropanol + acetone (5 : 4 : 1)

+

$NH_2(CH_2)_2NH(CH_2)_3Si(OR)_3$ (DIAMO : Au = 1:1)

mixing, stirring 4 h, RT + photocatalyst



UV curing (Hg-Xe lamp, 1500 W)
thermal curing (200 °C)
1 minute !

→

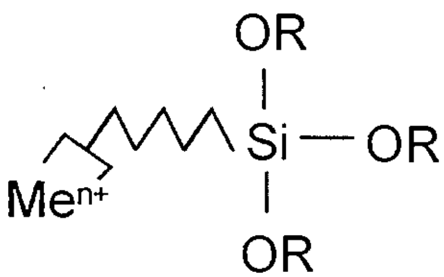
simultaneous
colloid formation
+
matrix densification

Au

Metal colloids for optical switching:

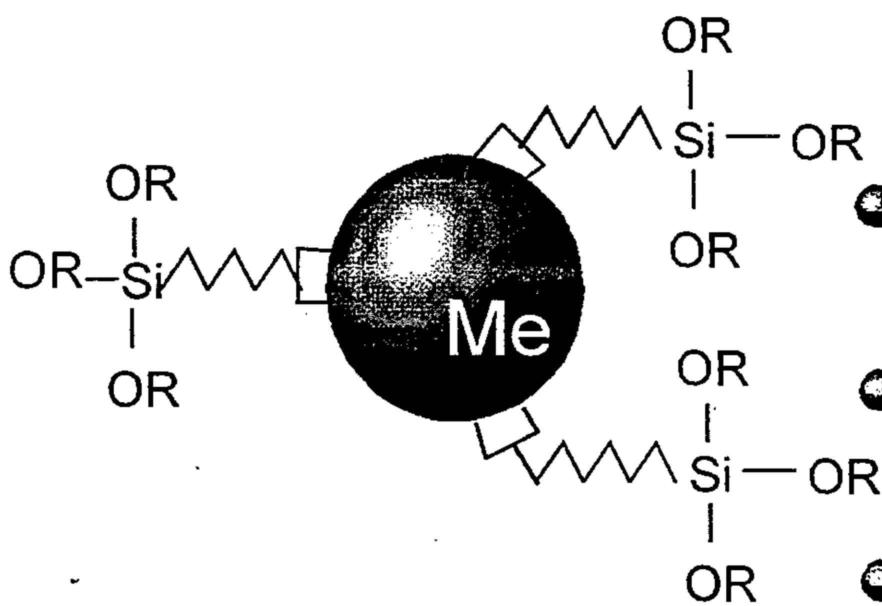
Synthesis of metal colloids in sol-gel matrices

problem: spontaneous reduction of Me-ions in solutions
uncontrolled agglomeration of colloids



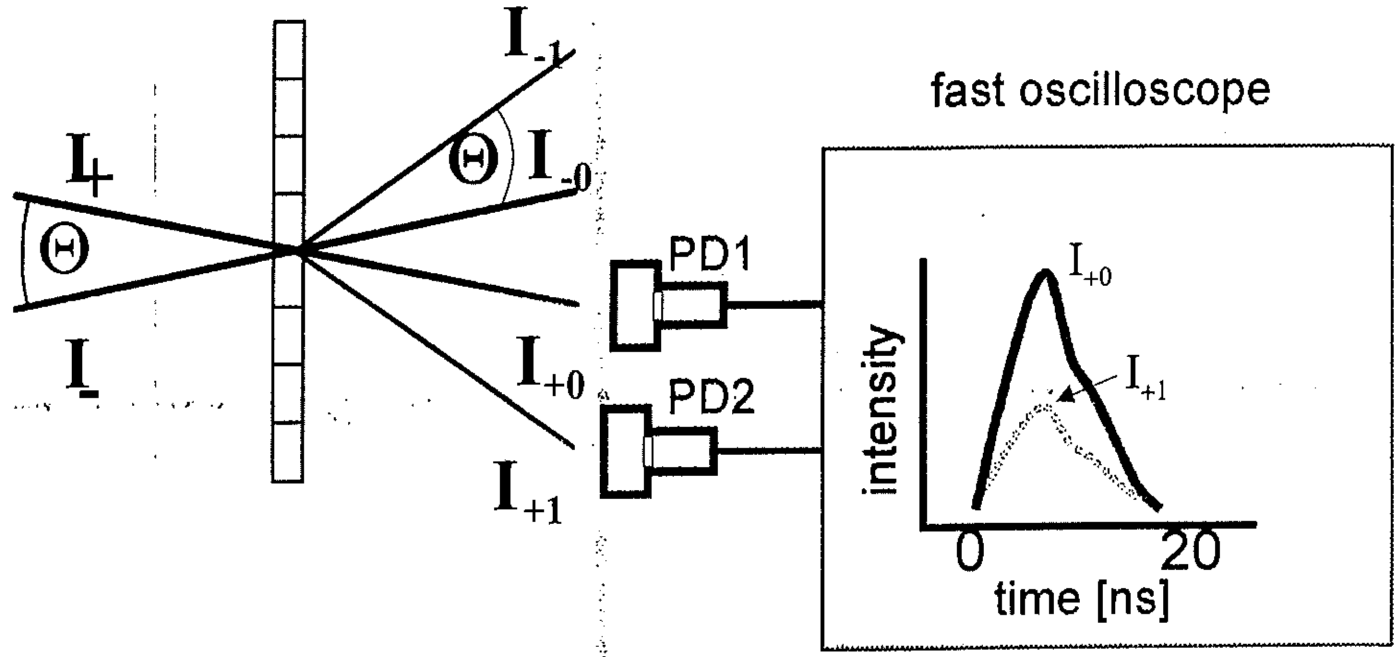
stabilization of Me-ions by complex formation with functionalized silanes

reduction step:
- UV-irradiation
- reducing agents
- thermal activation



- minimization of Gibbs Free Energy
- control of growth and agglomeration
- tailoring of interface

Determination of χ^3 by selfdiffraction experiment



PD = fast photodiode

response time: < 7ps

Au: $\chi^3_{(m)} = 2.6 \cdot 10^{-6}$

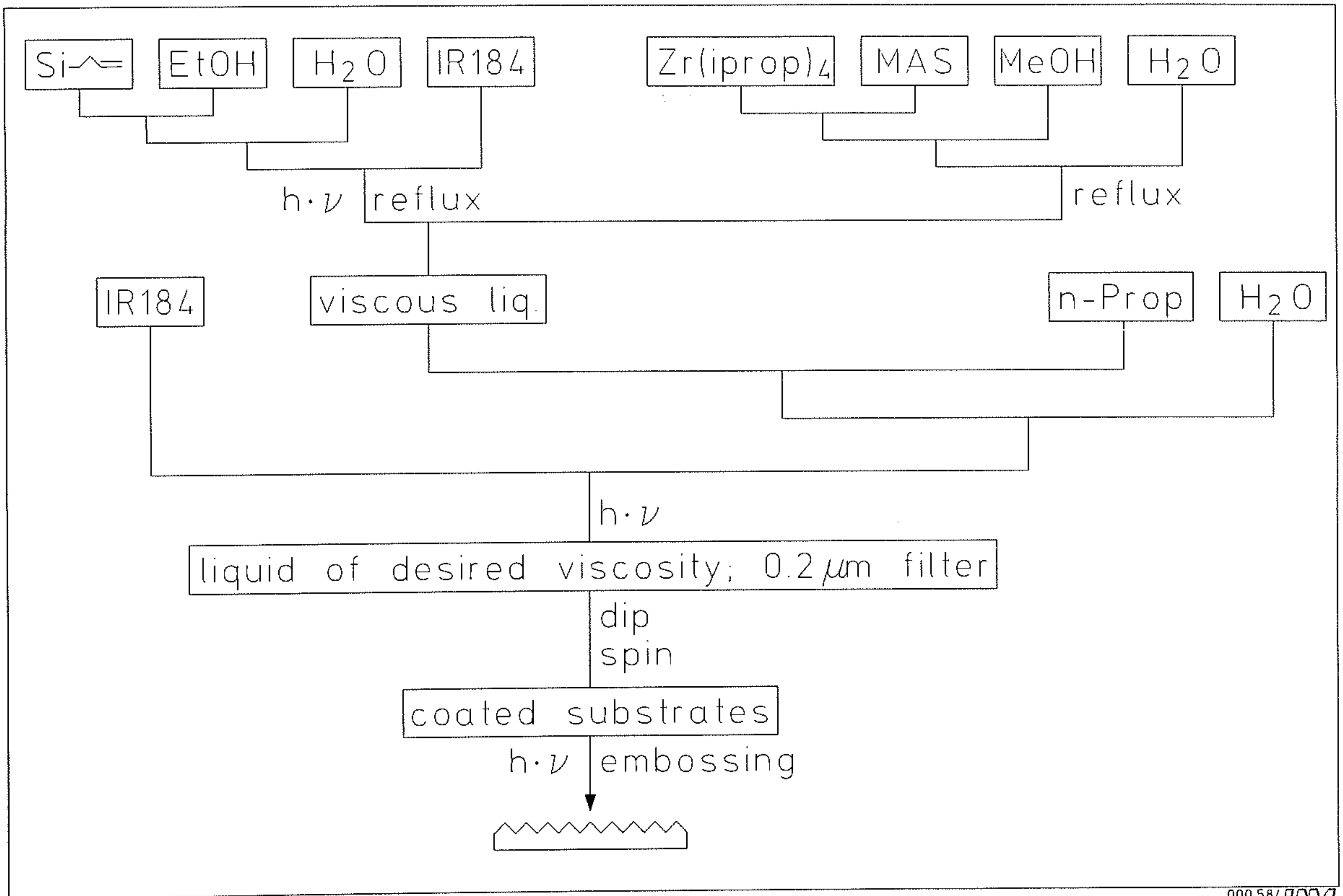
Cu: $\chi_{(m)} = 1.5 \cdot 10^{-5}$

Results:

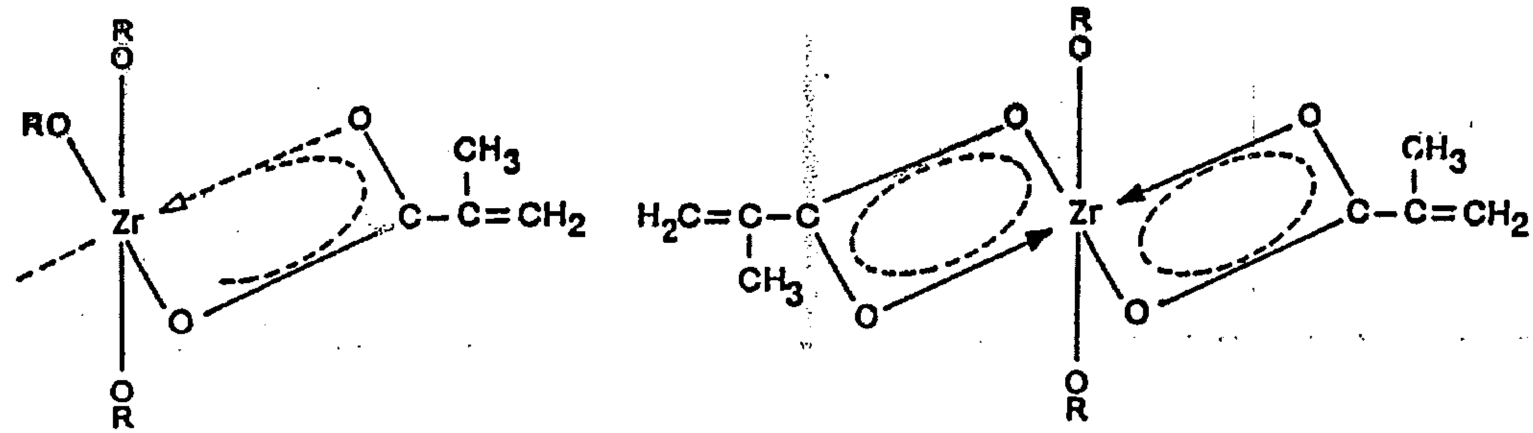
Matrix	ligand	$\chi^{(3)}_m$ [esu]
Ormocer	NH_2 -	2.0 10^{-6}
	SH-	9.0 10^{-7}
SiO_2	NH_2-	7.0 10^{-7}
	SH-	< 1 10^{-7}

Au colloids in glass: 1...5 10^{-8} esu

ZrO2 nanocomposite synthesis
for optical materials

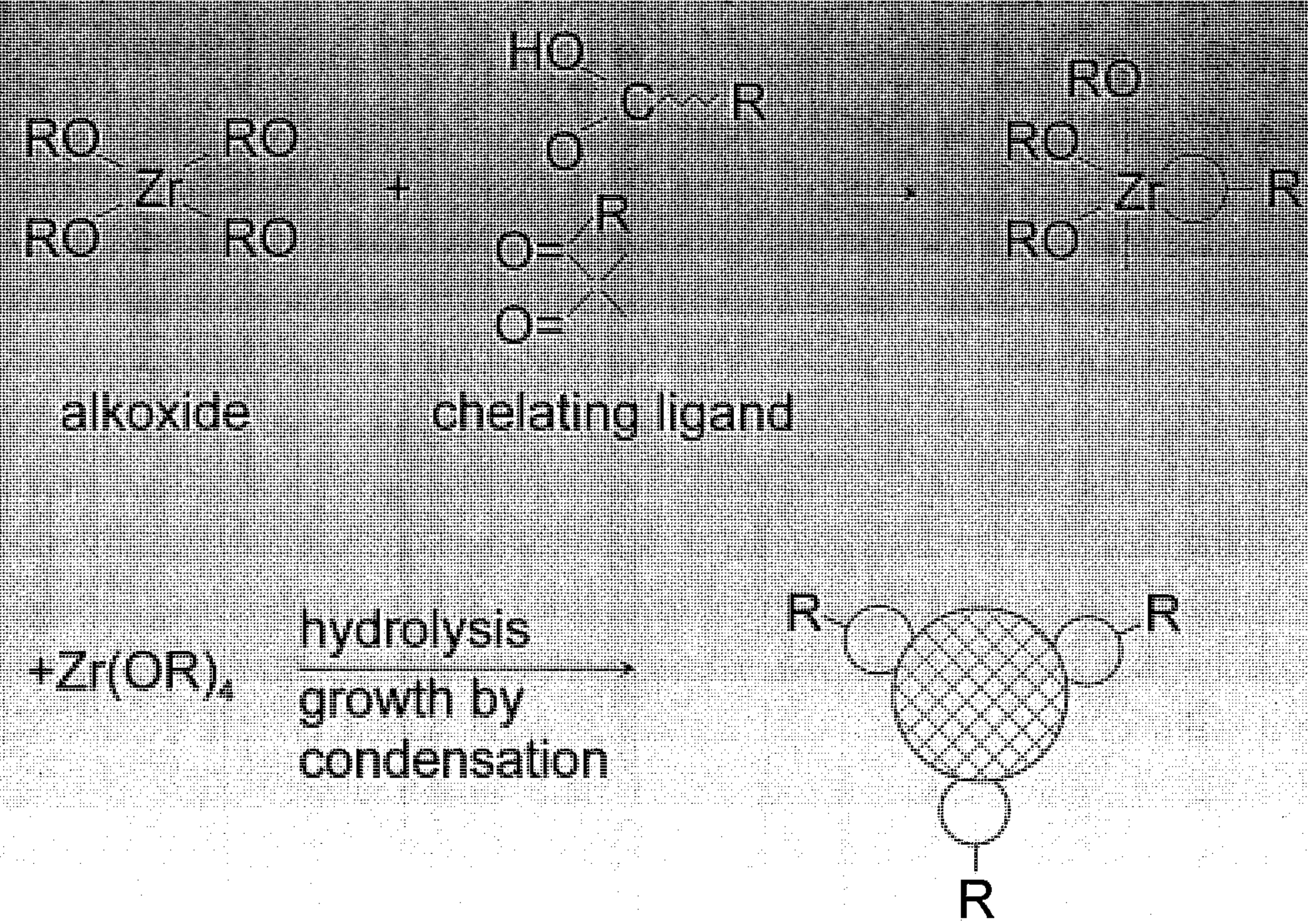


000 584 INM

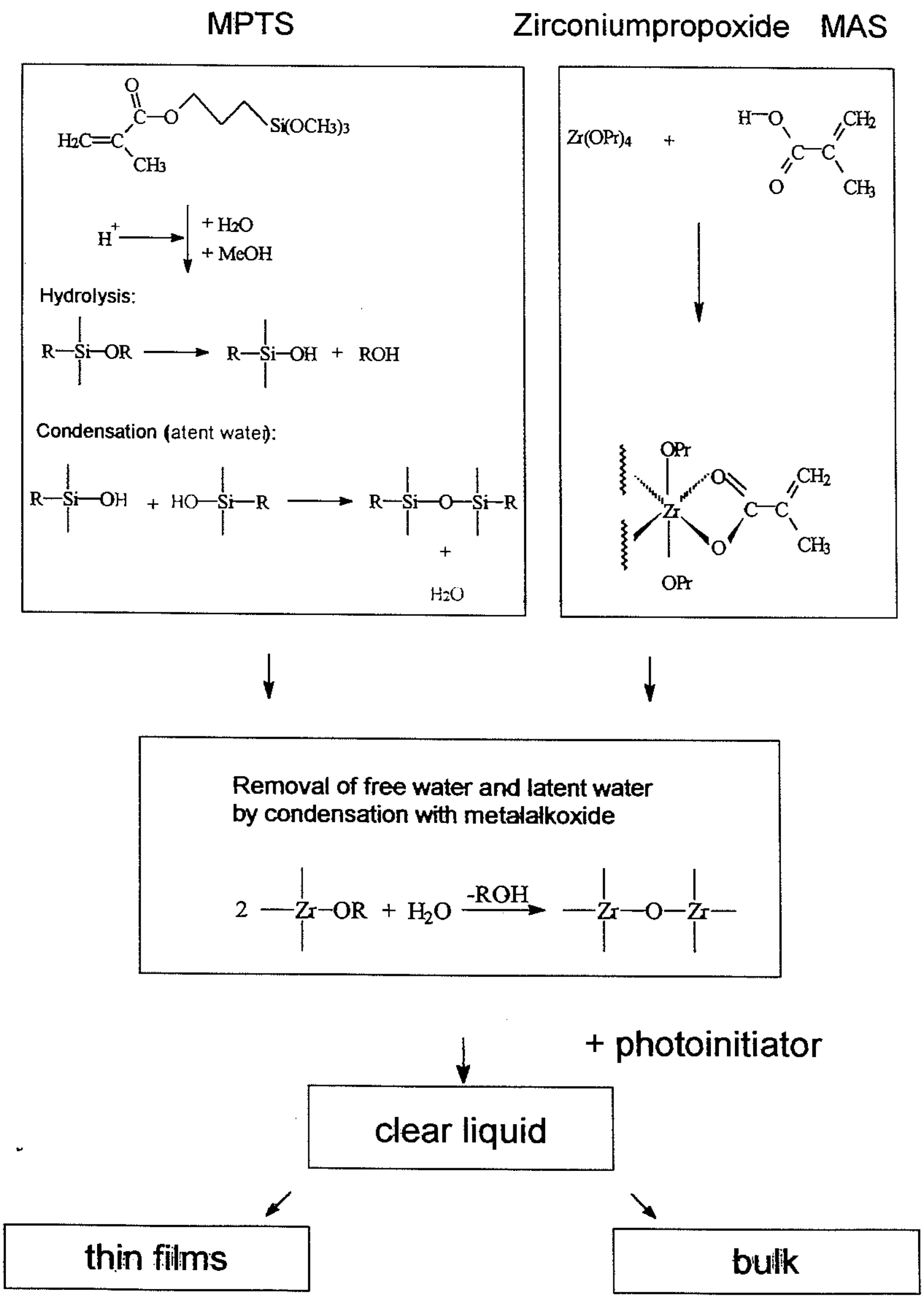


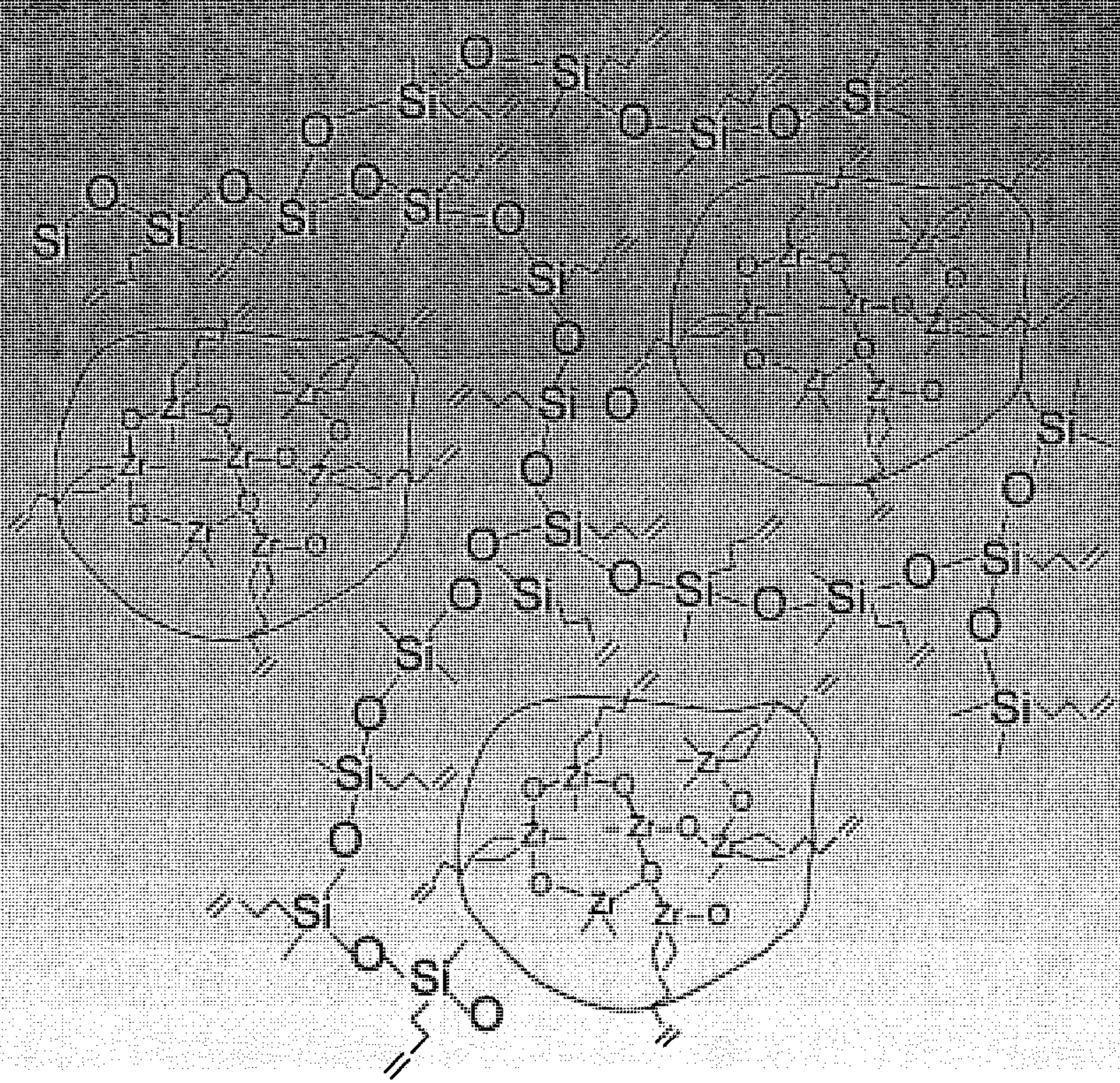
a b

Models for the "chelating" type of bonds between Zr and methacrylic acid a: ZR/MA = 1:1; b: ZR/MA = 1:2


RO
RO
Zr
RO
RO
+
HO
C
R
O
O=
R
O=
RO
RO
Zr
R
RO
alkoxide
chelating ligand
+Zr(OR)4
hydrolysis
growth by
condensation
R
R
R

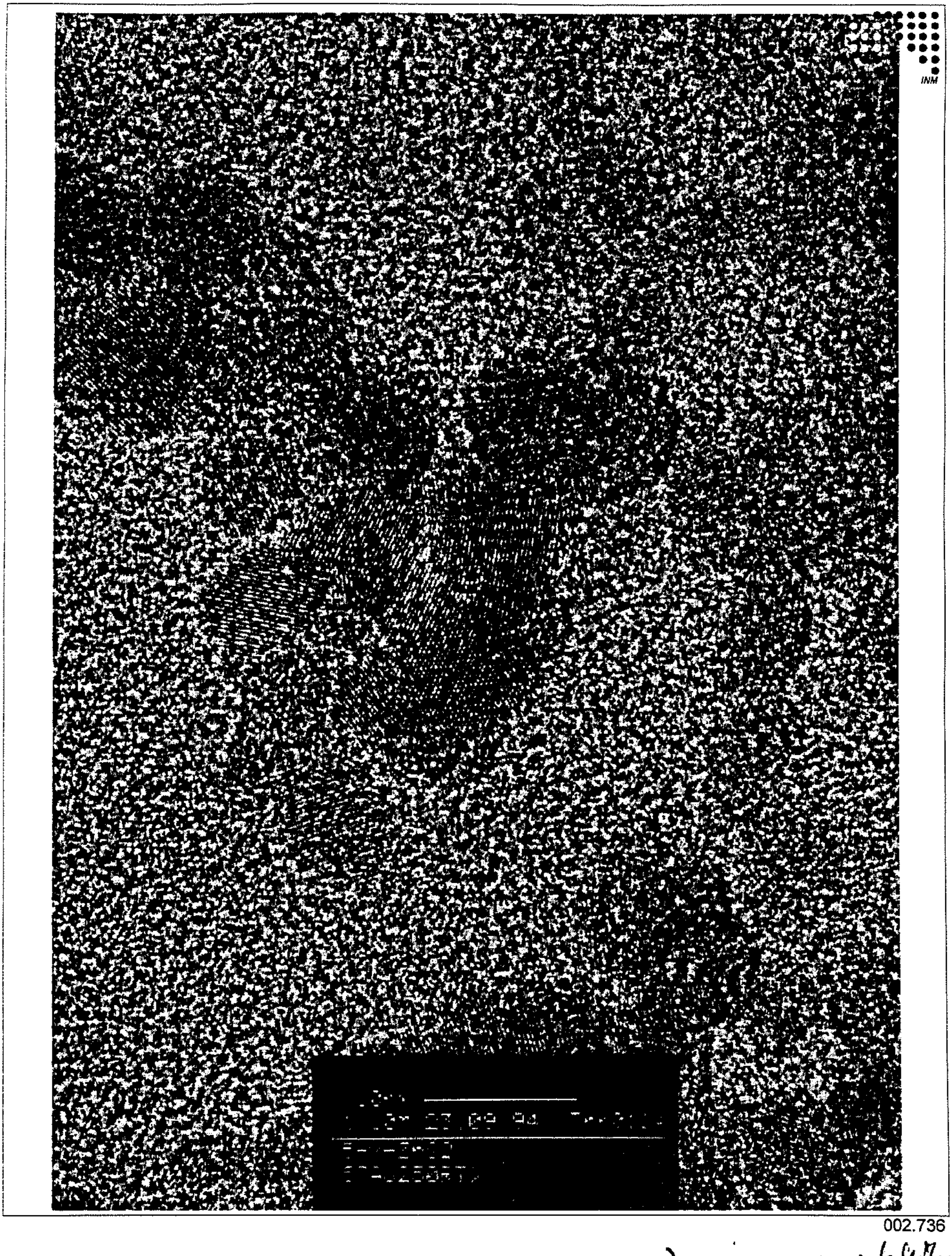
002.904


MPTS
Zirconiumpropoxide MAS
Si(OCH3)3
Zr(OPr)4
+ H2O
+ MeOH
Hydrolysis:
R—Si—OR → R—Si—OH + ROH
Condensation (latent water):
R—Si—OH + HO—Si—R → R—Si—O—Si—R + H2O
OPr
Zr
CH2
CH3
Removal of free water and latent water
by condensation with metalalkoxide
2 —Zr—OR + H2O -ROH → —Zr—O—Zr—
+ photoinitiator
clear liquid
thin films
bulk



Model for a colloidal organic-inorganic network interpenetrated by a siloxane network

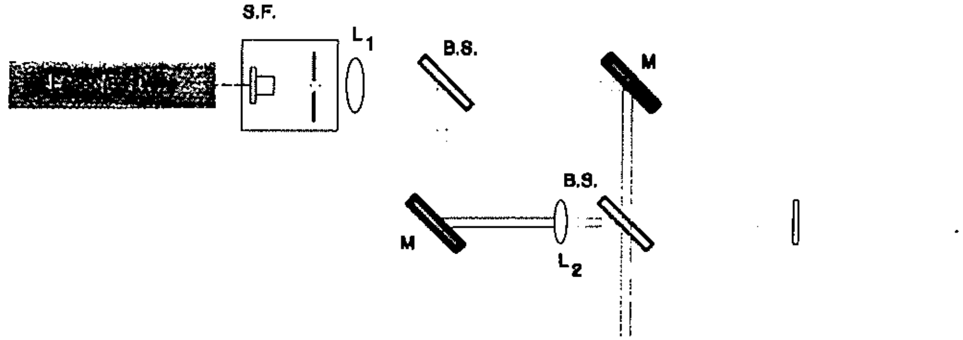
002.911



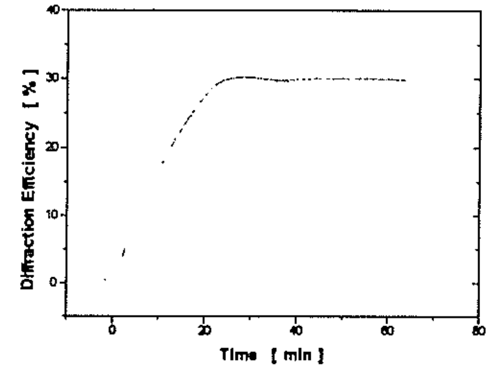
002.736

ZrO_2 nano crystallites

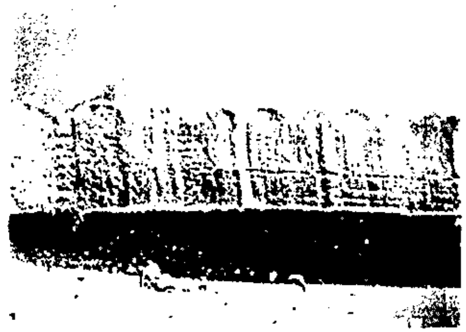
Mach-Zender-experiment

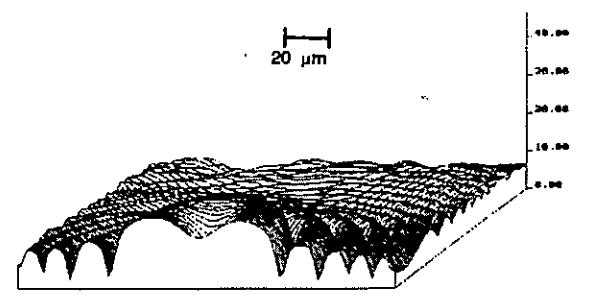


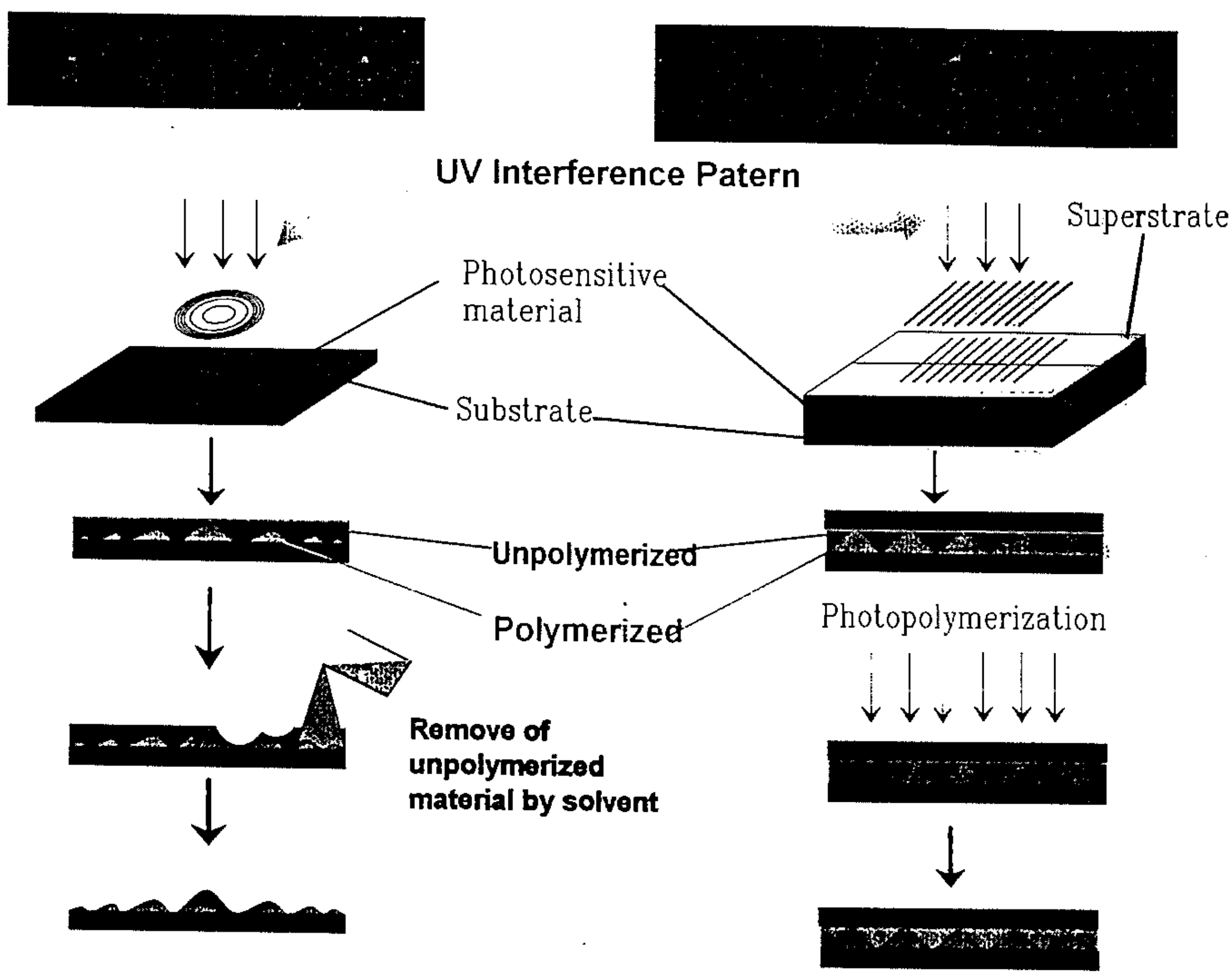
Diffraction efficiency



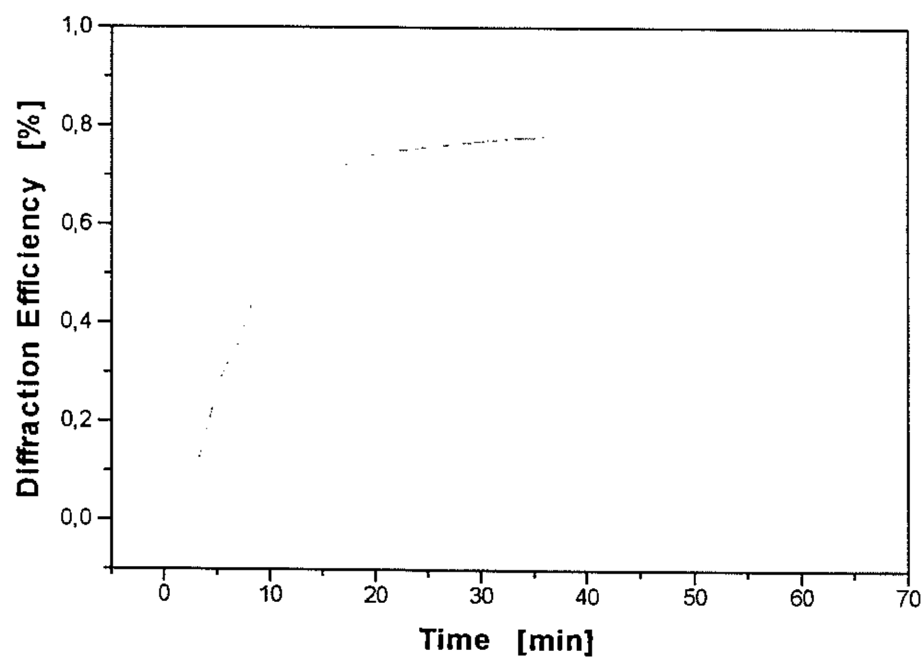
Results after subsequent development step





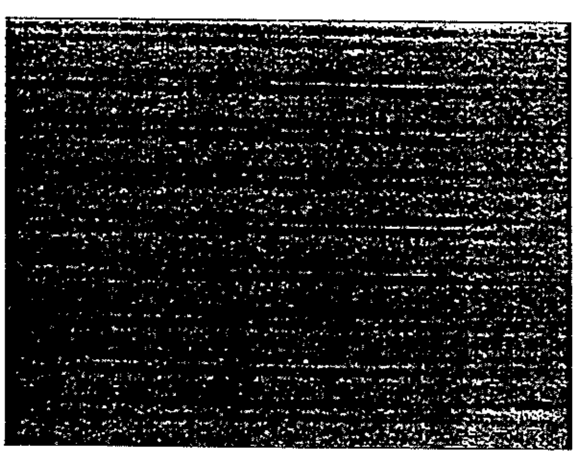

UV Interference Patern
Photosensitive material
Superstrate
Substrate
Unpolymerized
Polymerized
Photopolymerization
Remove of unpolymerized material by solvent

Fabrication [illegible] gratings as [illegible] elements [illegible]

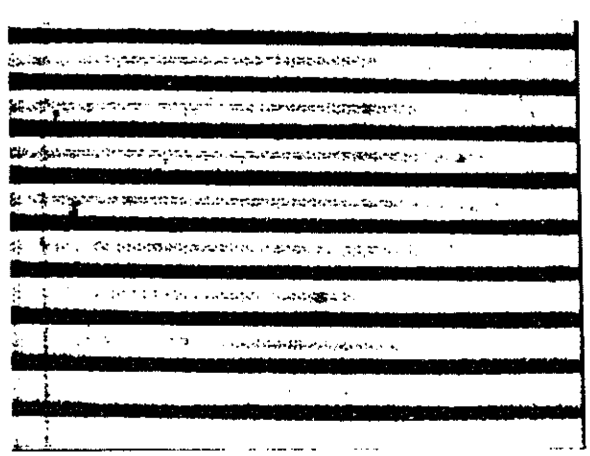


Light microscopy

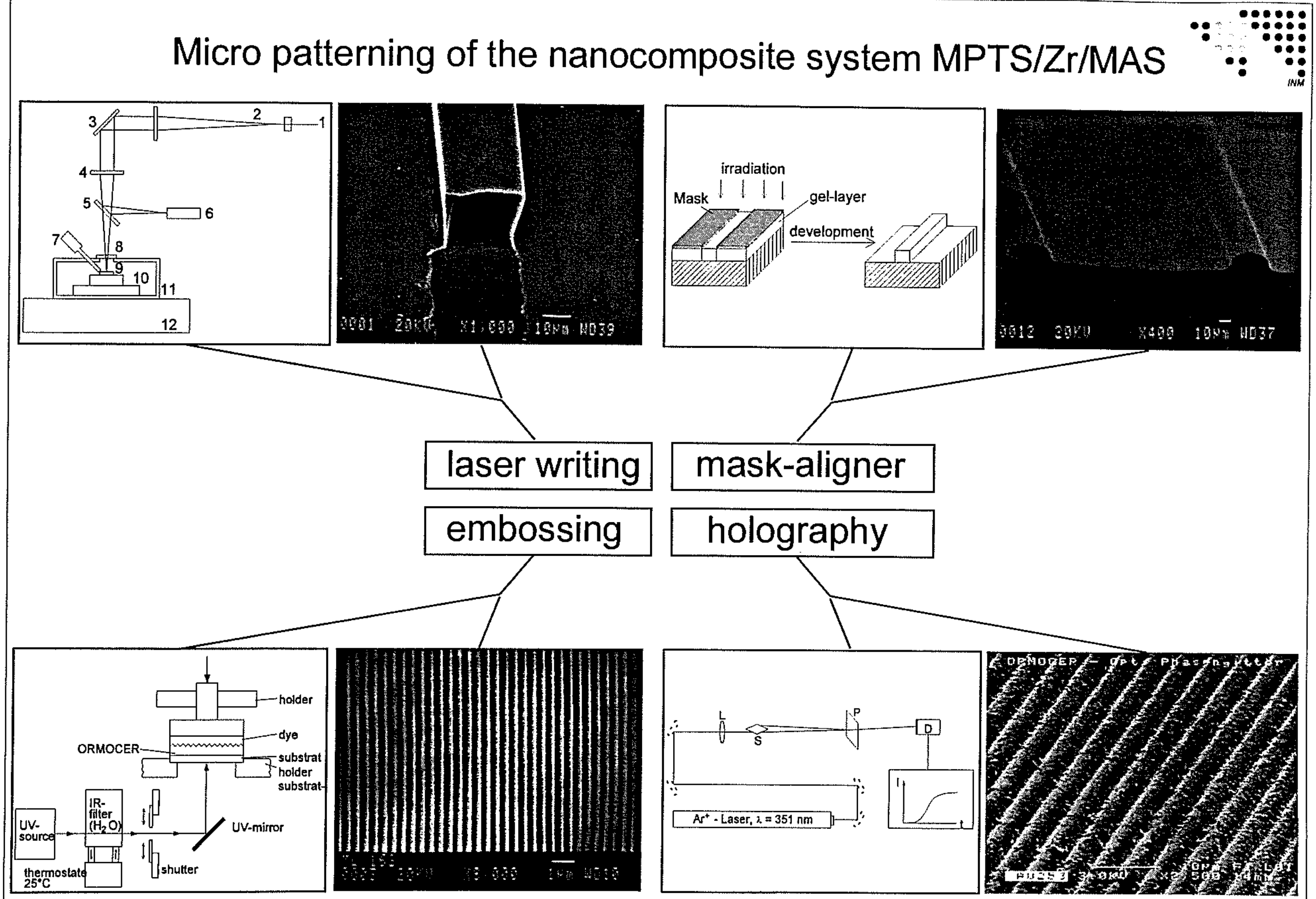
normal contrast



phase contrast

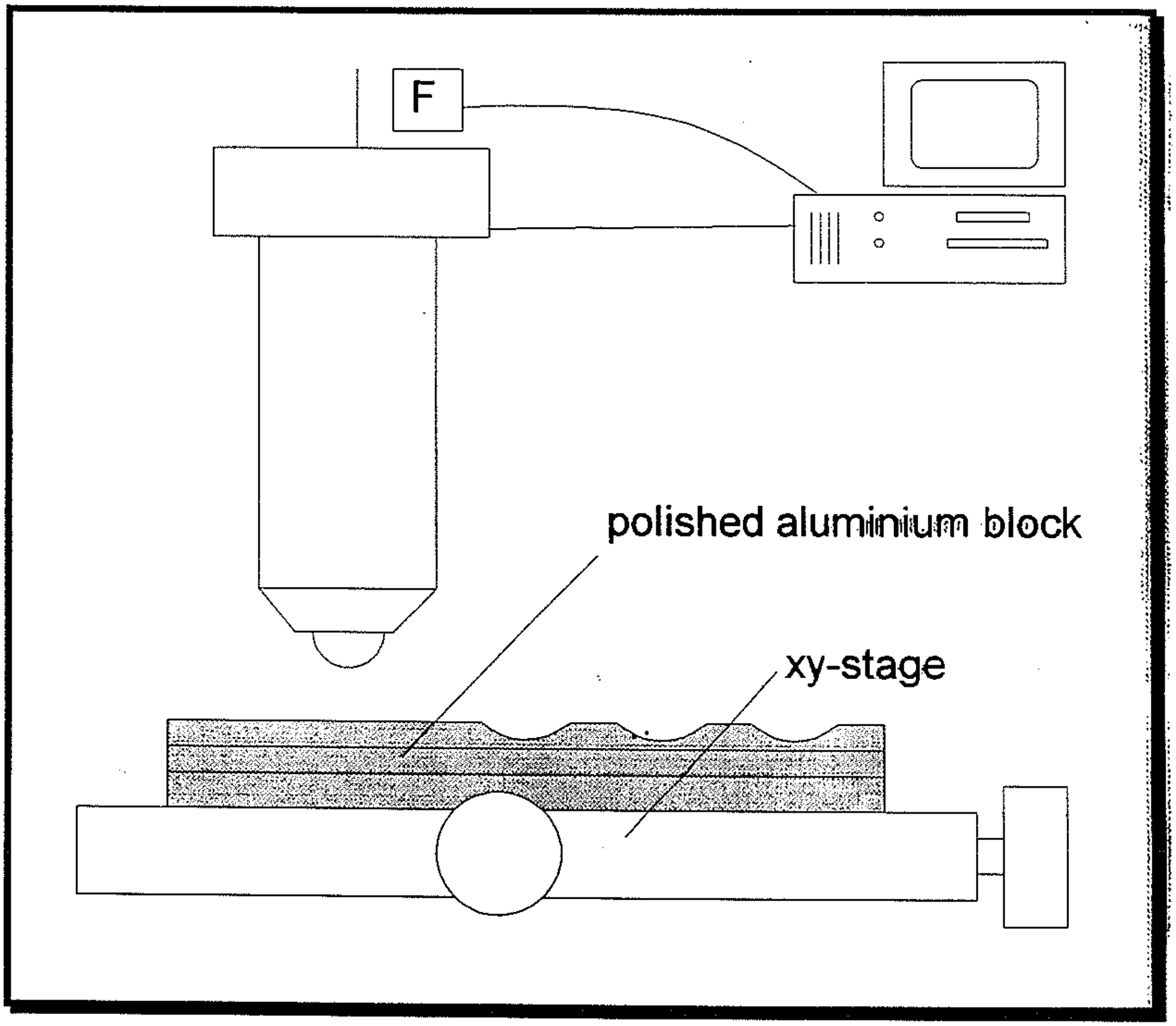


Micro patterning of the nanocomposite system MPTS/Zr/MAS

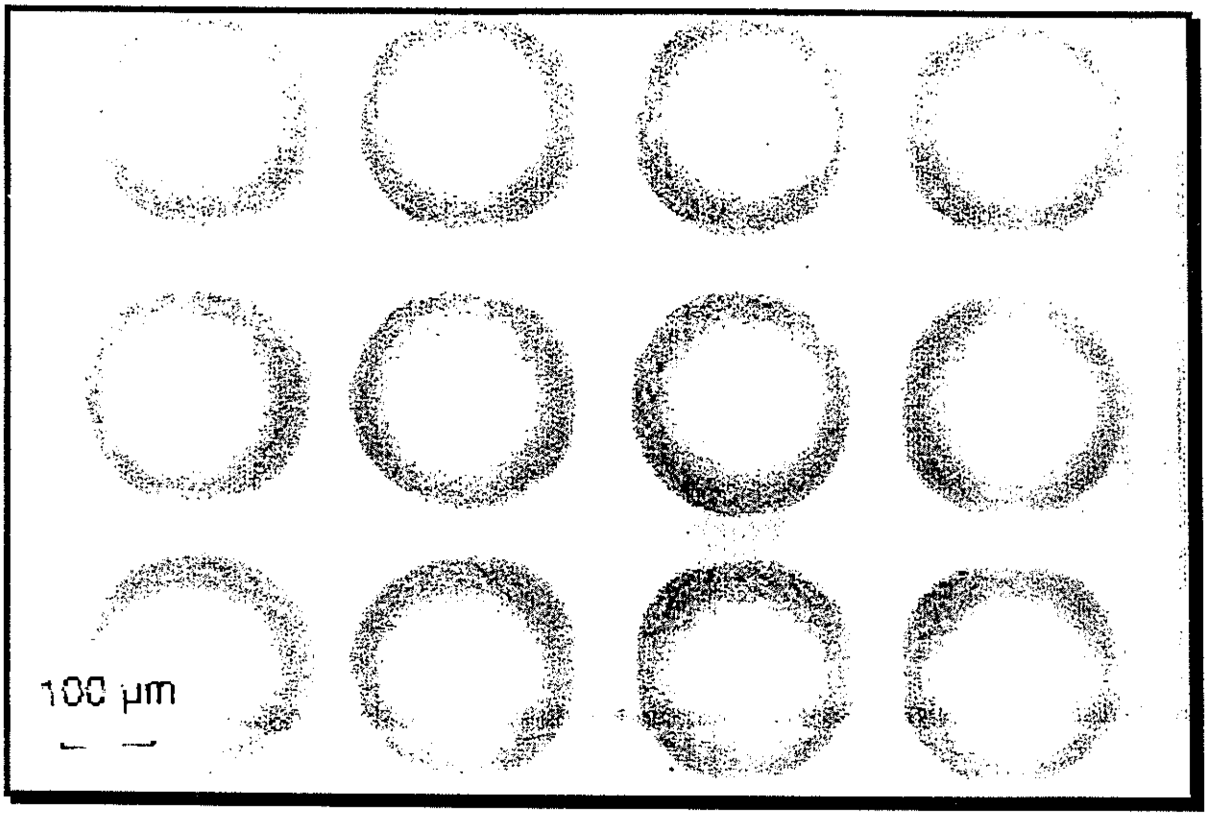


001.680

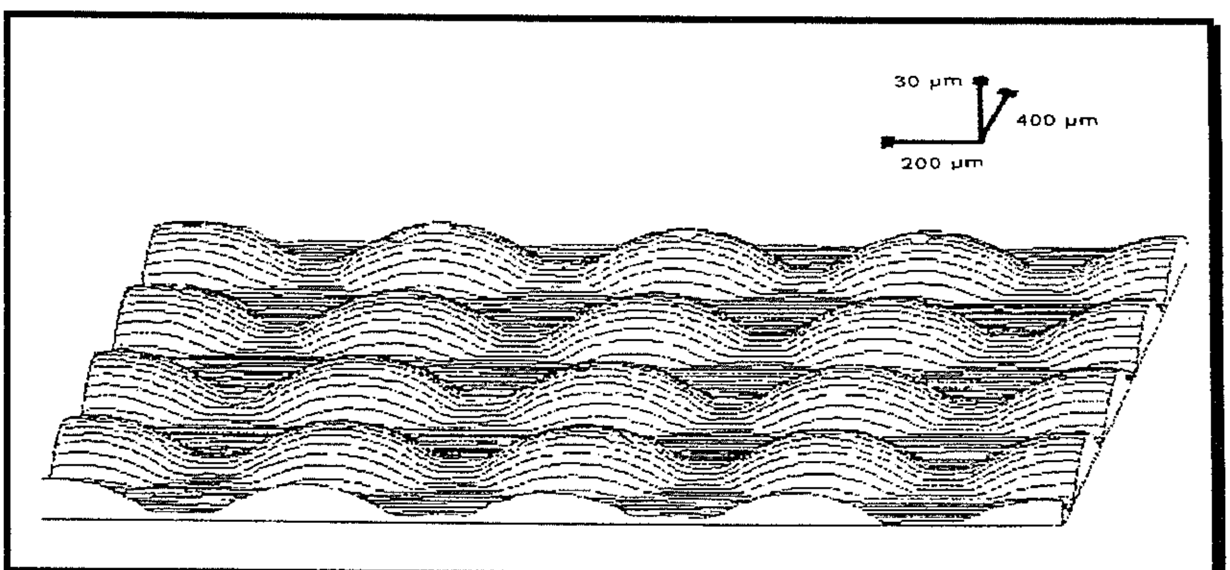
[redacted]



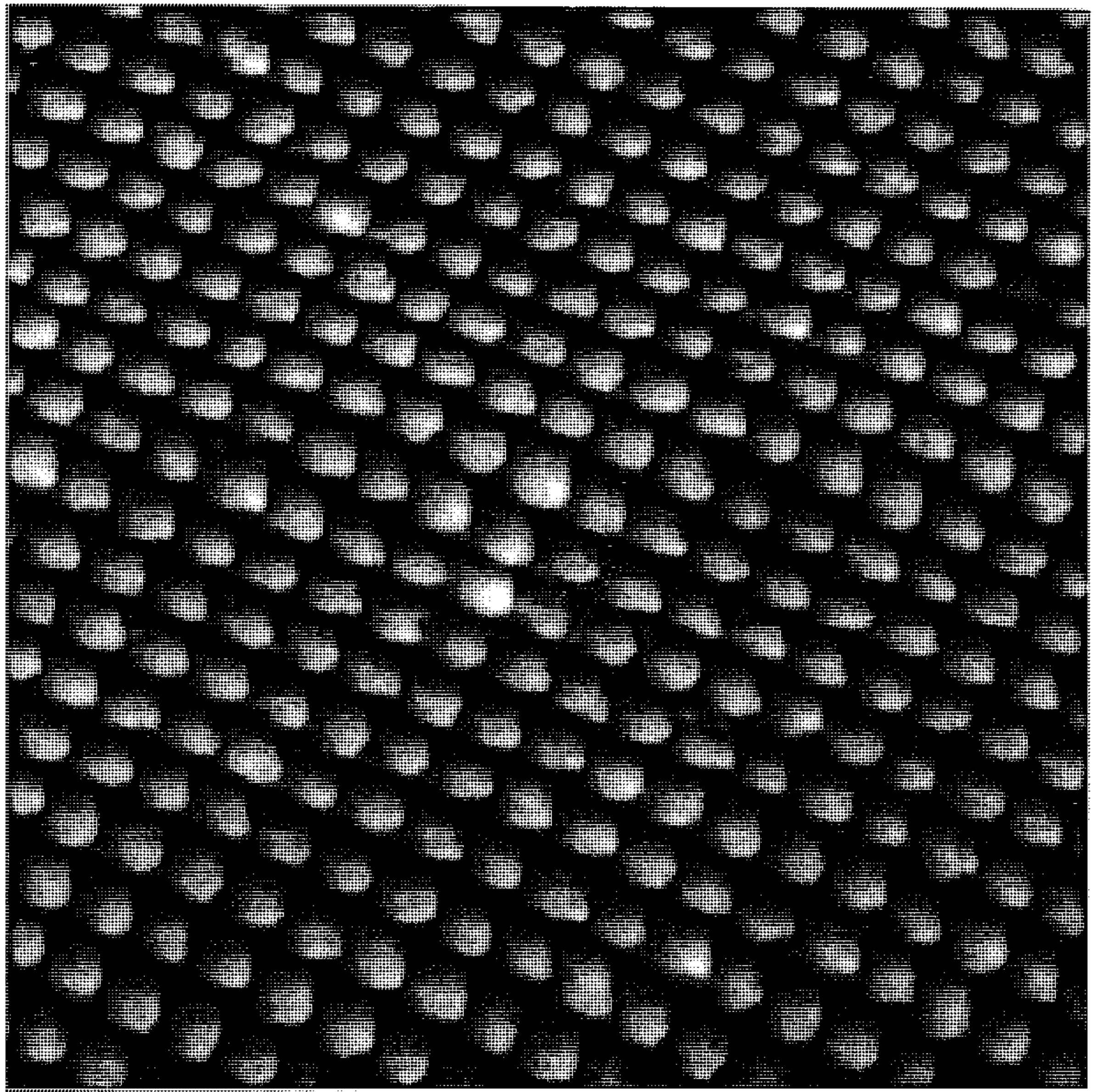
[illegible] OF AN EMB[illegible]SSED [illegible] LENS ARRA[illegible] [illegible] COMPOSITE MATERIAL

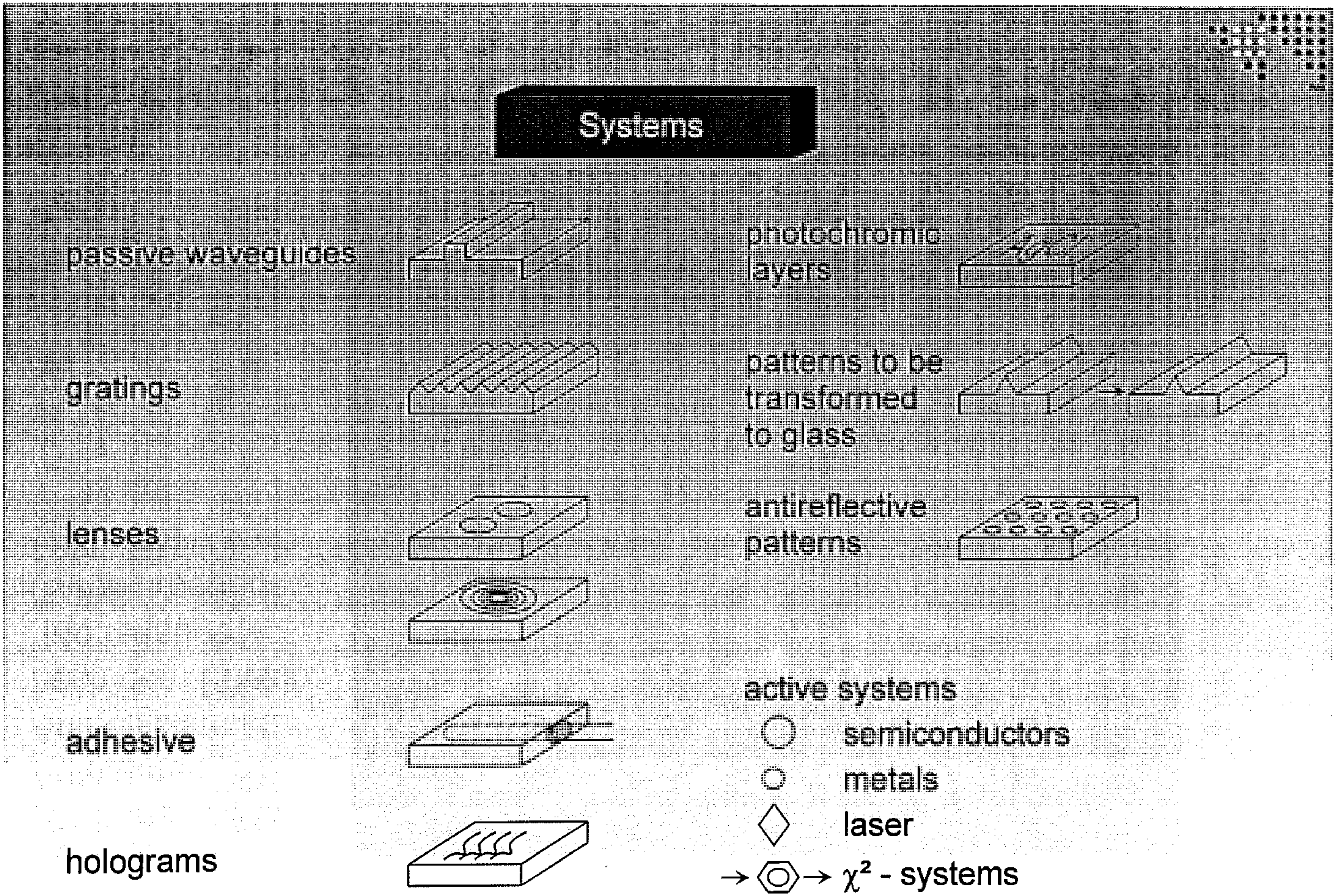


THREE DIMENSIONAL PROFILE OF A 3x4 [illegible]

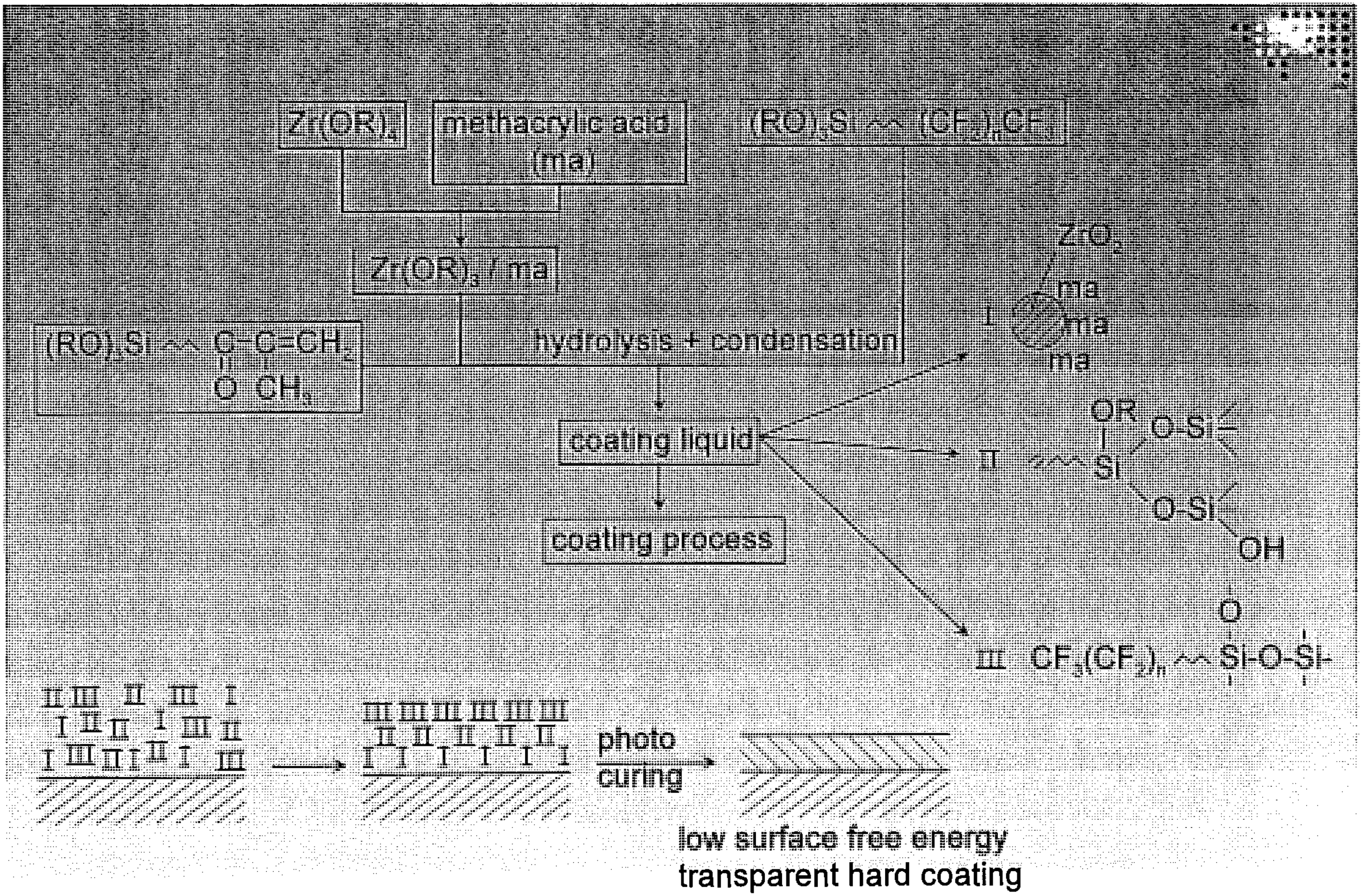


thermisch bzw. photochemisch Aushärten AFM-Aufnahme: Antireflexstruktur nach dem Prinzip "Mottenauge" (Strukturperiode: 285 nm)




Systems
passive waveguides
photochromic layers
gratings
patterns to be transformed to glass
lenses
antireflective patterns
adhesive
active systems
semiconductors
metals
laser
holograms
χ^2 - systems

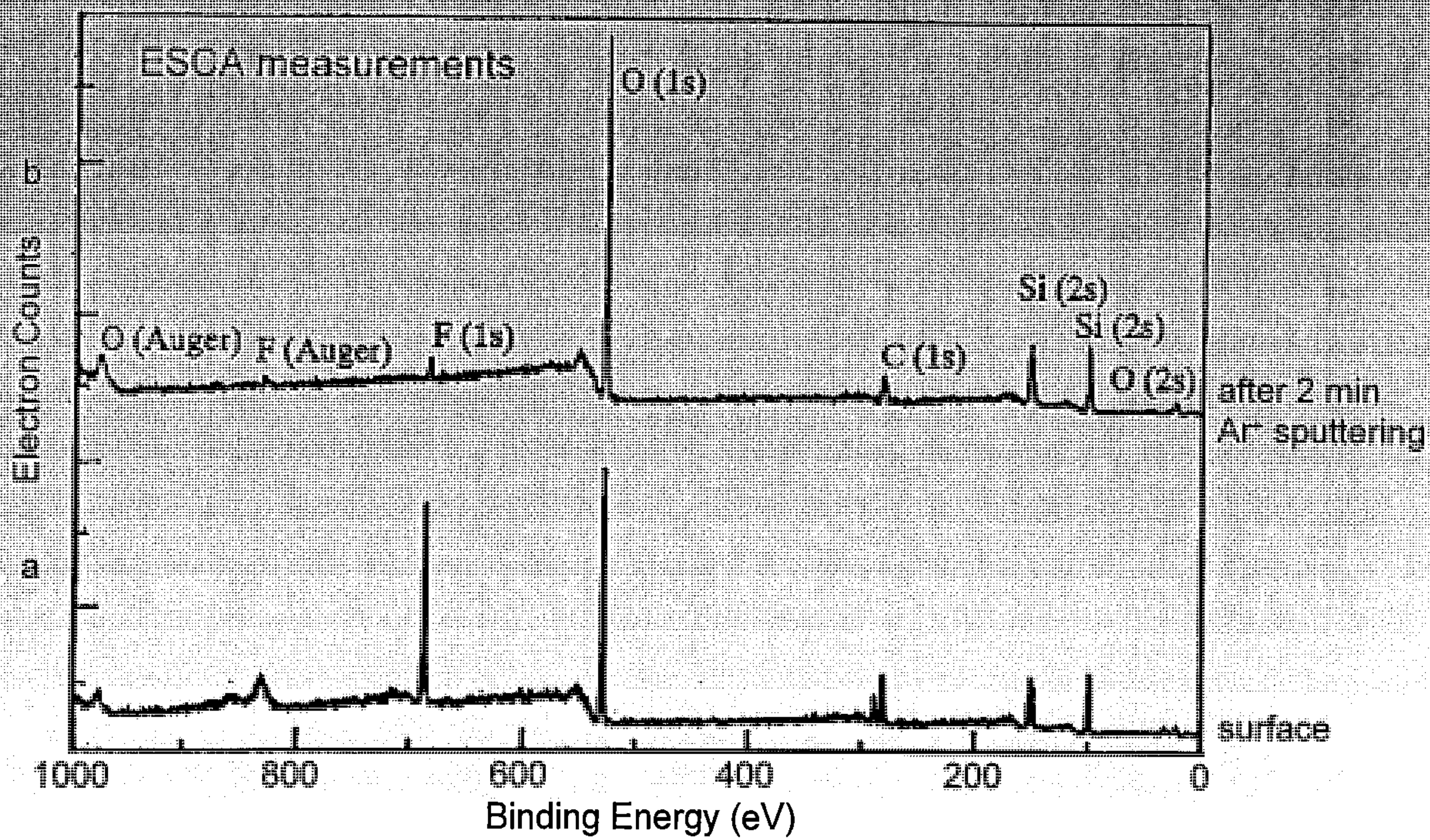
002.542



Zr(OR)4
methacrylic acid (ma)
(RO)3Si ~~ (CF2)nCF3
Zr(OR)3 / ma
(RO)3Si ~~ C–C=CH2 O CH3
hydrolysis + condensation
coating liquid
coating process
ZrO2
ma
ma
ma
I
II
III
OR
Si
O-Si
O-Si
OH
O
CF3(CF2)n ~~ Si-O-Si
photo curing
low surface free energy transparent hard coating

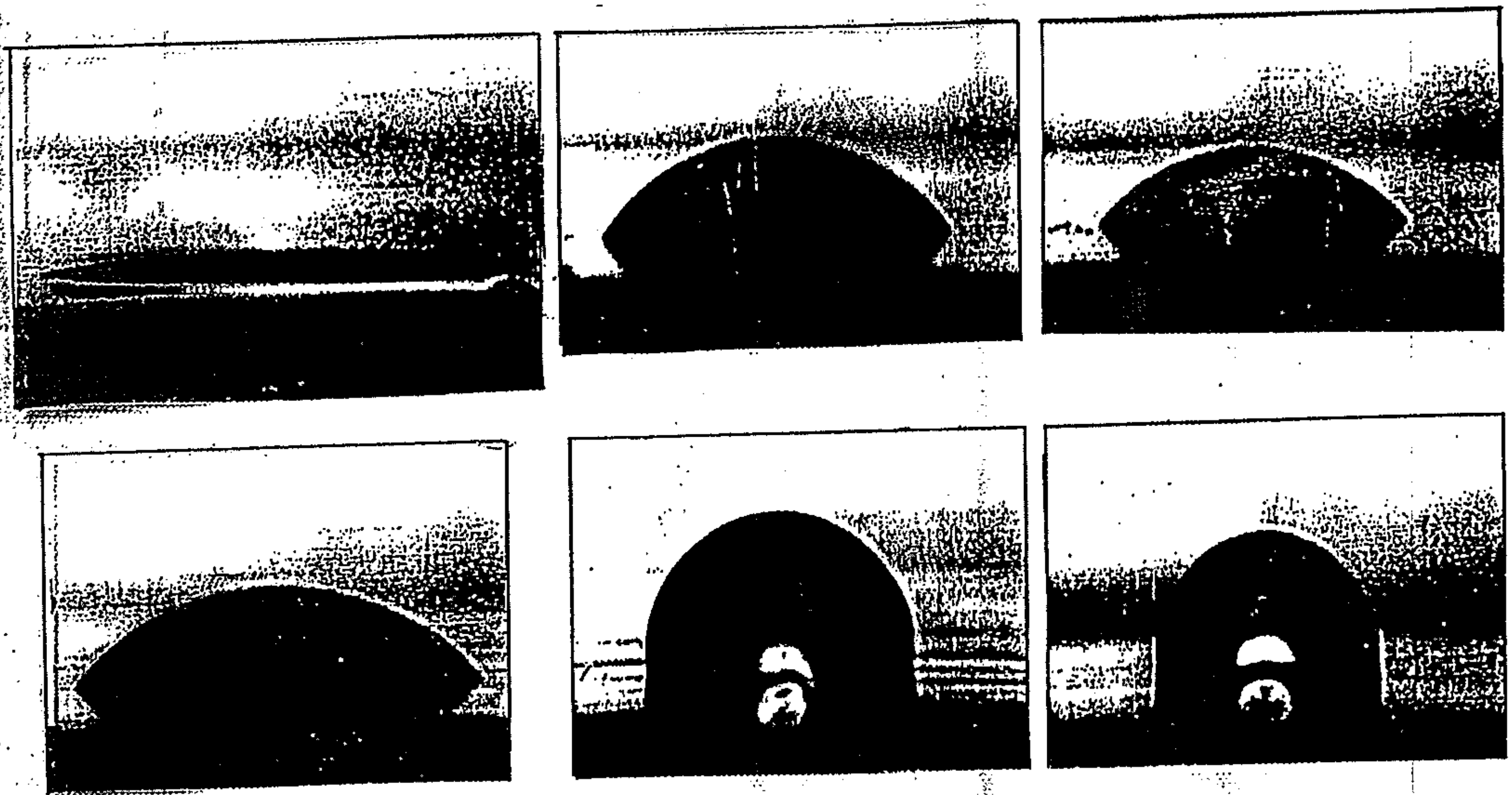
002.913

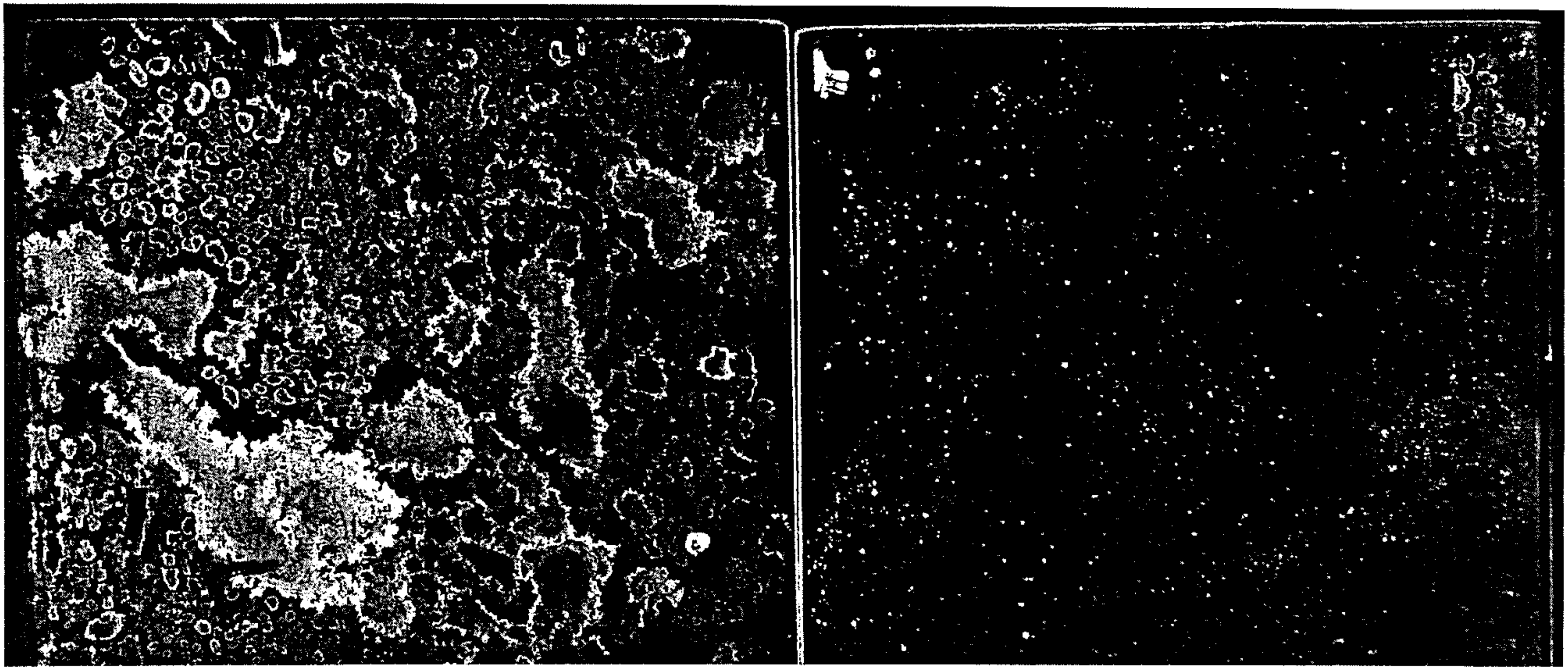
☐ Determination of the enrichment of fluorine chains at the surface by ESCA (Electron Spectroscopy for Chemical Applications) measurements



002.914

Fluorine Modification of ORMOCERs





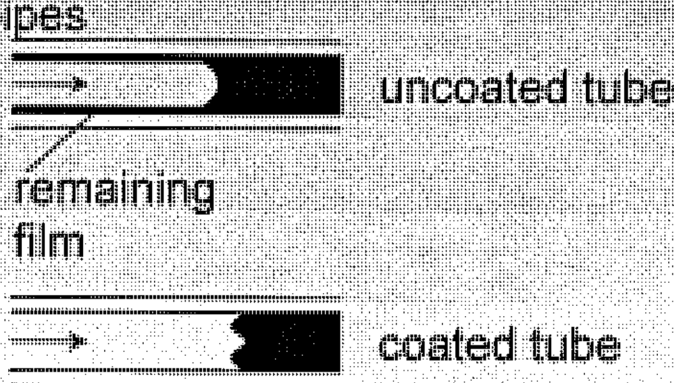
Unbeschichtet (uncoated) | Beschichtet (coated)

soiling experiment of glass (after soiling)

000.977 INM

surface free energy

- self aligning systems driven by interfacial free energy
- use of fuorinated silanes
- thermally curable systems (up to 400 °C) for glasses, ceramics
- photocurable systems, UV stable for plastic surfaces
  - dust repellent
  - antisoiling
  - deforming
    - conveyor belts
    - pipes



essential for automated analytics

Routes for Preparation and Utilization of Nano-Scale Systems

particle synthesis	matrix synthesis	composite fabrication
- controlled growth	- inorganic synthesis	- in-situ growth
- microemulsion	- inorganic-organic systems	- surface modification + mixing
- in-situ growth within the matrix	- organic systems	
- reduction processes		

metals reduction in solution
reduction in the solid matrix

- intensive colours (glass and composite films)
- catalytic films
- NLO films (Au, Cu ≡ χ^3)
- conductive films

ceramics

- passive optics
- micro systems (microlenses, gratings, fresnel lenses, holograms)
- NLO (χ^2)
- third functions (low surface free energy, anti-fogging, scratch resistance, anti-corrosive)

semiconductors

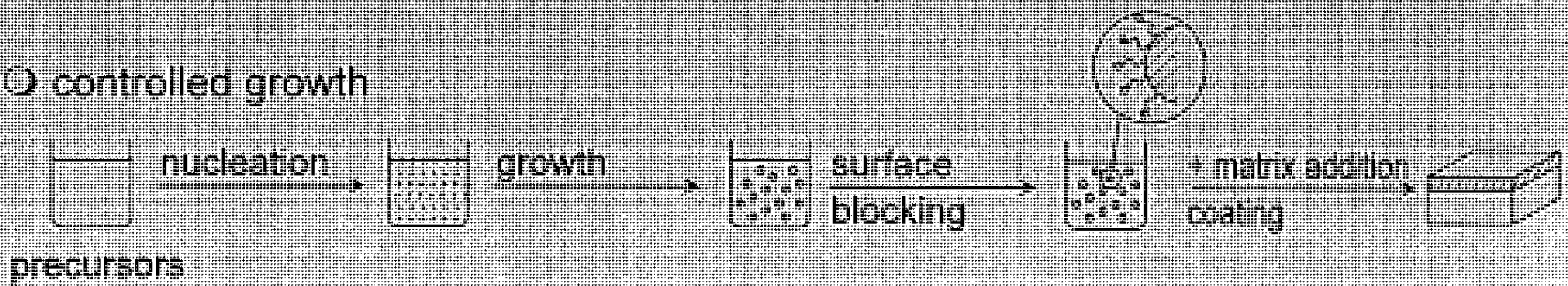
- laser materials
- χ^3 materials

Synthesis of Nano composites

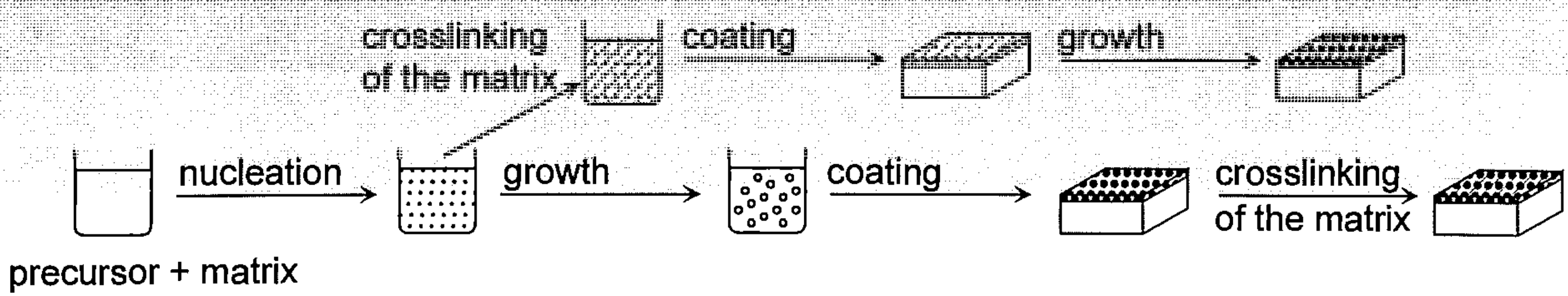
Synthesis of inorganic components

- microemulsion techniques

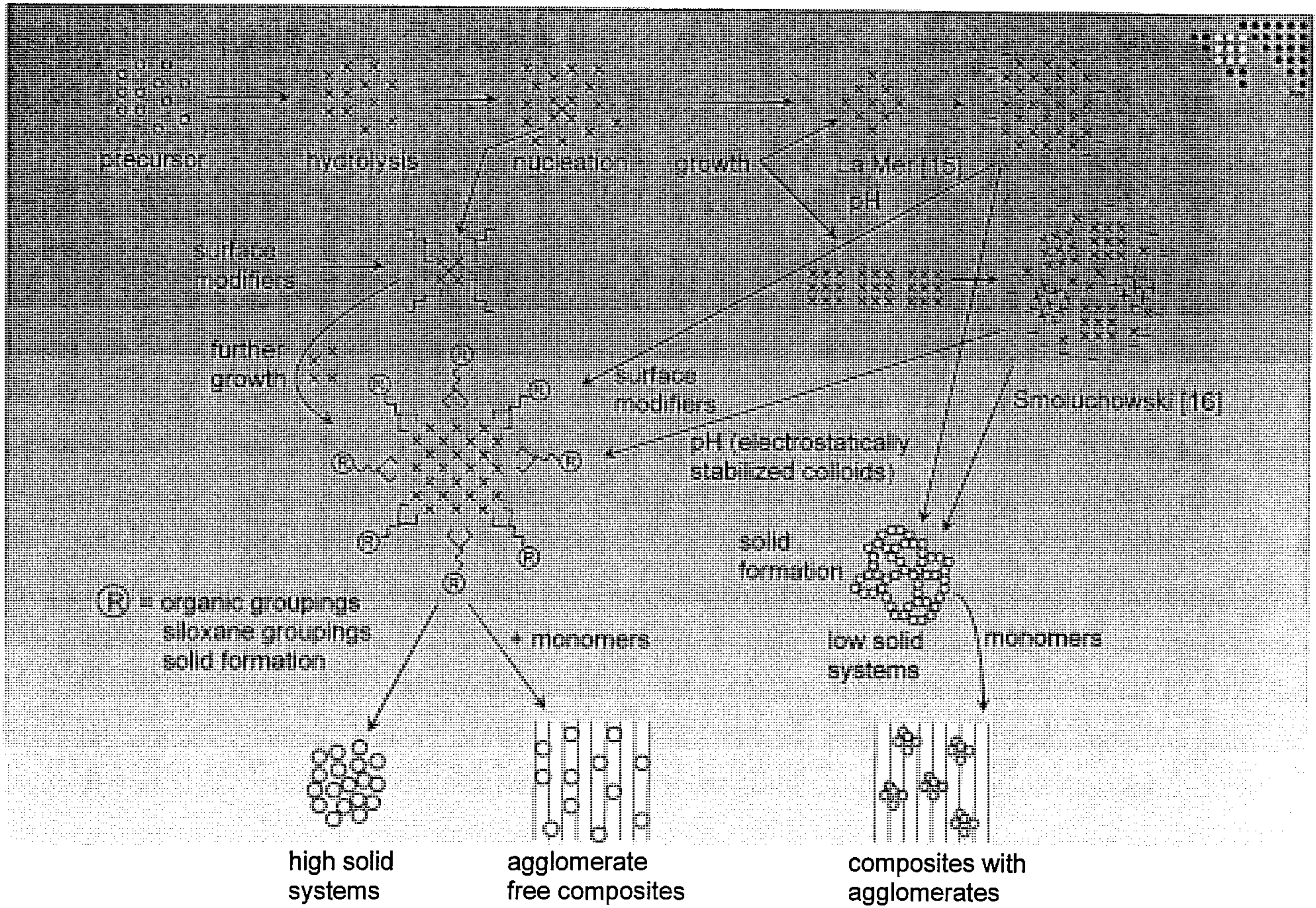
- controlled growth



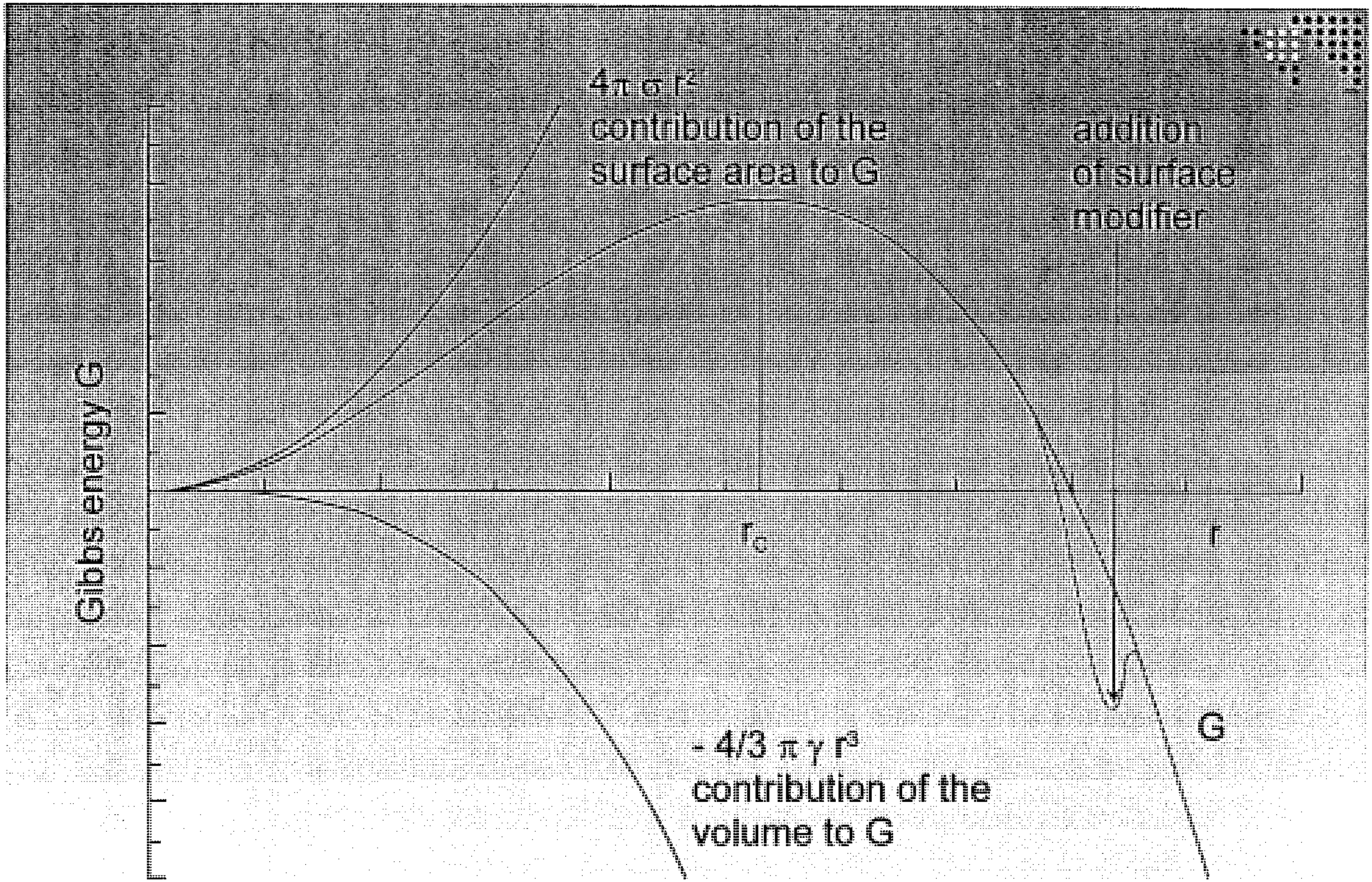
- "in-situ" - synthesis



002.554

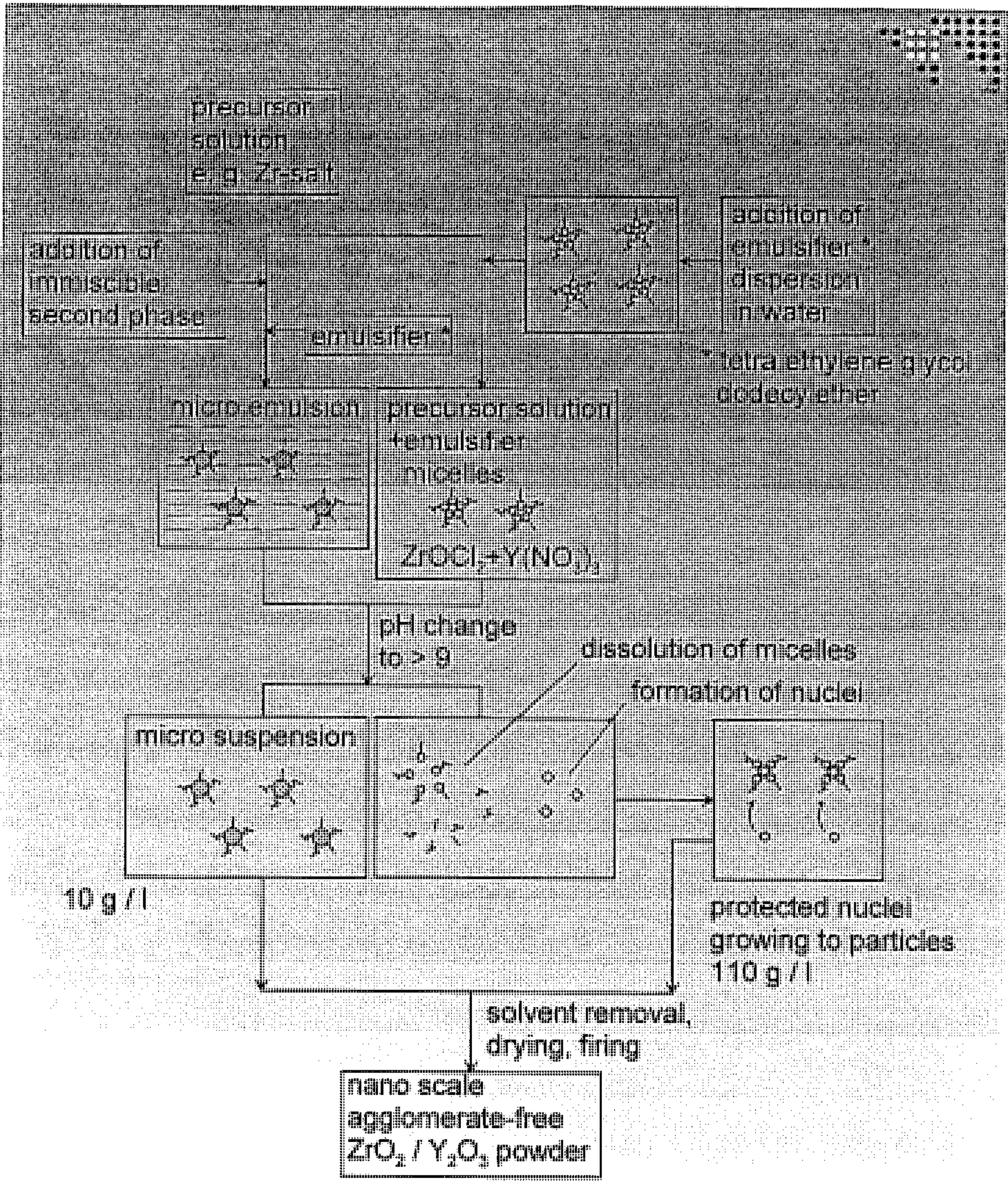

precursor
hydrolysis
nucleation
growth
La Mer [15]
pH
surface
modifiers
further
growth
surface
modifiers
Smoluchowski [16]
pH (electrostatically
stabilized colloids)
solid
formation
Ⓡ = organic groupings
siloxane groupings
solid formation
+ monomers
low solid
systems
monomers
high solid
systems
agglomerate
free composites
composites with
agglomerates

002.804



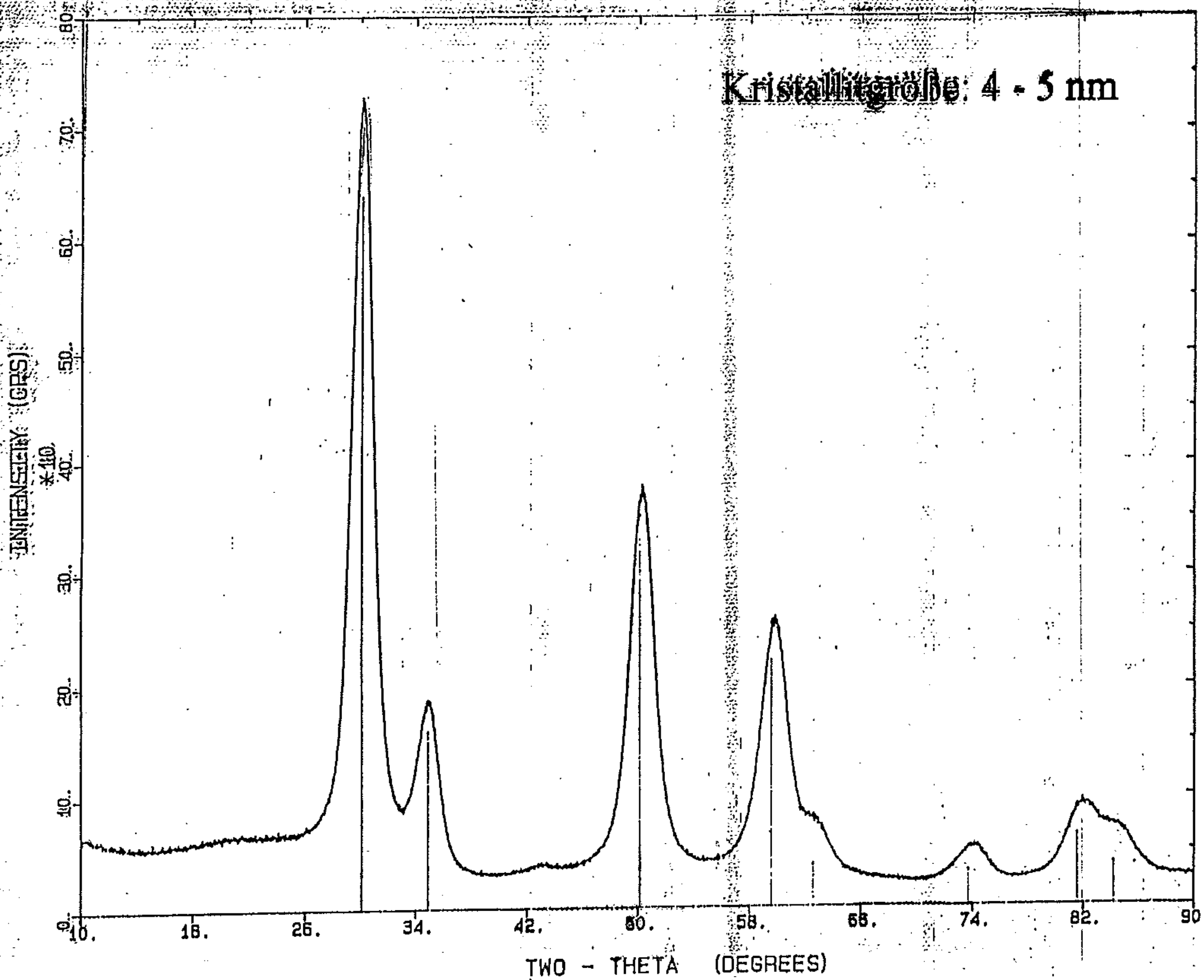
r_C= critical nucleation radius

002.748



micro emulsion and controlled growth route
for fabrication of nanopowders

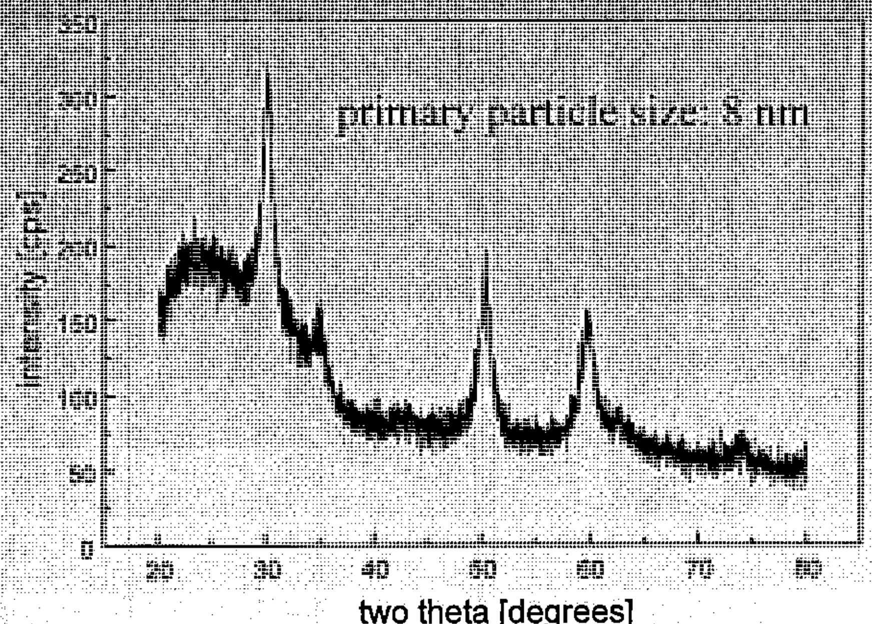
Röntgendiagramm des nanokristallinen tetragonalen 5 - Y_2O_3 - ZrO_2 by controlled growth



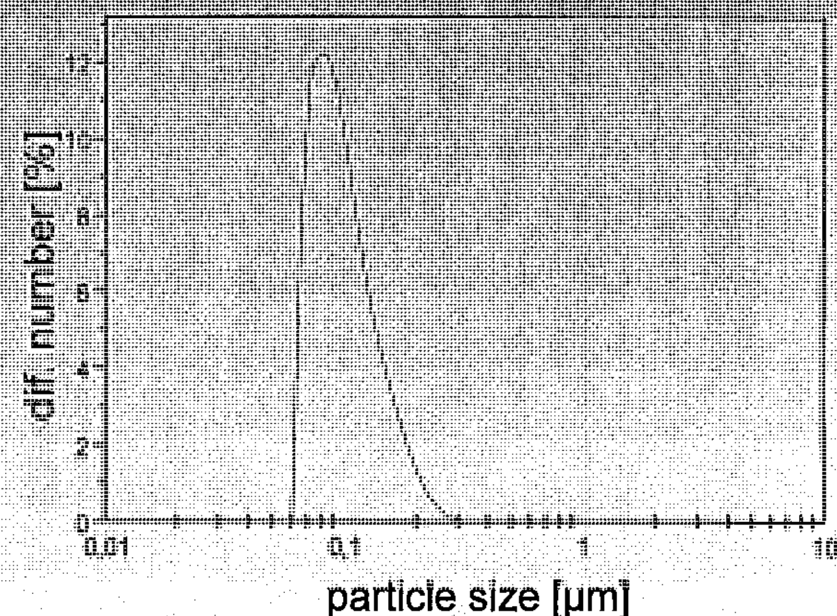
Powder synthesis by w/o microemulsions

❑ Y stabilized ZrO_2 prepared by a w/o microemulsion

O X-Ray diagram



O particle size distribution after redispersing

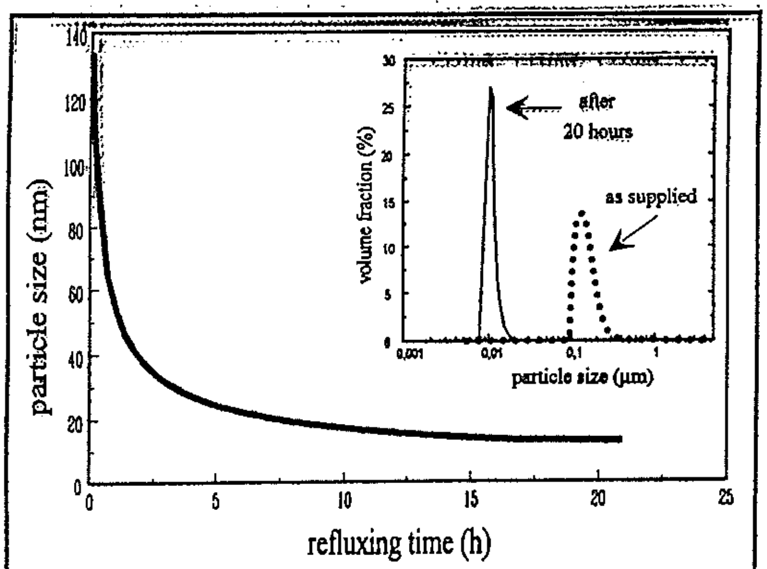


- O weakly agglomerated
- O redispersible to primary particle size
- O shaping by dry pressing possible

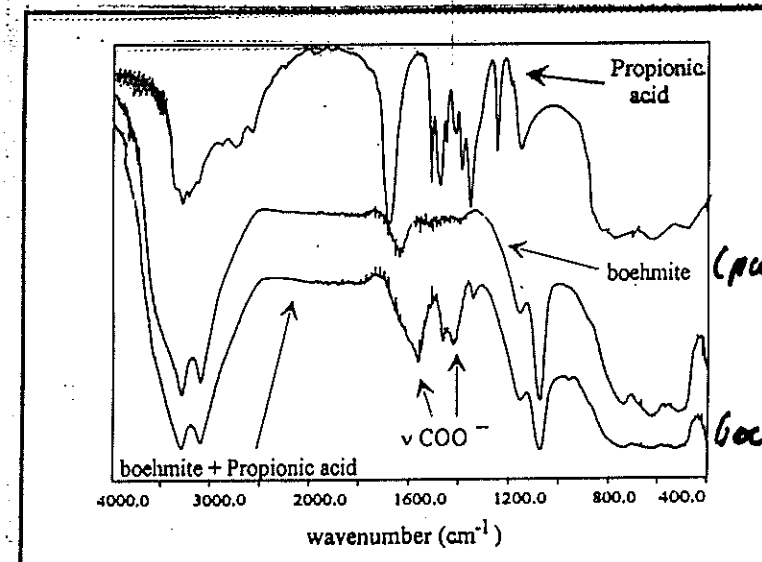
002.597

surface modification of boehmite

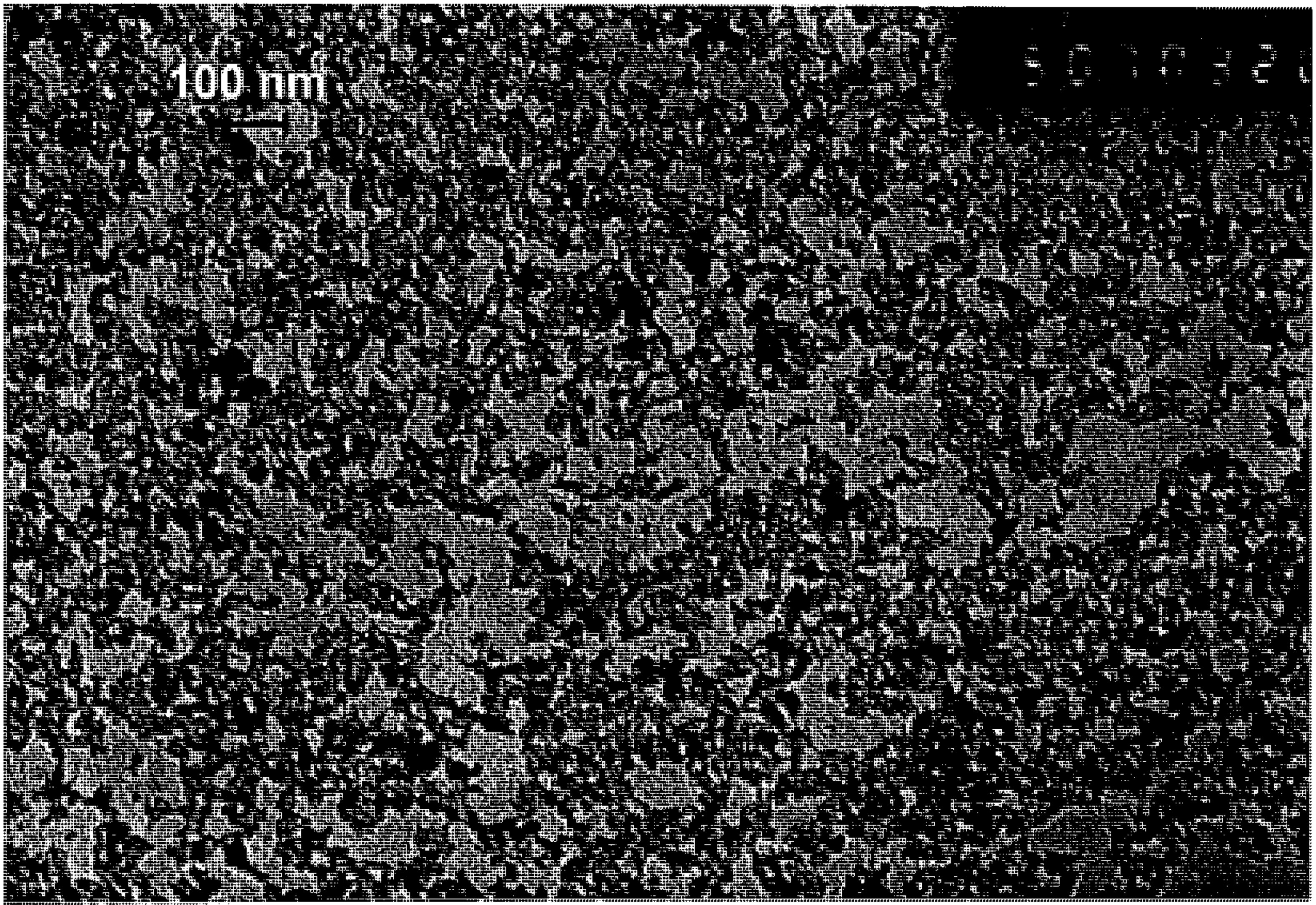
RESULTS



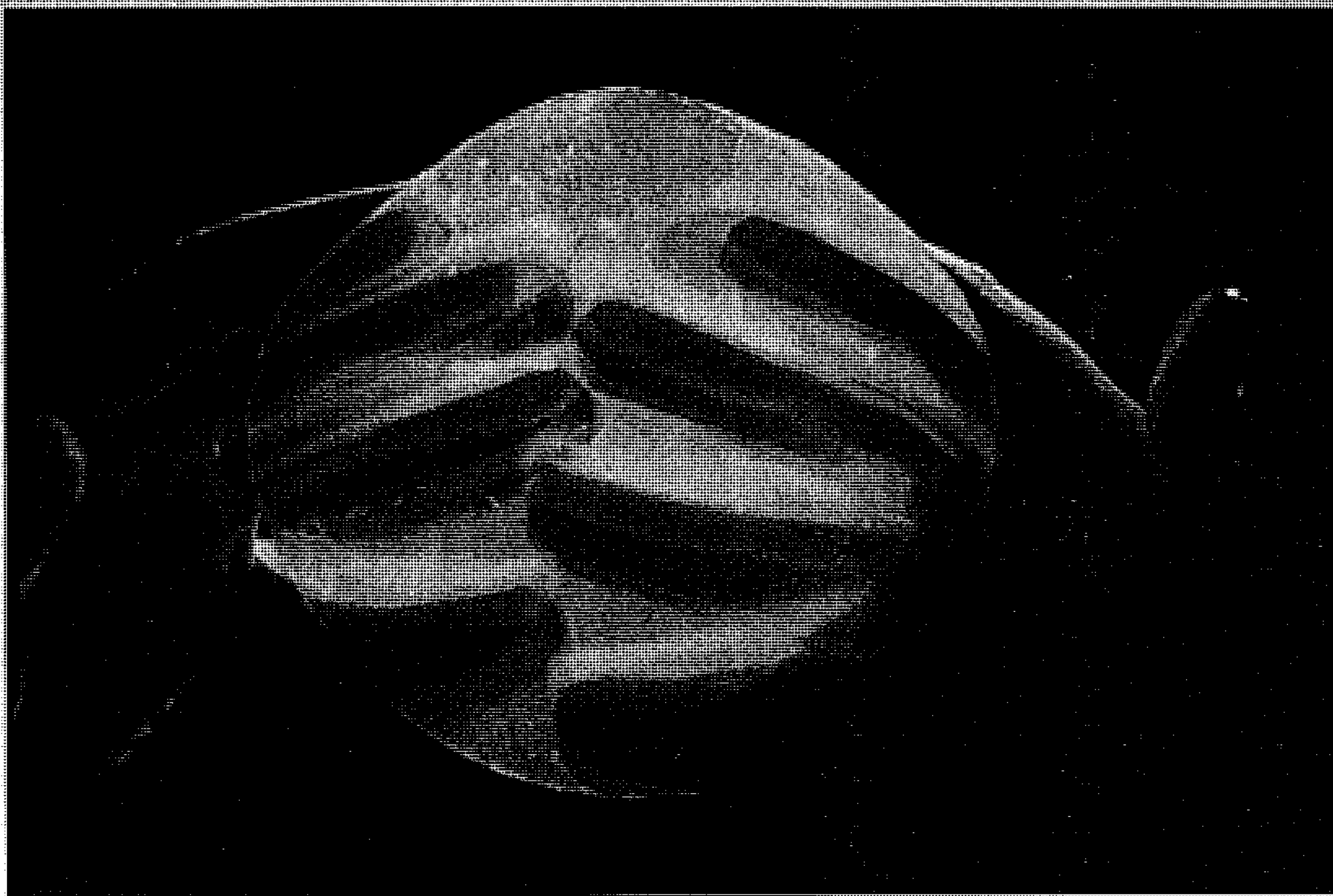
Deagglomeration down to primary crystallite size is obtained after 20 h refluxing time.



Coupling of carboxylic functional groups to the powder surface is demonstrated by characteristic decrease of the carbonyl absorption band.



nano ellipsoid boehmite

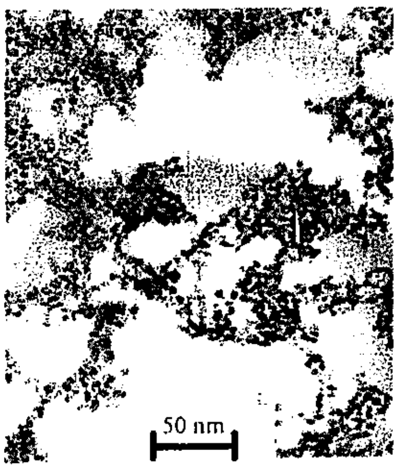


Translucent green body of modified boehmite ≈ 50% solid content by volume

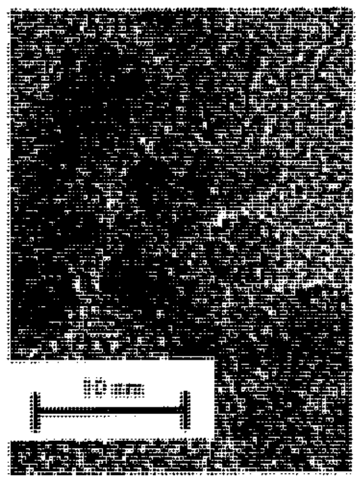
002.581

Ausgangspulver

❑ TEM

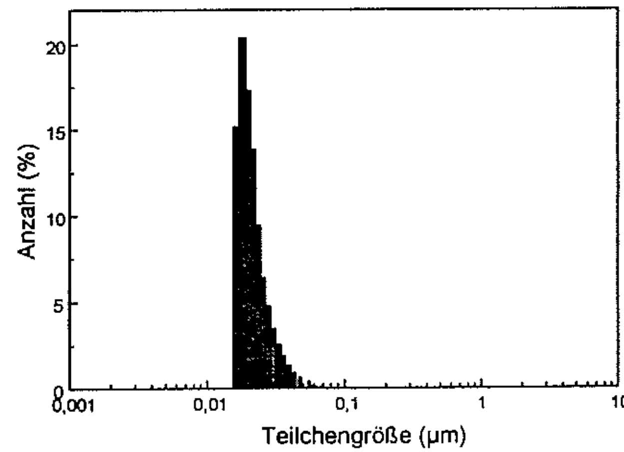


❑ Netzebenenabbildung



❑ Teilchengrößenverteilung (wäßrige Suspension)

size distribution (aques suspension)



particle size

❑ 8 Y - ZrO_2

- Modifikation: kubisch (c - ZrO_2)
- BET : 132 m^2/g
- Teilchengröße: 5 - 10 nm (size)
- oberflächenmodifiziert (surface modified)

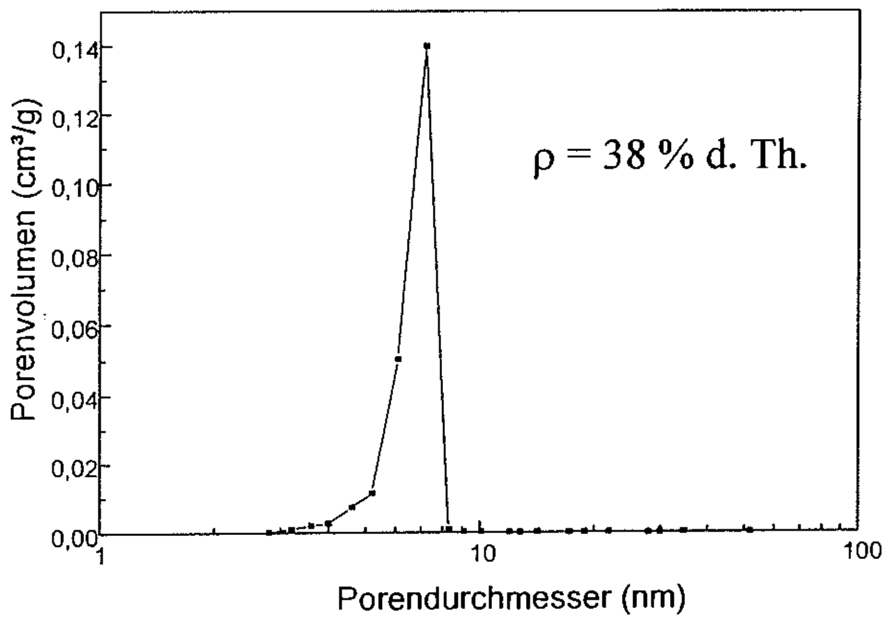
→ ❑ Formgießen

Grünkörper

Y_2O_3/ZrO_2
greenbodies
from nano particles

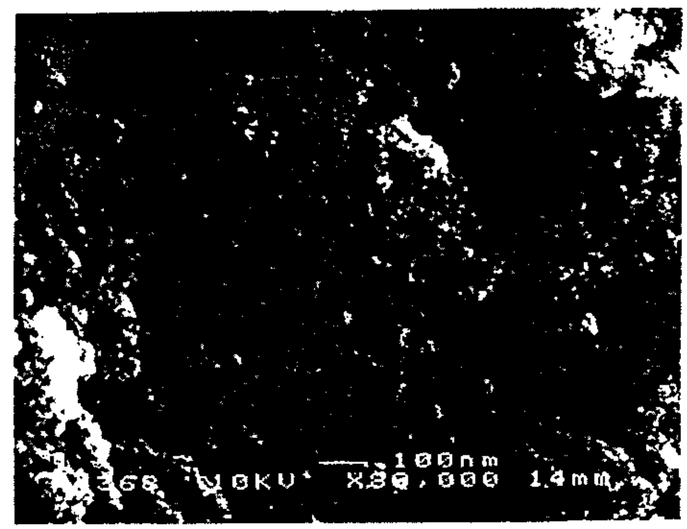
❑ Porengrößenverteilung

pore radii

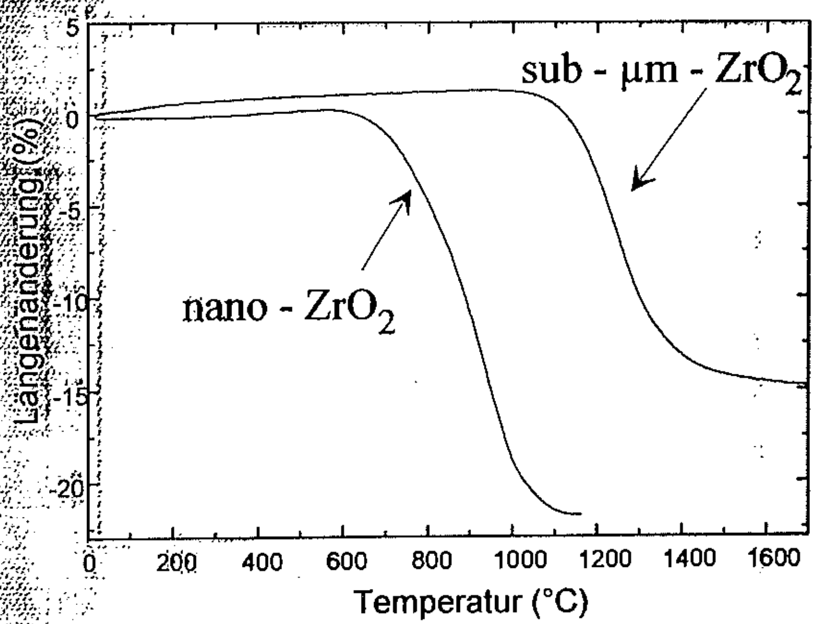


❑ HREM - Gefügeaufnahme

microstructure



Sintereigenschaften

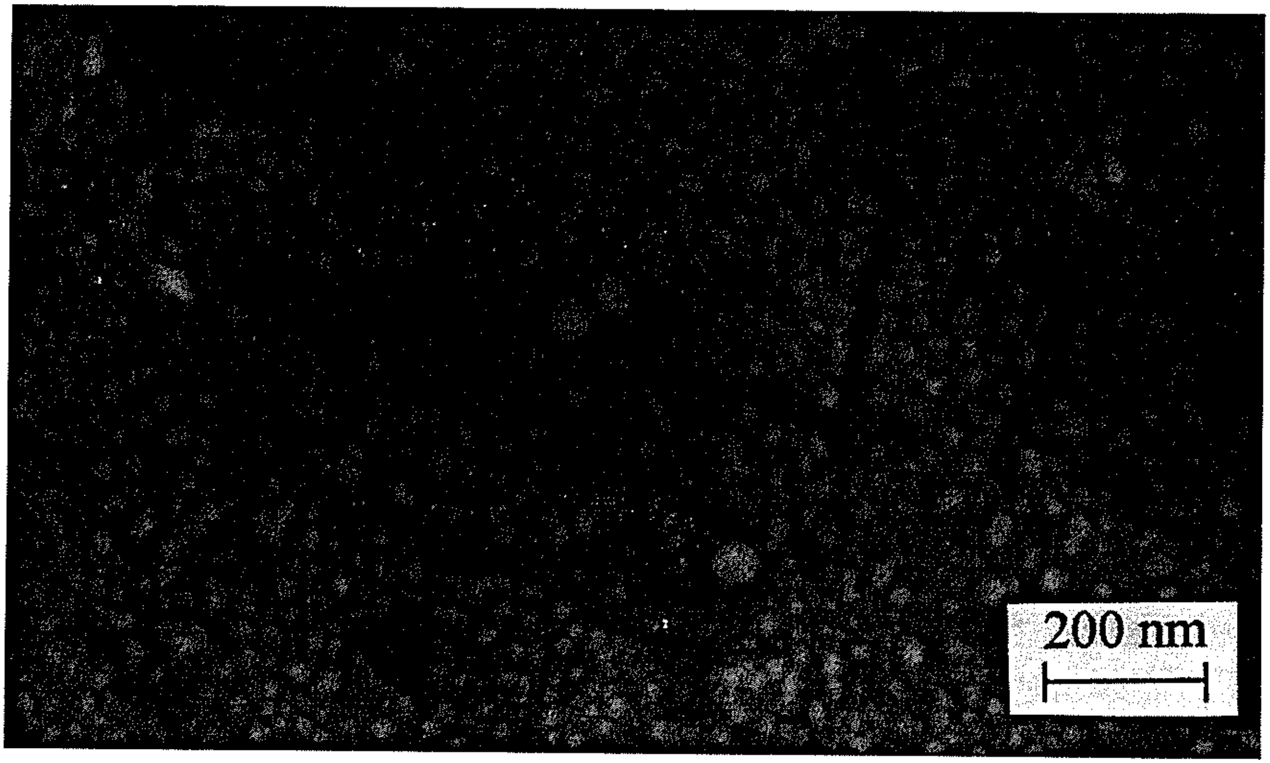


- ⇨ Cofiring - Techniken
- ⇨ Substrate
- ⇨ Beschichtungen

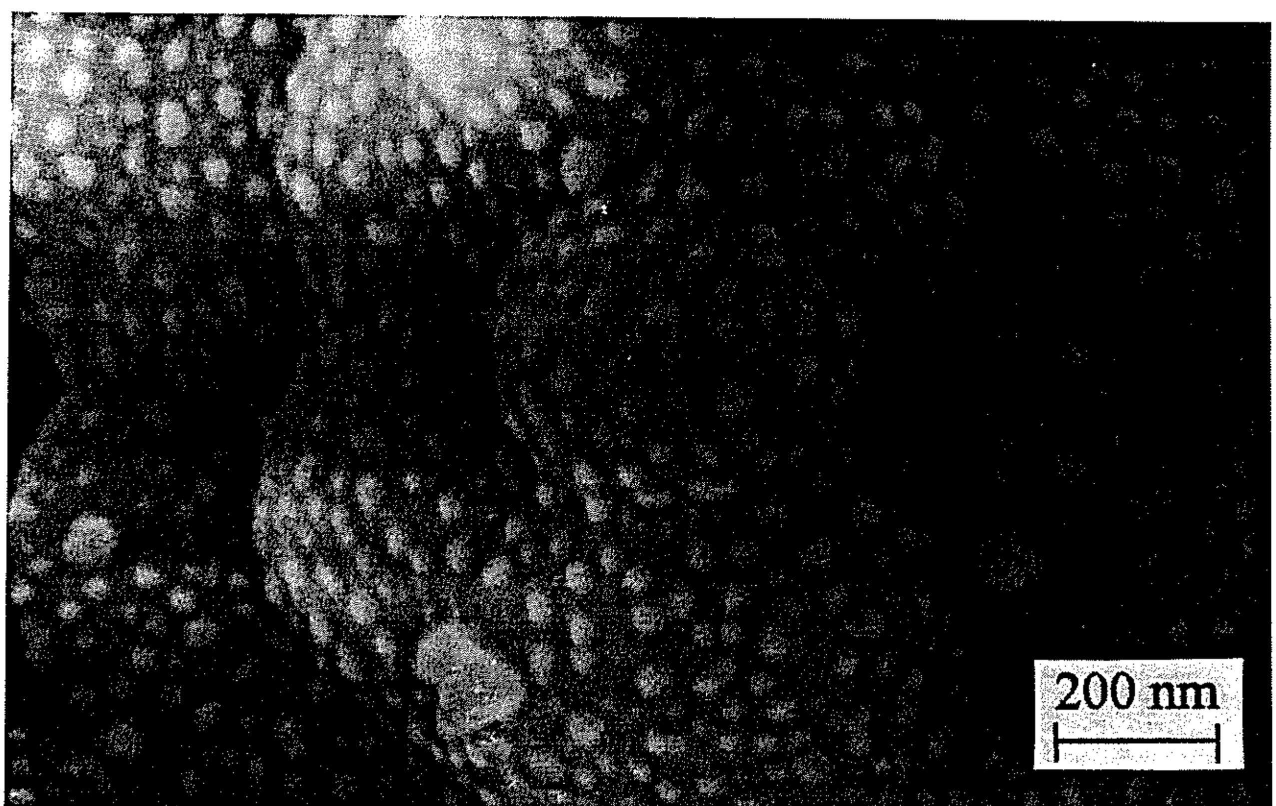
$\rho > 99$ % d. Th.
$d < 100$ nm

Microstructure of cold isostatically pressed Y_2O_3 / ZrO_2 particle size 4 - 5 nm

green body

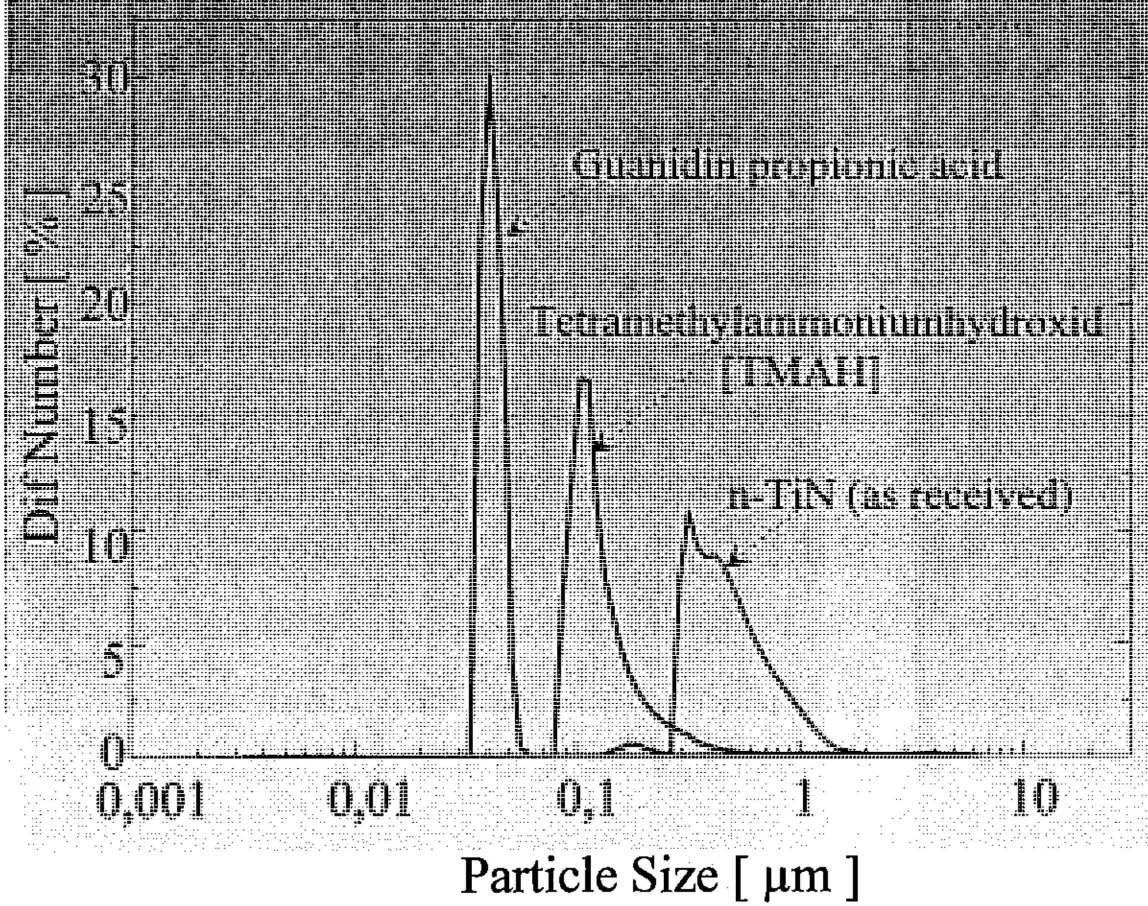


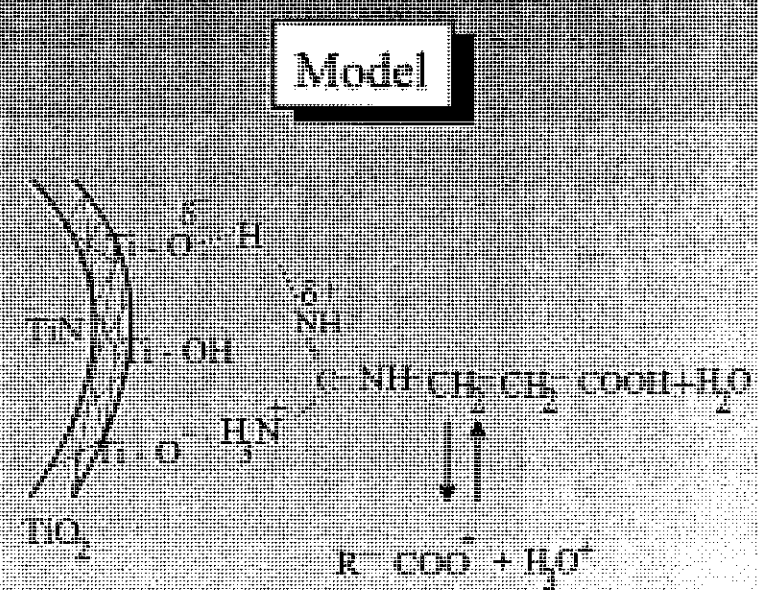
sintered body



Particle size distribution

- Ethanolic slurry with 40 wt% solid content

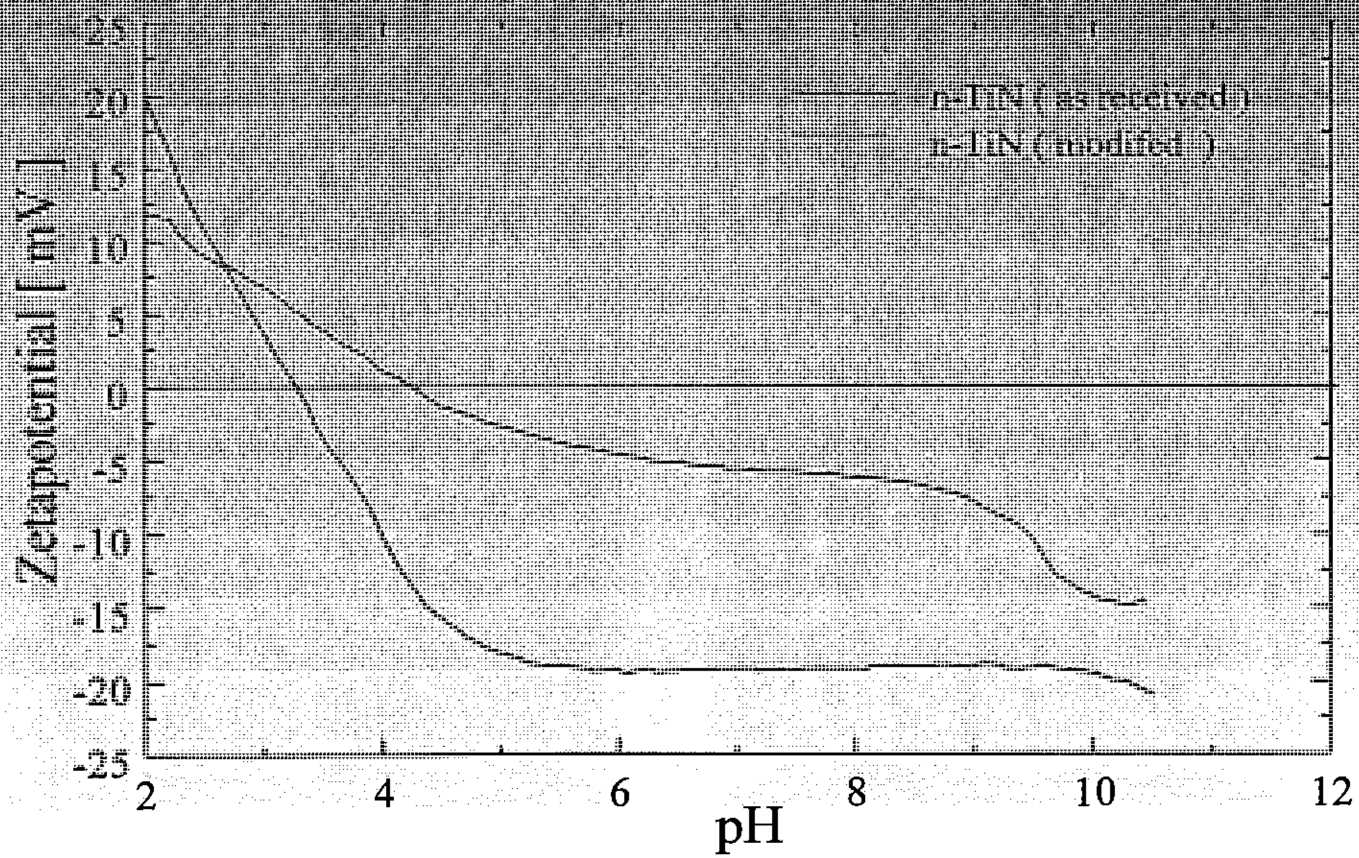




002.593

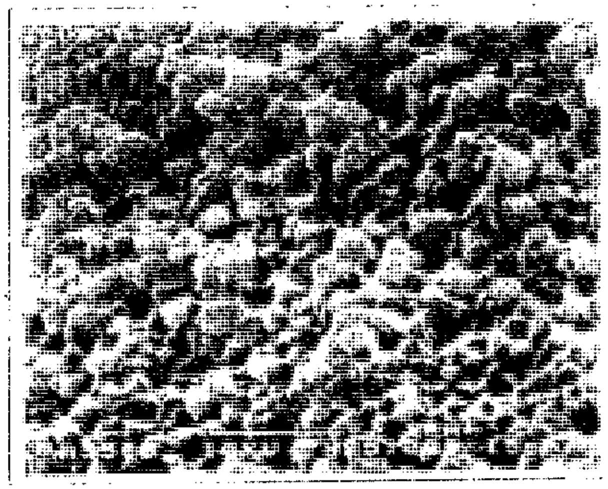
Zeta-Potential

- pH dependence of the zeta-potential of nanoscaled TiN

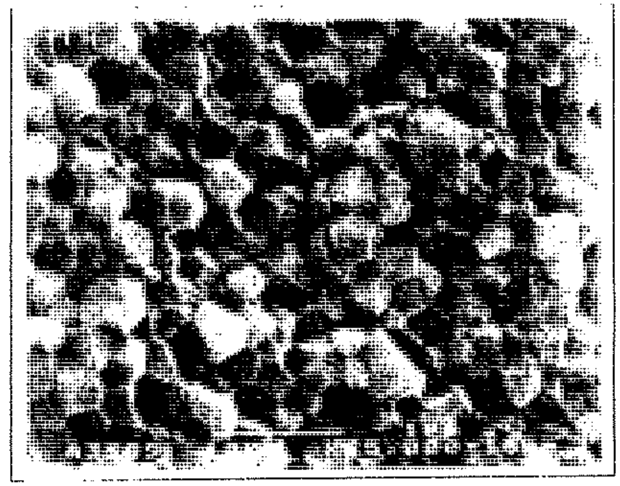


002.591

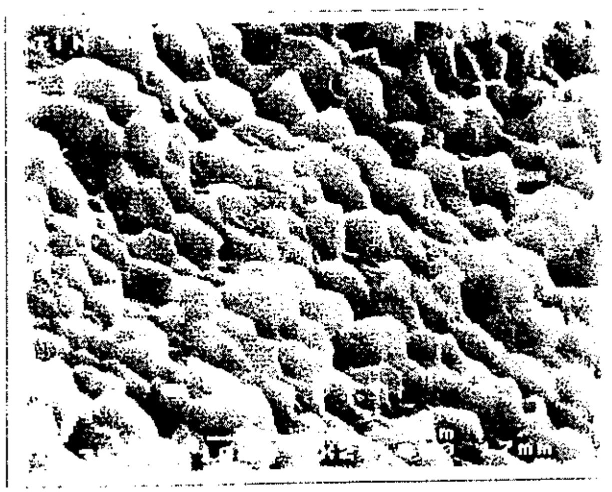
Grain Growth of Pressureles Sintered n-TiN



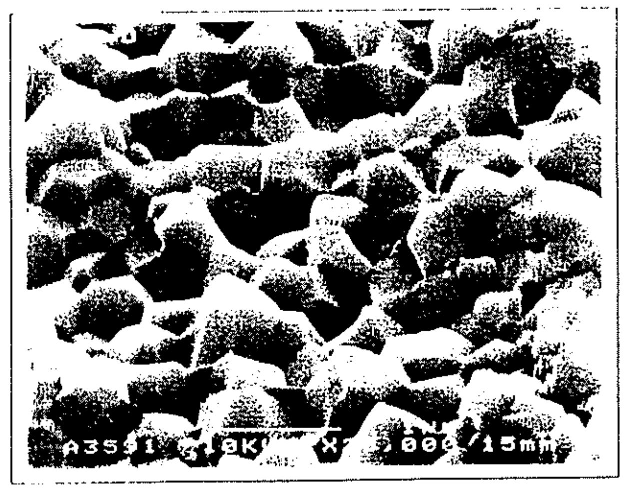
as sintered, 1400 °C , 2 min
D = 98.8   G = 263 nm



1400 °C , 30 min
D = 99,2   G = 356 nm



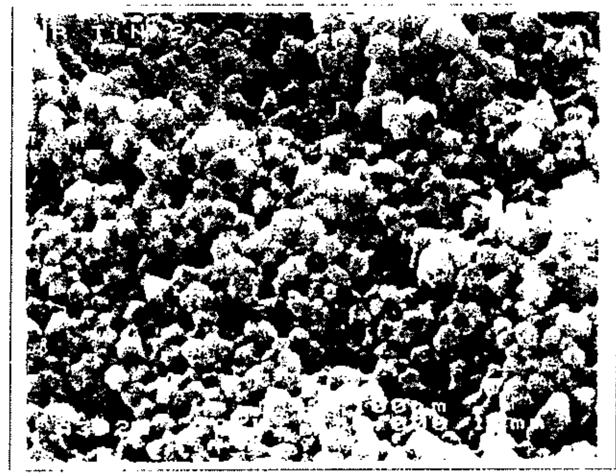
1400 °C , 60 min
D = 99,3   G = 414 nm



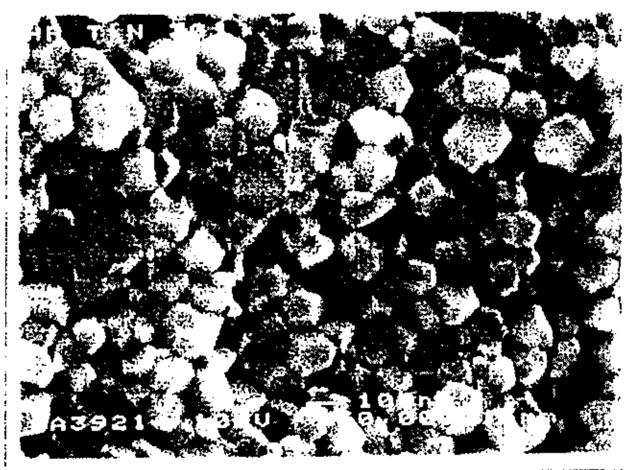
1400 °C , 120 min
D = 99,40   G =600 nm

Grain Growth of Hot Pressed n-TiN

as hot pressed
D = 97   G = 56 nm



1300 °C, 2 min
D = 98   G = 81 nm



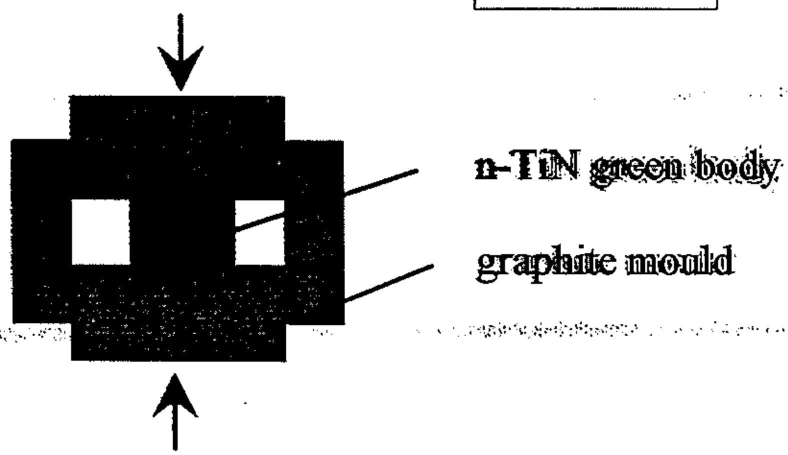
1300 °C , 30 min
D = 98,5   G = 140 nm

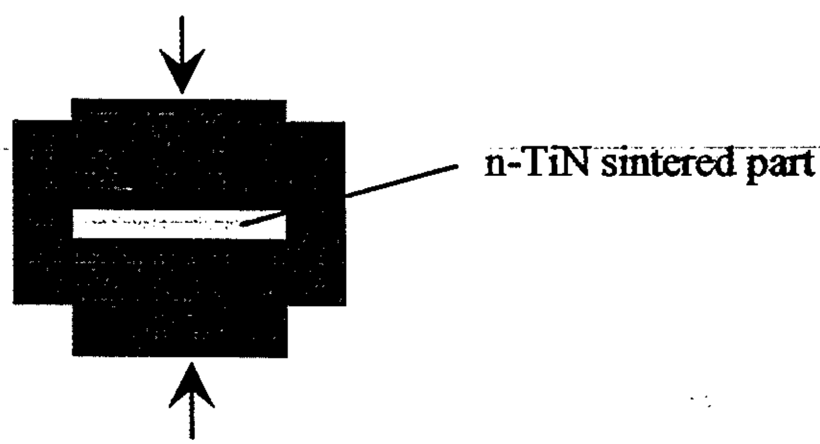
1300 °C , 60 min
D = 98,6   G = 170 nm

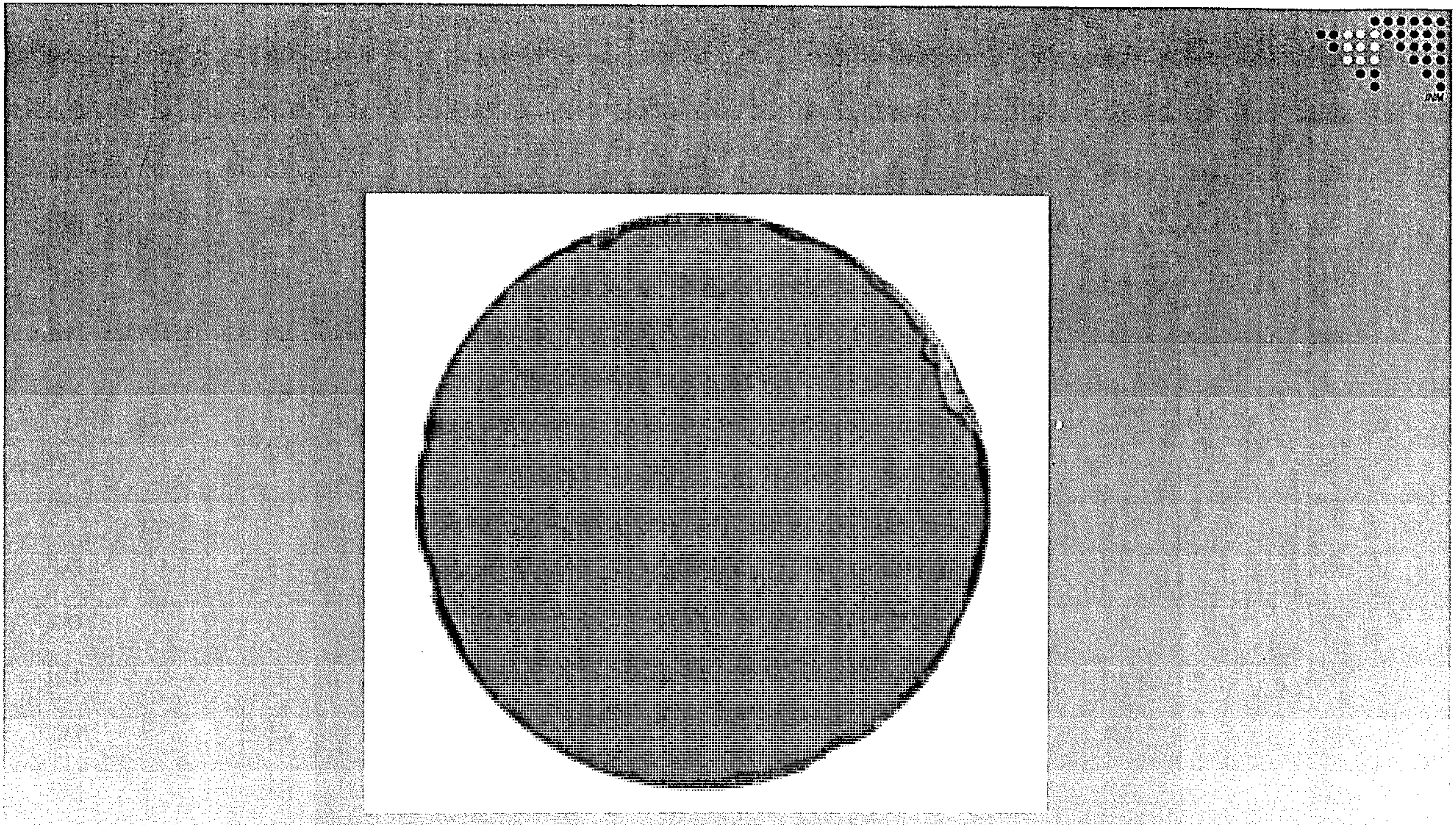
Plastic Deformation of n-TiN

- hot pressing of n-TiN

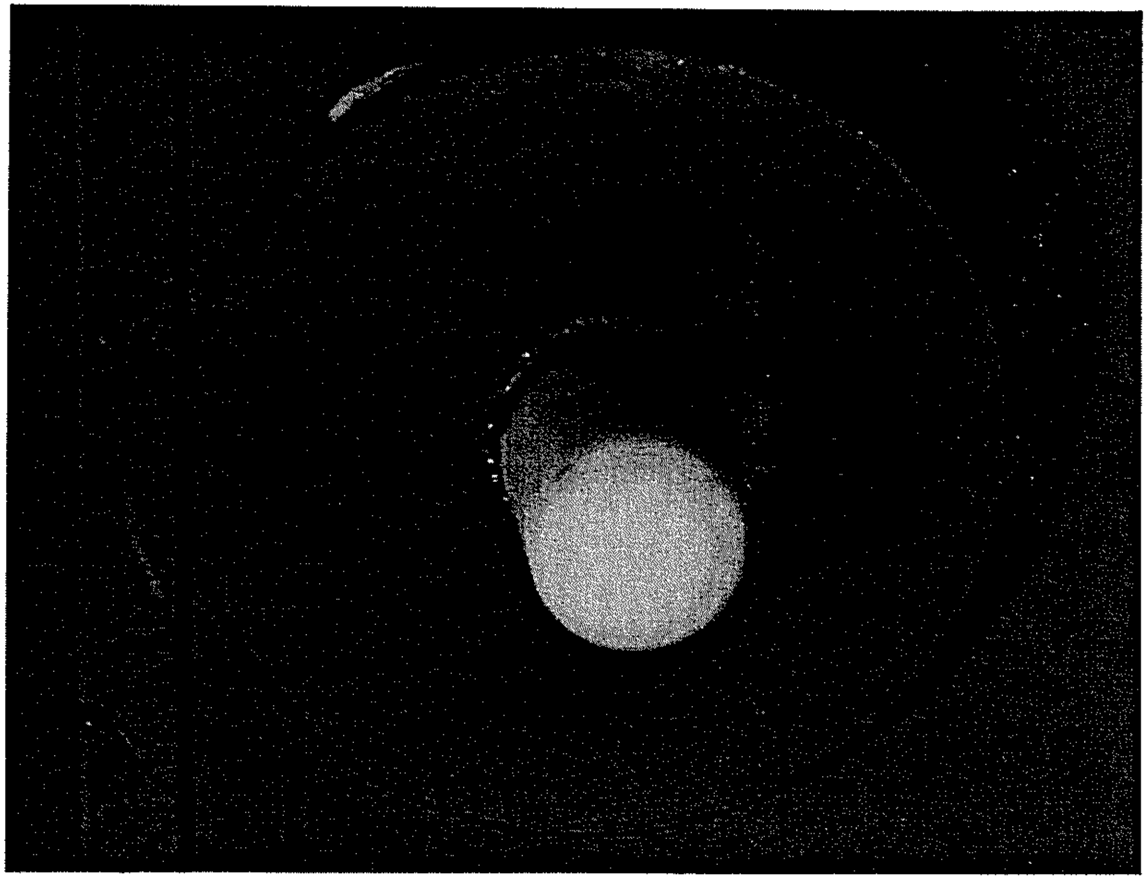
P = 20 MPa
T = 1150 °C
t = 30 min







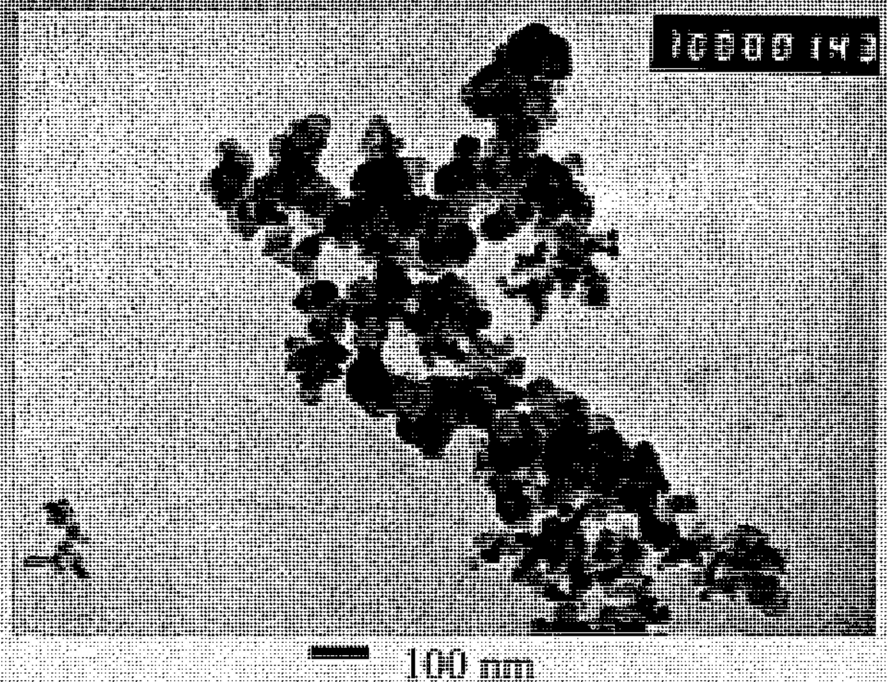
TiN solid plate



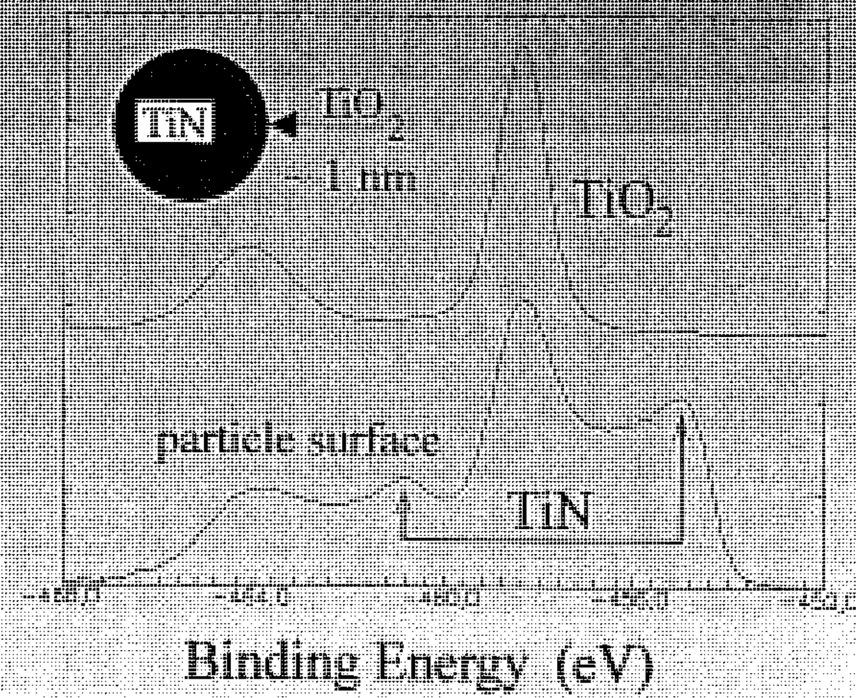
Al_2O_3 : sol-gel coated with TiN

Starting powder

TEM

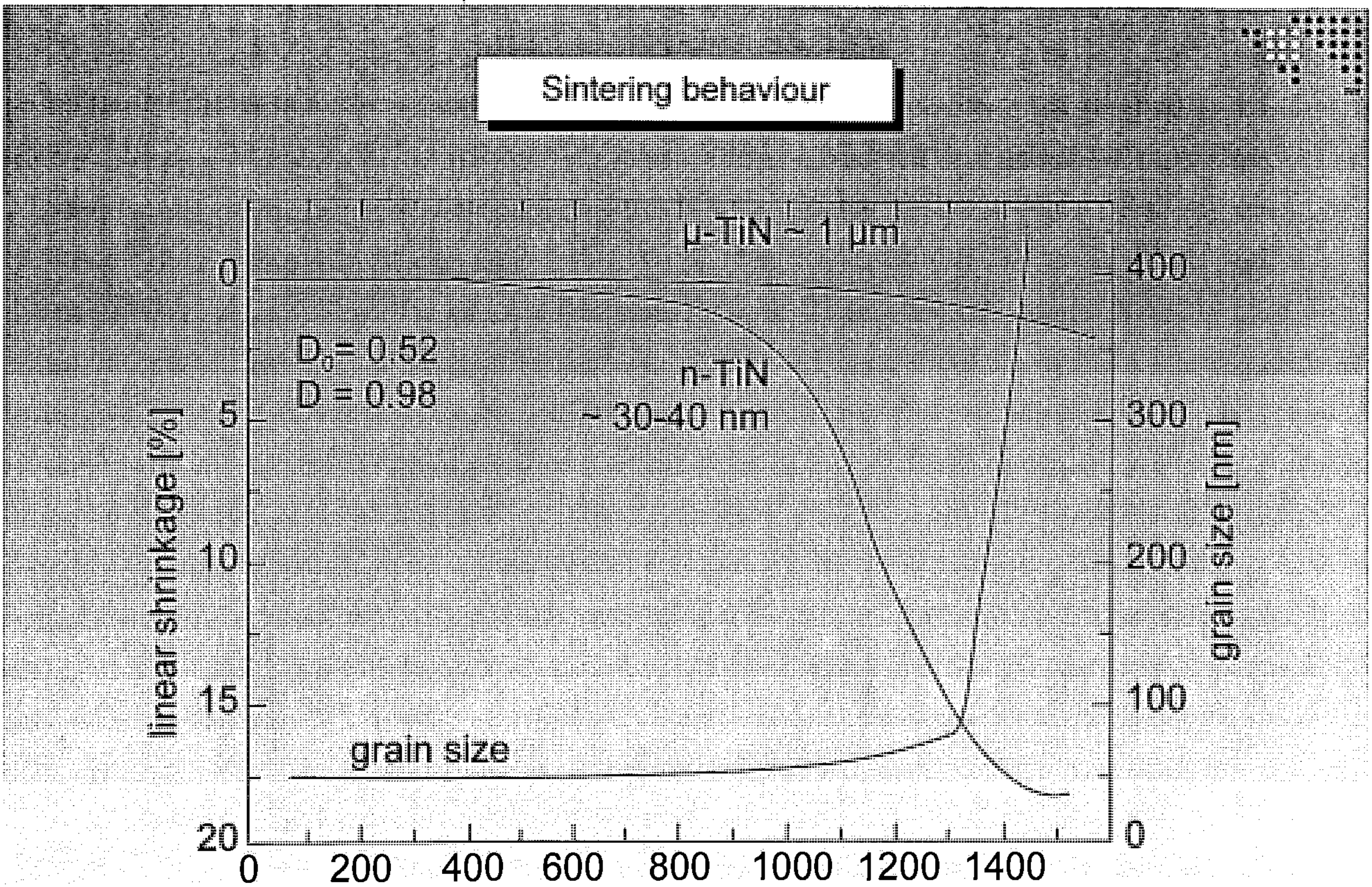


ESCA



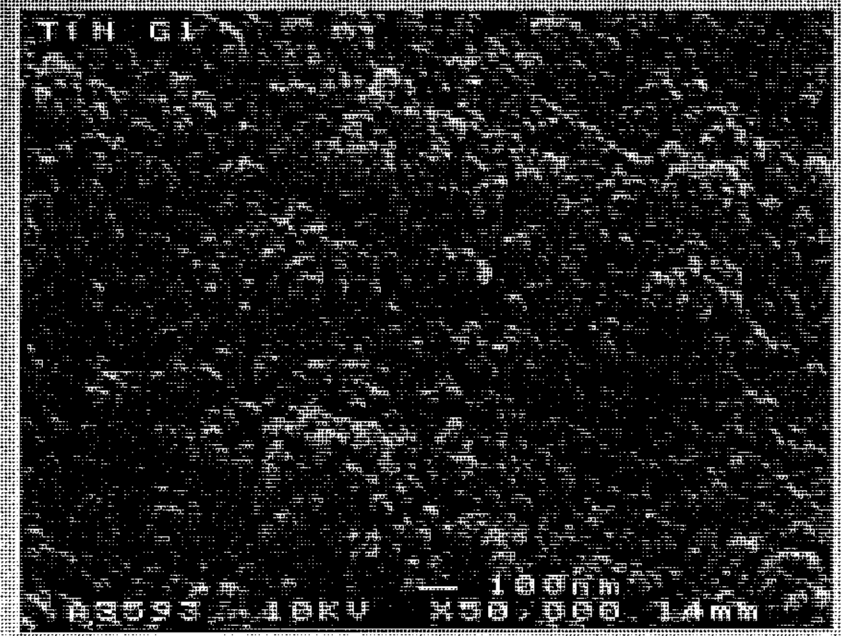
- particle size: 30-40 nm
- prepared by the CVR-process (H. C. Starck company)
- oxygen content: < 1 wt.-%
- crystal structure: osbornite
- specific surface area: 54 m2/g
- acidic surface properties

002.531

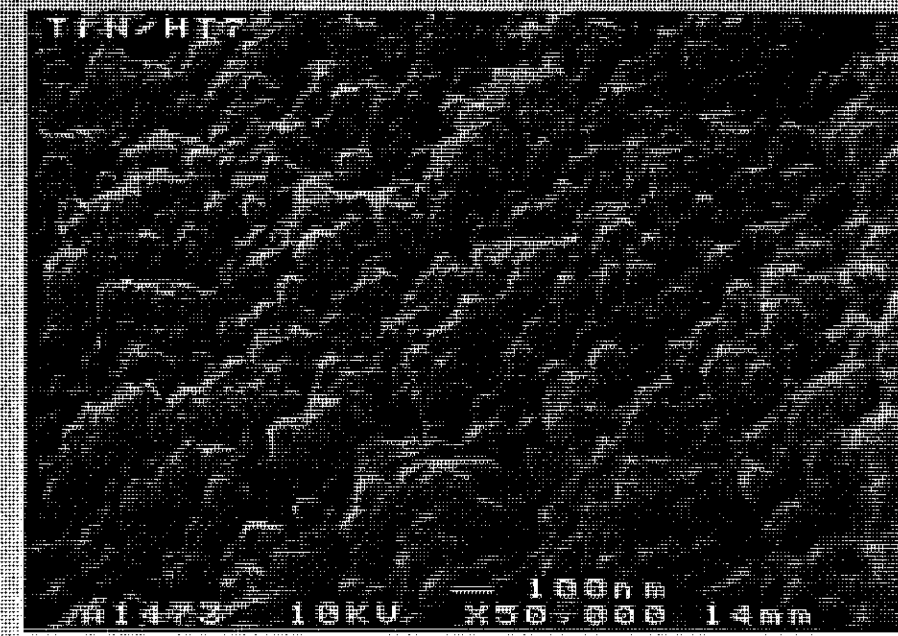

Sintering behaviour
µ-TiN ~ 1 µm
D0 = 0.52
D = 0.98
n-TiN
~ 30-40 nm
grain size
linear shrinkage [%]
0
5
10
15
20
grain size [nm]
400
300
200
100
0
0
200
400
600
800
1000
1200
1400
temperature [°C]

002.530

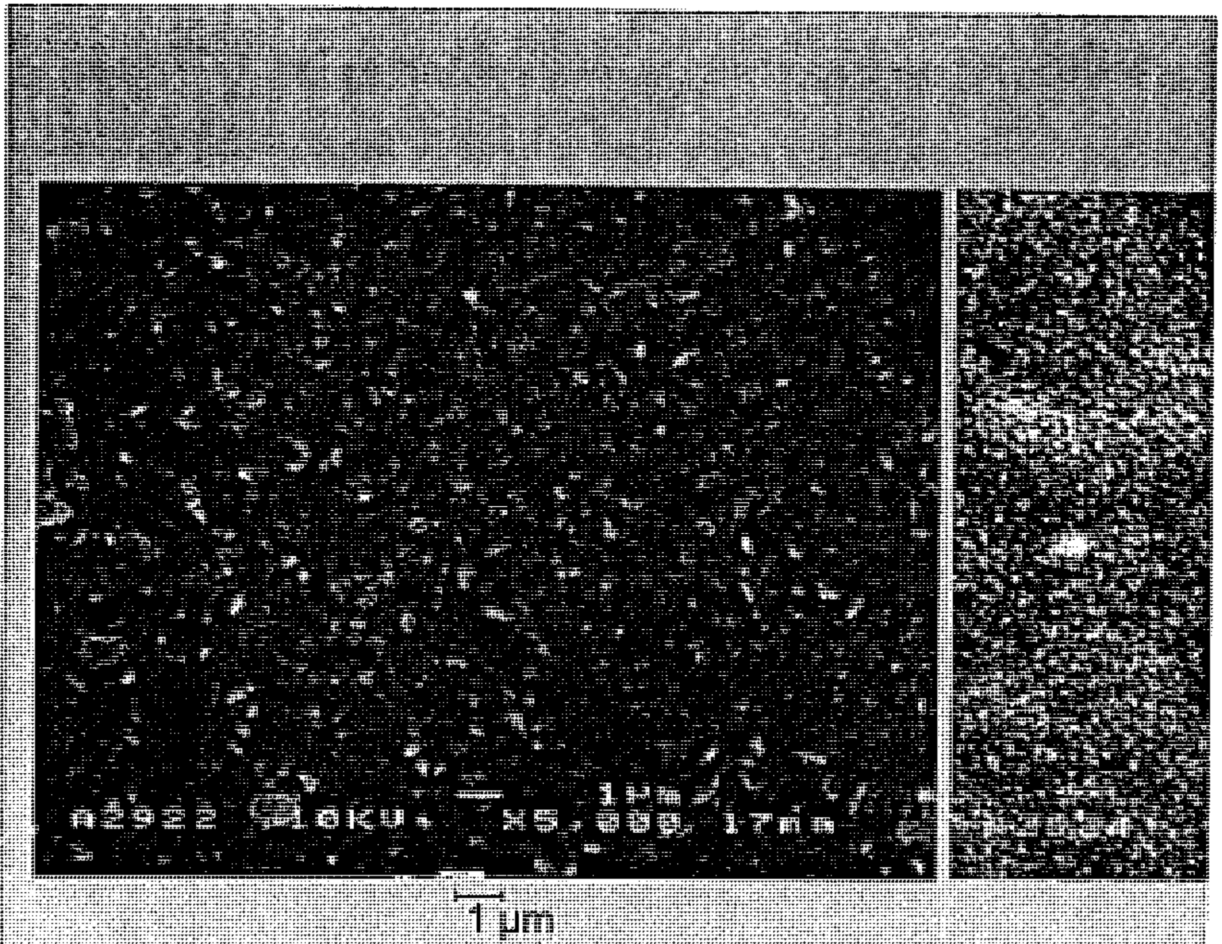
Microstructure of n-TiN

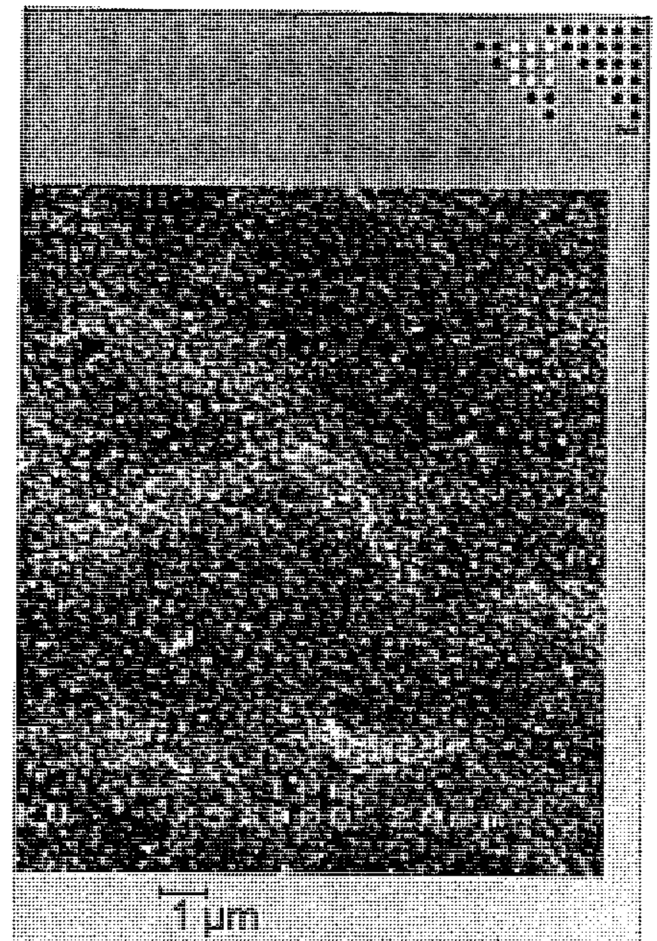


Green part



Sintered part
(1300 °C, D = 0.98, G = 70 nm)





SEM micrographs of the microstructure of titanium nit e coatings on an alumina substrate prepared by CVD (a) and dip coating follow by sintering (b)

Mechanical Properties of pressureless sintered n-TiN

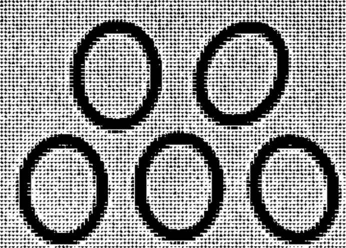
Porosity [%]	1.2	0.8	0.7	literature
E-Modul [GPa]	430	435	448	260-400
$H_{V0.5}$ [GPa]	16.0	16.2	16.5	12-15

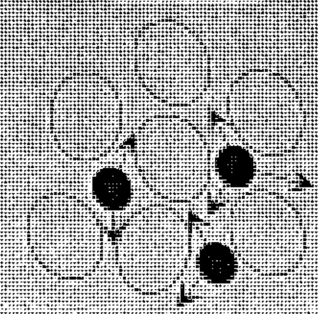
Distribution of Sintering Additives

- Activation of mass-transport

⟶ Effect on particle-surface / bulk-material

ideal ⟷ **real**



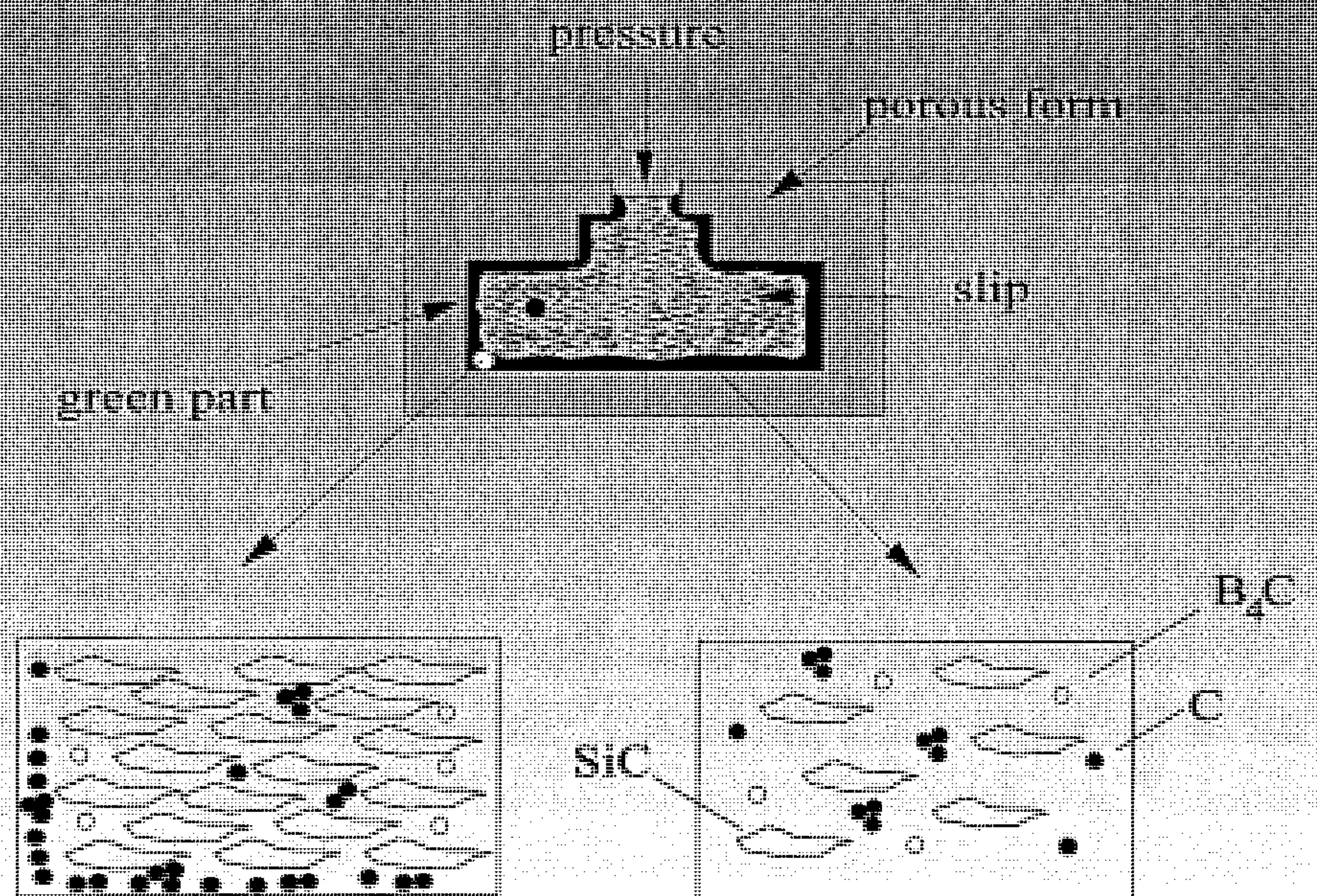


- thin layers

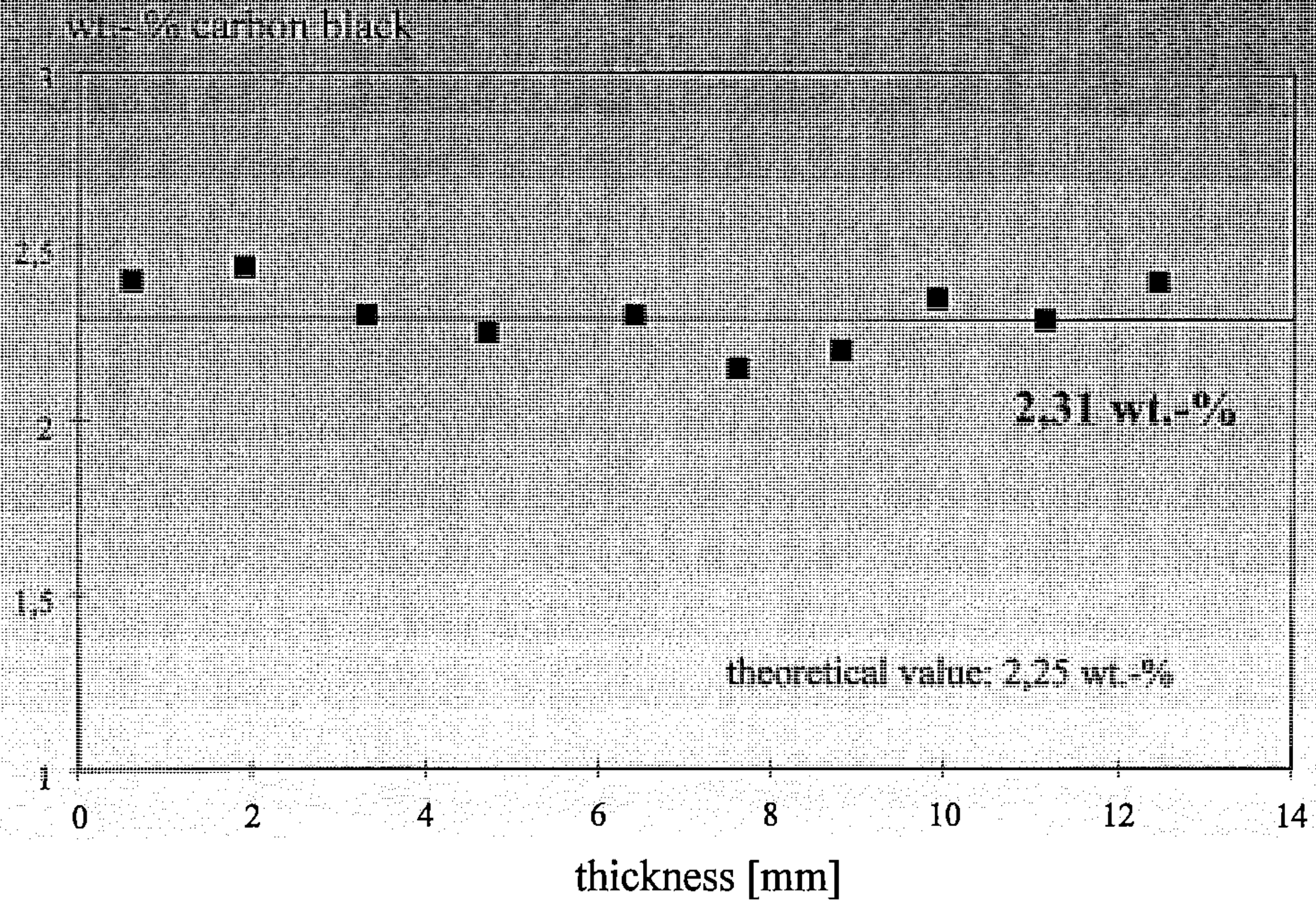
* by using „nano com-posite" particle structures

- density gradient
- random distribution
- additive transport to particle surface
  - ⟶ liquid-phase (capillary-forces)
  - ⟶ gas-phase and solid-state-diffusion

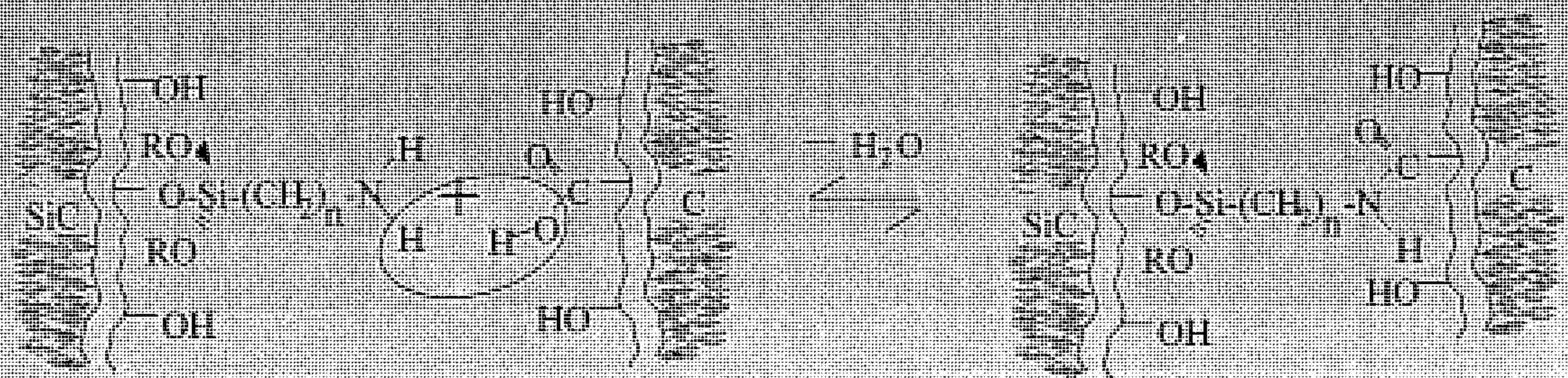
Pressure Slip Casting of $SiC/C/B_4C$



Distribution of Carbon Black



Model of Chemical Coupling

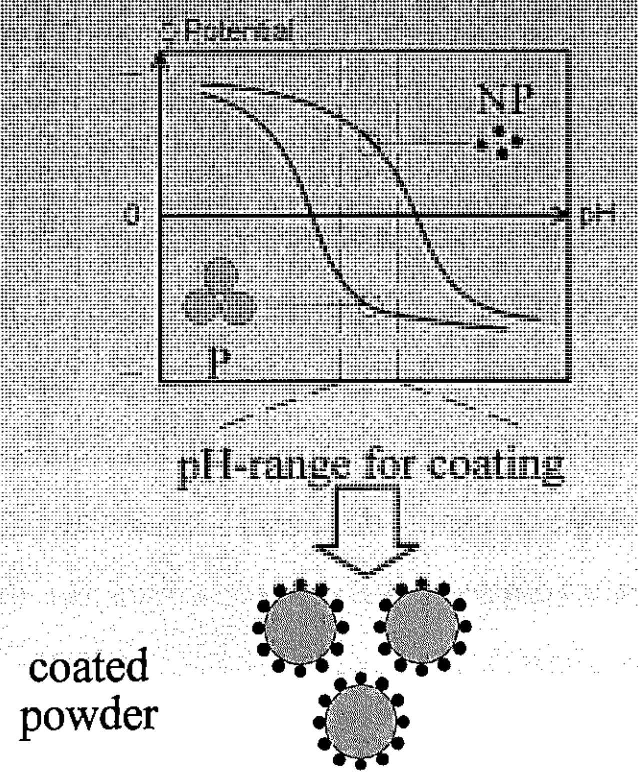


002.619

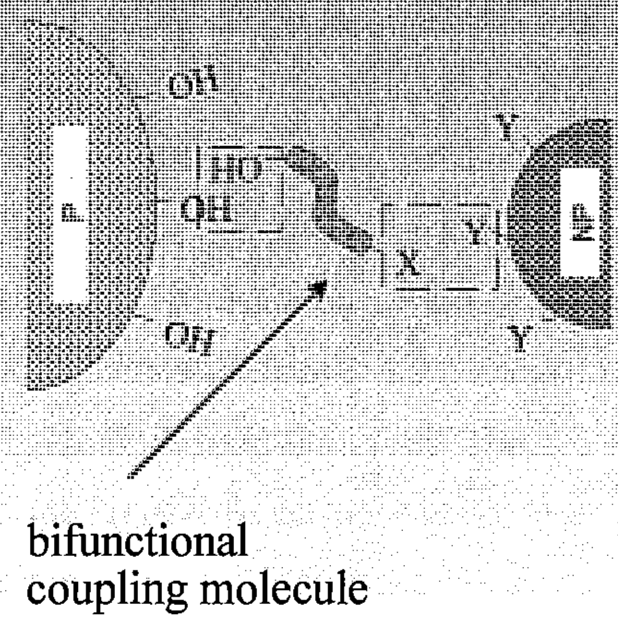
Multicomponent Monophasic Systems

○ coating of powder (P) with nanoparticles (NP)

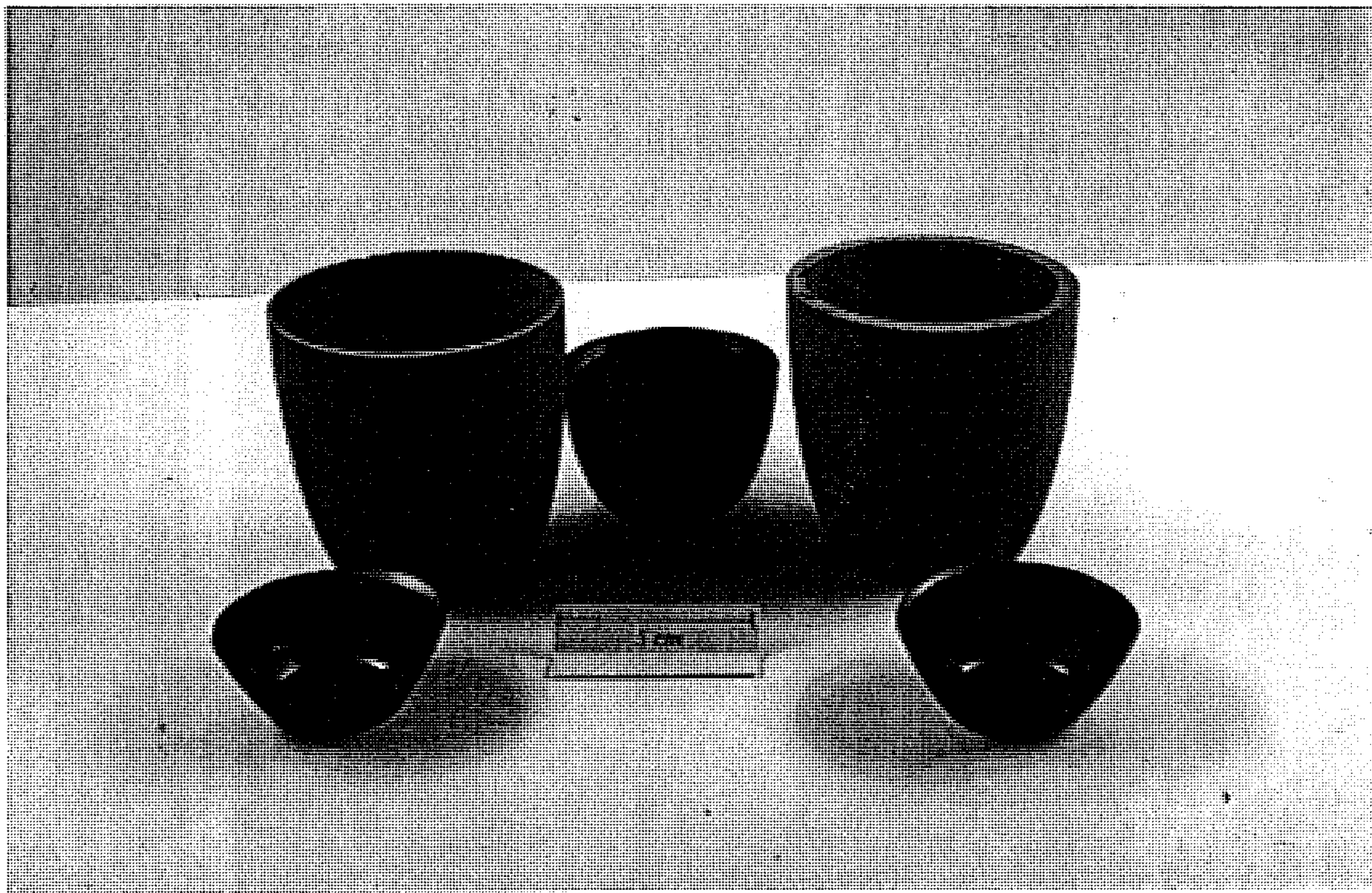
Electrostatic coating



Chemical Coupling

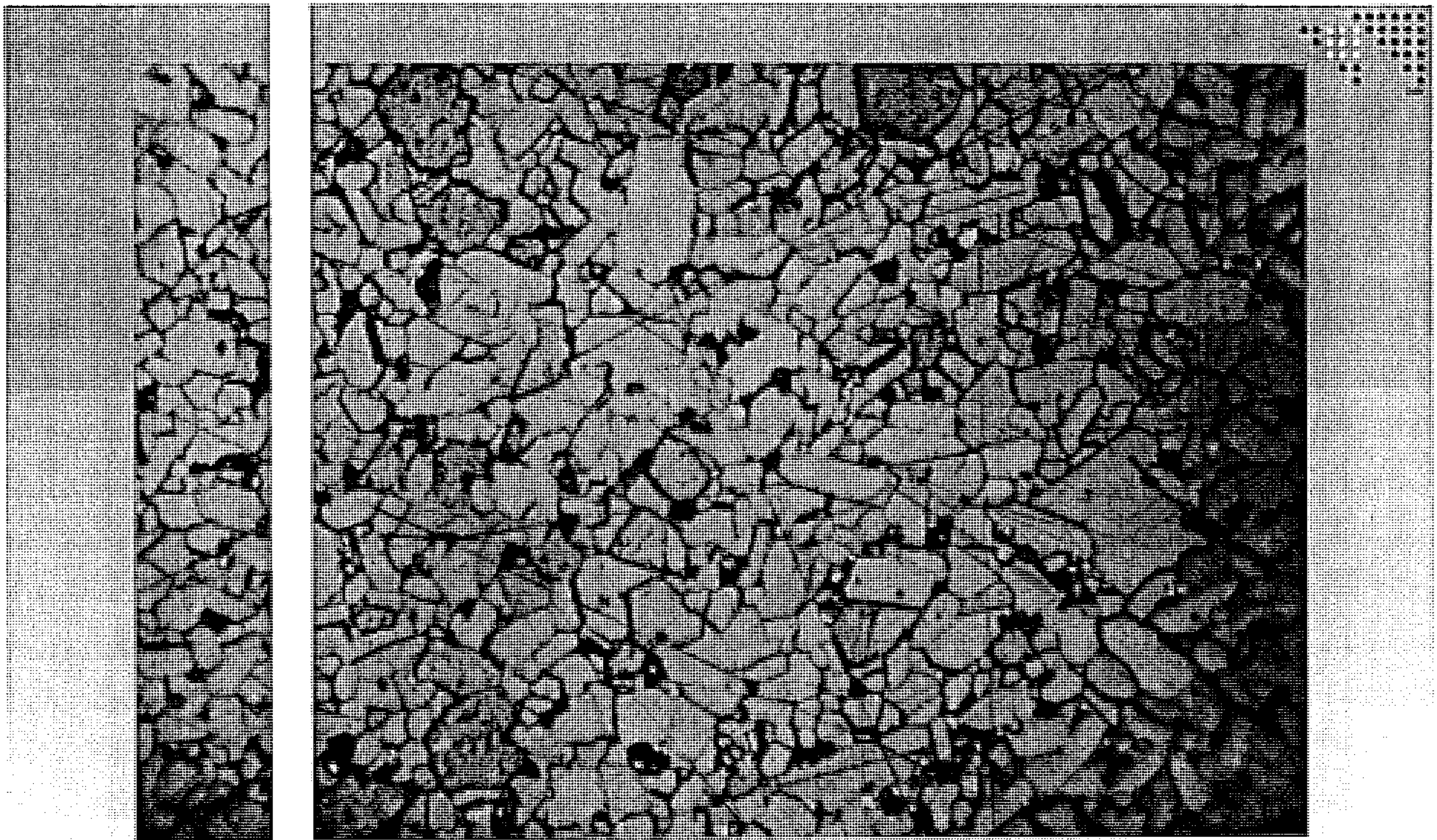


002.617

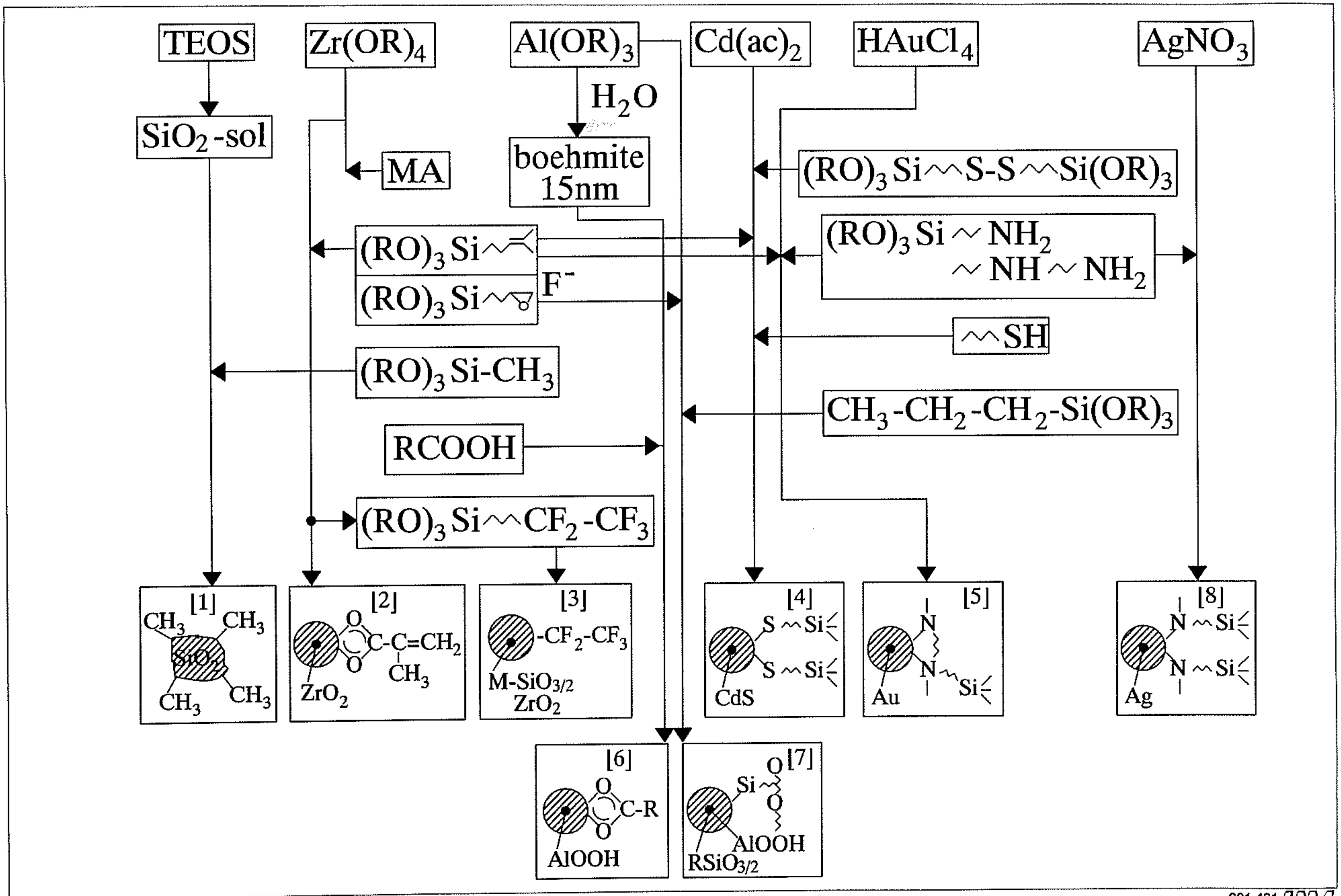


Part fabrication by the new
sub µm high pressure slip casting technique
on lab scale

001.844



S M micrograph of pressureless sintered SiC using carbon
b ck-modified SiC powder and B_4C as sintered aid


TEOS
Zr(OR)4
Al(OR)3
Cd(ac)2
HAuCl4
AgNO3
H2O
SiO2-sol
MA
boehmite 15nm
(RO)3Si~S-S~Si(OR)3
(RO)3Si~NH2 ~NH~NH2
F-
~SH
(RO)3Si-CH3
CH3-CH2-CH2-Si(OR)3
RCOOH
(RO)3Si~CF2-CF3
[1]
[2]
[3]
[4]
[5]
[6]
[7]
[8]
ZrO2
M-SiO3/2
CdS
Au
Ag
AlOOH
RSiO3/2

001.491 INM

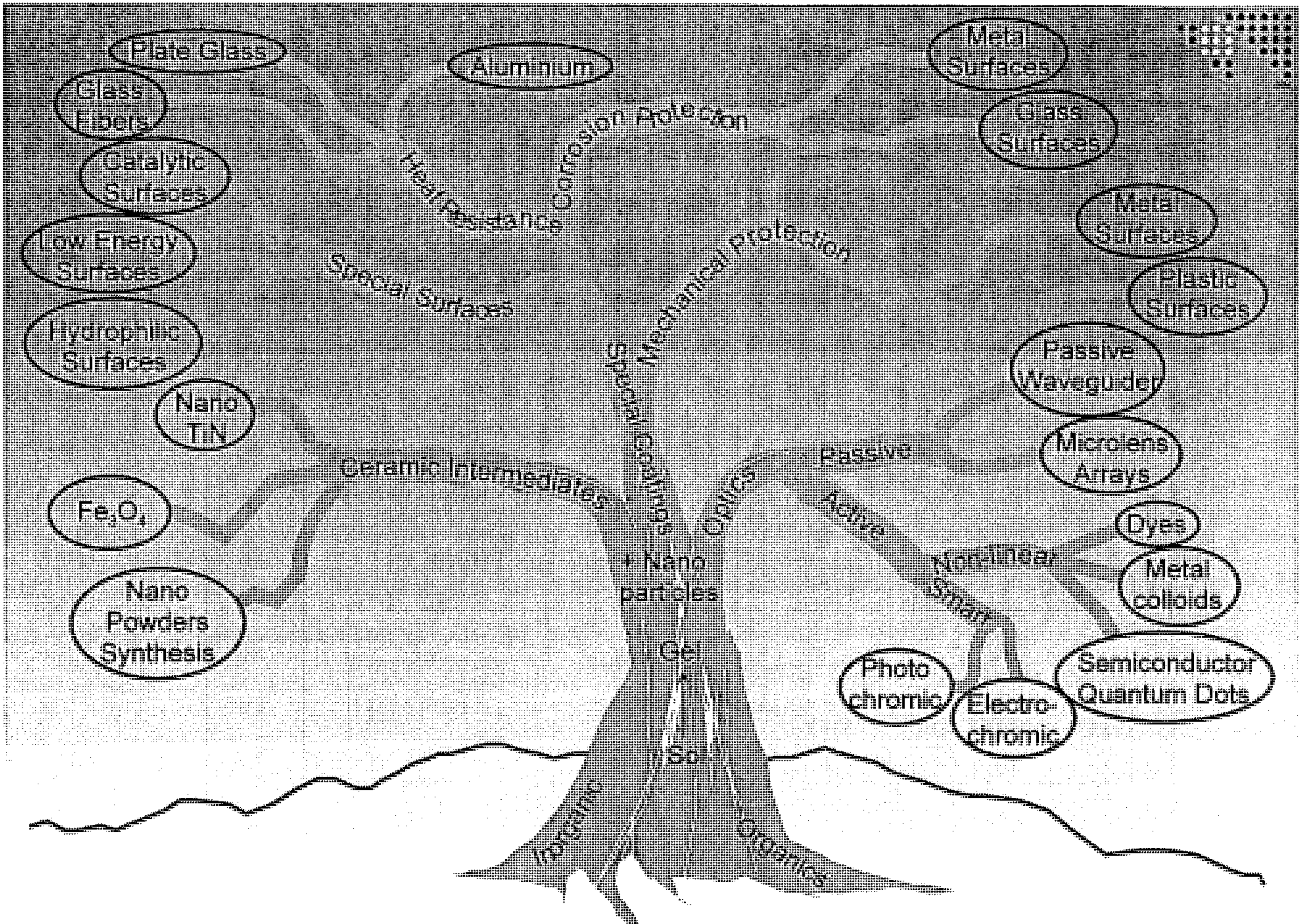


Plate Glass
Aluminium
Metal Surfaces
Glass Fibers
Corrosion Protection
Glass Surfaces
Catalytic Surfaces
Heat Resistance
Metal Surfaces
Low Energy Surfaces
Mechanical Protection
Special Surfaces
Plastic Surfaces
Hydrophilic Surfaces
Special Coatings
Passive Waveguides
Nano TiN
Microlens Arrays
Ceramic Intermediates
Passive
Optics
Fe_3O_4
Active
Dyes
+ Nano particles
Non-linear
Metal colloids
Nano Powders Synthesis
Smart
Gel
Photo chromic
Semiconductor Quantum Dots
Electro-chromic
Sol
Inorganic
Organics

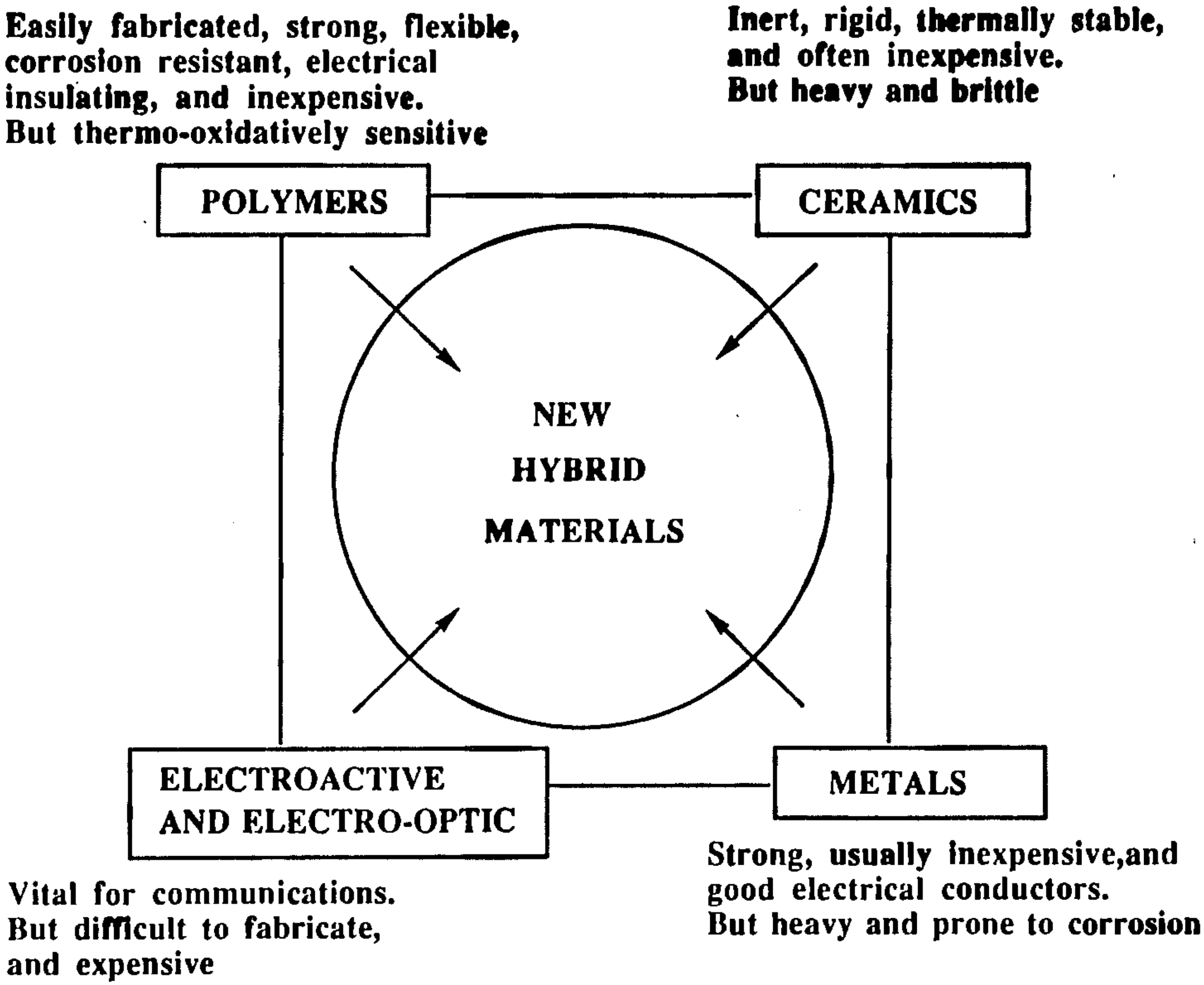
002.540

Inorganic/Organometallic Polymers

Harry Allcock	Polyphosphazenes, Properties and Application
James E. Mark	Properties of Inorganic Polymers with Bimodal Chain Distributions
Len Interrante	Preceramics Polymers
Rick Laine	Chemicals, Polymers and Ceramics from the Beach. I & II.

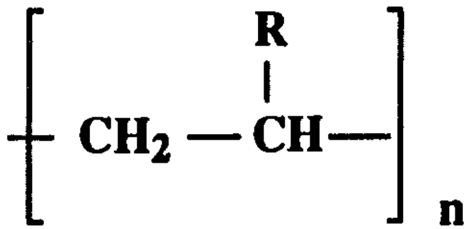
MOST AREAS OF ENGINEERING AND BIOMEDICINE ARE MATERIALS LIMITED - MATERIALS DO NOT YET EXIST THAT HAVE THE REQUIRED COMBINATIONS OF PROPERTIES.

TYPES OF MATERIALS

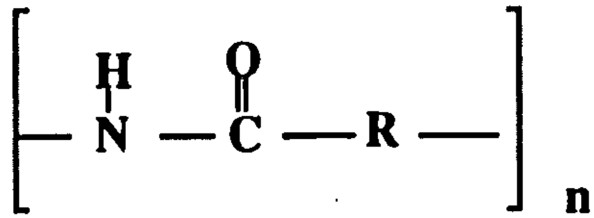


H. R. ALLCOCK

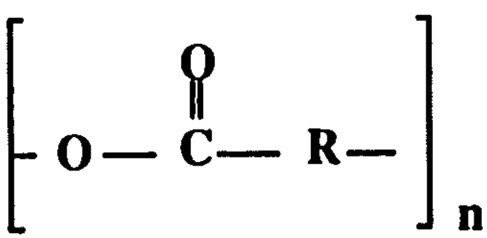
LONG - EXISTING POLYMER SYSTEMS



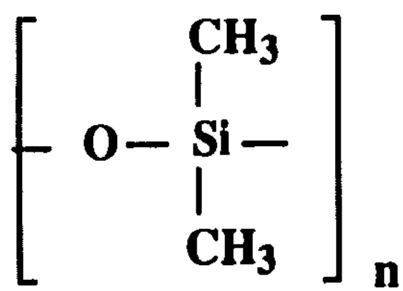
POLYVINYL POLYMERS



POLYAMIDES



POLYESTERS



SILICONES

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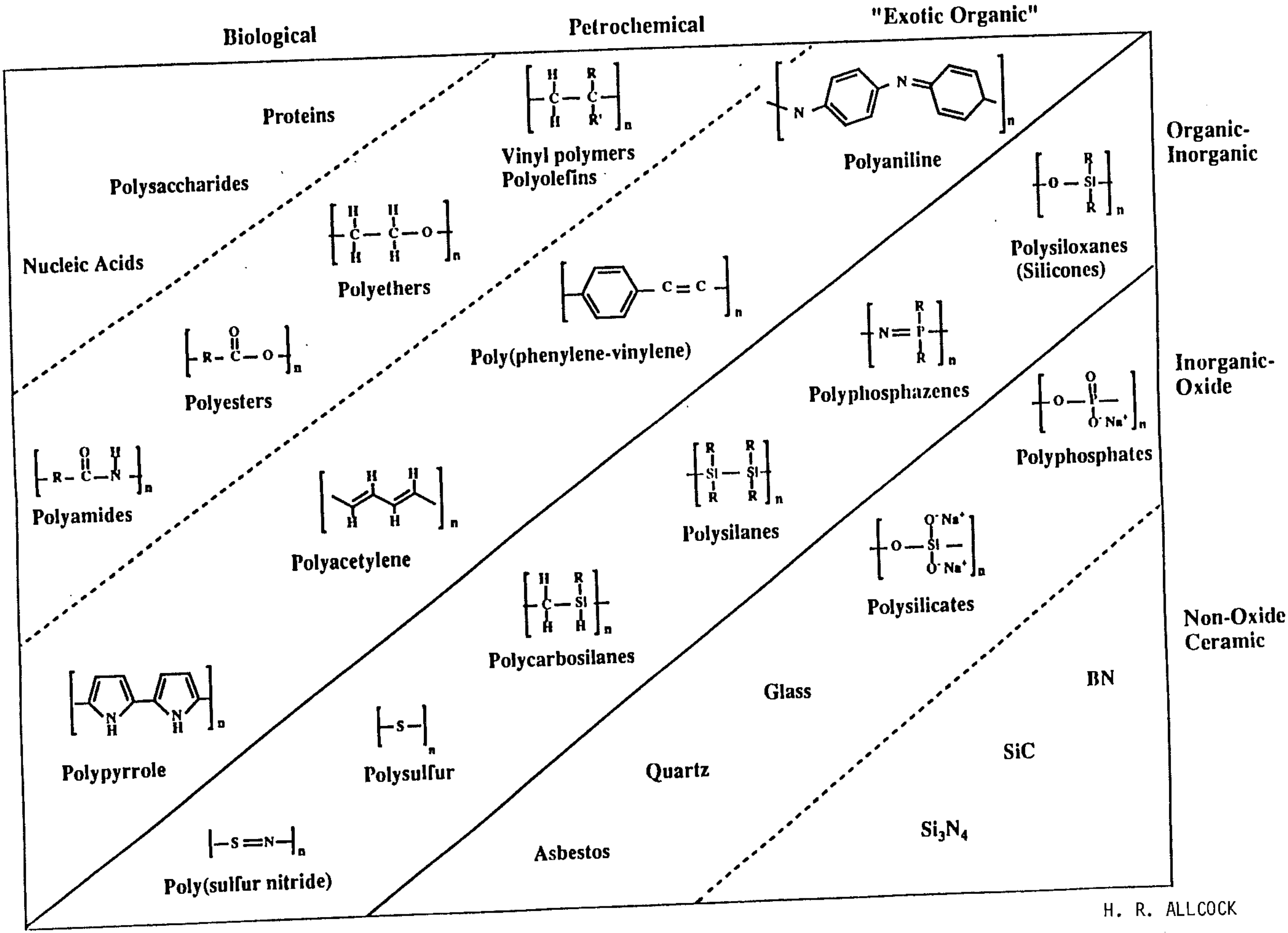
2-68-G


Biological
Petrochemical
"Exotic Organic"
Organic-
Inorganic
Inorganic-
Oxide
Non-Oxide
Ceramic
Proteins
Polysaccharides
Nucleic Acids
Vinyl polymers
Polyolefins
Polyaniline
Polyethers
Polyesters
Polyamides
Poly(phenylene-vinylene)
Polysiloxanes
(Silicones)
Polyphosphazenes
Polyphosphates
Polyacetylene
Polysilanes
Polysilicates
Polycarbosilanes
Polypyrrole
Polysulfur
Poly(sulfur nitride)
Glass
Quartz
Asbestos
BN
SiC
Si_3N_4
H. R. ALLCOCK

TWO WAYS TO VIEW INORGANIC POLYMERS AND THEIR PROPERTIES

1. INTRINSIC PROPERTIES OF THE INORGANIC BACKBONE
2. THE BACKBONE AS A "PLATFORM" FOR ACTIVE SIDE GROUPS

POLYMER DESIGN

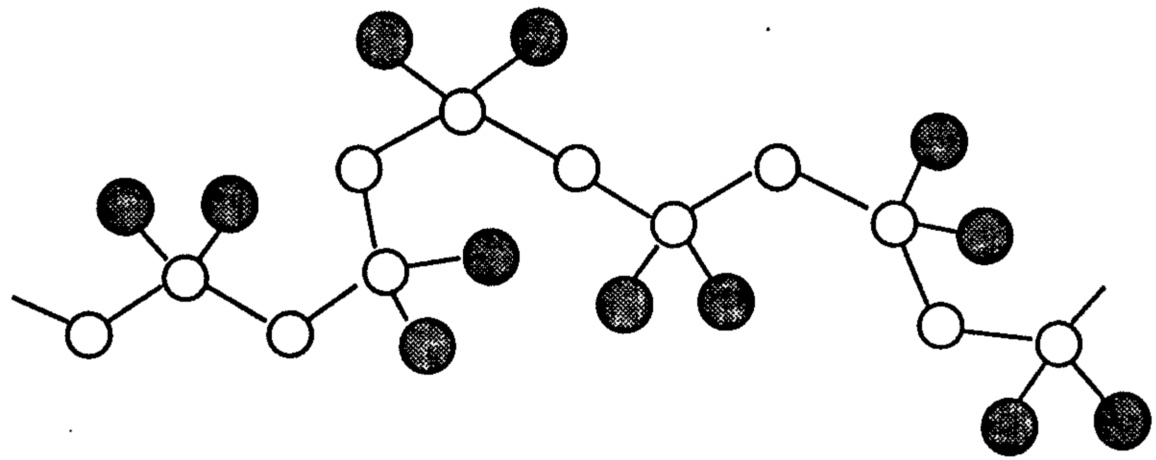
1. CHOICE OF POLYMER BACKBONE
   (Controls inherent chain flexibility, glass transition temperature, electrical conductivity, and thermal- and radiation stability)

2. CHOICE OF SIDE GROUPS
   (Controls glass transition temperature, crystallinity, solubility, miscibility, crosslinking, and many other properties)

3. OPEN CHAIN OR CROSSLINKED STRUCTURE
   (Determines solubility, strength, elasticity, hydrogel or organogel properties)

4. SINGLE POLYMER SYSTEM OR HYBRID MATERIAL
   (Blends, IPN's, composites, etc.)

5. "ACCIDENTAL" OR TAILORED SURFACE
   (Hydrophilicity, hydrophobicity, adhesion, biocompatibility, etc.)



THE PROPERTIES OF A POLYMER DEPEND ON:

1. THE ELEMENTS AND BONDS IN THE MAIN CHAIN
2. THE TYPES OF SIDE GROUPS ATTACHED TO THE BACKBONE

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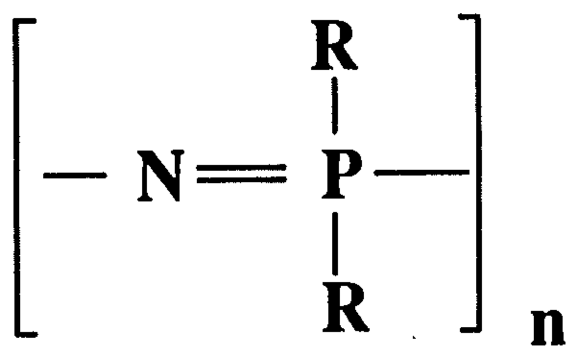
2-83-G

UNDERLYING IDEAS

1. GENERATION OF NEW PROPERTIES THROUGH POLYMERS WITH HETEROELEMENTS IN THE BACKBONE.
2. ACCESS TO BROAD RANGE OF NEW PROPERTIES THROUGH INTRODUCTION OF MANY DIFFERENT SIDE GROUPS VIA MACROMOLECULAR SUBSTITUTION.
3. TUNING OF PROPERTY COMBINATIONS VIA VARIATIONS IN RATIOS OF DIFFERENT SIDE GROUPS.
4. INTRODUCTION OF PROPERTY CHANGES BY SIDE GROUP EXCHANGE, ESPECIALLY AT SURFACES.

POLYPHOSPHAZENES



R = An organic group

n = Approx. 15,000

Molecular weights = 1 to 4 million

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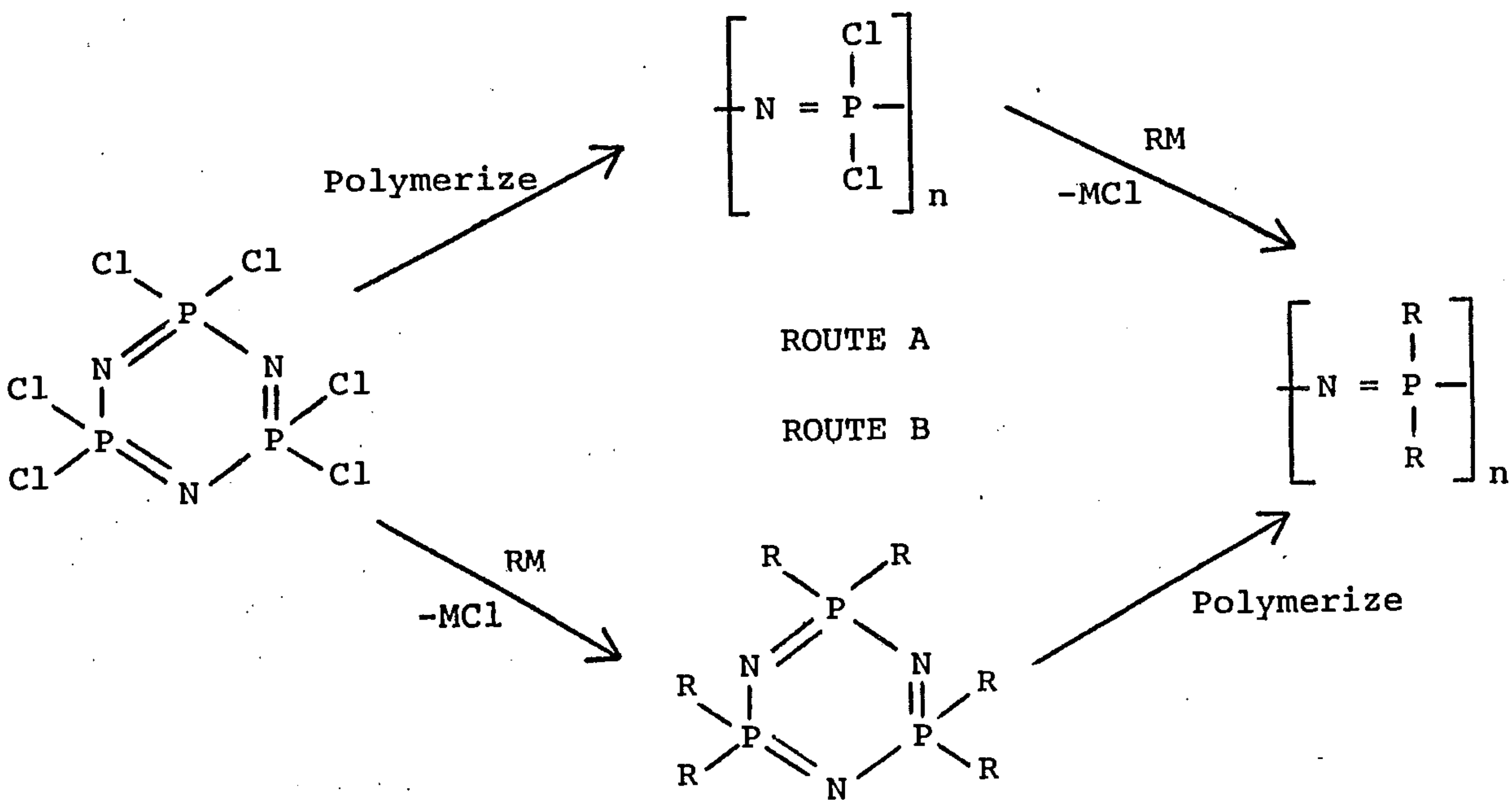
2-67-G

EXPERIMENTAL METHODS FOR REPLACEMENT OF ONE SIDE GROUP BY ANOTHER IN POLYMERS

1. USE A DIFFERENT MONOMER FOR POLYMERIZATION

2. REPLACEMENT OF SIDE GROUPS ON AN EXISTING POLYMER BY DIFFERENT GROUPS

TWO APPROACHES TO INORGANIC POLYMER SYNTHESIS



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ROUTE A

ADVANTAGES - CYCLIC SPECIES WITH F, Cl, OR Br SIDE GROUPS. POLYMERIZE READILY TO LINEAR HIGH POLYMERS.

DISADVANTAGES - REACTIONS ON POLYMERS MUST BE EXTREMELY "CLEAN" - NO CROSSLINKS OR CHAIN CLEAVAGE. REACTIVITY OF SUBSTRATE POLYMER MUST BE VERY HIGH. NEED FOR MODEL REACTIONS.

ROUTE B

ADVANTAGES - REACTIONS OF SMALL MOLECULES ARE EASIER TO CONTROL THAN REACTIONS OF HIGH POLYMERS. EASE OF CHARACTERIZATION.

DISADVANTAGES - LOWER TENDENCY FOR POLYMERIZATION OF NON-HALOGEN SUBSTITUTED CYCLIC SPECIES. MECHANISTIC AND STERIC PROBLEMS.

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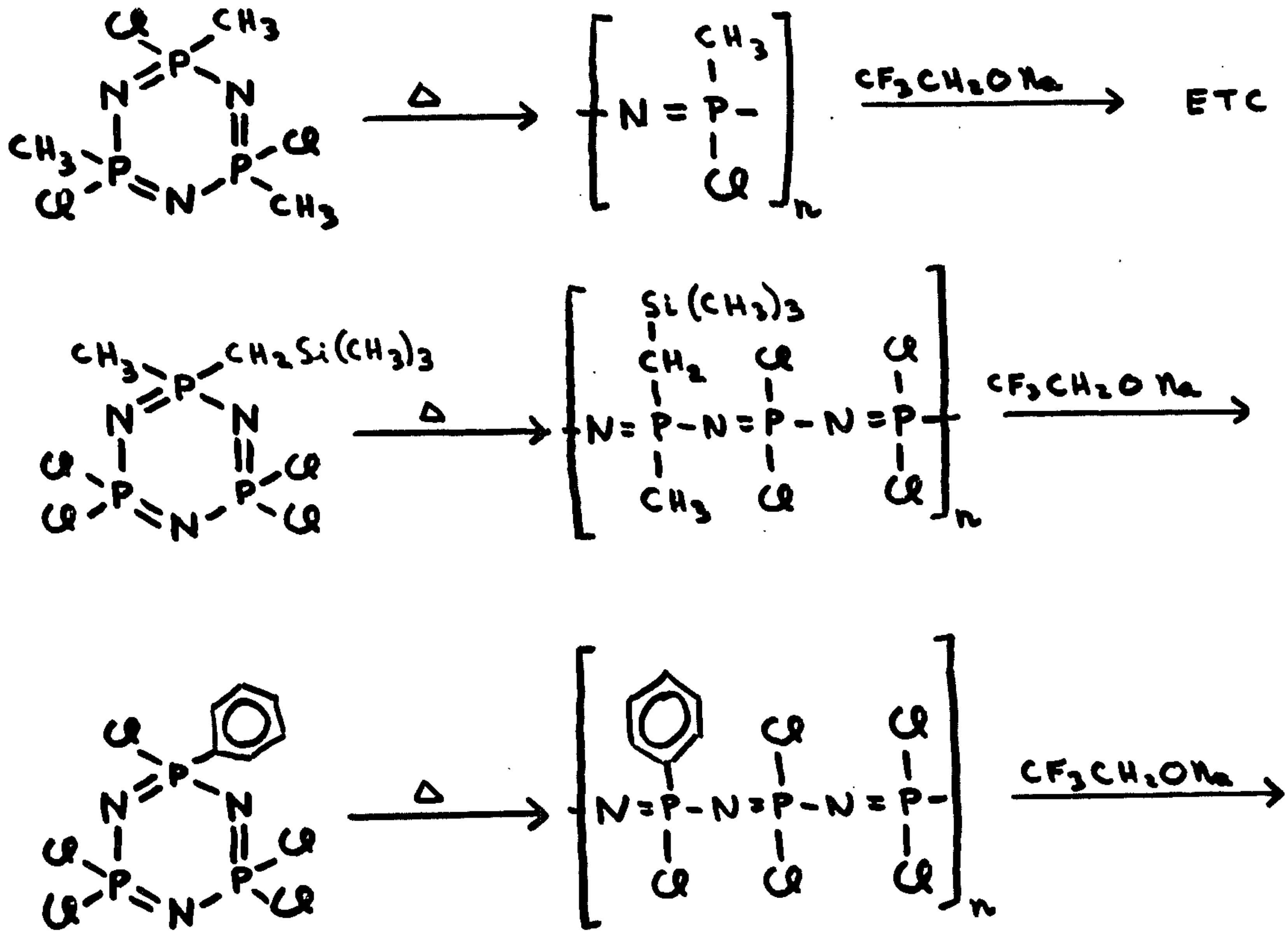

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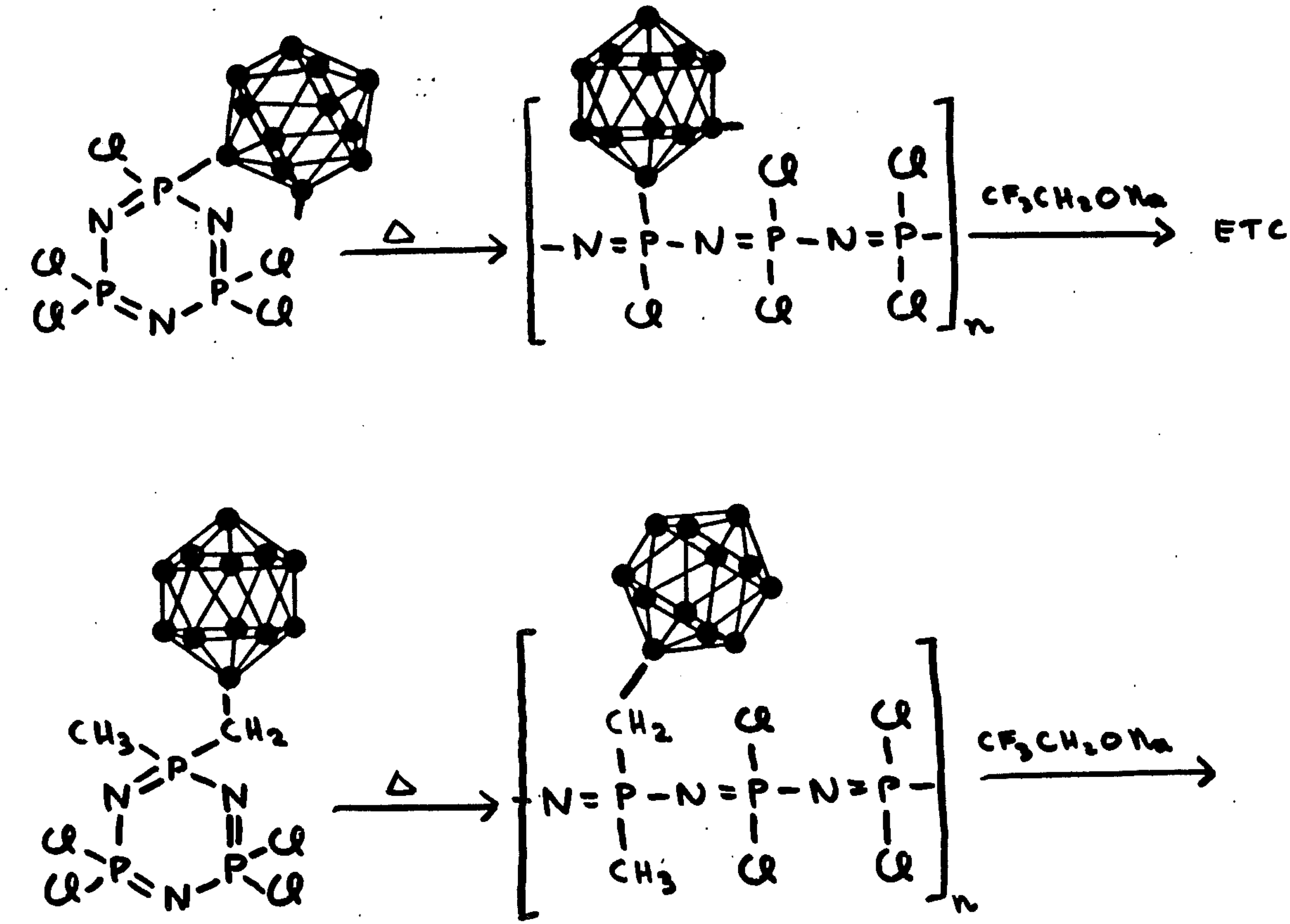

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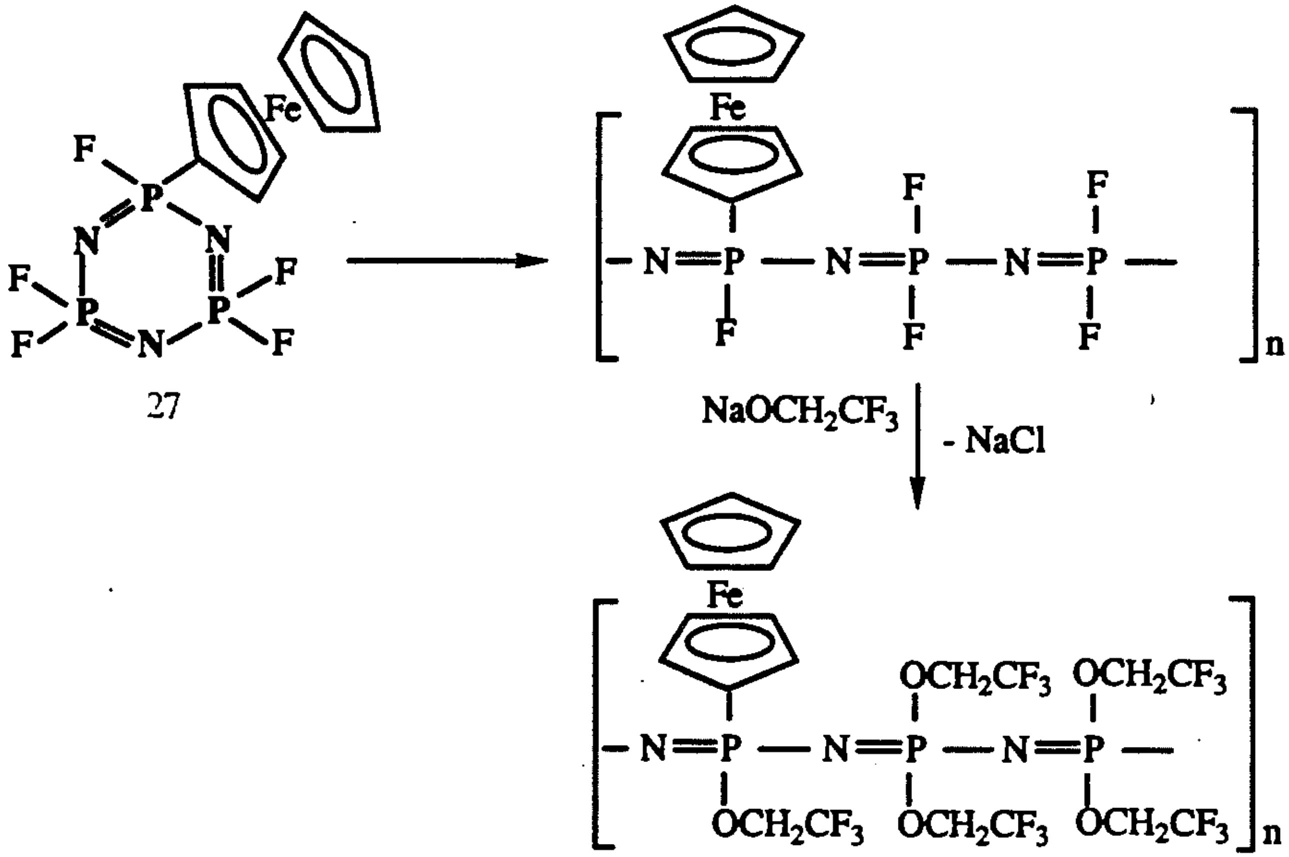
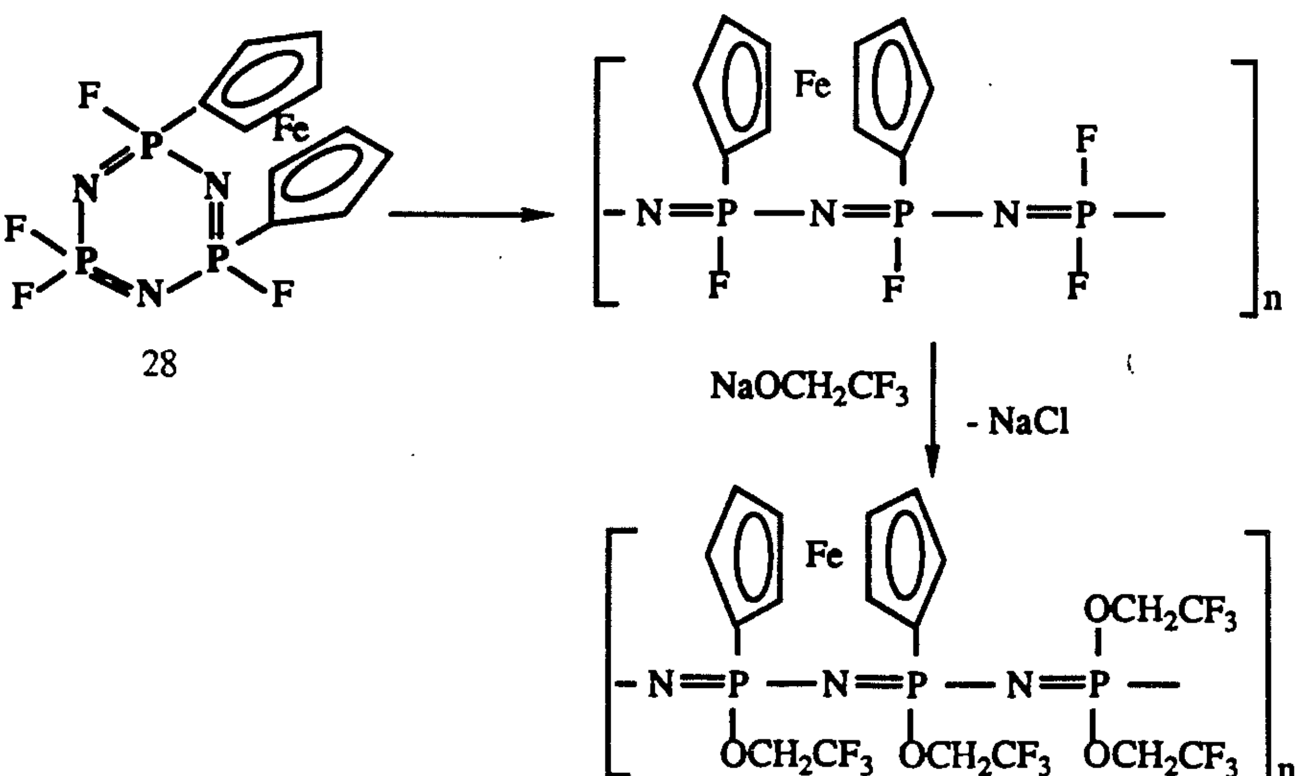
METALLOCENYLPHOSPHAZENES





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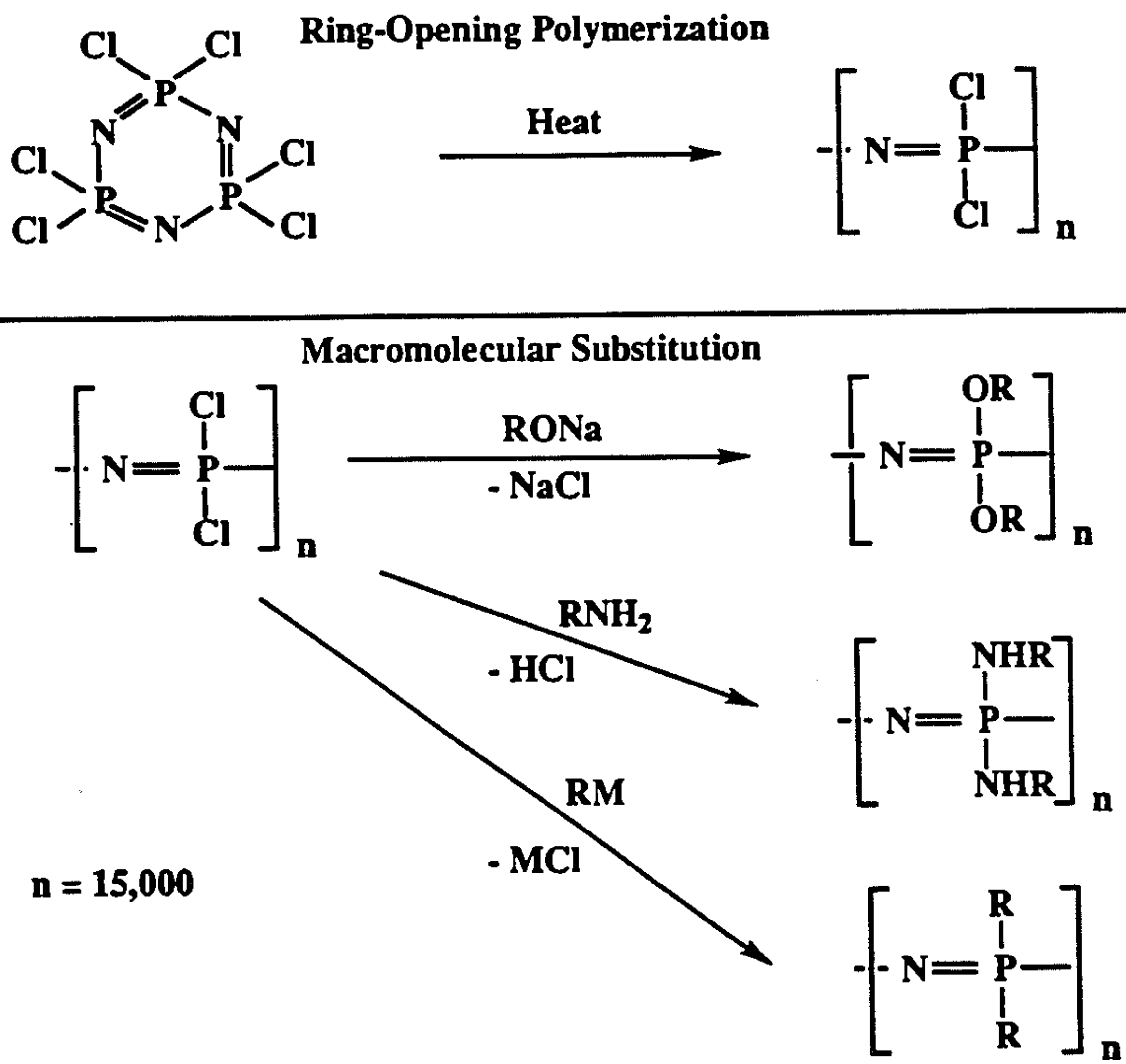
TWO STEP SYNTHESIS OF POLYPHOSPHAZENES



Note that, because all derivative polymers are made from one polymeric intermediate, the chain lengths of the final polymers are similar.

Note also that this type of macromolecular substitution chemistry is much easier and more versatile than similar reactions attempted with classical petrochemical polymers because of (a) the backbone stability and (b) the high reactivity of the P-Cl bonds.

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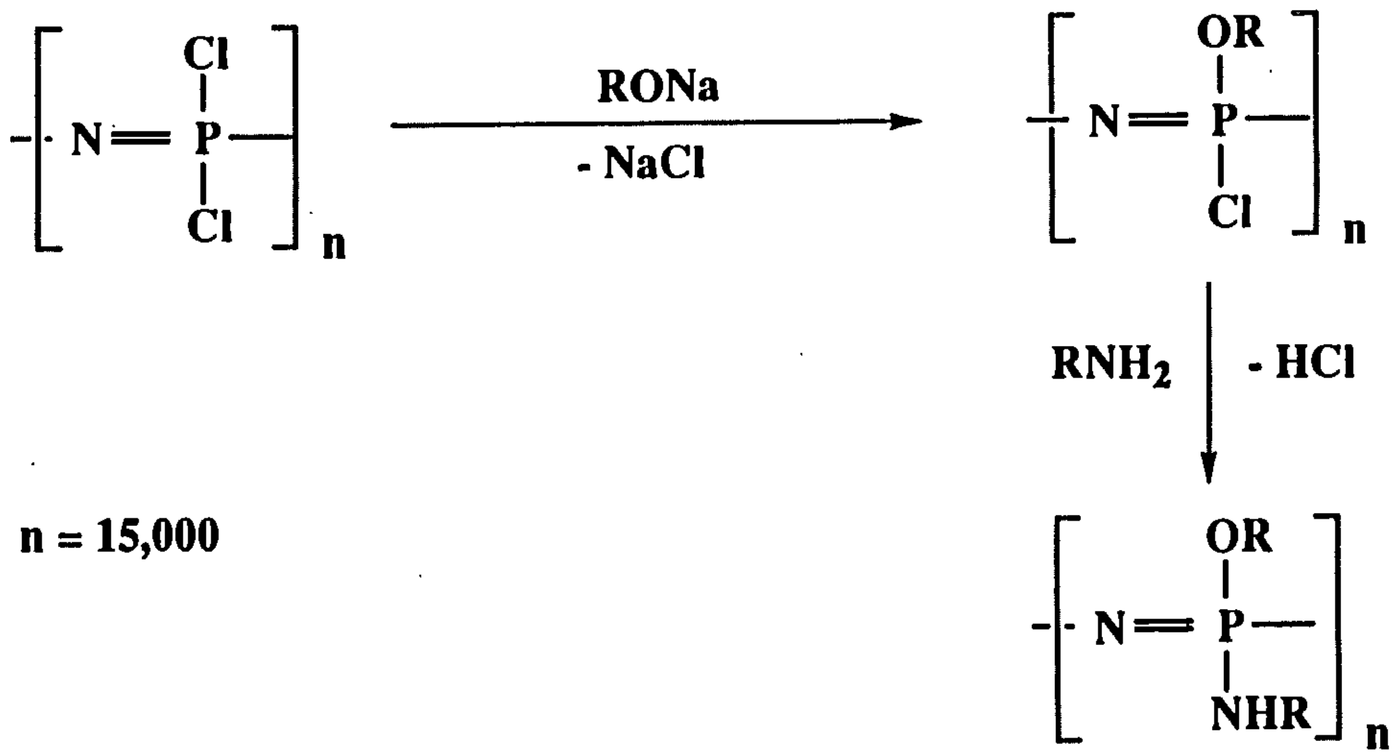
SEQUENTIAL SUBSTITUTION



n = 15,000

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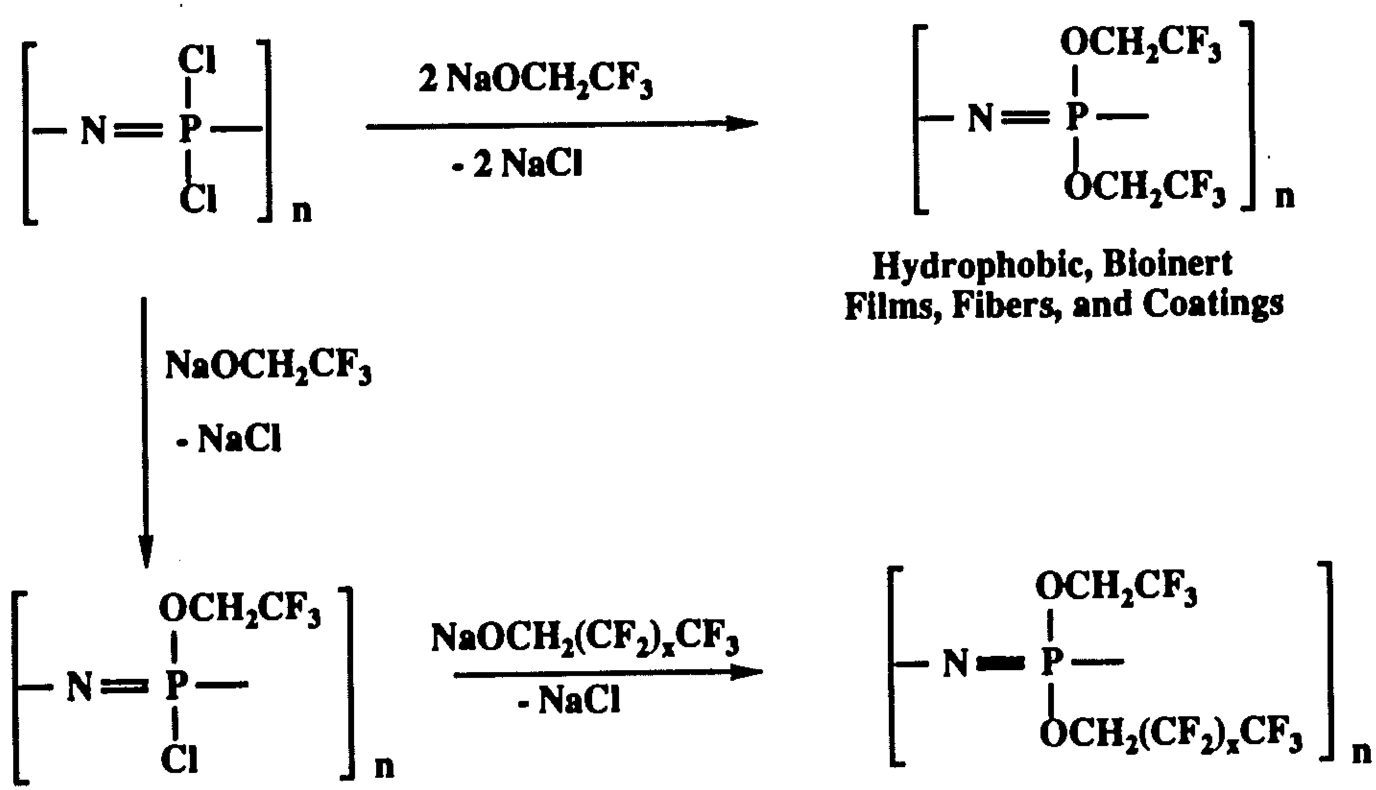
1-71-S

FLUOROALKOXYPHOSPHAZENES



Hydrophobic, Bioinert
Films, Fibers, and Coatings

Hydrophobic, Bioinert
Elastomer

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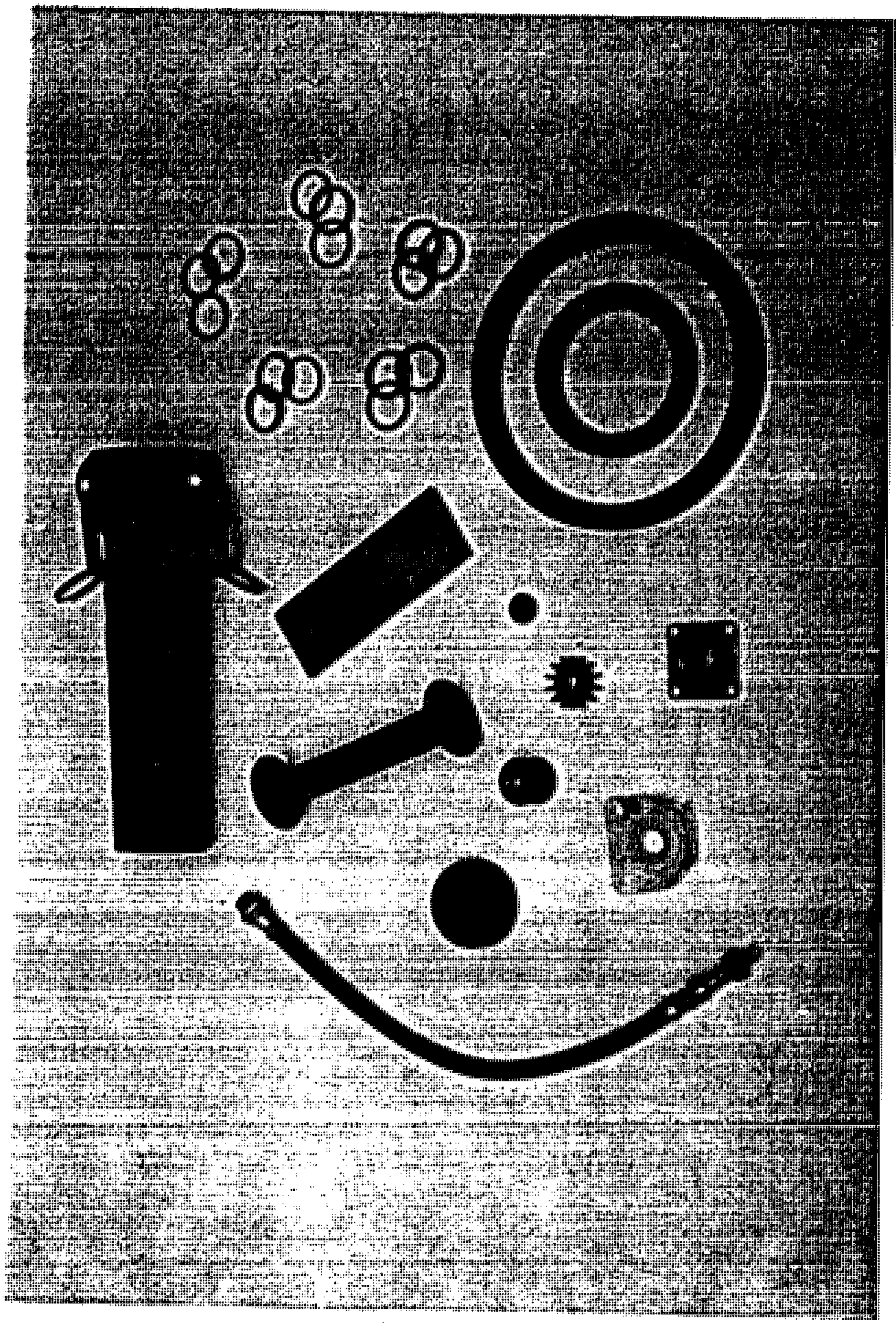

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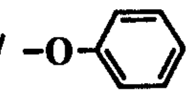
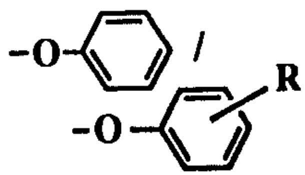
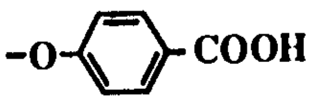
RELATIONSHIP BETWEEN SIDE GROUPS AND PROPERTIES

Side Groups for Elastomeric Properties	Side Groups for Water-Solubility or Hydrogels	Bioactive Side Groups	Side Groups for Bioerosion	Side Groups for Membranes
$-OC_2H_5$	$-NHCH_3$	Proteins	$-NHCH_2COOC_2H_5$	$-NHCH_3$/ $-OCH_2CF_3$
$-OCH_2CF_3$/ OCH_2-$(CF_2)_xCF_2H$	$-O(CH_2CH_2O)_2CH_3$ $-OCH_2CH(OH)CH_2OH$	Antibacterial agents	$-OCH_2CH(OH)CH_2OH$	$-NHCH_3$/ 
	-Glucosyl	Steroids	-Glucosyl	$-O(CH_2CH_2O)_2CH_3$/ $-OCH_2CF_3$
			(All generate P-OH)	
$-O(CH_2CH_2O)_2CH_3$		Catecholamines		Plus polymer alloys and interpenetrating networks

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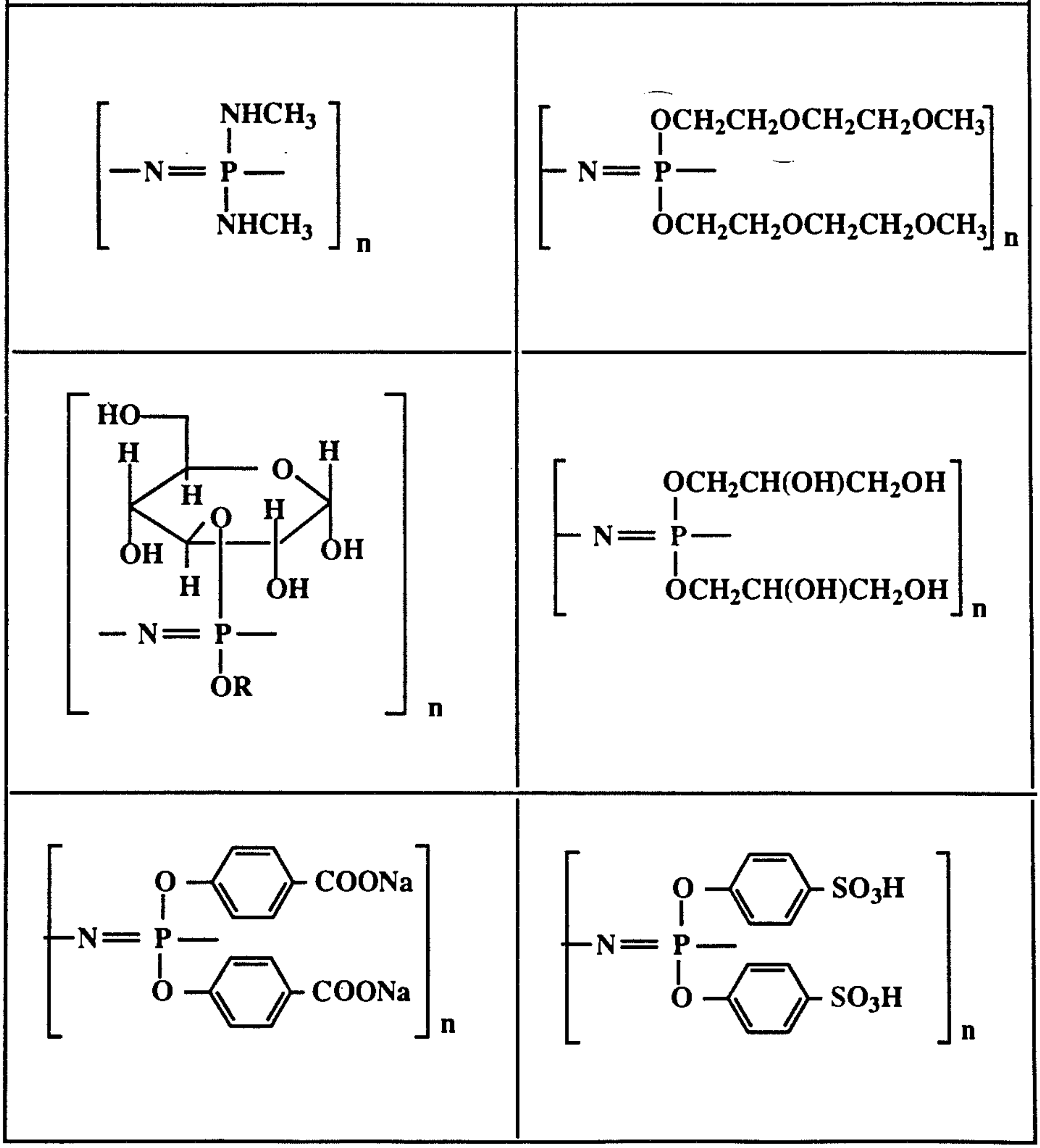
Bio-5

Water-Soluble Polyphosphazenes



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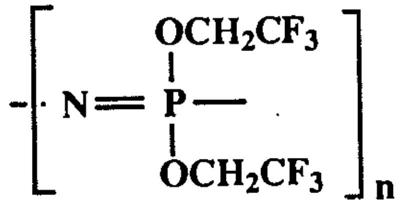
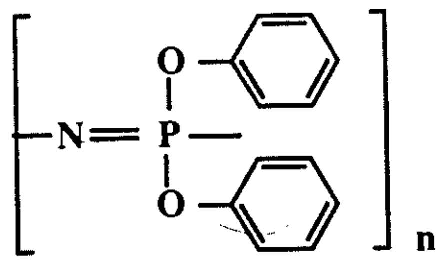
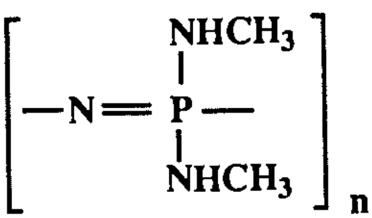
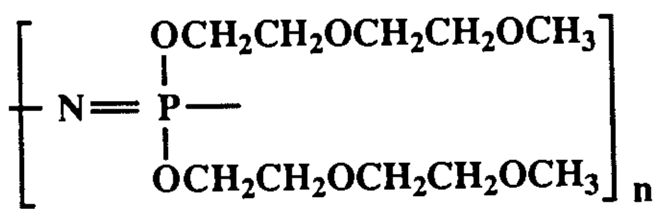
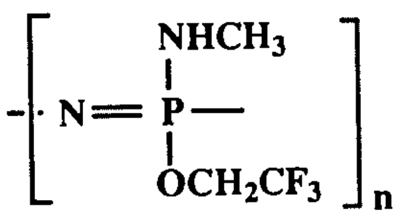
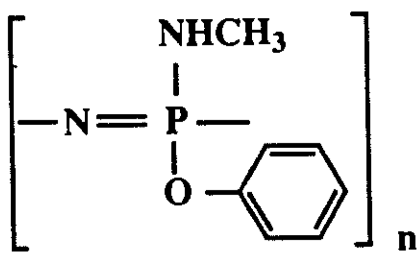
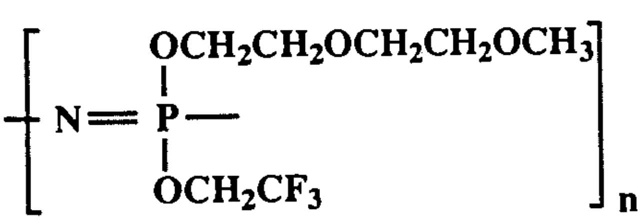
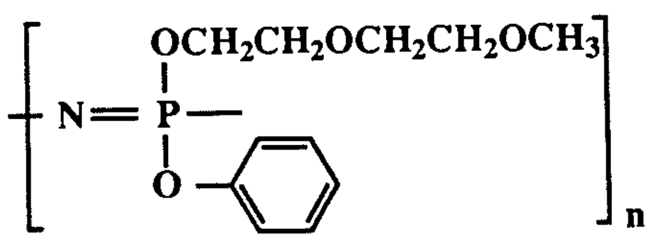
Hydrophobic, Hydrophilic, and Amphiphilic Polymers	
	
	
	
	

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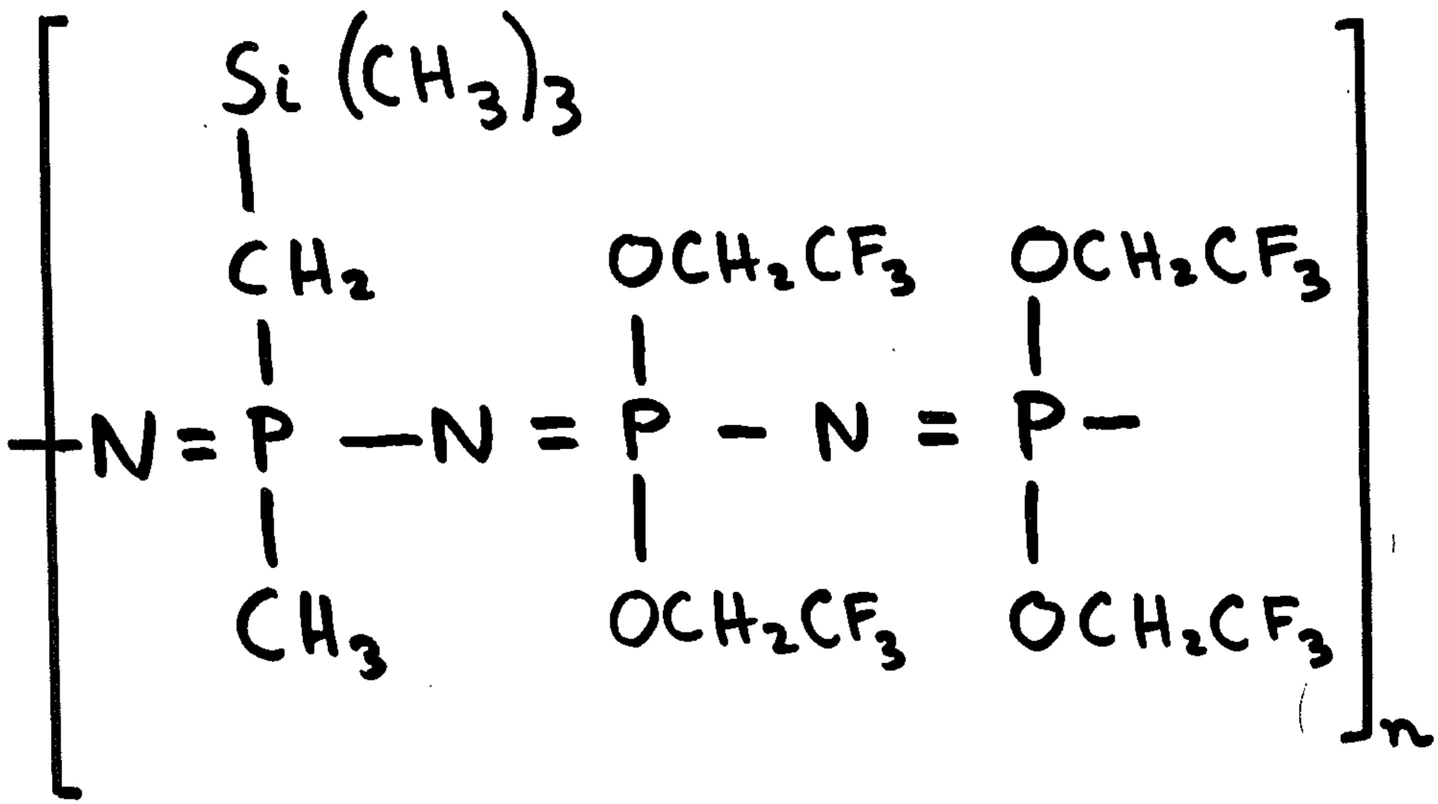

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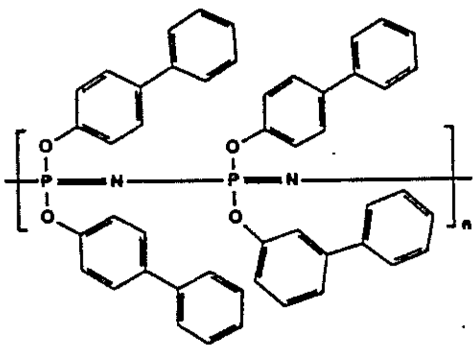
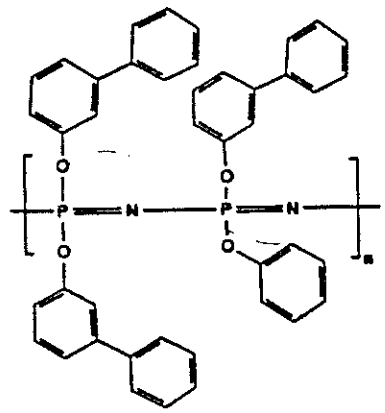
EXAMPLE HIGH POLYMERS, REFRACTIVE INDICES, AND GLASS TRANSITION TEMPERATURES



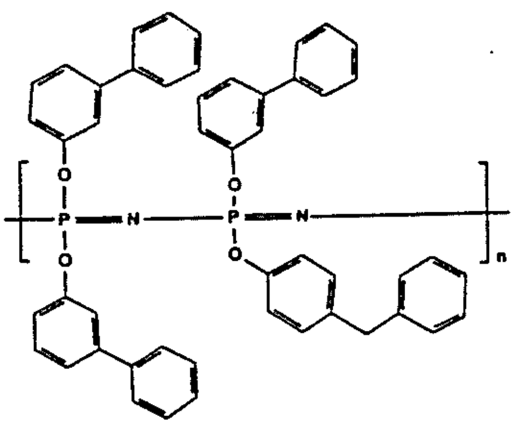
μ = 1.686

Tg = 64°C



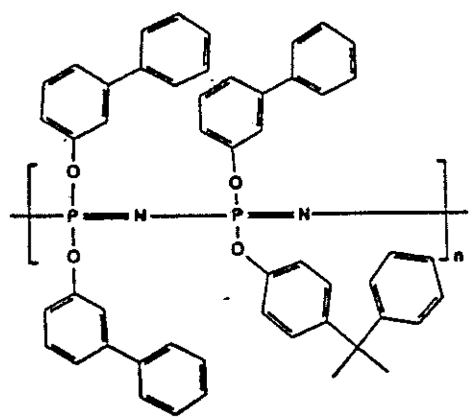
μ = 1.644

Tg = 27°C



μ = 1.648

Tg = 25°C



μ = 1.640

Tg = 32°C

μ values at 632 nm (25°C)

POLY(METHYL METHACRYLATE) μ = 1.490

POLYCARBONATE μ = 1.585

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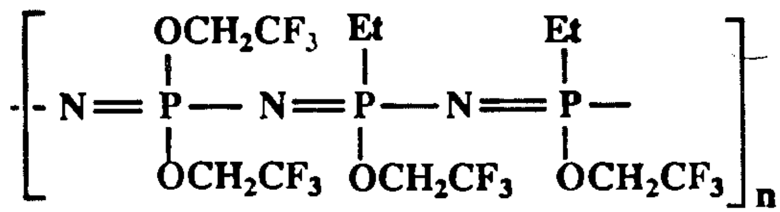
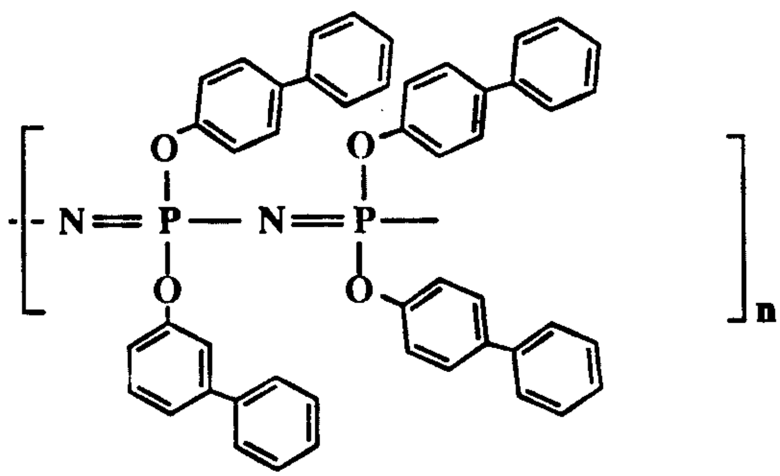
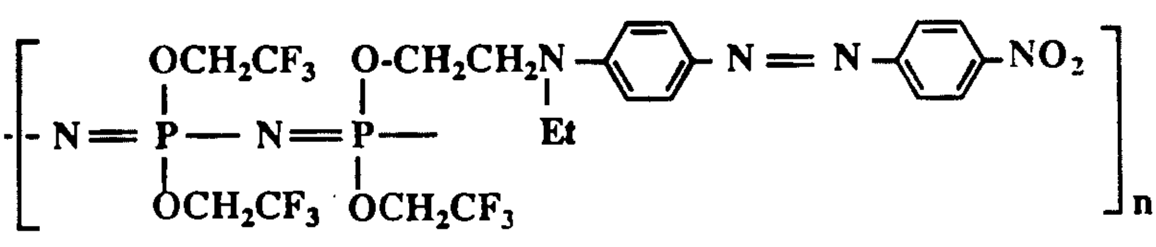
VARIATION OF PROPERTIES WITH POLYPHOSPHAZENE SIDE GROUPS



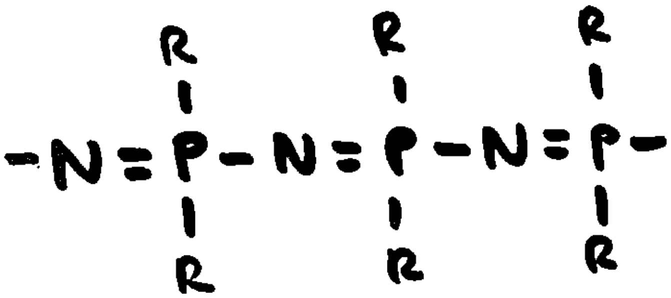
Elastomer. T_g = -65°C



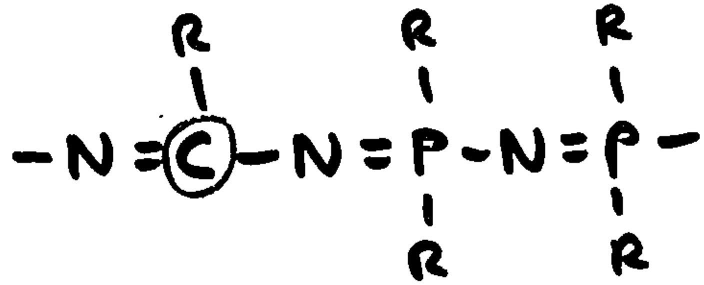
T_g = +64$_0$C. $n_{623\ nm}$ = 1.686



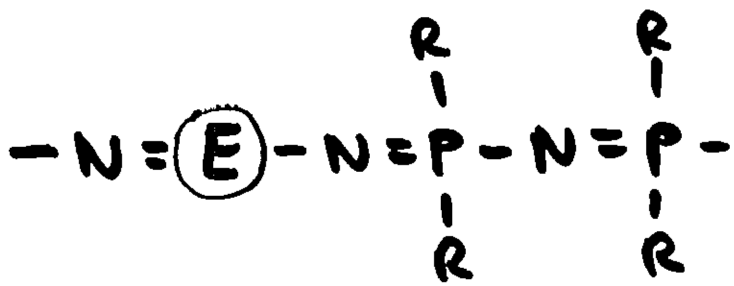
T_g = 44°C. d_{33} = 34 pm/V



PHOSPHAZENES



CARBOPHOSPHAZENES



"ELEMENTO" PHOSPHAZENES

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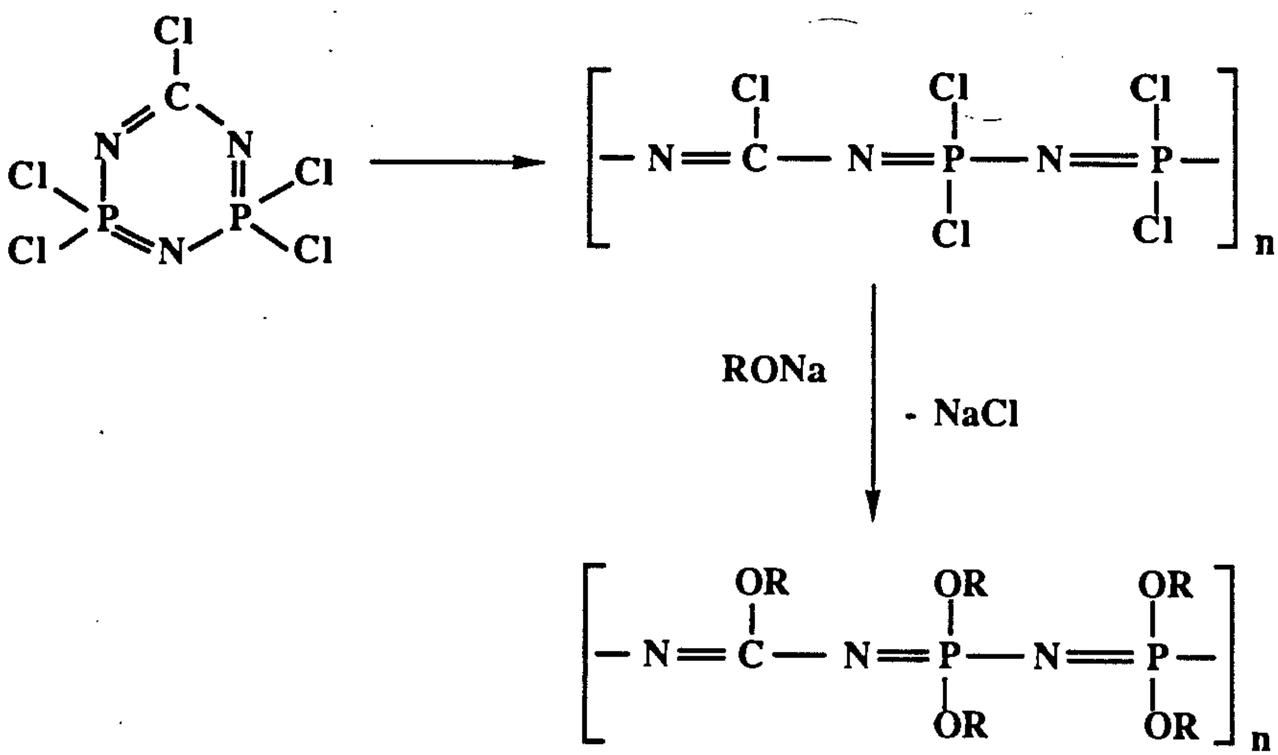
POLY(CARBOPHOSPHAZENES)



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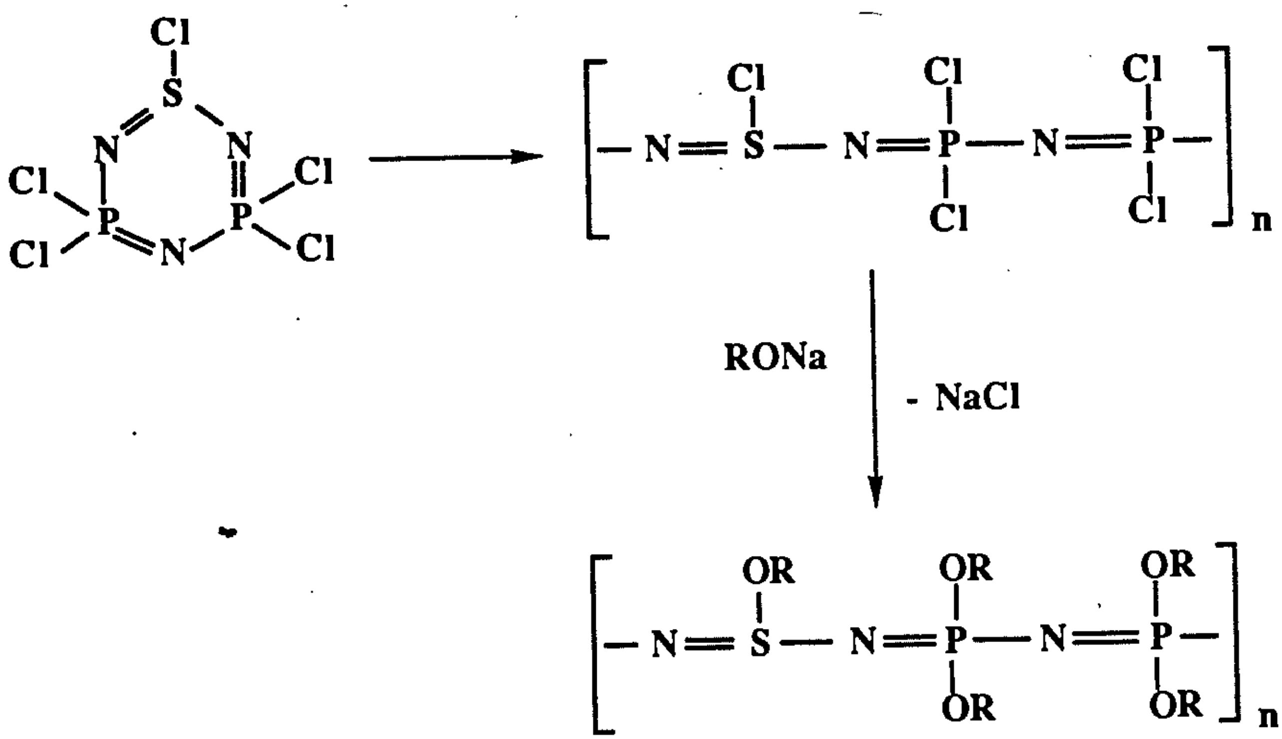
POLY(THIOPHOSPHAZENES)



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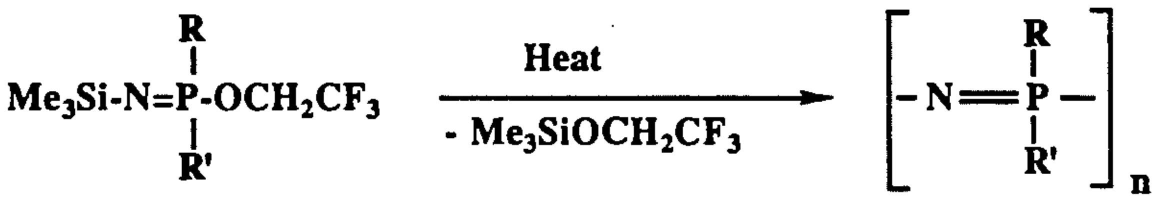
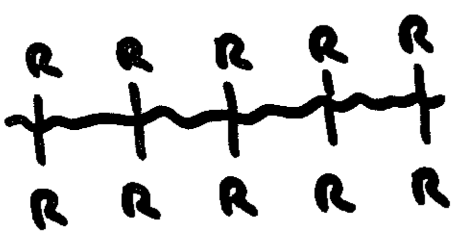
DIRECT SYNTHESIS OF POLY(ORGANOPHOSPHAZENES)



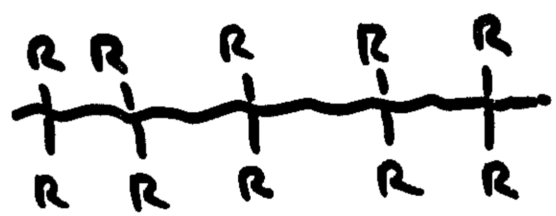
Wisian-Neilson, P.; Neilson, R. H. *J. Am Chem. Soc.* 1980, *102*, 2848

MEMBRANES

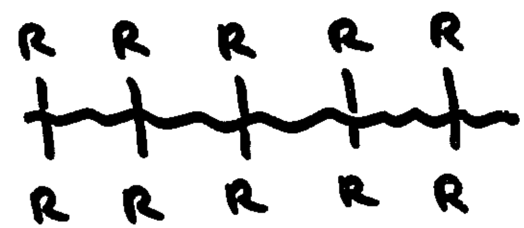
GAS SEPARATIONS, ION TRANSPORT, CONTROLLED RELEASE OF DRUG MOLECULES, CATALYST-MEMBRANE REACTORS.



HYDROPHILIC HOMOPOLYMERS



MIXED SUBSTITUENT POLYMERS



HYDROPHOBIC HOMOPOLYMERS

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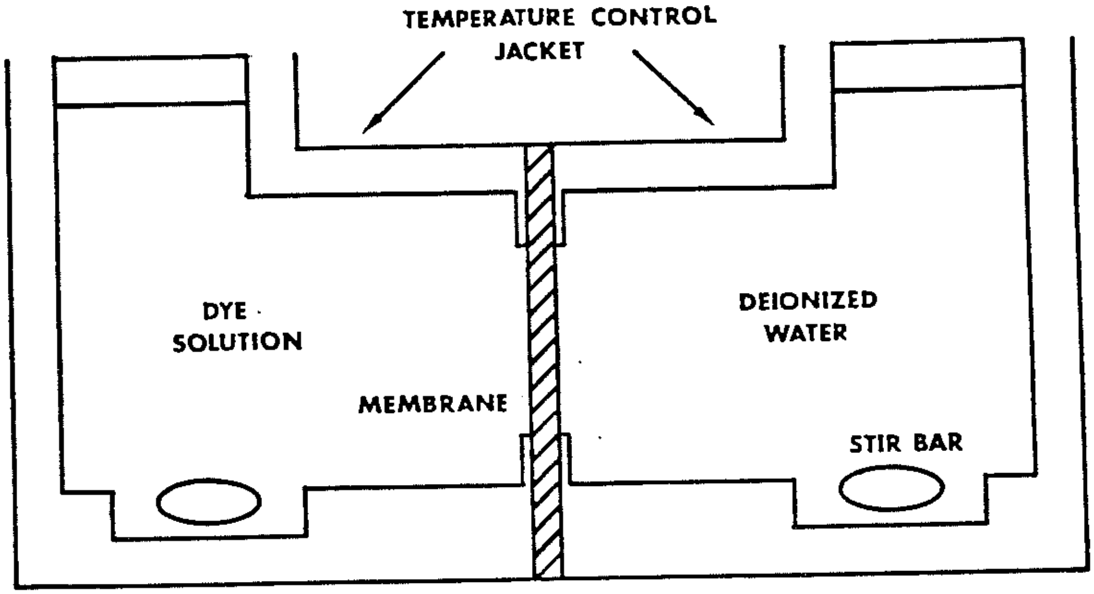
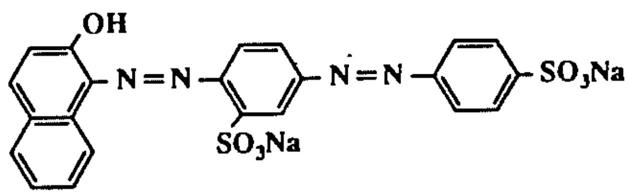
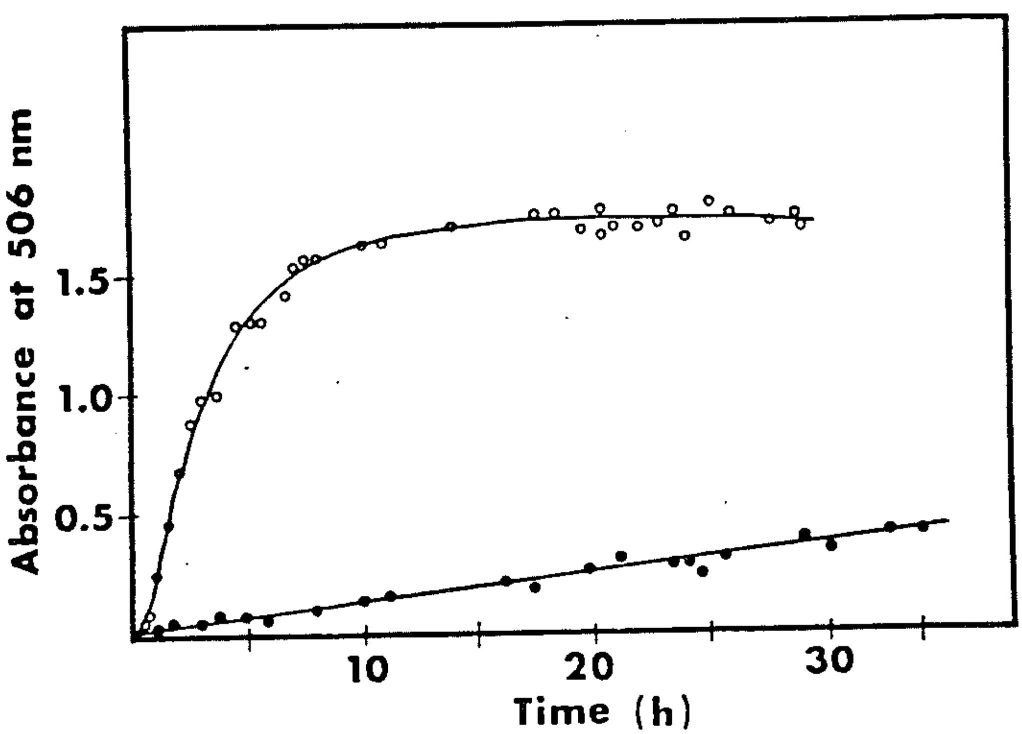




Biebrich Scarlet



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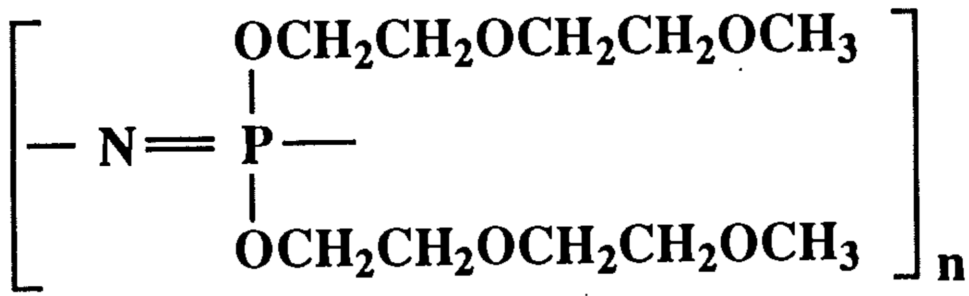

"MEEP"

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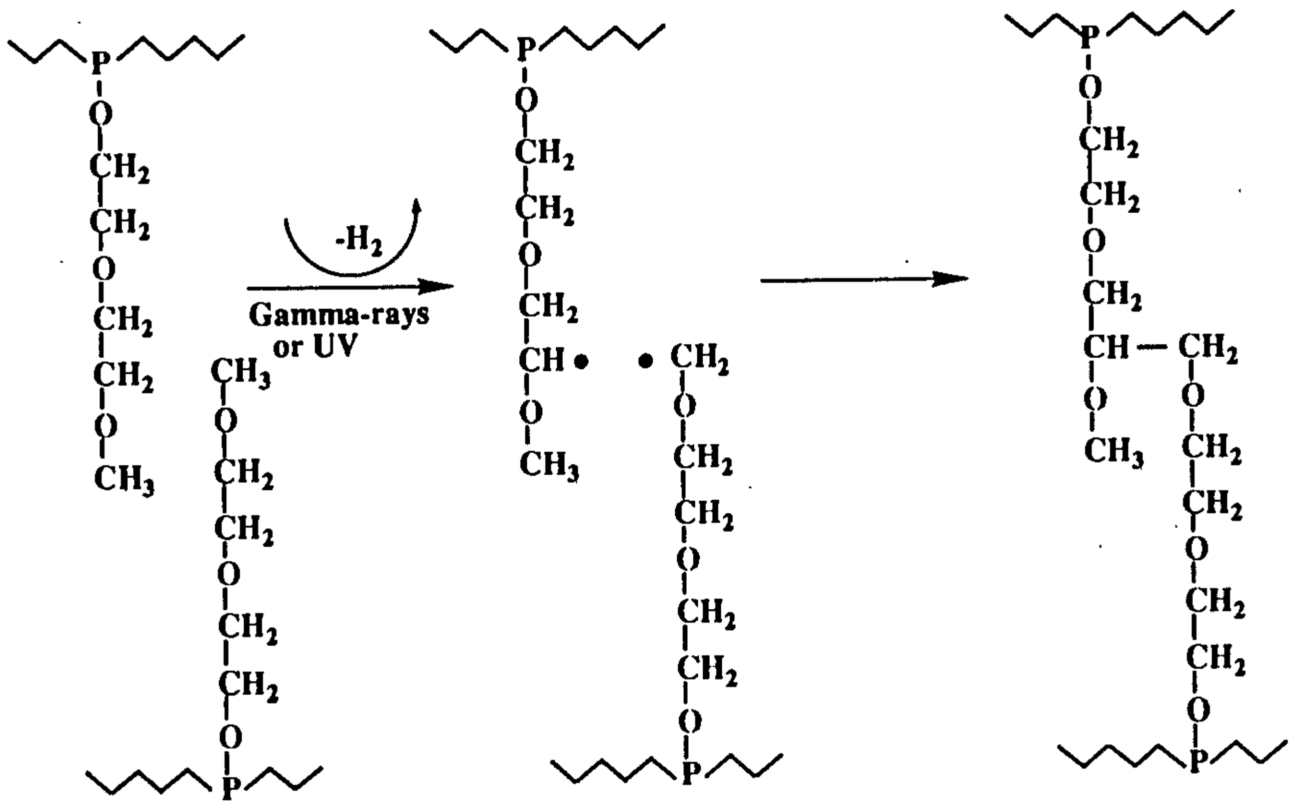
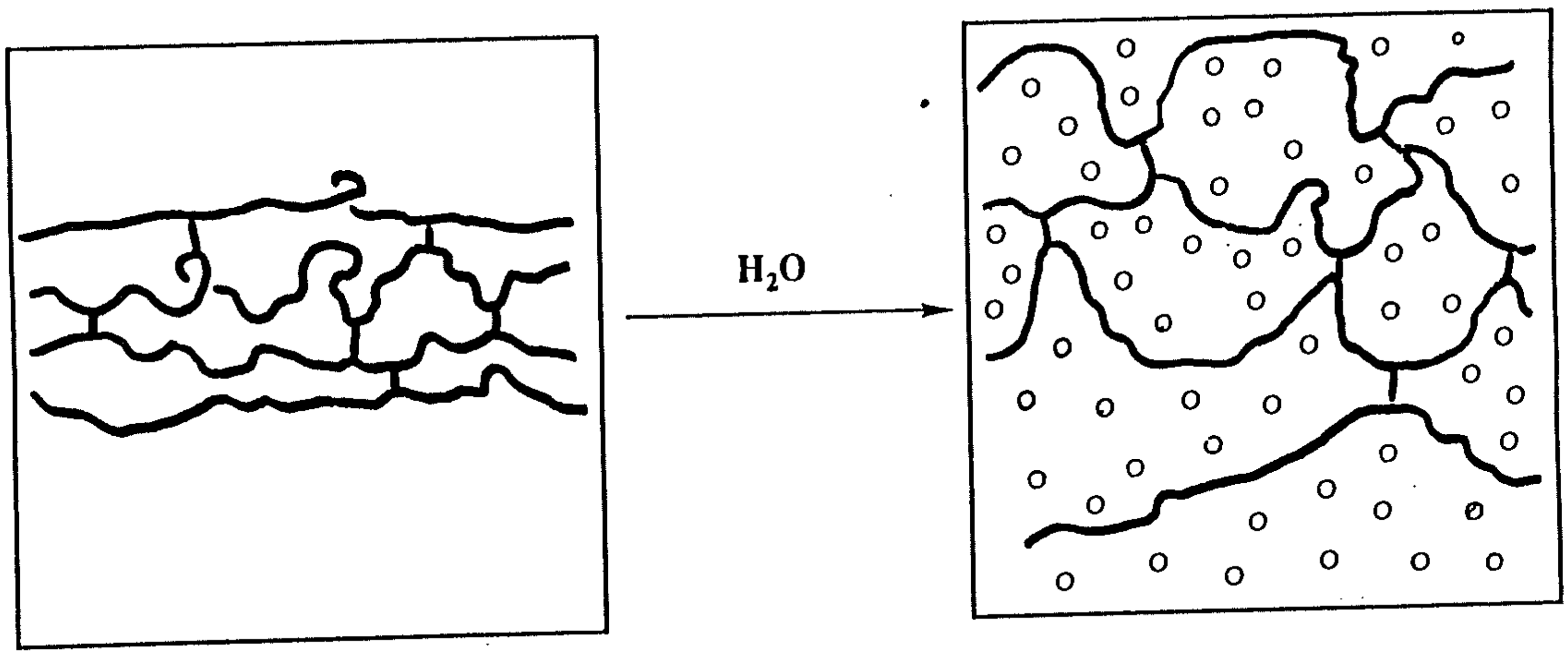
2-65-G

CROSSLINKING OF MEEP



γ-Ray - S. Kwon, G. H. Riding, R. J. Fitzpatrick, J. L. Bennett, A. A. Dembek, K. B. Visscher

UV - C. J. Nelson, W. D. Coggio



Crosslinking of water-soluble polymers generates hydrogels

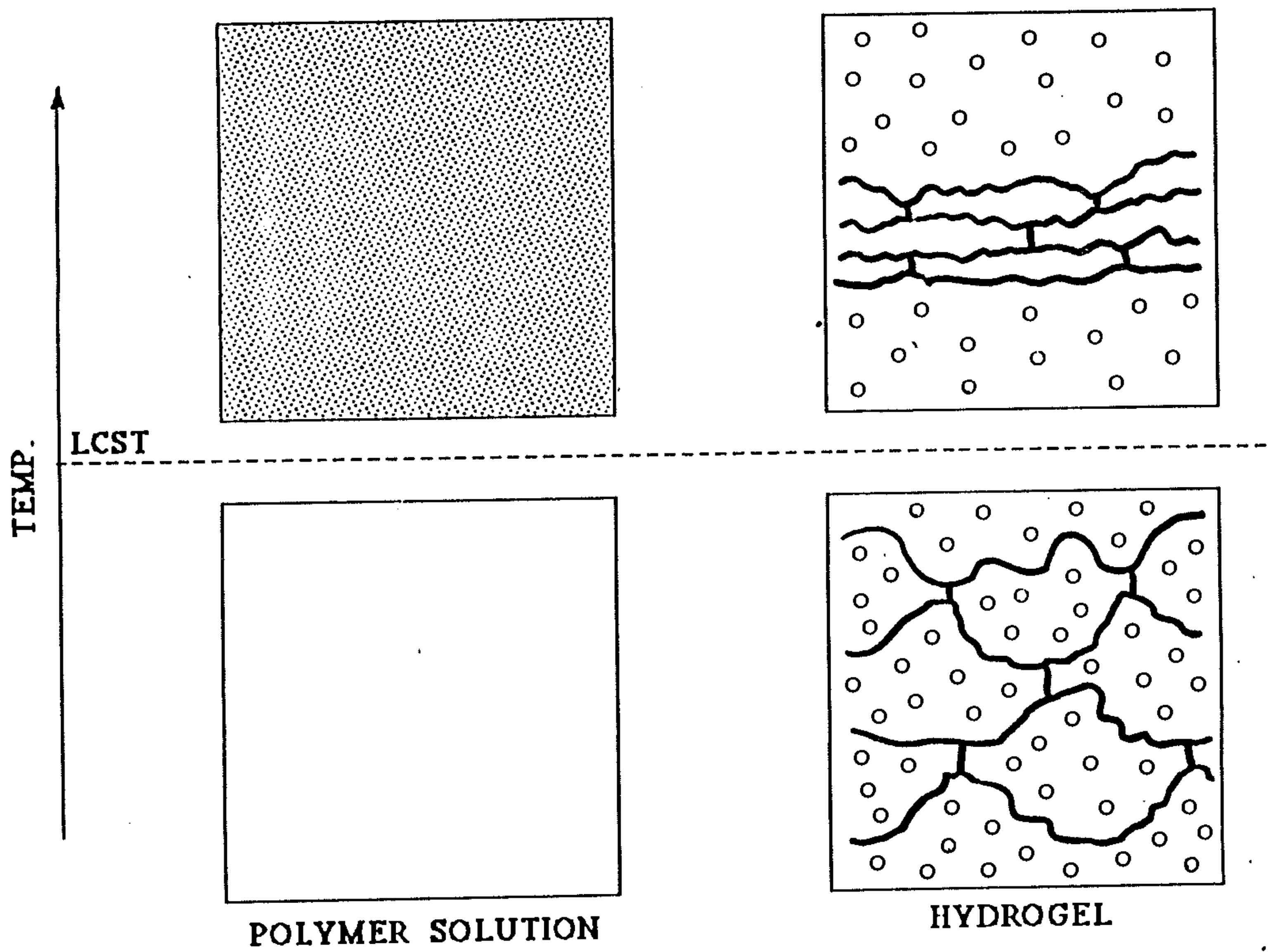
H. R. ALLCOCK

LCST FOR MEEP AND RELATED POLYMERS

Polymer	WATER SOLUBILITY 25°C	LCST (°C)
$[-N=P(OCH_2CH_2OCH_3)_2-]_n$	Sol.	30
$[-N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2-]_n$	Sol.	80
$[-N=P(OCH_2CH_2OCH_2CH_2OC_2H_5)_2-]_n$	Sol.	38
$[-N=P(OCH_2CH_2OCH_2CH_2OC_4H_9)_2-]_n$	Sol.	51
$[-N=P(OCH_2CH_2OCH_2CH_2NH_2)_2-]_n$	Sol.	None

HYDROGELS EXTRUDE WATER AT SAME TEMPERATURES AS LCST

S. R. Pucher, M. L. Turner, R. J. Fitzpatrick



Lower critical solution temperature (LCST) for a polymer solution and hydrogel.

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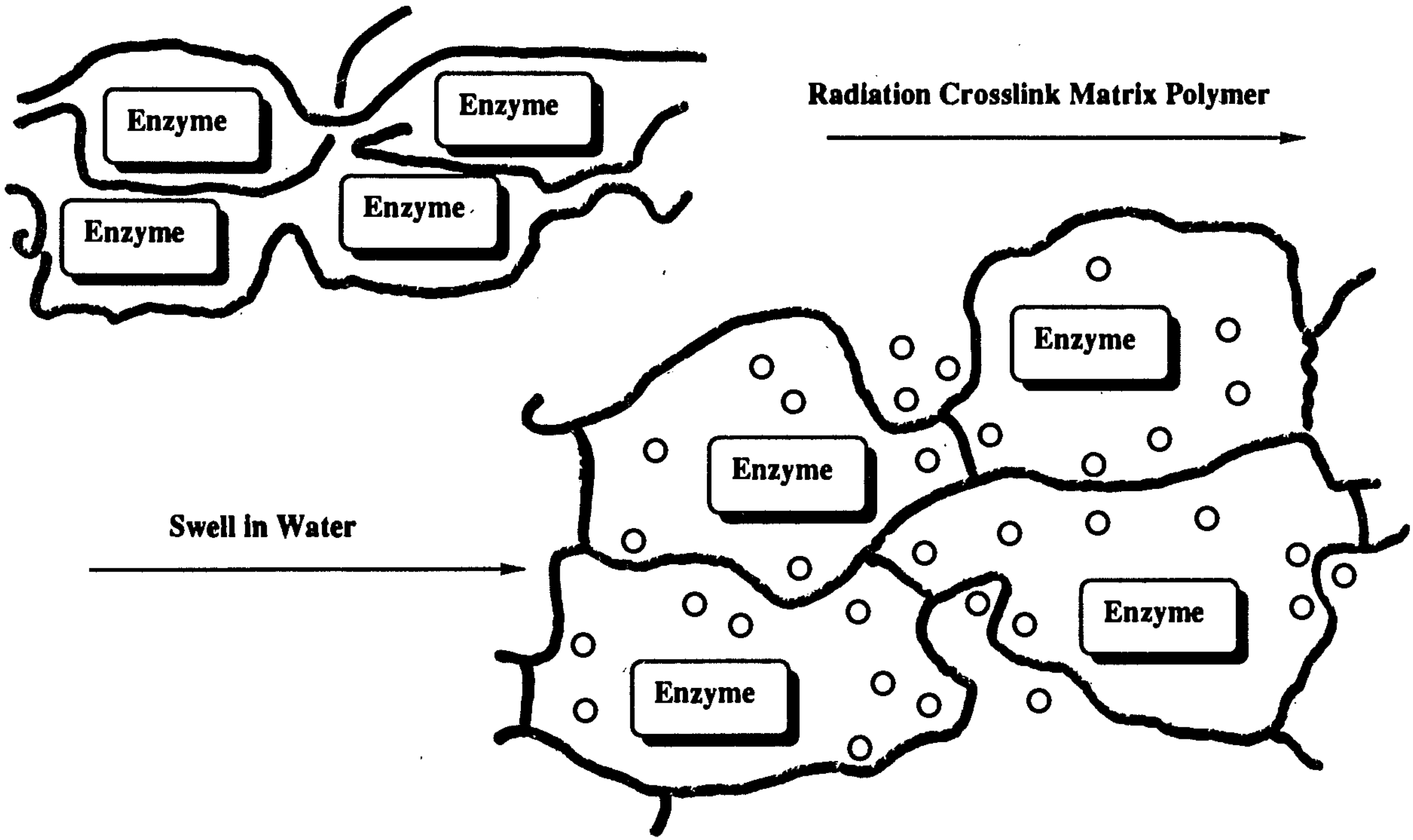
GEL ENTRAPPMENT OF ENZYMES
(UREASE)



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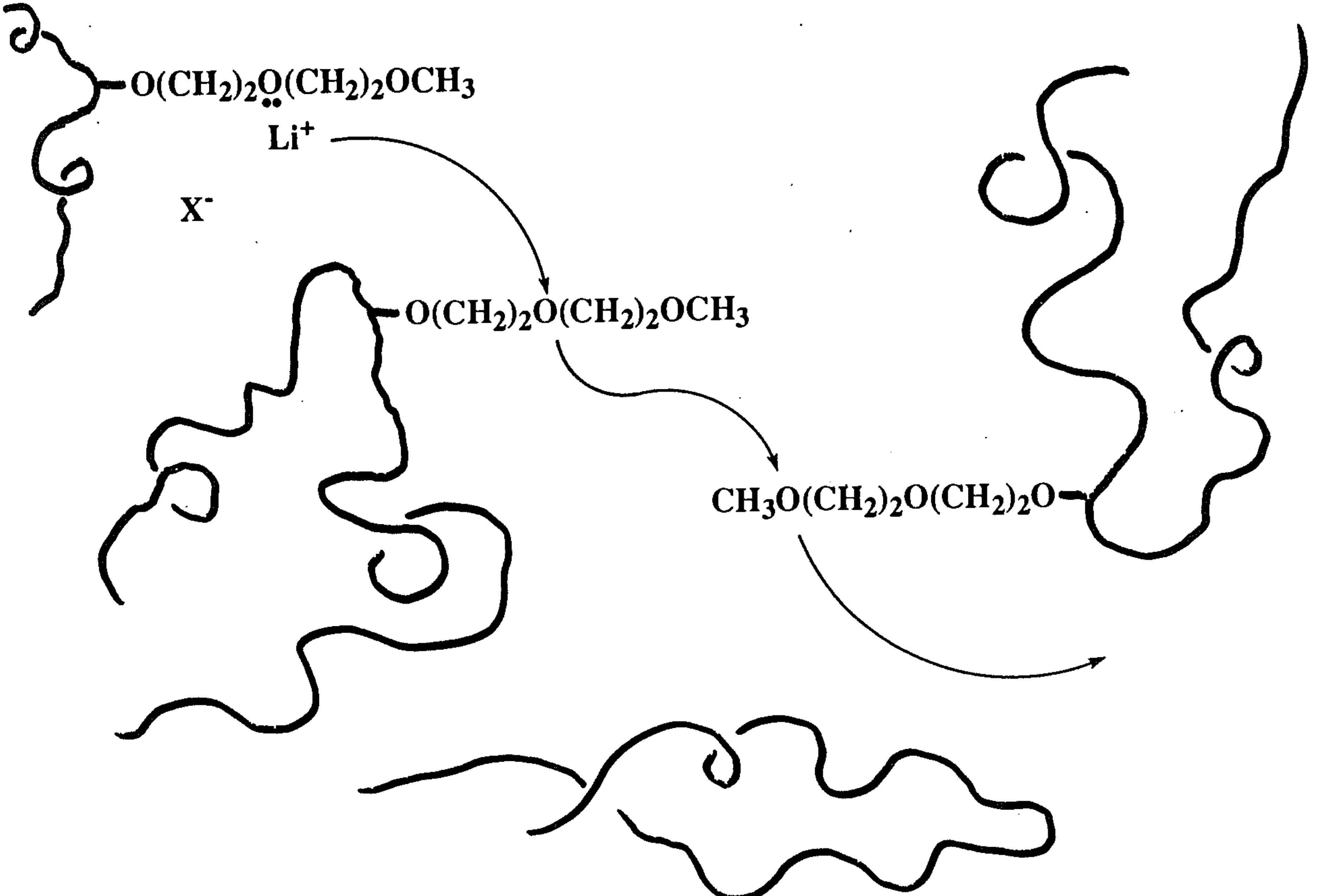
Cation Transport Through Solid MEEP



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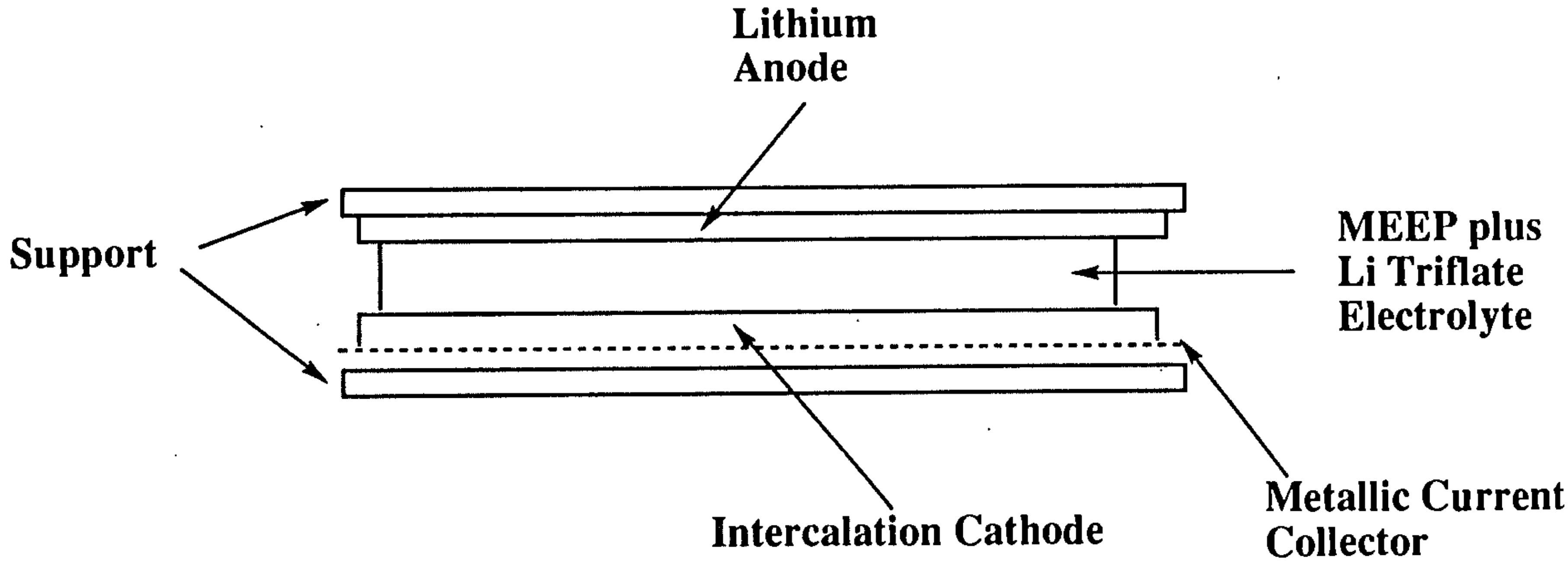
MEEP-Based Rechargeable Lithium Battery



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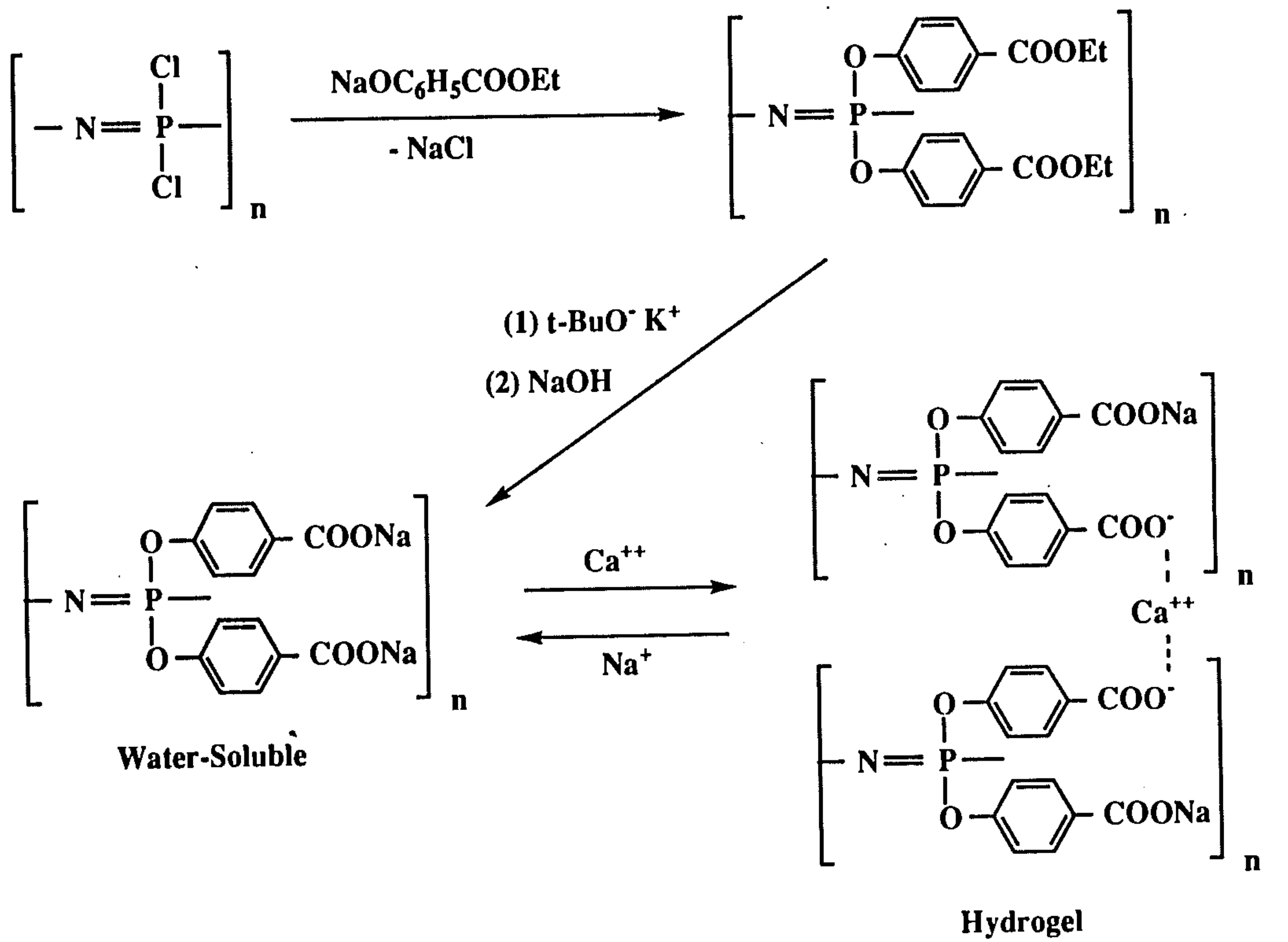
NaOC6H5COOEt
- NaCl
COOEt
COOEt
(1) t-BuO- K+
(2) NaOH
COONa
COONa
Water-Soluble
Ca++
Na+
COONa
COO-
Ca++
COO-
COONa
Hydrogel

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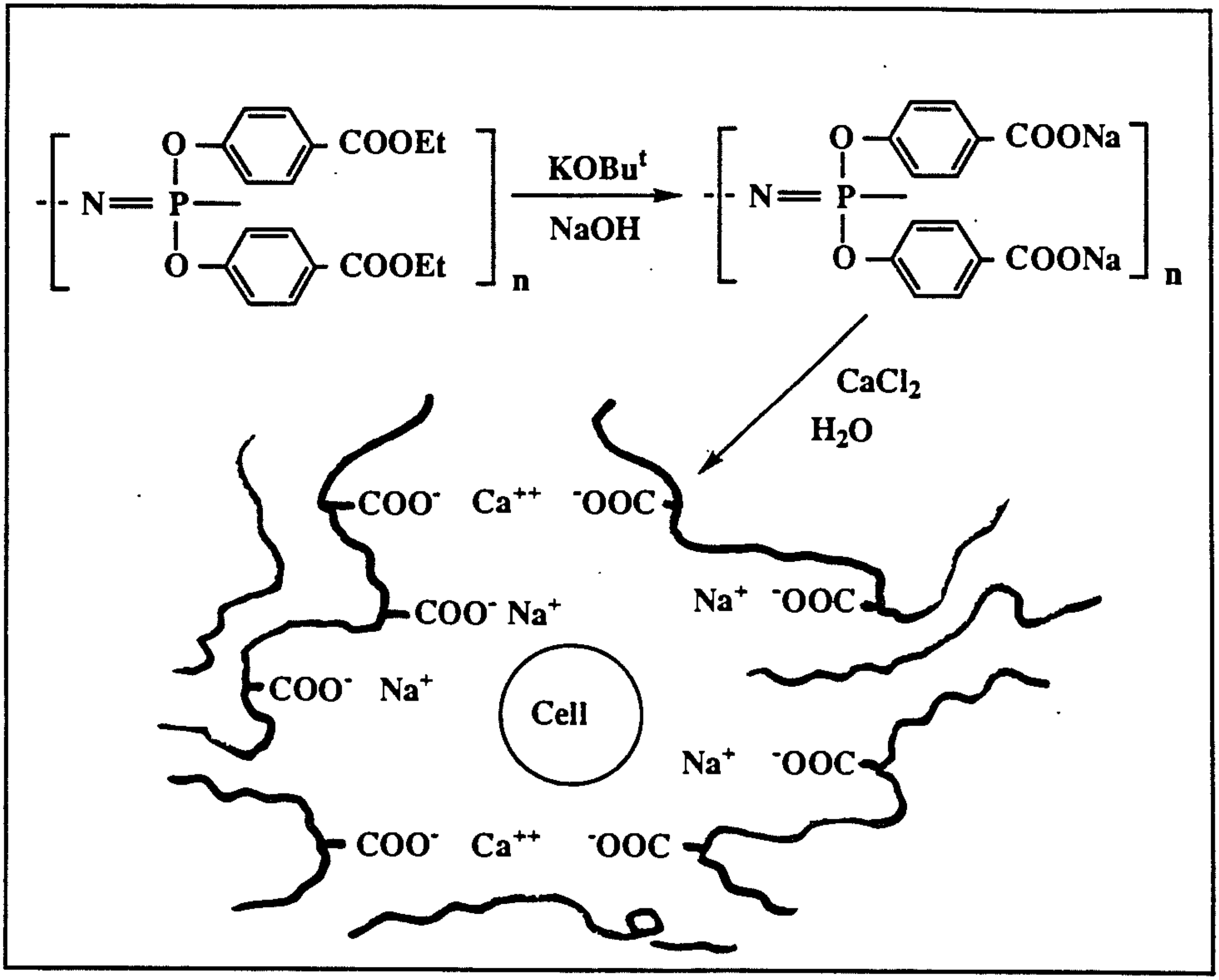
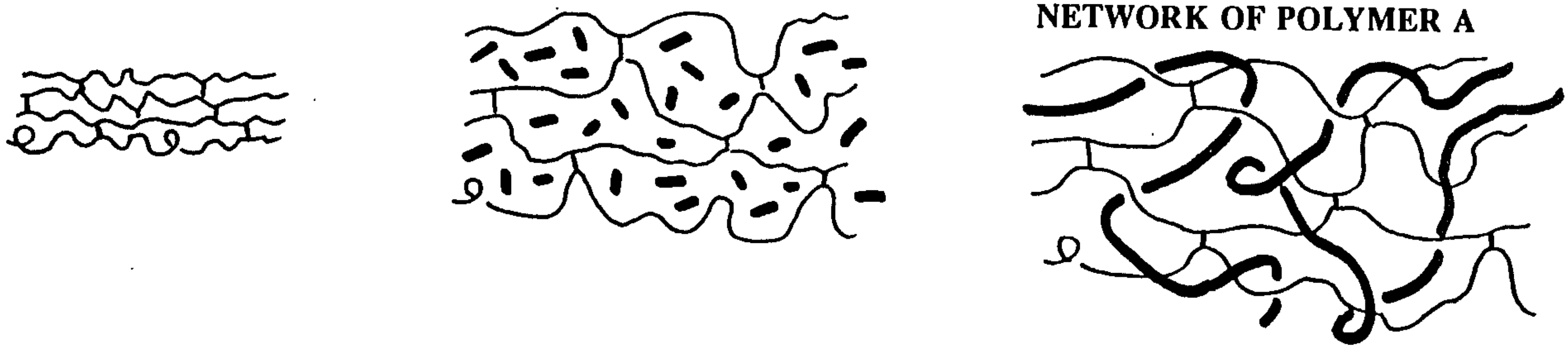

COOEt
COOEt
N
P
O
O
n
KOBu^t
NaOH
COONa
COONa
n
CaCl2
H2O
COO- Ca++ -OOC
COO- Na+
Na+ -OOC
COO- Na+
Cell
Na+ -OOC
COO- Ca++ -OOC

INTERPENETRATING POLYMER NETWORKS
FOR
CONTROL OF INTERNAL AND SURFACE PROPERTIES

CROSSLINKED POLYMER A	NETWORK OF POLYMER A SWELLED BY POLYMER B	POLYMER B POLYMERIZED AND / OR CROSSLINKED IN NETWORK OF POLYMER A



POLYMER A = POLY[BIS(METHOXYETHOXYETHOXY)PHOSPHAZENE] (MEEP)

POLYMER B = METHYL METHACRYLATE, POLYSTYRENE, ETC.

K. B. Visscher, I. Manners, H. R. Allcock. Macromolecules, 1990, *23*, 4885

PURPOSE OF SURFACE REACTIONS

1. TO COMBINE THE BEST "INTERNAL" POLYMER PROPERTIES, SUCH AS
   - (a) Elasticity, flexibility, and strength
   - (b) Electrical resistance
   - (c) Low lipid absorption

     etc.

   WITH THE BEST SURFACE PROPERTIES, SUCH AS
   - (a) Biocompatibility
   - (b) Tailored hydrophilic/hydrophobic
   - (c) Resistance to bacterial colonization
   - (d) Hydrogel character to encourage cell overgrowth

     etc.

2. TO DEVELOP WAYS TO TAILOR THE SURFACE CHARACTER WITHIN FINELY-TUNED LIMITS

3. TO BIND BIOACTIVE AGENTS TO THE SURFACE OR GENERATE BIOCOMPATIBLE SURFACE SITES

4. TO PROVIDE A "FOOTHOLD" FOR MAMMALIAN CELL OVERGROWTH

5. TO PREPARE SURFACES THAT RESIST BACTERIAL OR FUNGAL COLONIZATION

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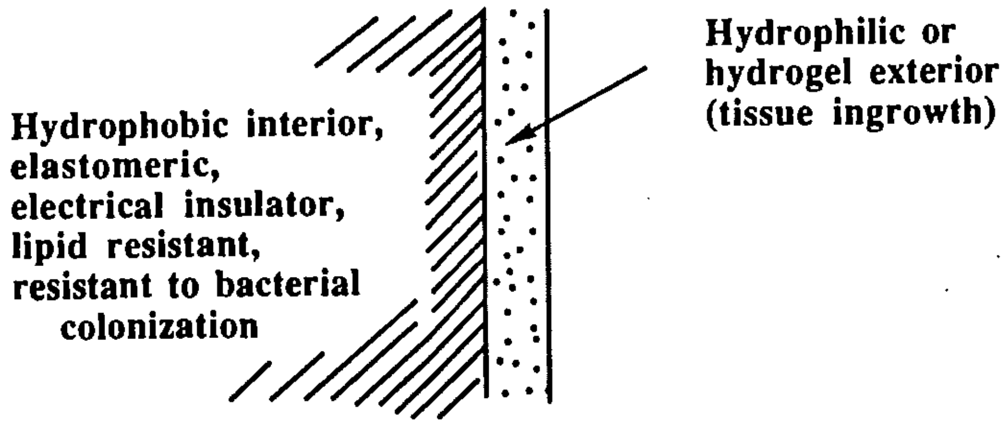
A TARGET BIOMEDICAL MATERIAL



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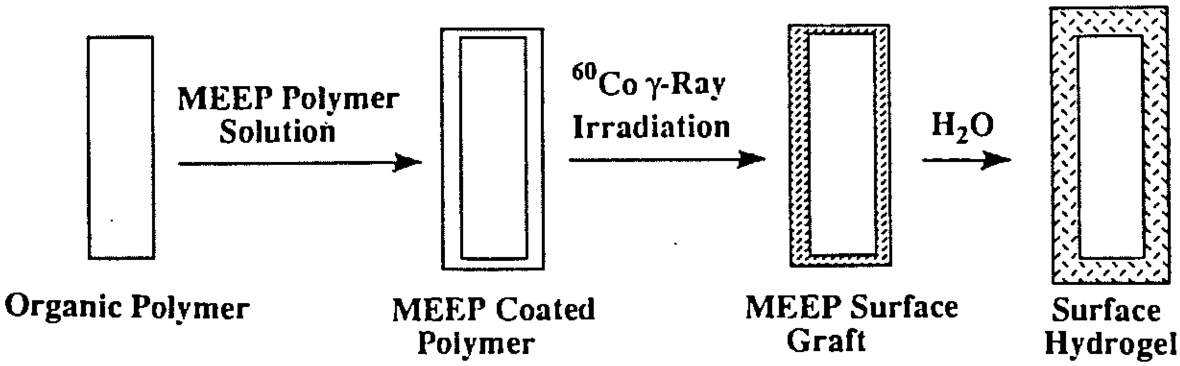
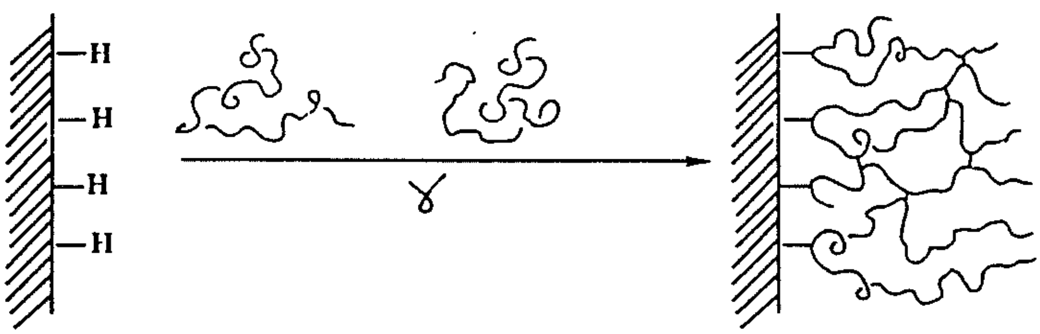
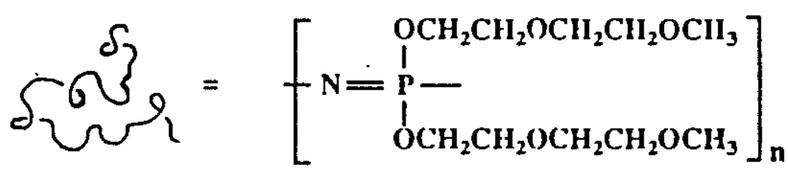
SURFACE GRAFTED MEEP HYDROGELS ON ORGANIC POLYMERS







SUBSTRATE POLYMER
(CONTACT ANGLE)

POLYPROPYLENE	94°	→	27°
PVC	78°	→	34°
POLYCARBONATE	65°	→	43°
PMMA	65°	→	35°
MYLAR	63°	→	31°

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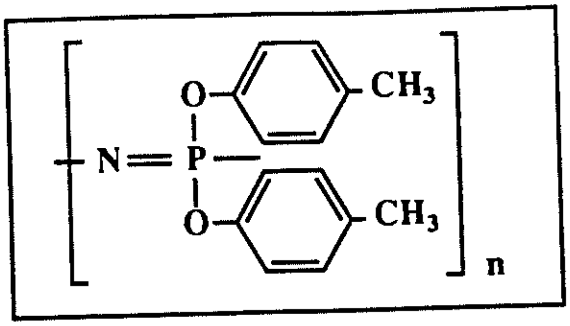
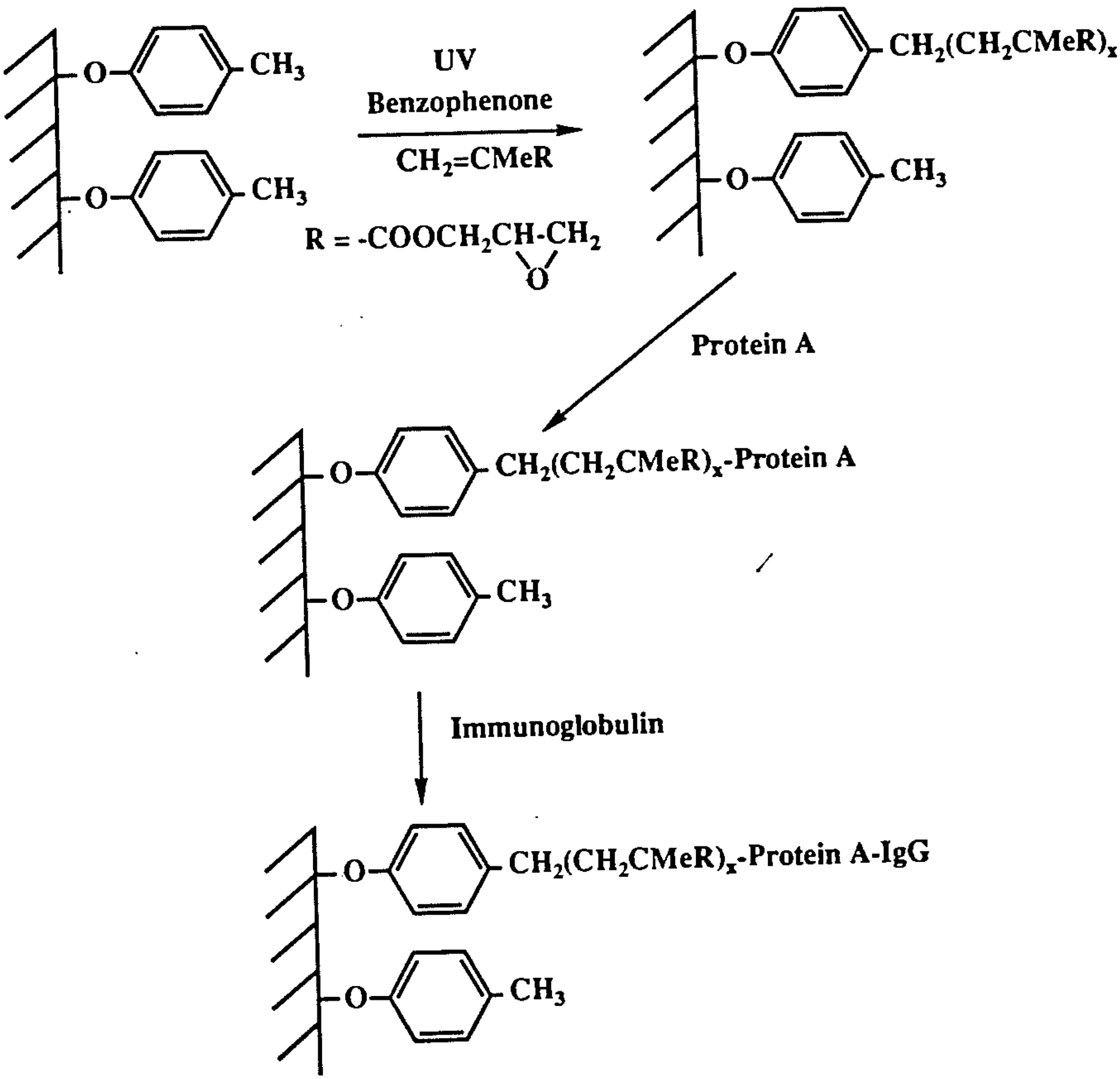
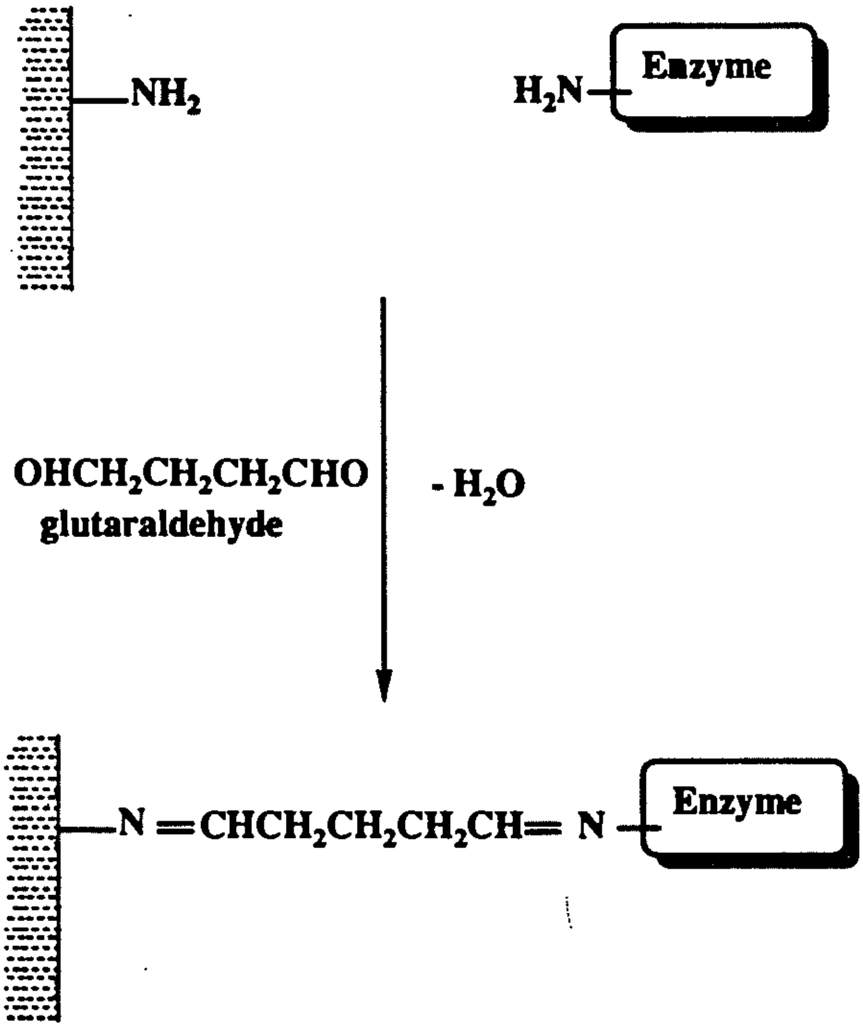




C. J. Nelson, W. D. Coggio, J. P. O'Brien, L. F. Palosi

SURFACE IMMOBILIZATION OF TRYPSIN AND 6-GLUCOSE PHOSPHATE DEHYDROGENASE



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SURFACE CHARACTERIZATION

BY

- T.I.R. FOURIER TRANSFORM INFRARED SPECTROSCOPY (1 mm depth)
- X-RAY PHOTOELECTRON SPECTROSCOPY (50 A depth)
- SCANNING ELECTRON MICROSCOPY
- TRANSMISSION ELECTRON MICROSCOPY
- OPTICAL MICROSCOPY (with staining)
- CONTACT ANGLES
- ADHESION TO OTHER POLYMERS AND METALS
- CHEMICAL REACTIONS AT FUNCTIONALIZED SITES
- SOLUTION NMR STUDIES OF SURFACE MODIFIED THIN FILMS
- MODEL REACTIONS IN SOLUTION FOR NMR AND IR COMPARISONS
- BACTERIAL INHIBITION AND COLONIZATION STUDIES

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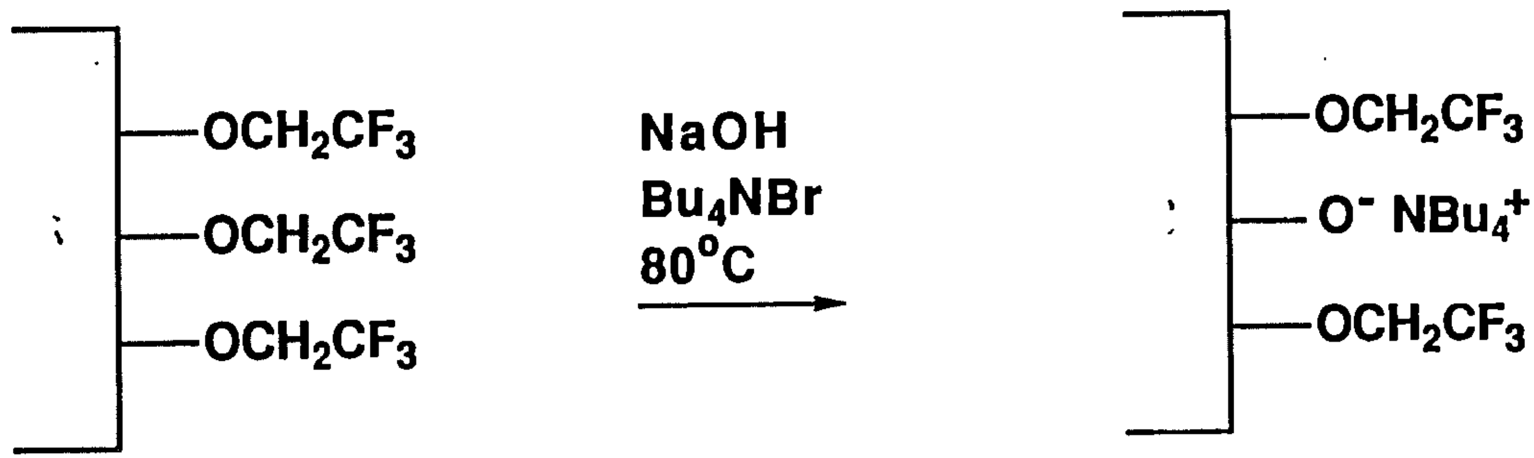

CONTACT ANGLE = 108°

NON-ADHESIVE

CONTACT ANGLE = 90° OR LOWER

HIGHLY ADHESIVE TO METALS, CERAMICS, AND SKIN

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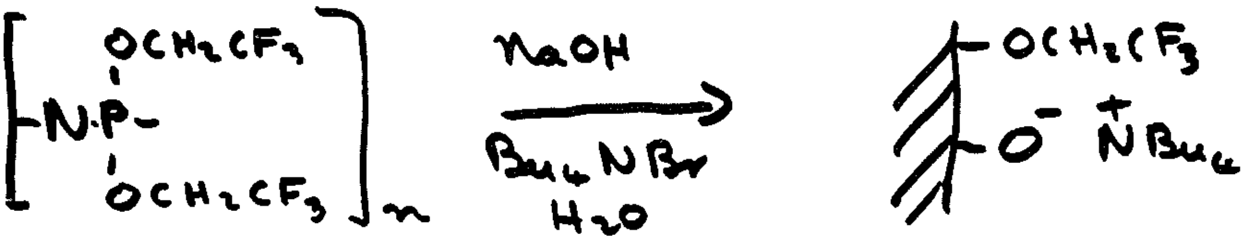
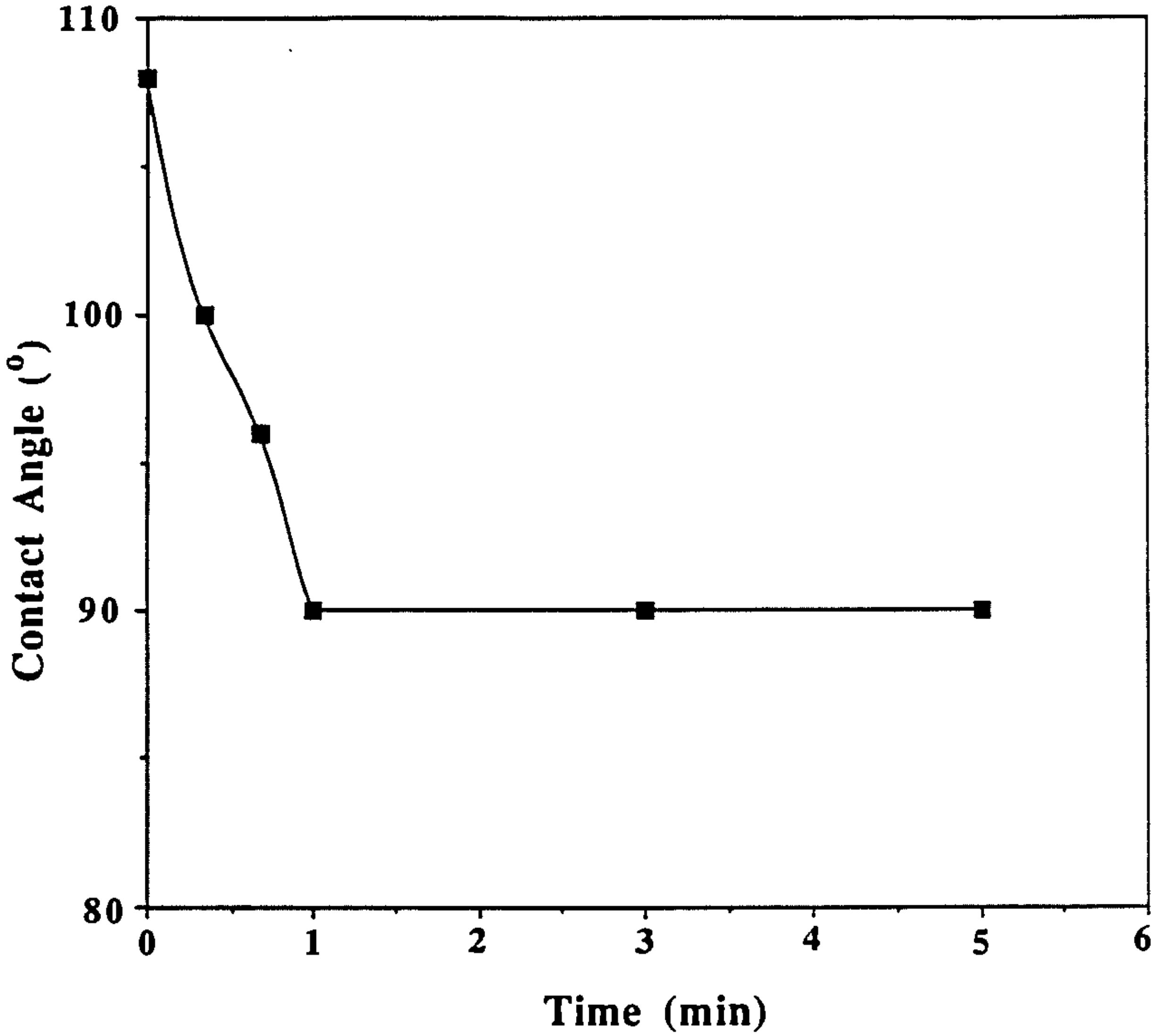


OCH2CF3
N=P
OCH2CF3
n
NaOH
Bu4NBr
H2O
OCH2CF3
O⁻ ⁺NBu4



110
100
90
80
Contact Angle (°)
0
1
2
3
4
5
6
Time (min)

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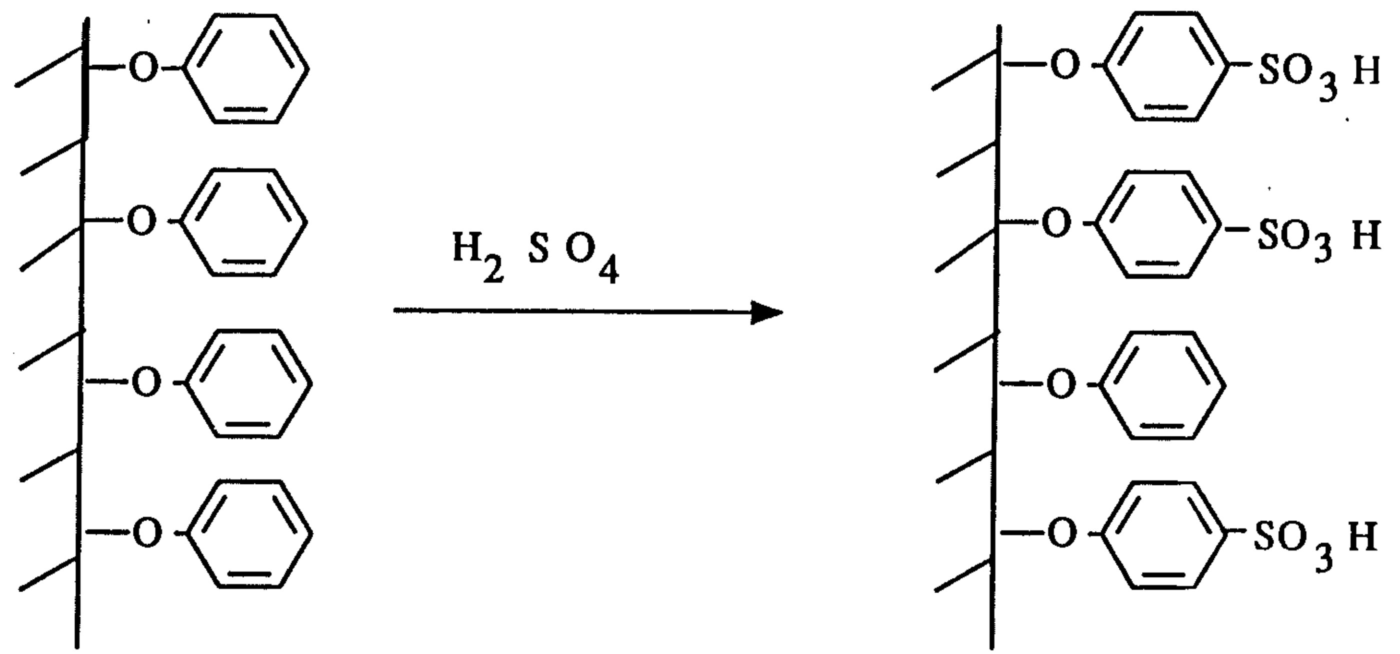

CONTACT ANGLE = > 103°

CONTACT ANGLE = 45-10°

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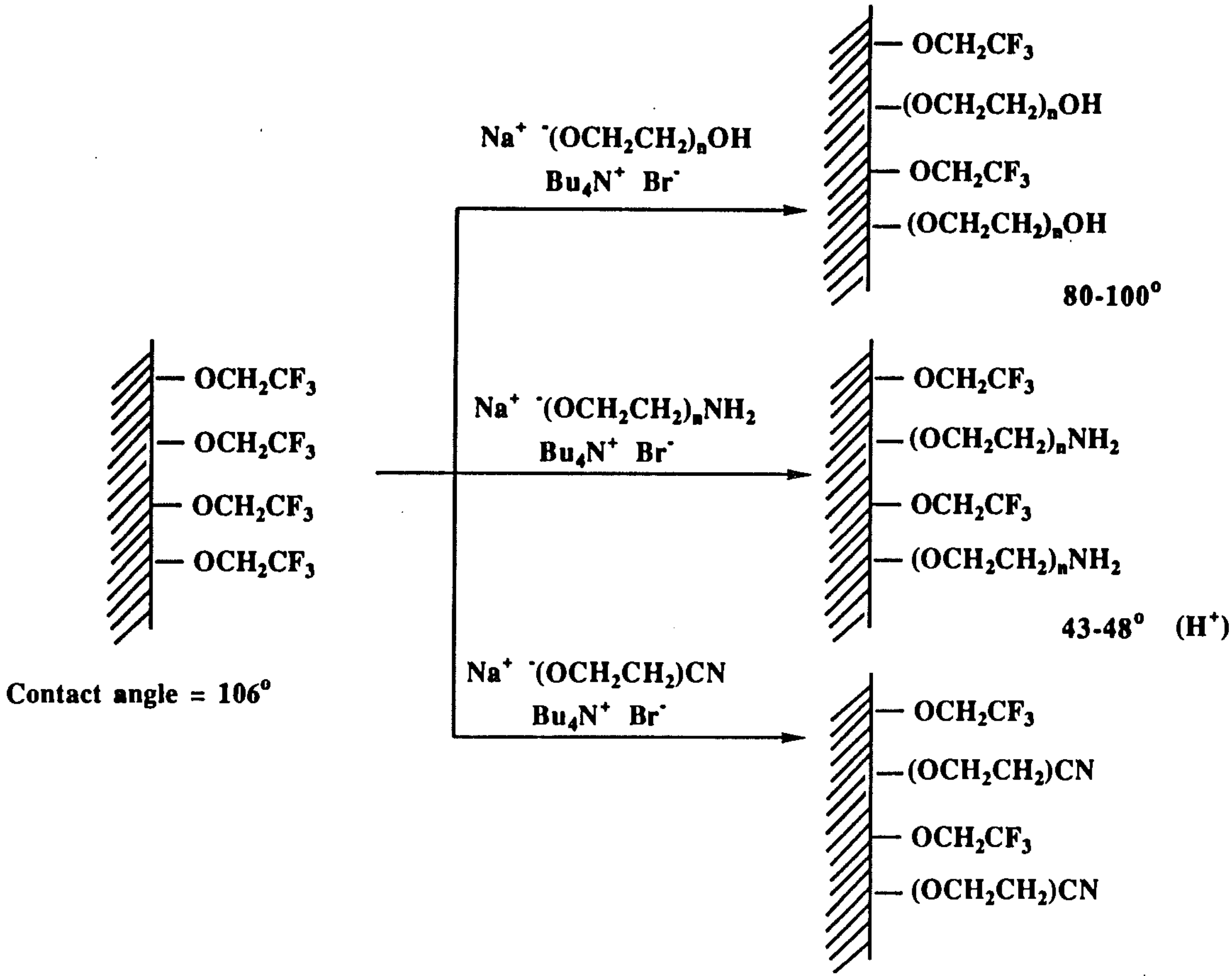
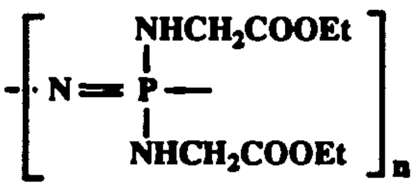
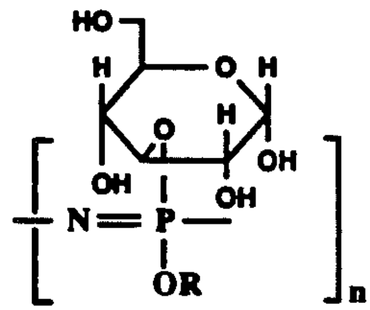
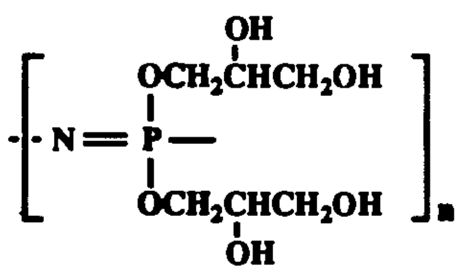

OCH2CF3
OCH2CF3
OCH2CF3
OCH2CF3
Contact angle = 106°
Na+ -(OCH2CH2)nOH
Bu4N+ Br-
Na+ -(OCH2CH2)nNH2
Bu4N+ Br-
Na+ -(OCH2CH2)CN
Bu4N+ Br-
OCH2CF3
(OCH2CH2)nOH
OCH2CF3
(OCH2CH2)nOH
80-100°
OCH2CF3
(OCH2CH2)nNH2
OCH2CF3
(OCH2CH2)nNH2
43-48° (H+)
OCH2CF3
(OCH2CH2)CN
OCH2CF3
(OCH2CH2)CN



NHCH₂COOEt
N
P
NHCH₂COOEt
n

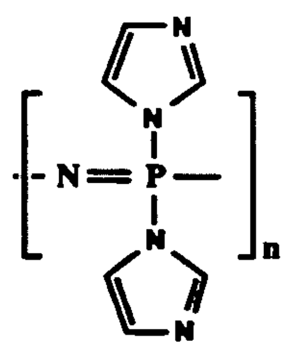


HO
H
O
H
O
H
OH
OH
OH
OH
N
P
OR
n



OH
OCH₂CHCH₂OH
N
P
OCH₂CHCH₂OH
OH
n

4



N
N
N
P
N
N
n

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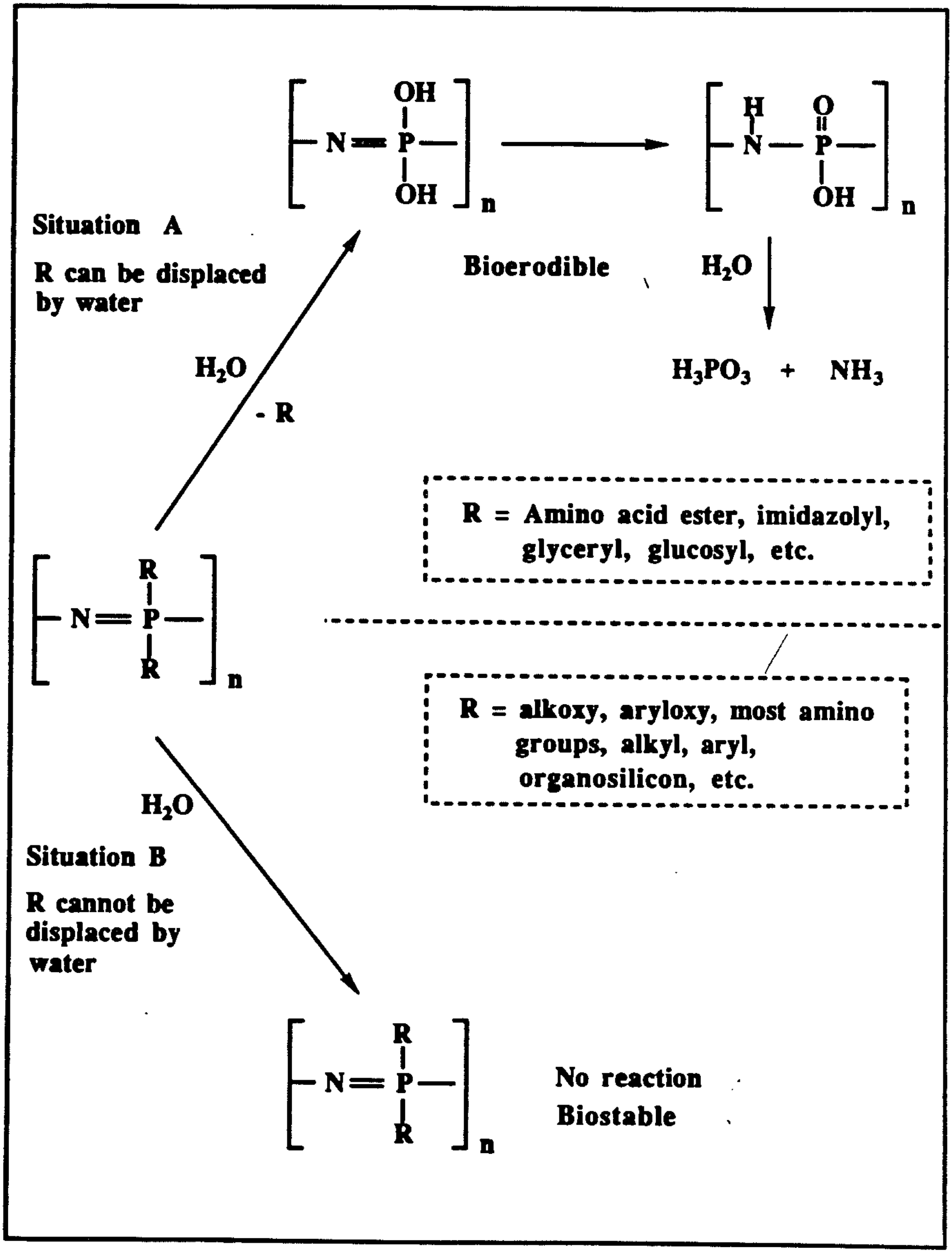
Situation A
R can be displaced by water
H2O
- R
Bioerodible
H2O
H3PO3 + NH3
R = Amino acid ester, imidazolyl, glyceryl, glucosyl, etc.
R = alkoxy, aryloxy, most amino groups, alkyl, aryl, organosilicon, etc.
H2O
Situation B
R cannot be displaced by water
No reaction
Biostable

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ADVANTAGES OF POLYPHOSPHAZENES OVER OTHER POLYMER SYSTEMS

Very high molecular weights (1 to 4 million)

Versatile synthetic method that allows hundreds of different side groups and combinations of side groups to be linked to the chain

Bioinertness with some side groups

Bioerosion with other side groups

Hydrogels with yet others

Ease of surface modification to change biological response

Combinations of properties not accessible in petrochemical polymers, biological polymers, or silicones.

H. R. ALLCOCK

2-70-G/B

Preceramic Polymers

With Special Focus on SiC Precursors – Their Synthesis, Pyrolysis and Application

Leonard V. Interrante

Chemistry Department
Rensselaer Polytechnic Institute
Troy, NY

Chris Whitmarsh
Walt Sherwood

Starfire Systems, Inc.
Glenville, NY

Advantages of Ceramic Materials:

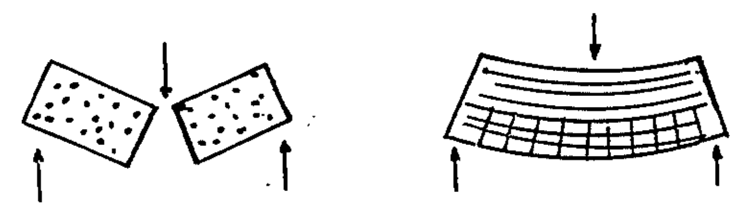
- Low density (40% of super alloys).
- High strength and stiffness to weight ratio at high temperatures.
- Good thermal stability.
- Good thermal stress resistance (low CTE).
- Excellent resistance to oxidation, corrosion, and erosion.
- Near net shape manufacturing.

Disadvantages of Ceramic Materials:

- Brittle, low strain to failure ratio. **Catastrophic!**
- High temperature preparation and processing.
- Difficult to control composition and purity,
- Difficult and/or expensive to fabricate required shapes.

Solution One:

Ceramic Matrix Composites



Dispersion of the reinforcing phase in the ceramic matrix provides a toughening mechanism,

Reinforcing phases—carbon, glass, or ceramic fiber; ceramic rods, whiskers, or platelets.

Solution Two:

Polymeric Precursors to Ceramic Materials

- o Improved product purity and compositional homogeneity
- o Greater control over ceramic microstructure
- o Lower temperature preparation
- o Solubility and/or themoplasticity allowing the preparation of:
  - continuous ceramic fibers
  - ceramic or preceramic coatings
  - binders/sintering aids for ceramics
  - ceramic matrices for composites as well as the
  - joining/bonding of ceramics/metals

Design Criteria for Organometallic Precursors

- Single molecule with an elemental composition and stoichiometry near that of the desired ceramic phase.
- Conversion to ceramic should occur cleanly, with only the loss of the organic component, at low temperatures.
- Change in volume/shape on conversion should be as small as possible, (high ceramic yield).

Table II. Important Actual and Potential Ceramics Produced by Polymer Pyrolysis

Product	Approx. theor. density (g/cm³)
Products demonstrated	
SiC	3.2
Si_3N_4	3.2
BN	2.2
B_4C	2.5
Desired products that may be possible	
AlB_{12}	2.6
CaB_6	2.5
TiB_2	4.4
SiB_6	2.4
TiC	4.9
AlN	3.3
TiN	5.2
B_6P	3.0
B	2.6
TiSi	4.2
$TiSi_2$	4.0

Table III. Forms and Applications of Ceramics from Polymer Pyrolysis

- Fibers
  - Reinforcement
  - Filters, insulation
- Coating, sealing
  - (e.g., for oxidation resistance)
- Joining
- Foams
  - (e.g., for filtering or heaters)
- Bulk bodies
  - From powders via pyrolysis
  - Using product-producing polymers as binder
  - Directly via pyrolysis
  - Composites

R.W. Rice, Ceramic Bulletin *62*, 889 (1983)

Key Developments in the Preparation of Silicon Carbide via Polymer Pyrolysis

o $[(Me_2Si]_n \longrightarrow$ "$[MeSi(H)CH_2]_n$" ("Polycarbosilane")
Yajima - 1975

melt-spinnable solid PCS intermediate -->
air-cured Si-O-C fibers (Nicalon™)

o $[(MeSi\equiv)_x(Me_2Si=)_y(Me)_z]$ (MPS)
Baney (Dow Corning) - 1982

o $[\{(C_6H_6)MeSi\}_m\{(Me_2Si\}_n]$ (Polysilastyrene)
West - 1983

o $[\{Me_2Si\}_x\{Me(H)Si\}_y\{Me(CH_2=CH)Si\}_z]$ (VPS)
Schilling and Wesson - 1984

ref.: Wynne and Rice, Ann Rev. Mater. Sci., 1984, 14, 297

Recent Developments

1987 – Seyferth – polymethylsilane $[(CH_3)(H)Si]_n$ – via dehalocoupling with K – gives a Si-rich SiC

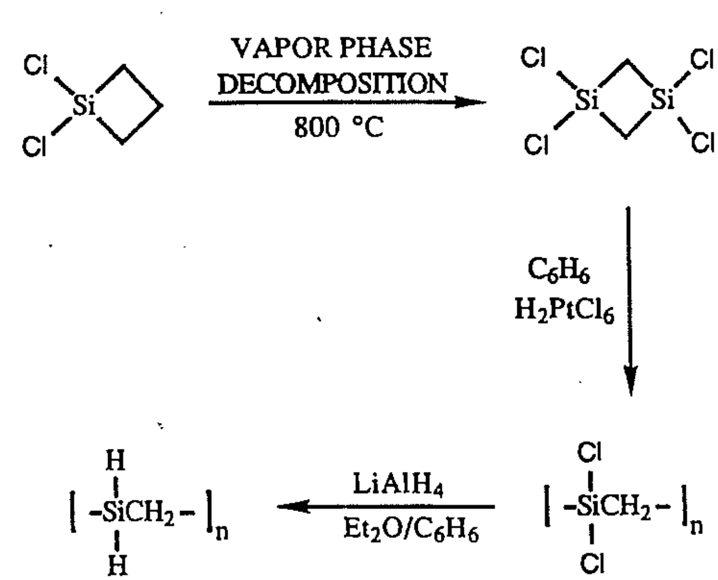
1990 – Corriu – polycarbosilanes $[Si(H)_2CH_2CH_2]_n$ – from $SiH(CH=CH_2)Cl_2$ – gives C-rich SiC

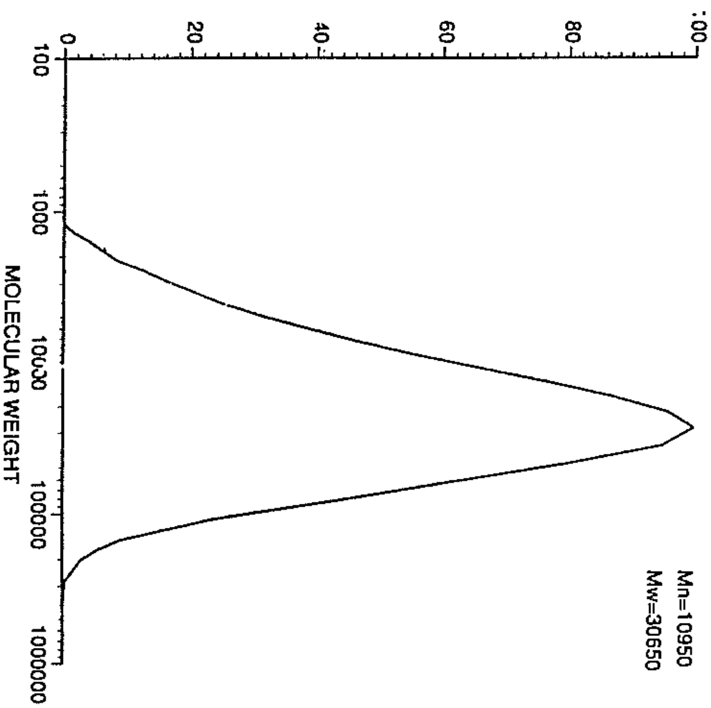
1990 – Barton – polysilylacetylenes $[R_2SiC{=}C]_n$ – from R_2SiCl_2 + LiC≡CLi – gives C-rich SiC

1991 – Laine, Harrod – polymethylsilane – $[(CH_3)(H)Si]_n$ – via catalytic dehydrocoupling of $MeSiH_3$ – extremely air sensitive polymer; gives $SiC_{0.9}H_{<0.2}O_{0.1}$ in 77% ceramic yield on pyrolysis

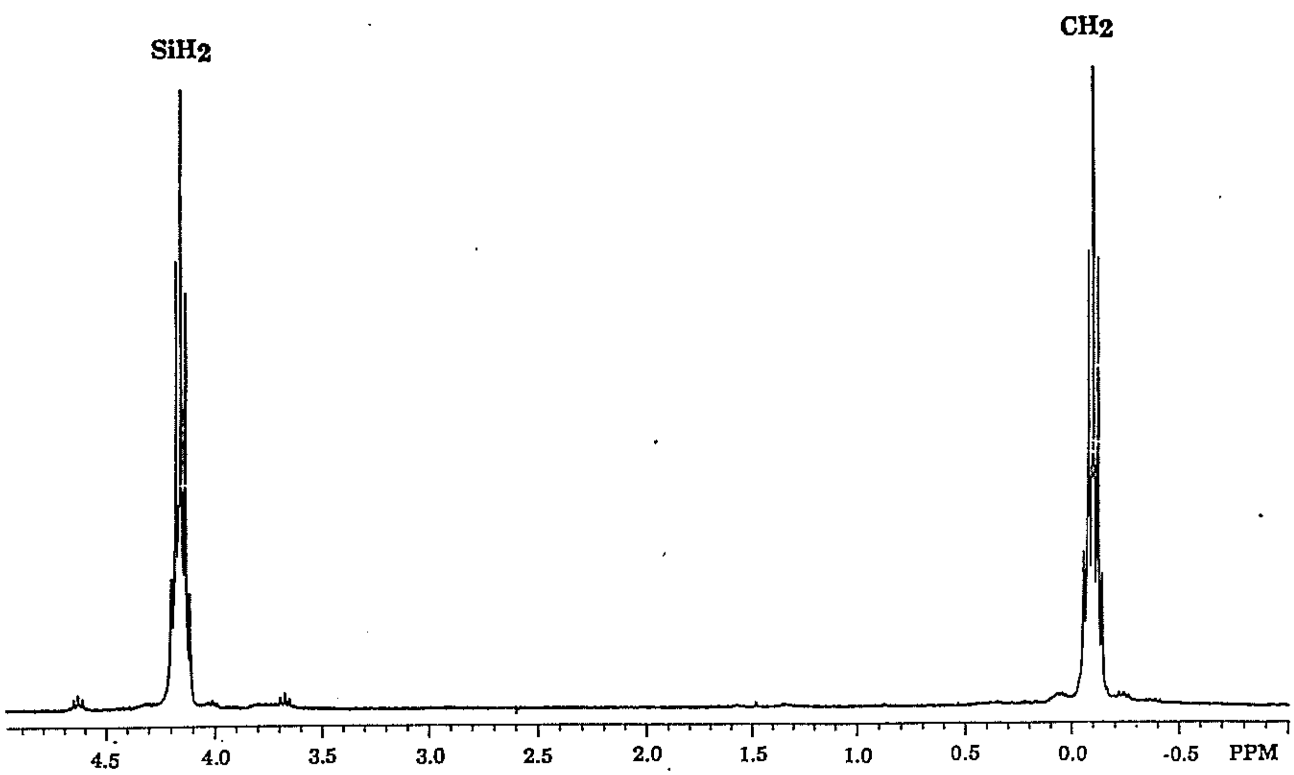
ref., Laine and Babonneau, Chem. Mater., 1993, 5, 260

PREPARATION OF THE LINEAR POLYMER $[SiH_2CH_2]_n$

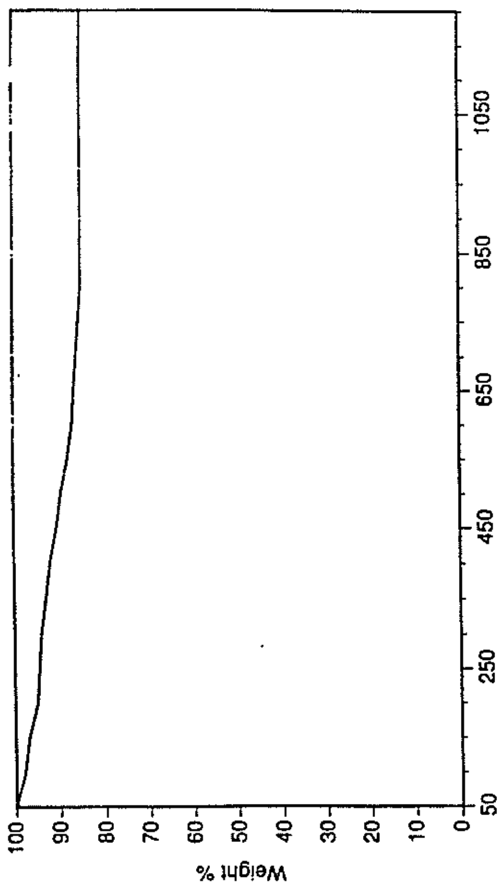




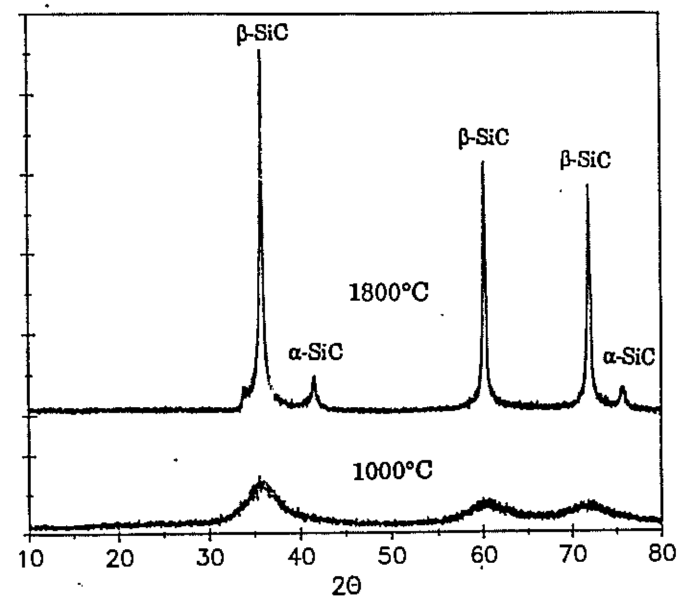
Molecular Weight Distribution of Poly(silaethylene), (-SiH_2CH_2-)n.



1H NMR Spectrum of Poly(silaethylene), (-SiH2CH2-)n, Obtained by Using a Varian XL-200 NMR Spectrometer.



TGA Plot of Poly(silaethylene), $(-SiH_2CH_2-)_n$.



XRD Patterns of Poly(Silaethylene), $(-SiH_2CH_2-)_n$ Heated to 1000°C and 1800°C under N_2.

Approach to the Study of the Pyrolysis Chemistry of Poly(silaethylene)

* Study of the evolution of gaseous species during the pyrolysis of poly(silaethylene) , $(SiH_2CH_2)_n$, and deuterated poly(silaethylene), $(SiD_2CH_2)_n$, by u ing mass spectrometry.

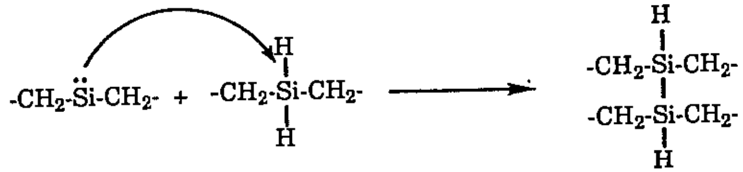
* Characterization of the samples prepared by pyrolyzing poly(silaethylene) to various temperatures with IR and solid state NMR.

CONCLUSIONS REGARDING THE PYROLYTIC CONVERSION OF POLYSILAETHYLENE TO SiC

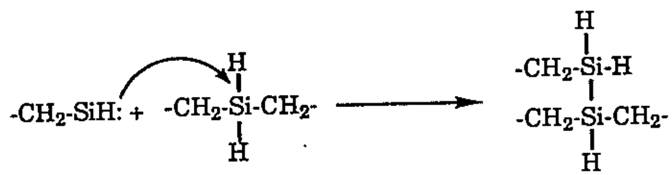
Temp Range/ (%wt loss)	
<300 °C: (ca. 5%)	THE SMALL WEIGHT LOSS IN THIS REGION IS ATTRIBUTED TO THE EVAPORATION OF OLIGIMERS
300 - 400 °C: (ca. 3%)	SILYLENE SPECIES (=Si:) ARE PRESUMED TO BE FORMED, MAINLY BY 1,1-H_2-ELIMINATION FROM $-SiH_2-$ GROUPS, CAUSING CHAIN BRANCHING AND CROSSLINKING
400 - 600 °C: (ca. 5%)	BOTH SILYLENE AND FREE RADICAL MECHANISMS ARE OPERATIVE, RESULTING IN A HIGHLY CROSSLINKED STRUCTURE
>600 °C: (ca. 2%)	ONLY A SLIGHT WEIGHT LOSS, DUE MAINLY TO H_2 EVOLUTION, IS OBSERVED, AS $HSiC_3$ AND REMAINING H_2SiC_2 SITES ARE CONVERTED TO SiC, FORMING A NANOCRYSTALLINE SiC STRUCTURE BY 1000 °C

$-CH_2\text{-}SiH_2\text{-}CH_2\text{-} \longrightarrow -CH_2\text{-}\ddot{S}i\text{-}CH_2\text{-}$ Equation 1

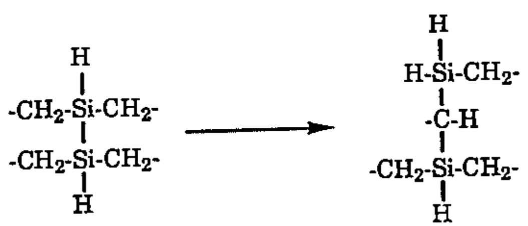
$-CH_2\text{-}SiH_2\text{-}CH_2\text{-} \longrightarrow -CH_2\text{-}SiH\text{:} + CH_3\text{-}$ Equation 2



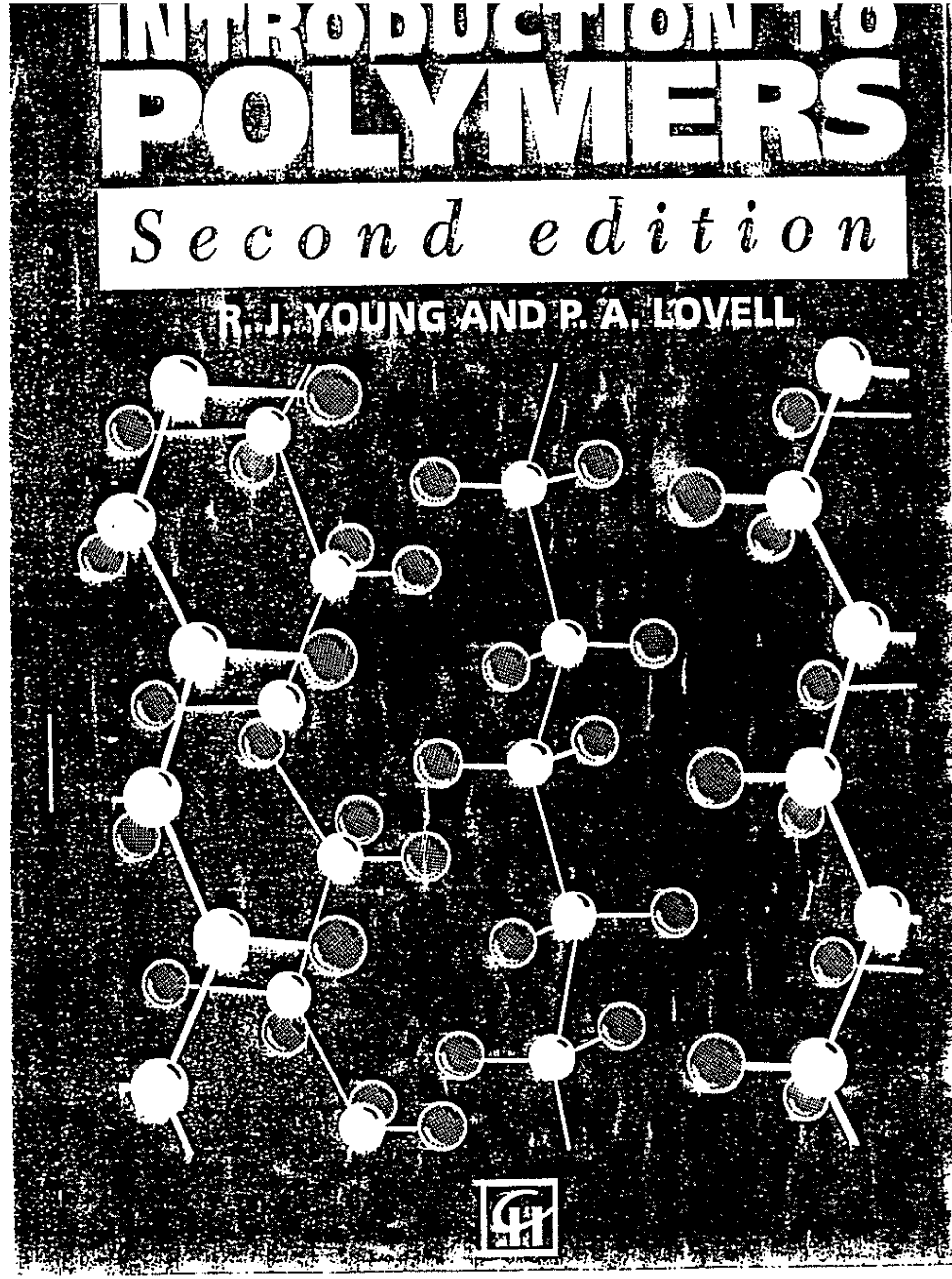
Equation 3

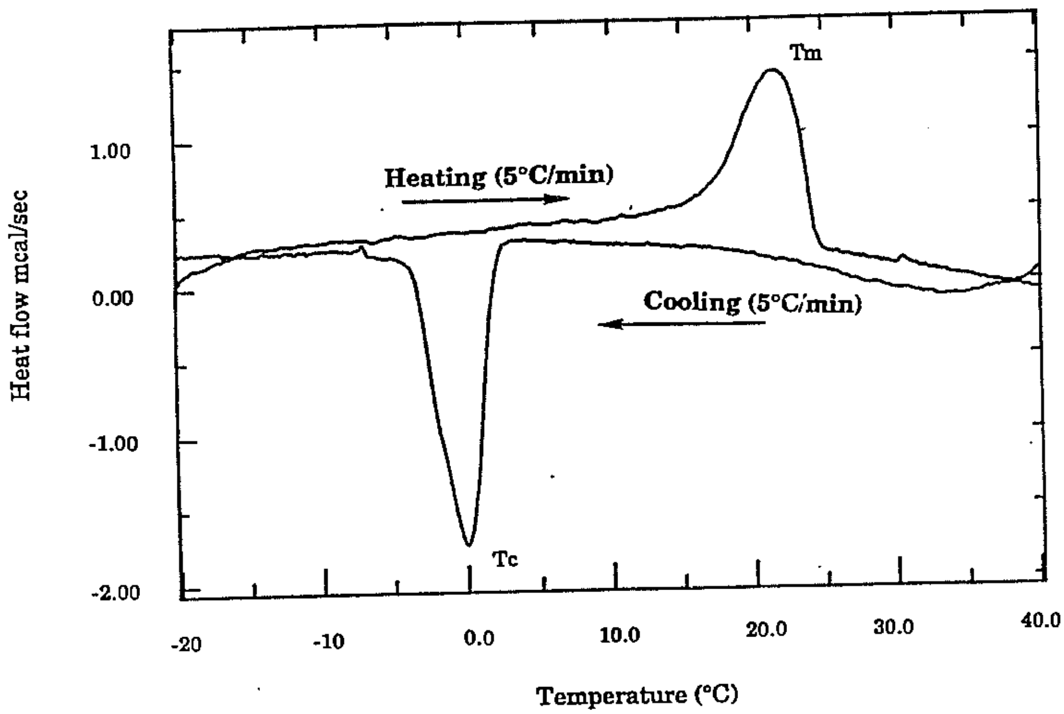


Equation 4



Equation 5





DSC Plots of Poly(silaethylene), $(SiH_2CH_2)_n$, with Mn=11800, Mw=470000.

Mn=900 , Mw=24140, at -2°C.

Mn=11200, Mw=81900, at 3°C.

Cross-Polarized Optical Microscope Photographs of Poly(silaethylene).

Results of a Molecular Mechanics Calculation on PSE

Dr. Kennith A. Smith
GE CRD, Schenectady

Performed ab initio HF calculations on $H_3SiCH_2SiH_2CH_2SiH_3$ using Gaussian 90

Results used to modify the molecular parameters for a molecular mechanics calculation on polysilaethylene (with Polygraf)

One of the minimized structures has an orthorhombic cell having two chains

An X-Ray powder diffraction pattern was calculated for this structure with CERIUS

Relationship Between Poly(silaethylene) and Polyethylene

PSE exhibits some significant similarities and differences compared to PE insofar as its structure and properties are concerned,

Similarities:

Like (HD)PE, PSE,

- crystallizes from the melt, exhibiting a spherulite structure by optical microscopy

- exhibits reversible melting and crystallization transitions in the DSC whose peak temperatures vary with MW and the heating(cooling) rate

- appears to crystallize in an orthorhombic structure which is related to that of PE

Differences:

- PSE is a liquid at rm. temp. and has a substantially lower melting temperature (by over 100 ^{o}) and $\Delta H_{s=l}$ than PE

- their XRD patterns appear quite different

SYNTHESIS OF THE BRANCHED "[SiH_2CH_2]" POLYMER

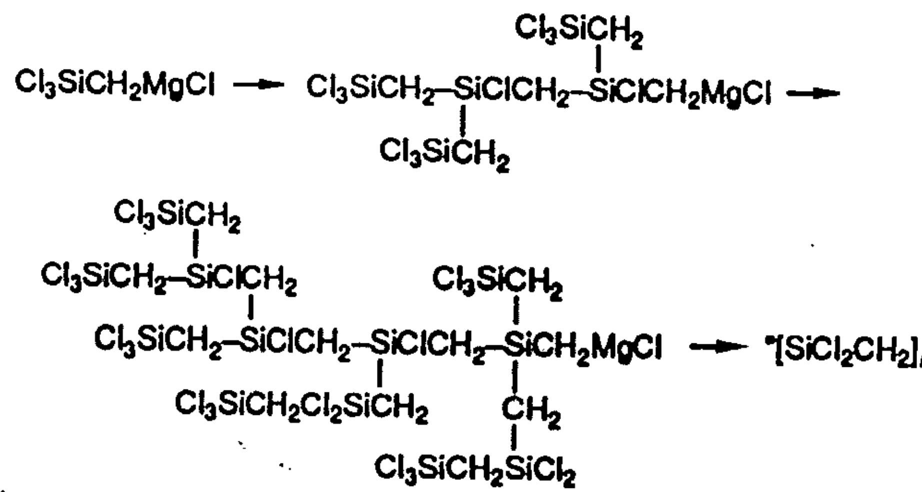
1] PREPARATION OF THE "CHLORO-POLYMER"

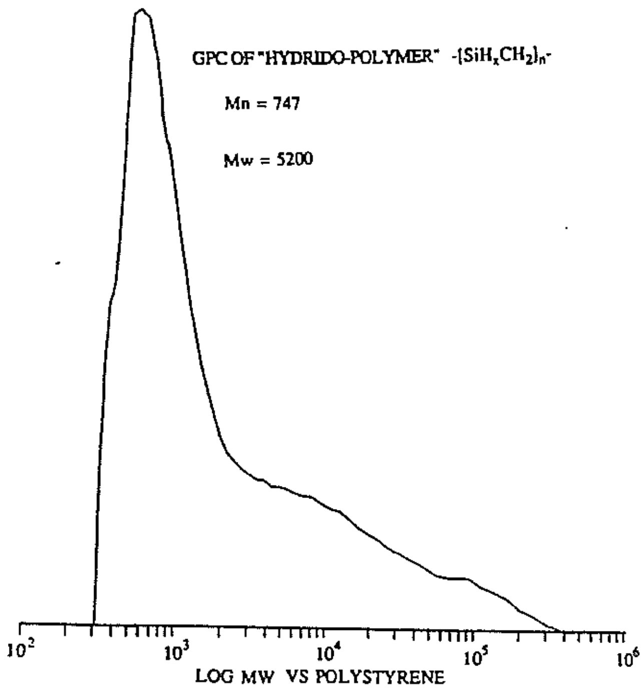
$$Cl_3SiCH_2Cl + Mg \xrightarrow[-MgCl_2]{Et_2O} \text{"}[SiCl_2CH_2]_n\text{"}$$

2] REDUCTION TO "[SiH_2CH_2]$_n$"

$$\text{"}[SiCl_2CH_2]_n\text{"} \xrightarrow{Et_2O/LiAlH_4} \text{"}[SiH_2CH_2]_n\text{"}$$

Organometallics, Vol. 10, No. 5, 1991





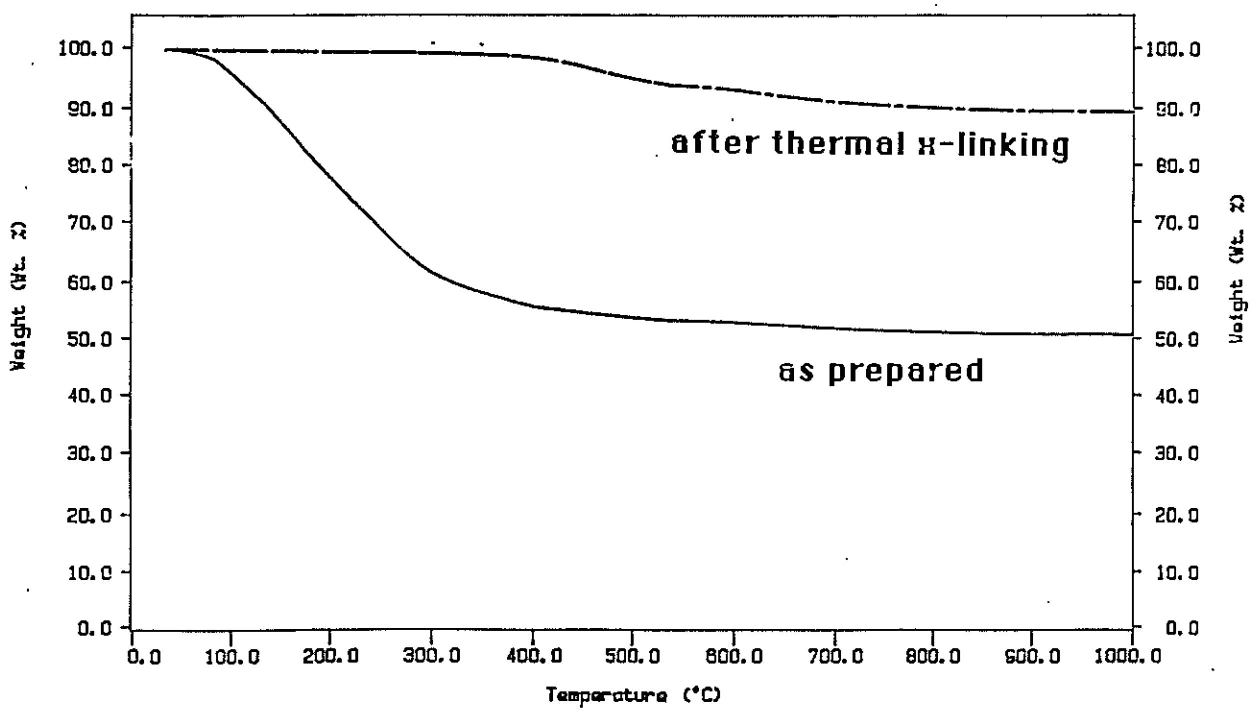
MODIFICATION OF THE POLYCARBOSILANE

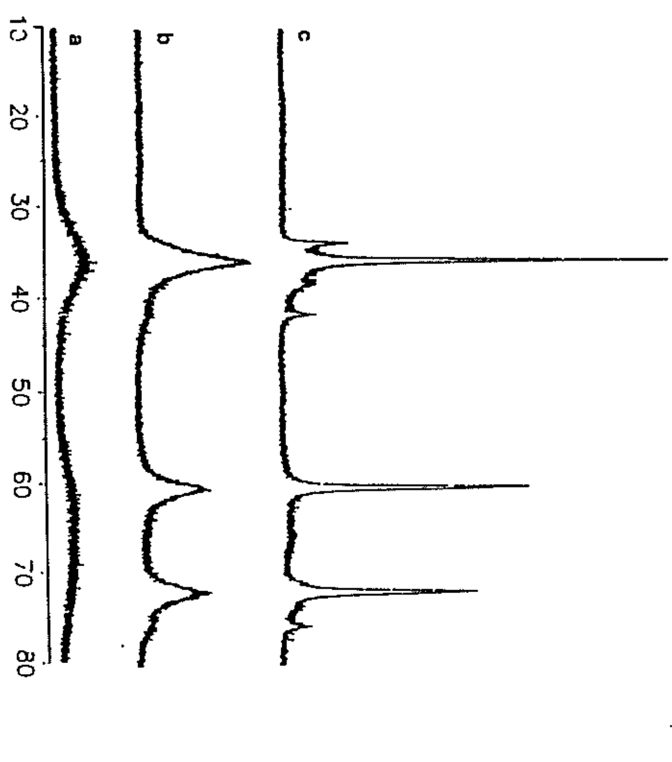
"$[SiCl_2CH_2]_n$" (branched chloropolymer)

x RMgBr ↓ LiAlH$_4$ ↓ → "$[SiR_xH_yCH_2]_n$" (XHPCS), R = allyl, vinyl, etc.

xs EtOH ↓ → "$[Si(EtO)_2CH_2]_n$" (EtOPCS)

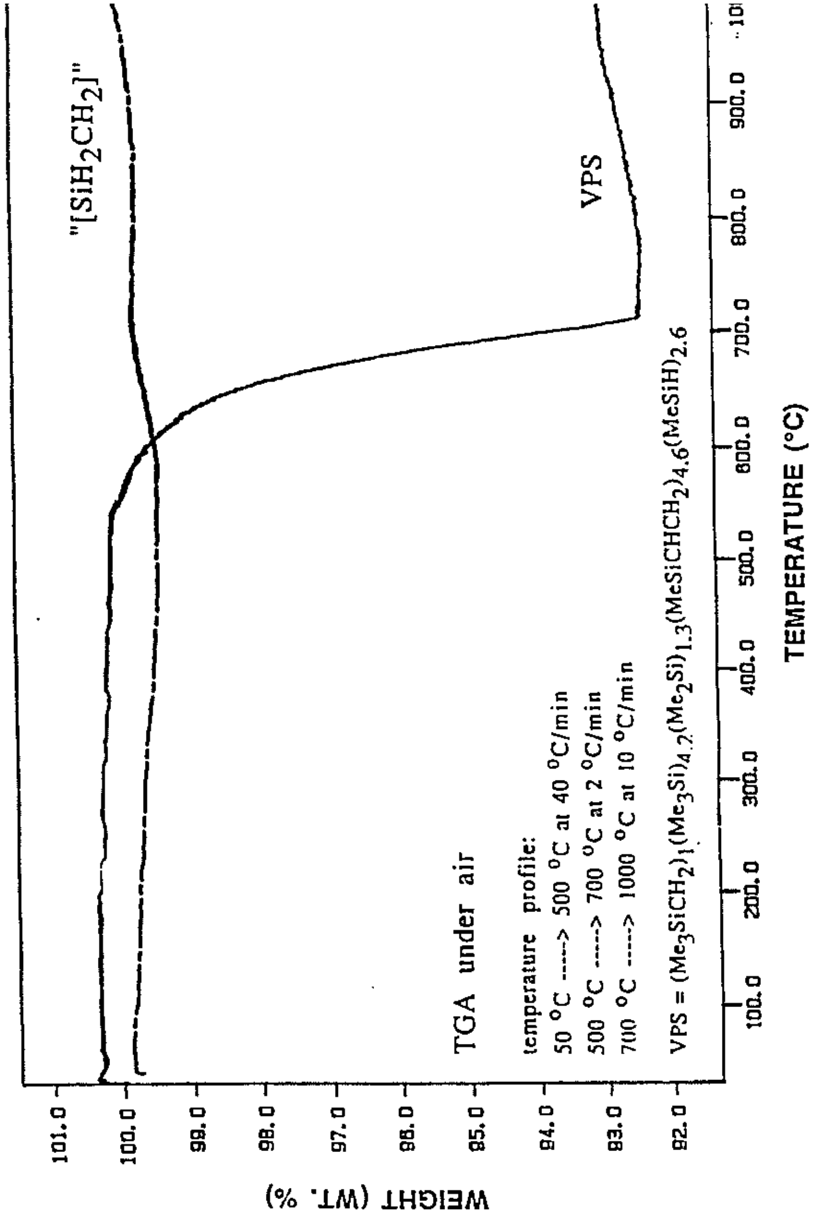
TGA PLOT FOR AHPCS (UNDER N_2; 10 °C/MIN)





X-ray diffraction of ceramic products from pyrolysis of HPCS:
(a) 1000°C, 10h; (b) 1600°C, 2h; (c) 1800°C, 2h.

OXIDATION OF $[SiH_2CH_2]_n$ and VPS N_2 CERAMICS



US005153295A

United States Patent [19]

Whitmarsh et al.

[11] Patent Number: 5,153,295

[45] Date of Patent: Oct. 6, 1992

[54] CARBOSILANE POLYMER PRECURSORS TO SILICON CARBIDE CERAMICS

[75] Inventors: Christopher K. Whitmarsh; Leonard V. Interrante, both of Schenectady, N.Y.

[73] Assignee: Rensselaer Polytechnic Institute, Troy, N.Y.

[21] Appl. No.: 556,599

[22] Filed: Jul. 20, 1990

[51] Int. Cl.[5] C08G 77/12

[52] U.S. Cl. 528/31; 525/475; 528/10; 528/32; 556/480

[58] Field of Search 525/475; 528/10, 31, 528/32; 556/480

[56] References Cited

U.S. PATENT DOCUMENTS

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4,472,591	9/1984	Schilling, Jr. et al.	528/14
4,631,179	12/1986	Smith, Jr.	423/345
4,783,516	11/1988	Schilling, Jr. et al.	528/32
4,923,716	5/1990	Brown et al.	427/249

OTHER PUBLICATIONS

S. Yajima et al., "Synthesis of Continuous Silicon Carbide Fibre with High Tensile Strength and High Young's Modulus", Journal of Materials Science 13 (1978) 2569-2576.

Primary Examiner—Melvyn I. Marquis
Attorney, Agent, or Firm—Richard P. Fennelly; Louis A. Morris

[57] ABSTRACT

Polycarbosilane compositions, which can serve as silicon carbide precursors, are formed by a Grignard coupling reaction of a halomethylcarbosilane followed by reduction using a metal hydride. The polycarbosilane compositions that result have a substantially 1:1 silicon to carbon stoichiometry, are substantially non-cyclic and branched, and comprise the repeat units SiH_3CH_2—, —SiH_2CH_2—, =$SiHCH_2$—, and ≡$SiCH_2$—.

19 Claims, 4 Drawing Sheets

SUMMARY

A BRANCHED HYDRIDOPOLYCARBOSILANE HAS BEEN PREPARED FROM A LOW COST STARTING MATERIAL (CH_3SiCl_3)

THIS POLYMER:

* HAS A NOMINAL 1:1 Si:C RATIO
* IS EASILY MODIFIED AT THE "CHLORO" STAGE
* IS A MOBILE LIQUID WHICH CAN BE HANDLED IN AIR
* UNDERGOES FACILE CROSSLINKING
* HAS A GOOD CERAMIC YIELD

POTENTIAL USES:

* SiC MATRIX SOURCE - VIA PIP
* SiC and SiO_xC_y COATINGS
* SiC FIBERS?

Advantages of (X)HPCS (X = Vinyl, Allyl) as a SiC Matrix Source

- o Highly fluid liquid at ca. 125 °C, wets C, SiC, SiO_2 surfaces
- o HPCS alone thermosets at 300-400 °C (110 °C with a catalyst) to produce a clear glass with little loss in weight
- o Pyrolysis of HPCS to 1000 °C gives near-stoichiometric "SiC" in 80% yield
- o XHPCS (X = 10% V or A) thermosets at 110 °C, without a catalyst, shows uniform shrinkage on pyrolysis to 1000 °C; SiC obtained contains 4-8 % xs C

Research Programs Involving Hydridopolycarbosilane (HPCS)
(continued)

o US Army Phase I SBIR Grant
to Starfire Systems, Inc.; 3/1/93-8/31/93

"Engineered, Ceramic Reinforced, Ceramic Matrix Composites"
Investigation of Polymer Infiltration and Pyrolysis as a route to C/SiC and SiC/SiC-structural composites

Objectives:

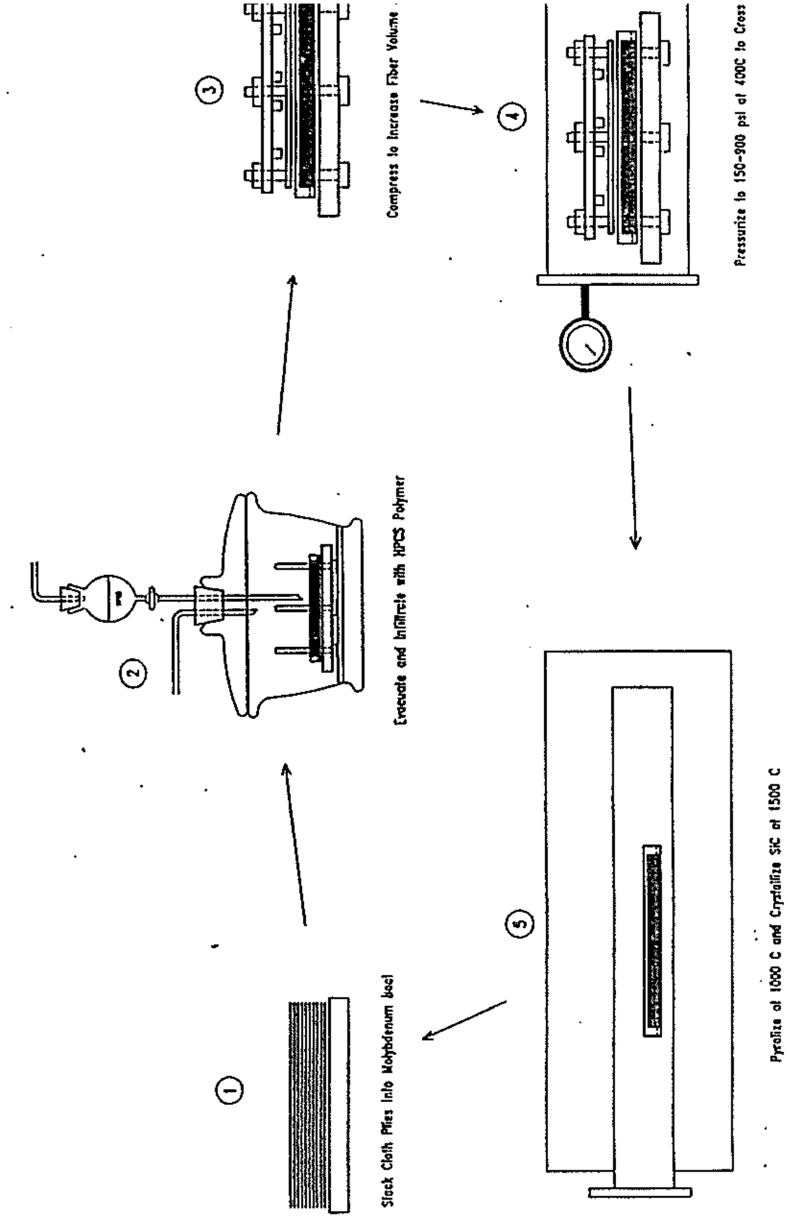
- o Use resin transfer moulding to produce ceramic matrix composite plates
- o Machining the plates into test specimens such as bend bars and interlaminar shear specimens
- o Characterization of the microstructure and mechanical properties of the materials to demonstrate reproducibility of properties and for comparison to CVI based ceramic composites
- o Demonstrate the thermal stability of the matrix material

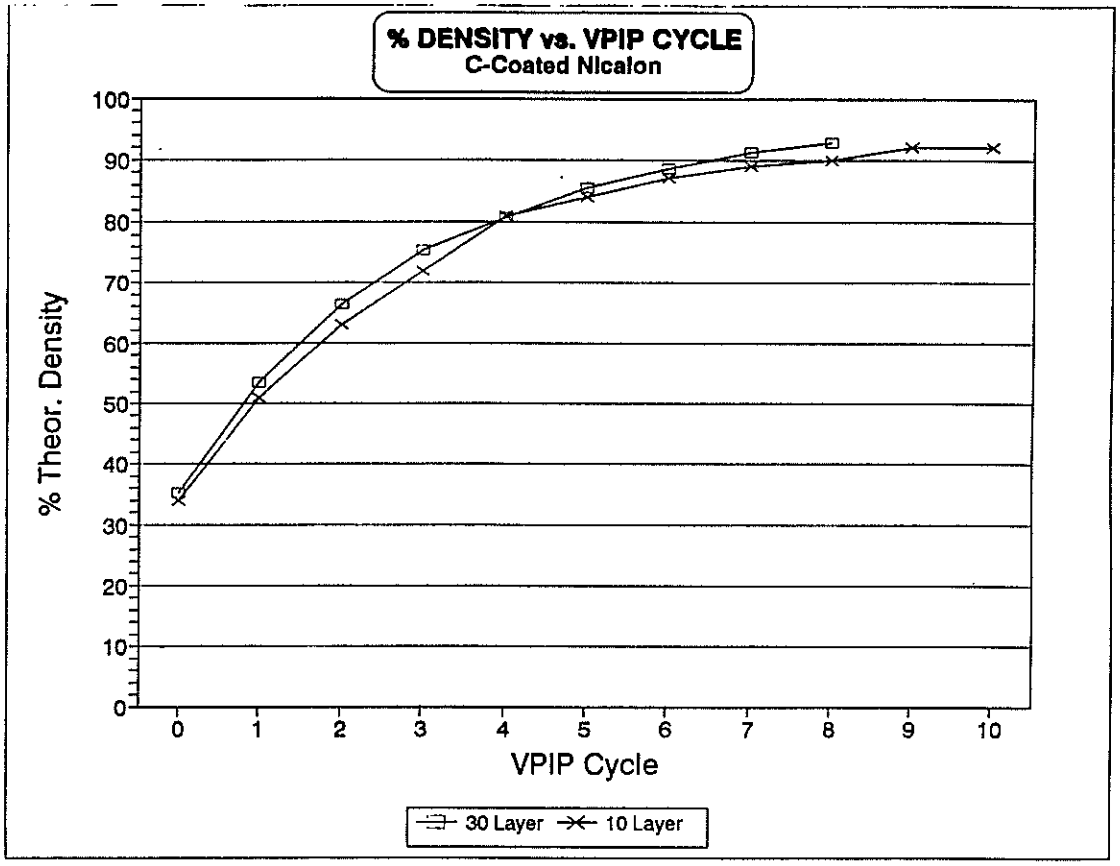
Deliverables:

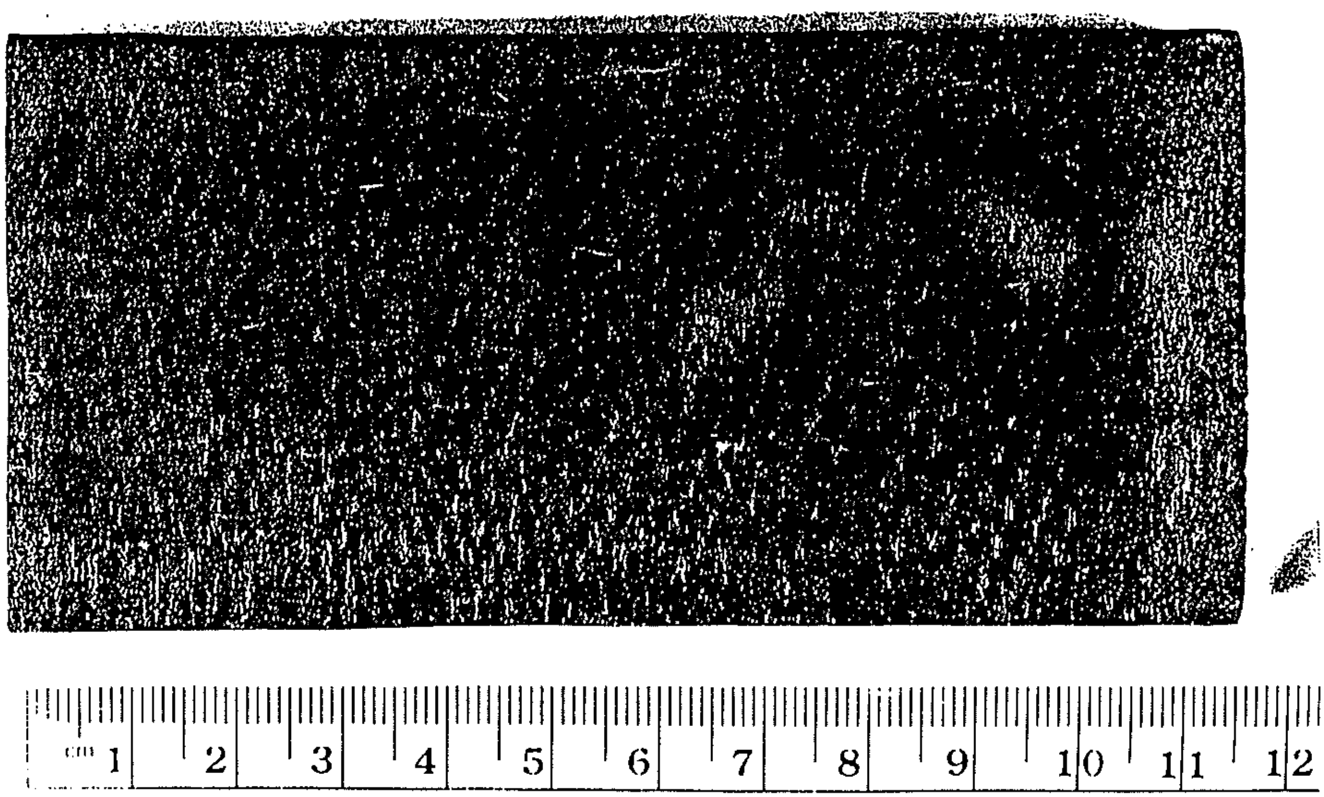
- o 3 bend bars of each of the following types:

  carbon fiber cloth-, Nicalon cloth-, and SiC whisker-reinforced SiC matrix composites

HPCS COMPOSITE FABRICATION FLOWCHART




% DENSITY vs. VPIP CYCLE
C-Coated Nicalon
% Theor. Density
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
10
VPIP Cycle
30 Layer
10 Layer



No. 18

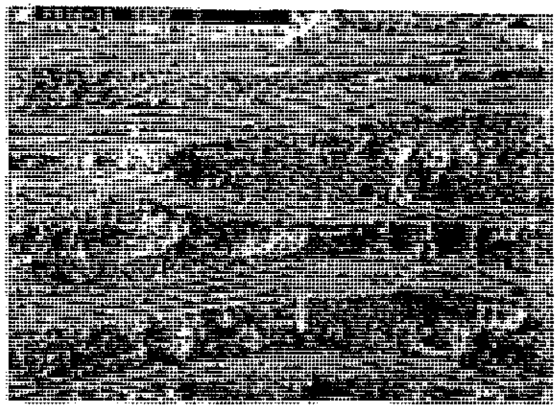


Figure 5a. SEM micrograph of a cross-section of a HPCS densified Nicalon fiber plate after 8 infiltration and pyrolysis cycles. (50X)

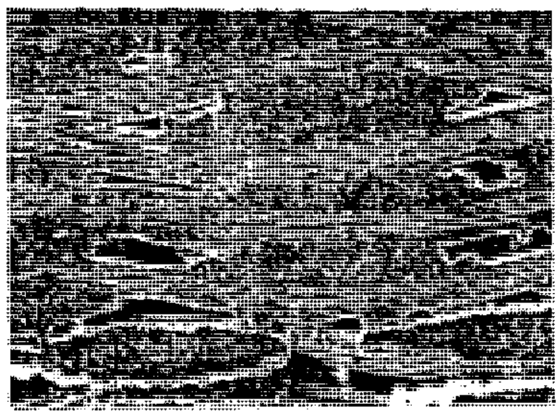


Figure 5b. SEM micrograph of a cross-section of a CVI densified Nicalon plate showing porosity and a density gradient. (50X)

Four Point Flexure Data for HPCS and CVI Composites

ID#	Width (in.)	Thickness (in.)	Max. Load (lbs)	Fracture Stress (ksi)	Extension (in.)
Nicalon/HPCS Bars					
1N-1	0.172	0.107	74.5	55.0	0.056
1N-2	0.213	0.105	81.0	50.4	0.068
1N-3	0.175	0.109	73.7	52.3	0.054
1N-4	0.151	0.106	69.1	60.5	0.064
1N-5	0.149	0.107	58.9	51.0	0.056
1N-6	0.148	0.108	66.7	57.0	0.065
3N-2	0.145	0.195	128	54.9	0.063
3N-3	0.186	0.151	93.3	51.9	0.066
3N-4	0.196	0.151	101.9	53.9	0.067
5N-1	0.135	0.12	52.8	60.8	0.045
			Average	54.8	
Nicalon/CVI Bars					
CVI-1	0.176	0.145	91.9	43.5	0.92
CVI-2	0.179	0.132	90.4	46.8	0.024
CVI-3	0.169	0.14	88.9	47.4	0.025
			Average	45.8	
Other Nicalon/CVI Bars			Average	43.3	
Other Nicalon/polymer-derived Avg. SiC Bars				16.7	

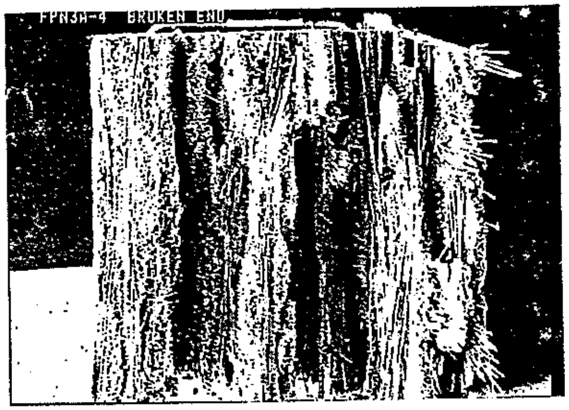


Figure 6a. SEM micrograph of the fracture surface of a Nicalon/HPCS flexure bar. (16X)

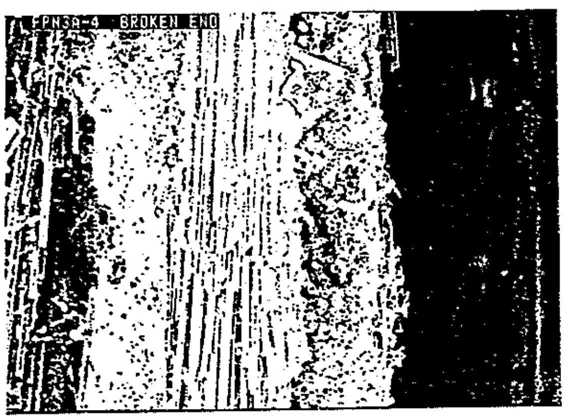


Figure 6b. Figure 6a. at 103X magnification

CONCLUSIONS

- o A simple, low cost, Resin Transfer Molding (RTM) Process has been developed for the fabrication of SiC-matrix composites which employs a new liquid, high-yield, polymeric precursor to SiC (AHPCS)

- o This process was used to fabricate Nicalon-, SCS-6-, and SiC whisker-reinforced SiC/SiC composites.

- o The Nicalon and SCS-6 composites showed improved mechanical properties and more uniform matrix filling relative to comparably reinforced CVI-matrix composites.

- o Composites up to ca. 1/2 in thickness incorporating 30 layers of Nicalon cloth were fabricated by this approach which showed comparable densification rates and final densities as the thinner (0.15") 10 layer plates)

Work In Progress

- Tensile test specimens of the Nicalon-SiC/AHPCS-SiC composites have been fabricated and have been submitted for tensile tests at both room temperature and 1000 °C
- The effect of interlaminar filler materials such as SiC whiskers and powder on densification rate, flexure and tensile strength, and inter-laminar shear are under evaluation
- Various alternatives to the carbon currently used as the interface material in these composites are also under evaluation so as to permit the meaningful study of these composites in high temperature oxidizing environments
- Modifications of the AHPCS synthesis procedure appear promising as a means of improving product quality while reducing its cost. These improvements should enable the synthesis of this material on a large scale at a relatively low cost

Key References

Polysilaethylene

L.V. Interrante, H.-J. Wu, T. Apple, Q. Shen, B. Ziemann, D.M. Narsavage, and K. Smith, "Polysilaethylene - A Novel Analog of Polyethylene", J. Amer. Chem. Soc. 116, 12085-12086 (1994).

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HPCS and Its Applications

L.V. Interrante, C.W. Whitmarsh, C-Y. Yang, W. Sherwood, W.R. Schmidt, P.S. Marchetti, and G.E. Maciel, "Processing of Si-Based Ceramics and Ceramic Composites Using Hydridopolycarbosilane (HPCS)", Proceedings, Symposium on "Silicon-Based Structural Ceramics", 1993 PACRIM Conference, Honolulu, November 7-9, 1993, Ceram. Trans., Vol 42 (1994) pp. 57-69.

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C. Whitmarsh and L.V. Interrante, "Synthesis and Structure of a Highly Branched Polycarbosilane Derived From Chloromethyltrichlorosilane, Organometallics, 10, 1336-1344 (1991).

Chemicals, Polymers and Ceramics from the Beach, I.

K. A. Blohowiak, T. Robinson, M. Hoppe, B. Mueller, P. Kansal, K. W. Chew, F. Babonneau,* R. M. Laine

Departments of Materials Science and Engineering, and Chemistry

Work Supported by ONR, AFOSR, ARL, ARO

Program Objectives:

- **Develop New Routes to Metal Containing Compounds Directly from Metal Oxides**
- **Develop New, Polymeric Species That Exhibit Ion Conducting, Liquid Crystalline or Preceramic Properties**
- **Process Powders, Films, Fibers**

Outline

Chemicals, Polymers & Ceramics from the Beach, I.

Basic Science

Simple Complexes

What Can You Do With $M_2Si_2(OCHCHO)_5$?

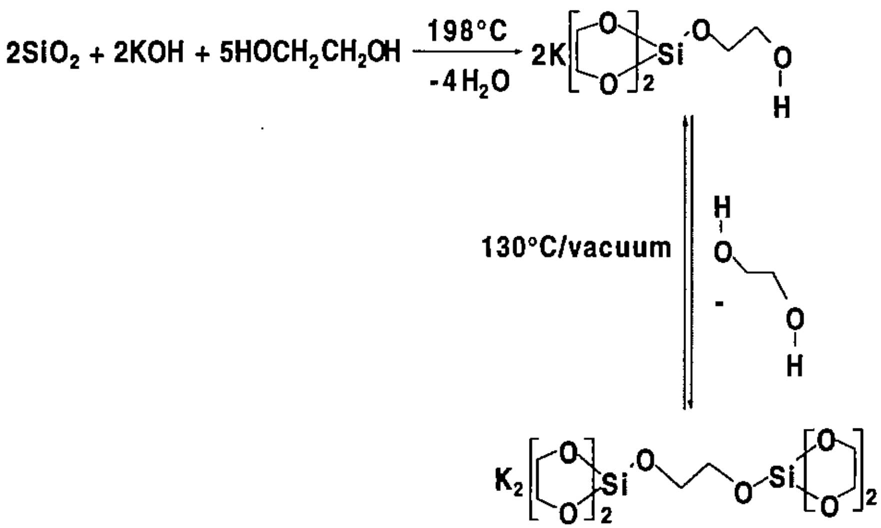
Chemicals, Polymers & Ceramics from the Beach, II.

Oxide One Pot Synthesis Process

Basic Science

What can you do with it?

Dissolving the Beach with Antifreeze and Liquid Plumr®



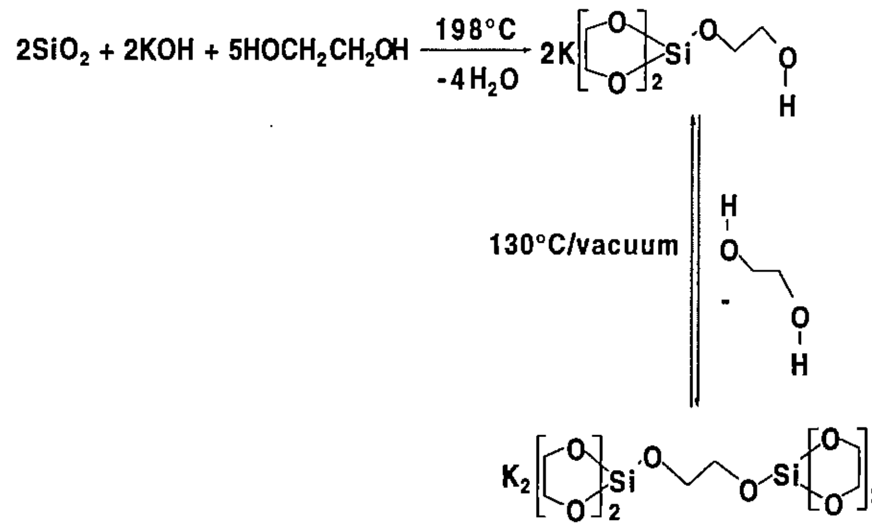
- SiO_2 as Silica Gel, Fused Silica or Sand, or *Rice Hulls*
  - Rxn Also Works With MOH = Li, Na, Cs,

    or MO = Mg, Ca, Sr, Ba
  - 1,2- and 1,3 diols also work

Nature <u>353</u>, 640-2 (1991)

What Can You Do With $M_2Si_2(OCHCHO)_5$?

Dissolving the Beach with Antifreeze and Liquid Plumr®



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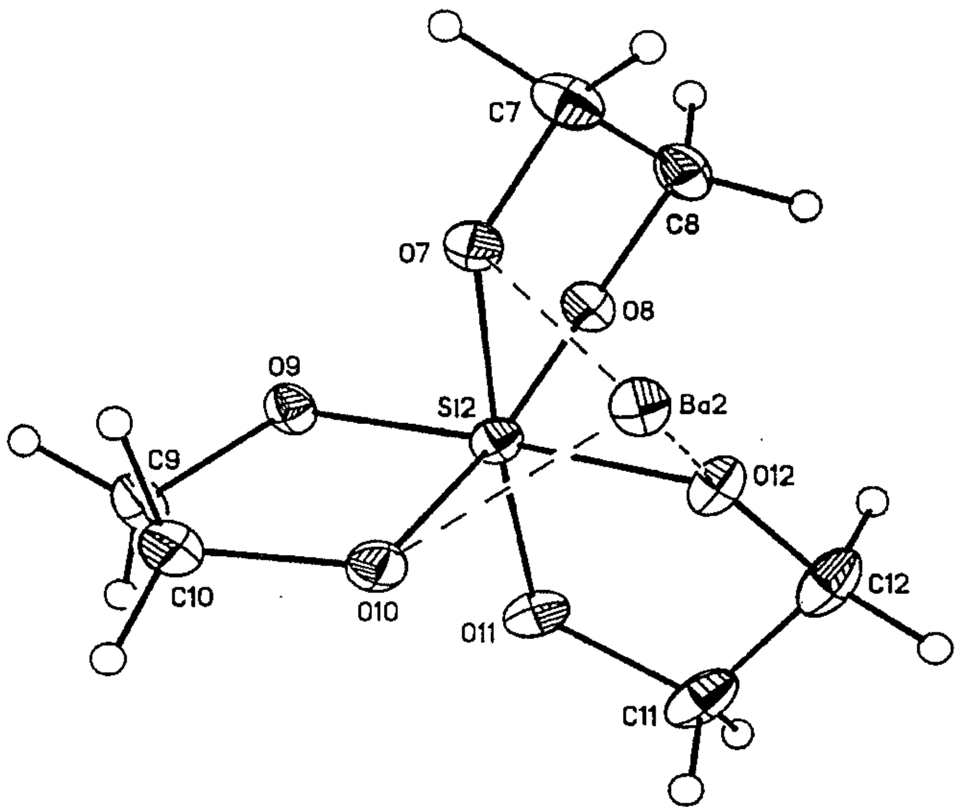
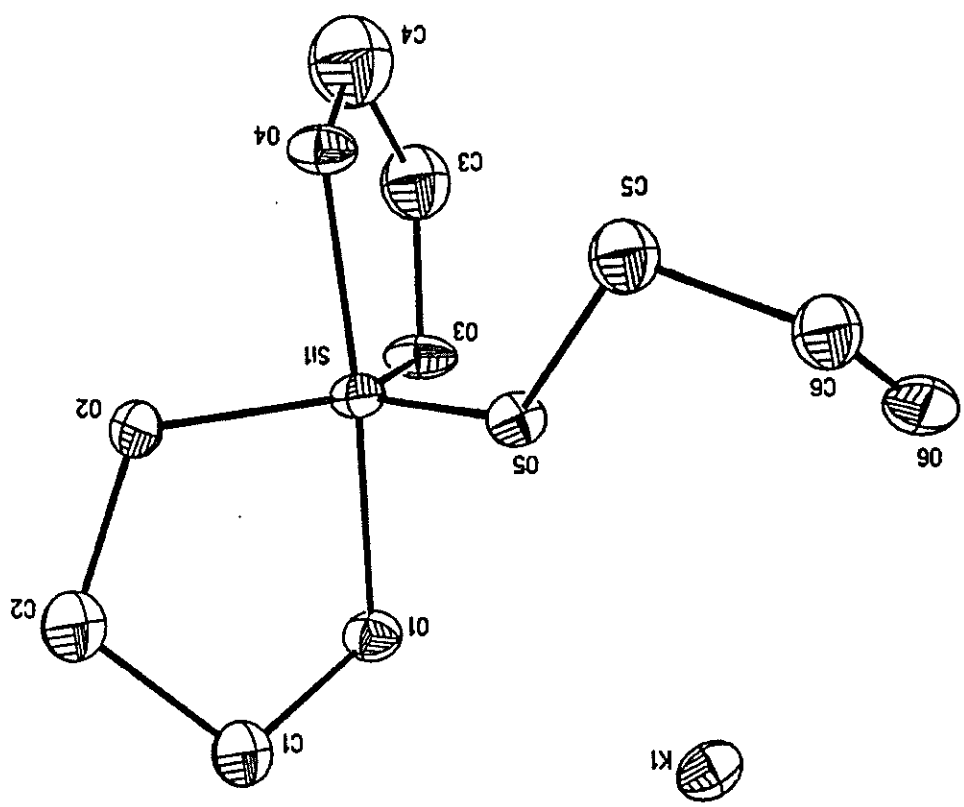
Nature <u>353</u>, 640-2 (1991)

What Can You Do With $M_2Si_2(OCHCHO)_5$?

4


C7
C8
O7
O8
O9
Si2
Ba2
C9
O12
C12
C10
O10
O11
C11

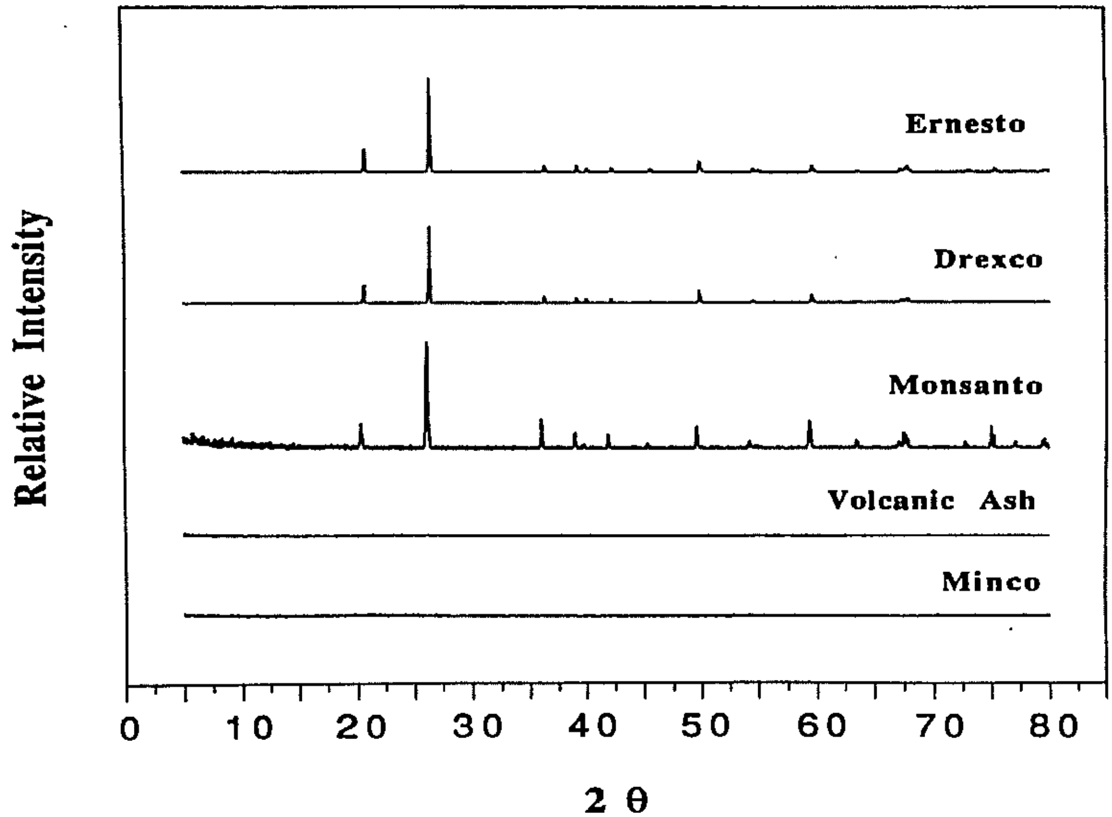
6


C4
O4
C3
C5
O3
Si1
O2
C6
O5
O6
C2
O1
C1
K1

5

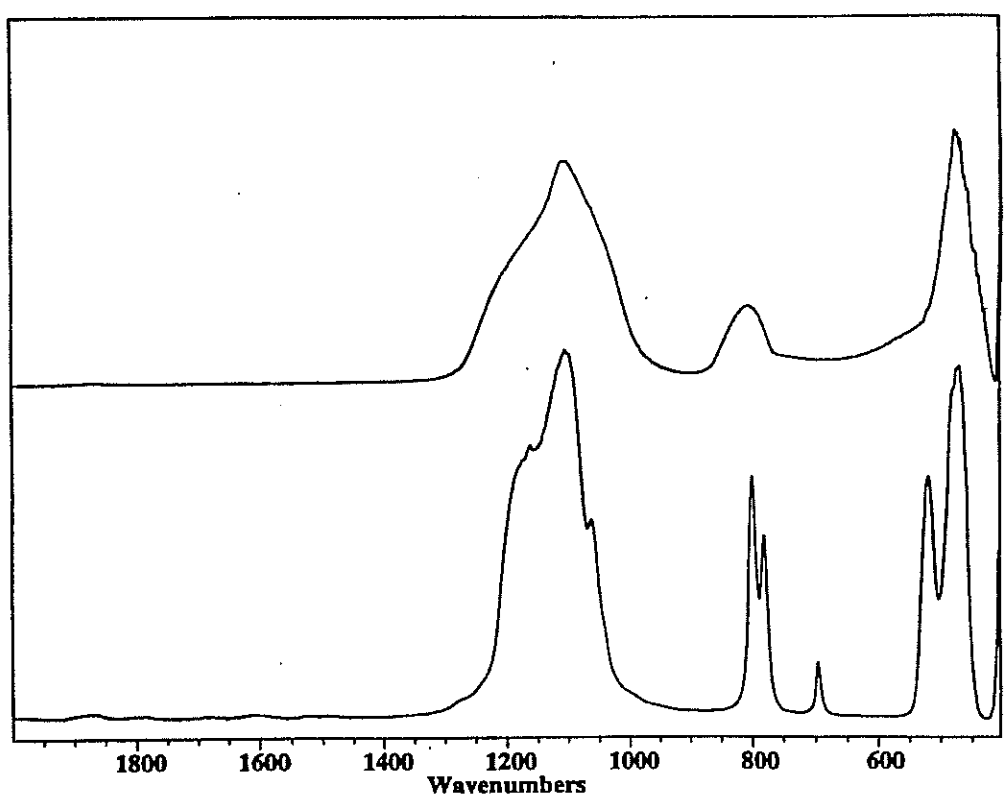
7

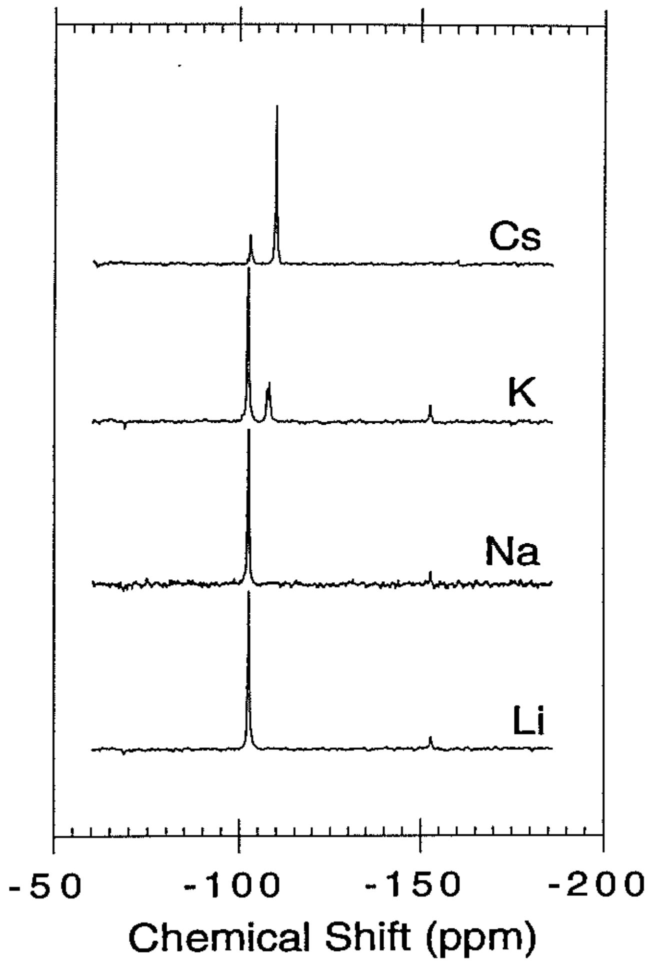
XRD of various sand samples



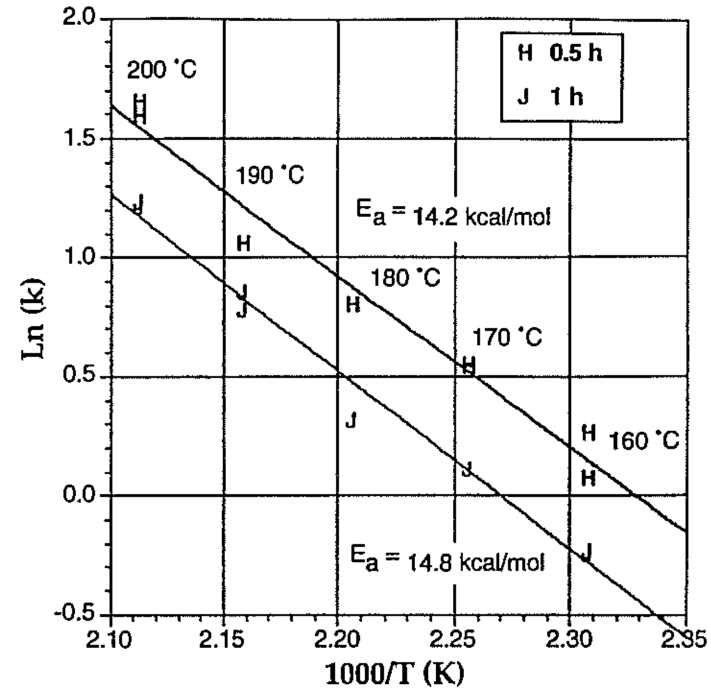
8

DRIFTS of Raw Fused Silica and Quartz.





Minco SiO_2 525 mesh Dissolution Studies



SiO_2 Dissolution in $HOCH_2CH_2OH$

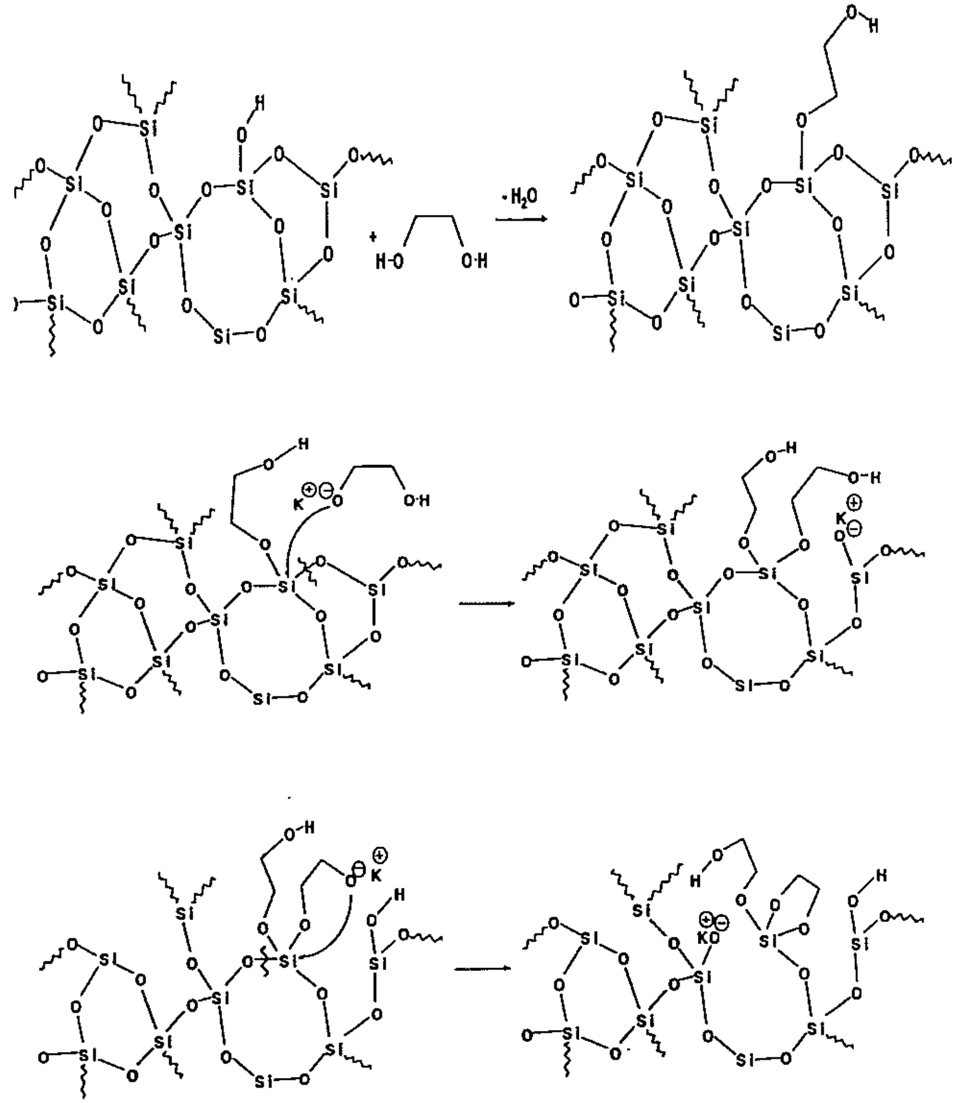
- First order in [$KOCH_2CH_2OH$]
- First order in Surface Area

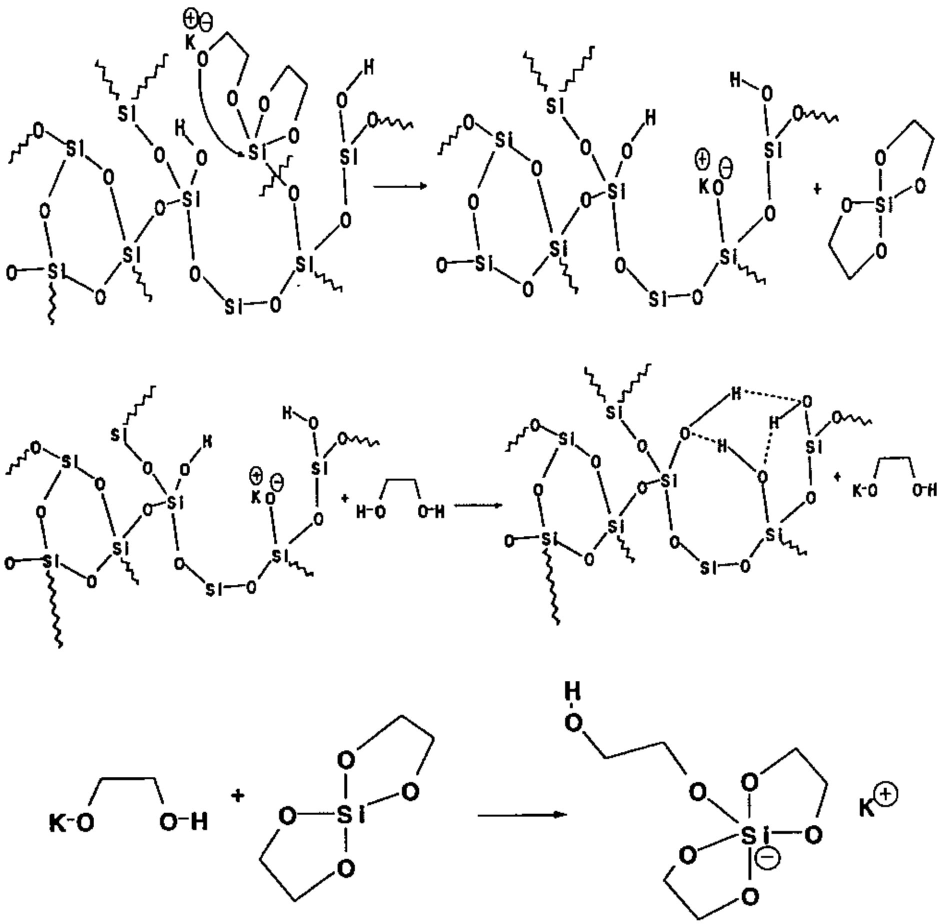
∴ <u>Slow Step After $KOCH_2CH_2OH$ Reacts with Surface</u>

- $E_a \approx 14 \pm 2$ kcal/mol
- Without Base, Surface Covered with Pendant $Si\text{-}OCH_2CH_2OH$ Groups
- With Base, Surface Covered with Si-OH Groups
- FTIR Shows No Evidence of $Si\text{-}O^-K^+$ Groups

    ∴ No K^+ on Surface

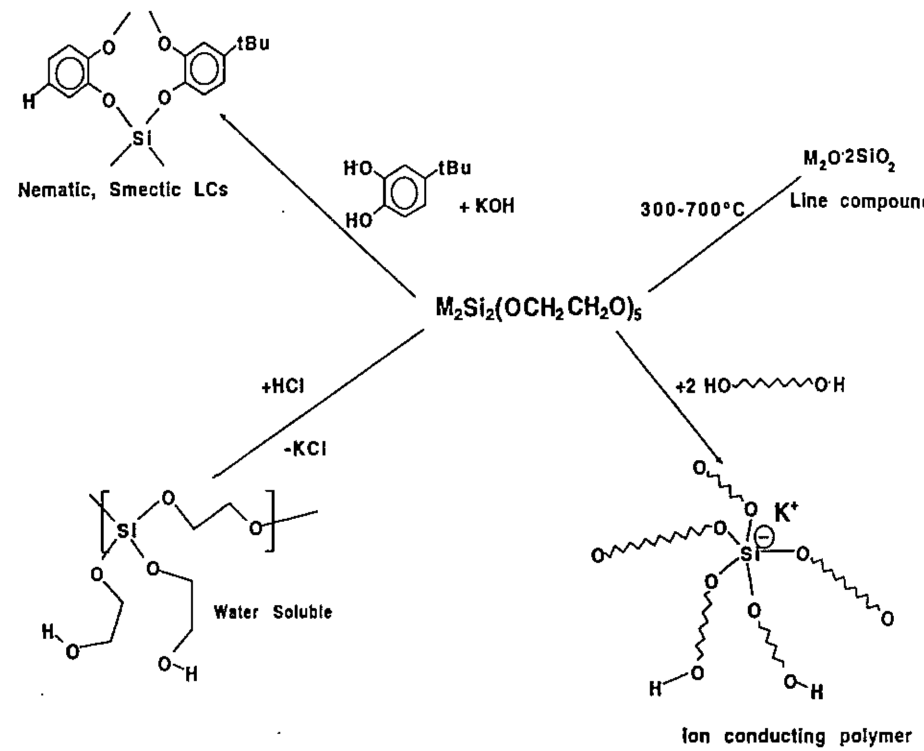
What is the dissolution process?



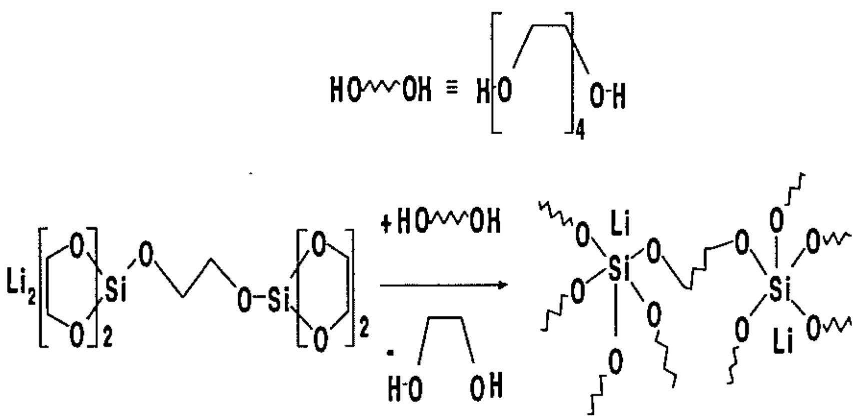


Chem. Mater., Nov. 1994

What Can You Do With $M_2Si_2(OCHCHO)_5$?



What Can You Do With $M_2Si_2(OCHCHO)_5$?



T_gs ≈ -25°C, T_m ≈ 15-25°C

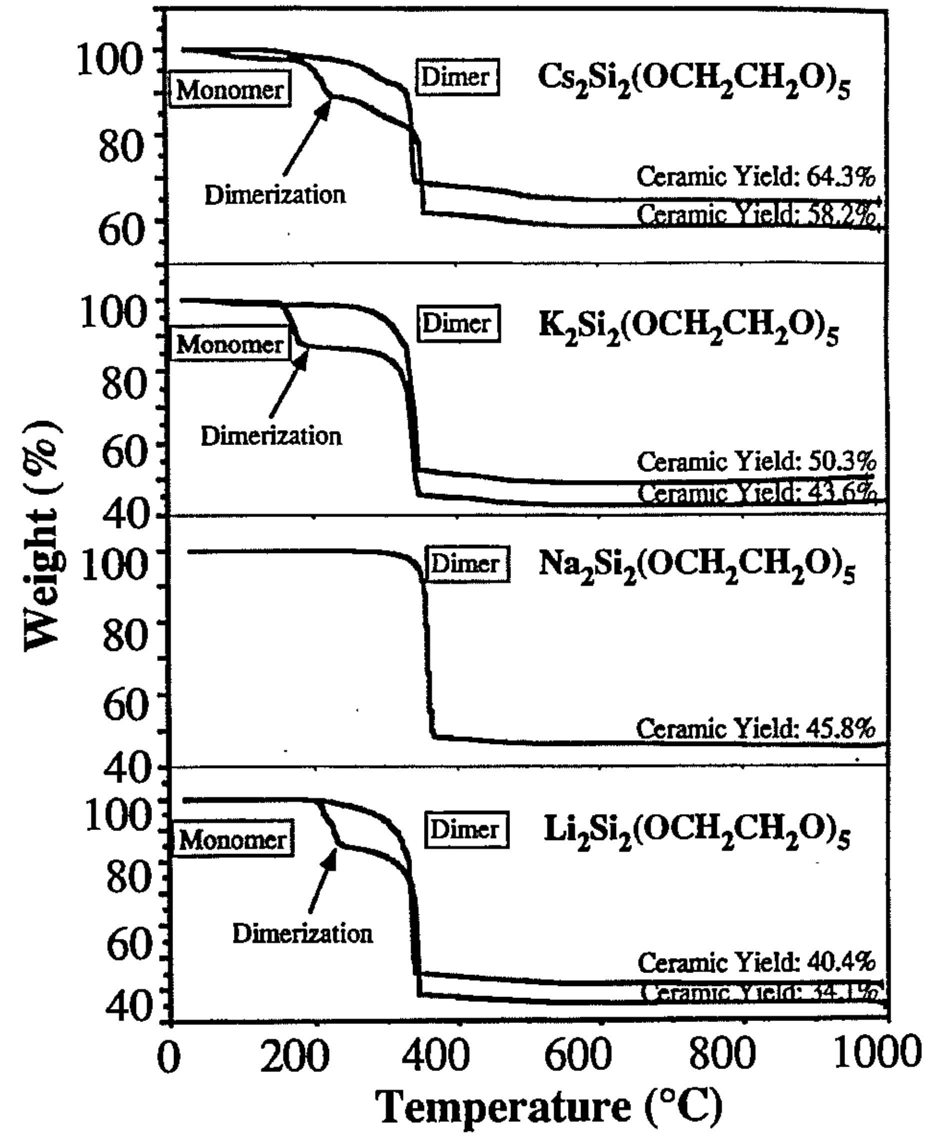
AC Impedance at 25°C

Over Frequency Range of 10-10 ^{5} Hz

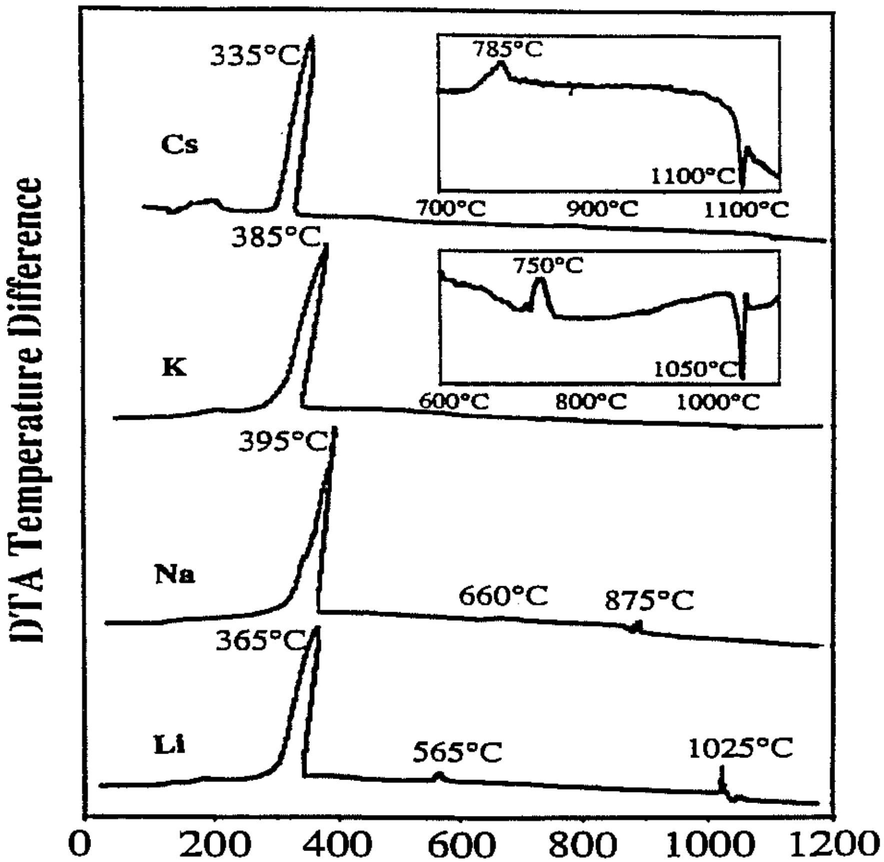
Polymer	Conductivities	^{29}Si NMR(ppm)
Li^+	7×10^{-7} S/cm	-103
K^+	3×10^{-5} S/cm	-107
Ba^{2+}	6×10^{-6} S/cm	

B. Dunn, T. Faltens--UCLA, 1994

What Can You Do With $M_2Si_2(OCHCHO)_5$?



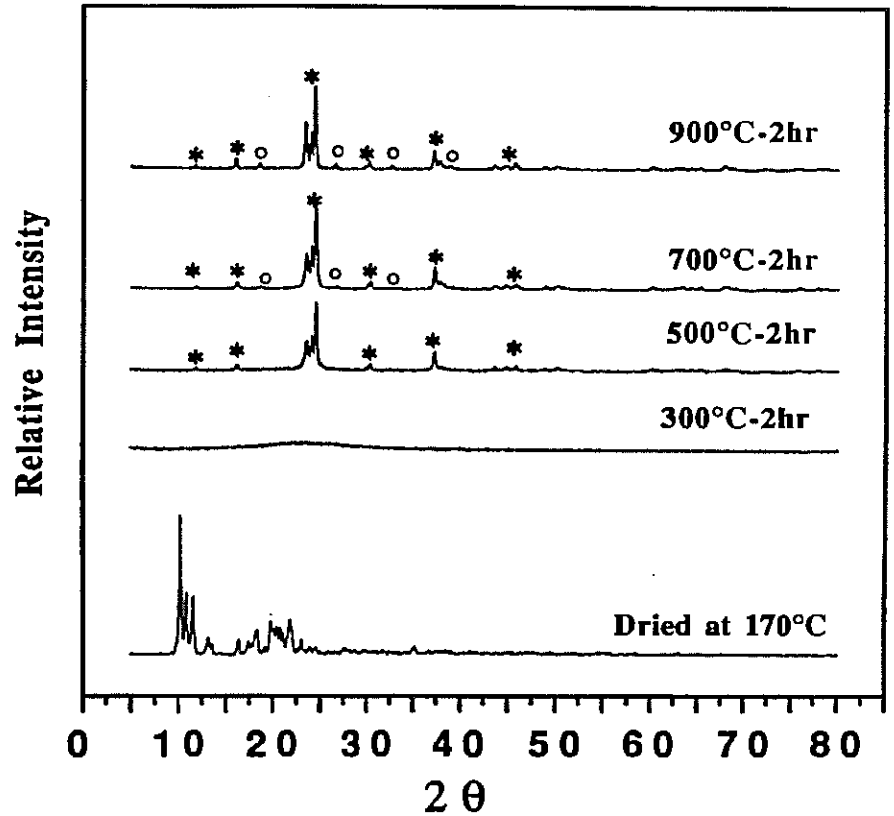
What Can You Do With $M_2Si_2(OCHCHO)_5$?



DTA of $M_2Si_2(OCH_2CH_2O)_5$

What Can You Do With $M_2Si_2(OCHCHO)_5$?

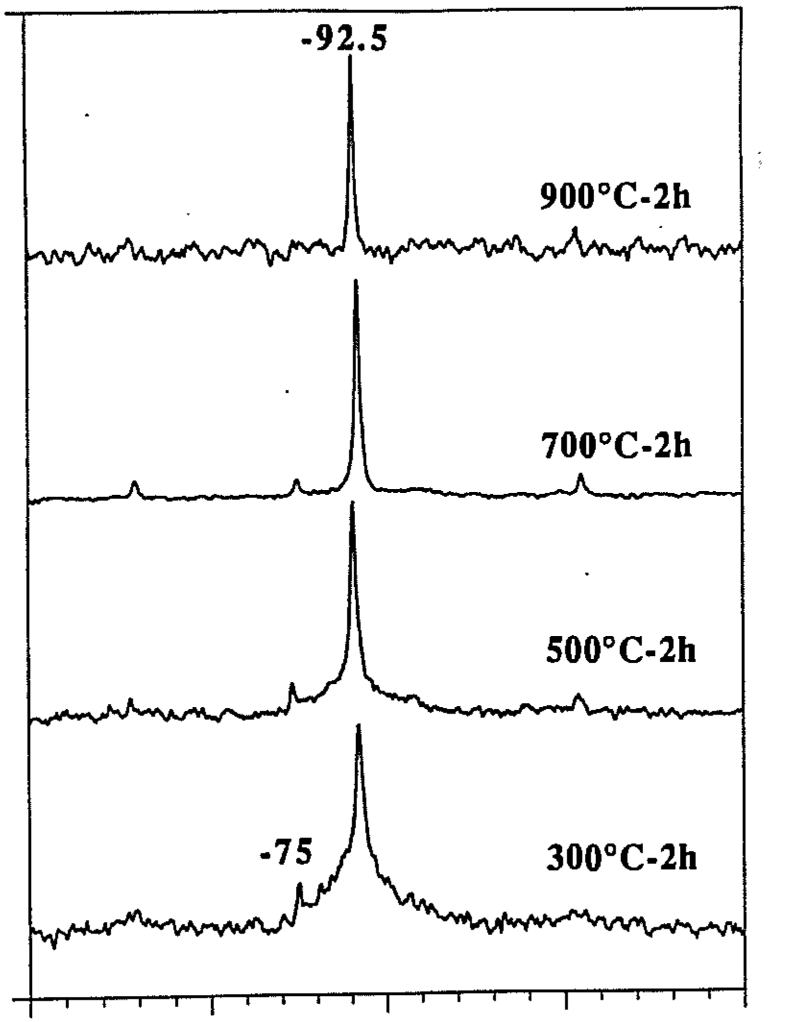
XRD of $Li_2Si_2(OCH_2CH_2O)_5$



*orthorhombic α-$Li_2Si_2O_5$, JCPDS File 17-447

°orthorhombic Li_2SiO_3, JCPDS File 29-829

^{29}Si Solid state NMR of $Li_2Si_2(OCH_2CH_2O)_5$

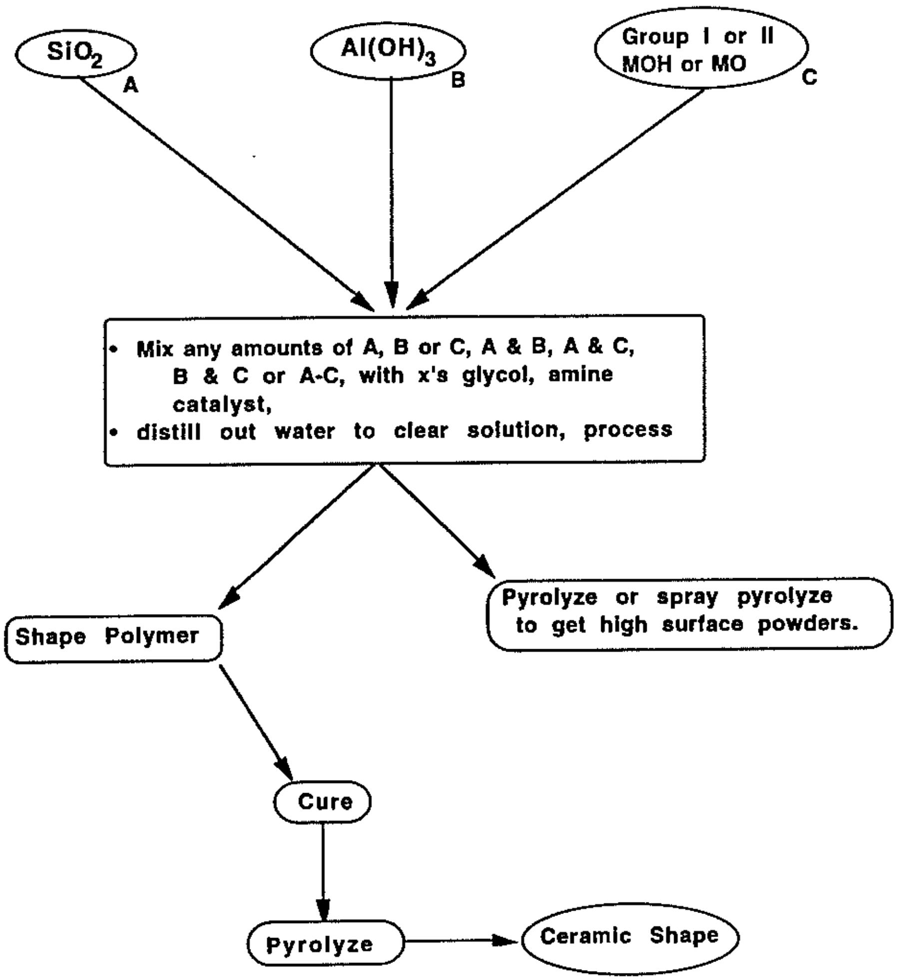


Chemicals, Polymers and Ceramics from the Beach, II.

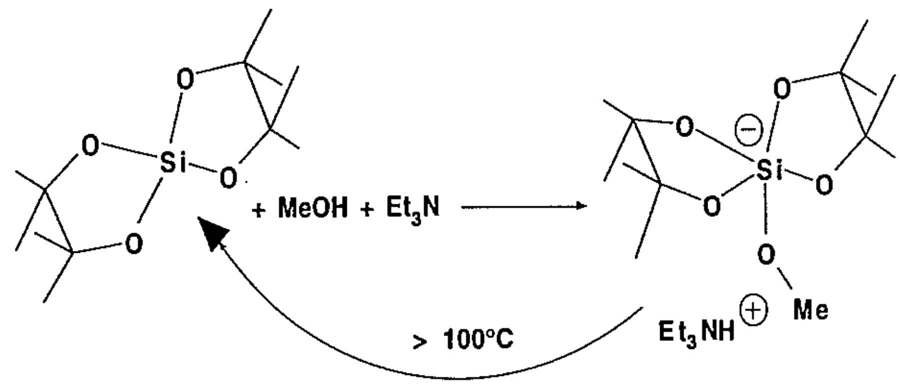
C. Bickmore, K. W. Chew, P. Kansal, T. Hinklin,
B. Mueller, D. Treadwell, K. Waldner,
R. M. Laine & F. Babonneau

Dissolving the Beach with Antifreeze ~~and Liquid Plumr~~

OOPS Process



Background



Frye et al '71

SiO_2

Can we use a catalytic amount of amine to dissolve silica and form neutral tetra-alkoxy silanes?

Requirements:

- High boiling amine--b.p. >> 200°C
- Soluble in polar solvents--ethylene glycol
- Strong base--no aromatic amines

Solution:

Triethylenetetramine: $H(NHCH_2CH_2)_3NH$ bp 266 TETA

Triethanolamine: $HN(CH_2CH_2OH)_3$ bp 277^{150} TEA

SiO_2 + x's $HOCH_2CH_2OH$ $\xrightarrow{\text{TETA/200°C}}$?

Solution clears in 2-100 h of distillation depending on SiO_2:

- Surface area,
- Crystallinity,
- Total volume of $HOCH_2CH_2OH$
- If too much solvent is removed early--gels
- *Also depends on [TETA]*

Recover polymer that:

Crosslinks on vacuum drying with heat

Gives clear, hard plastic

Soluble in Ethylene Glycol

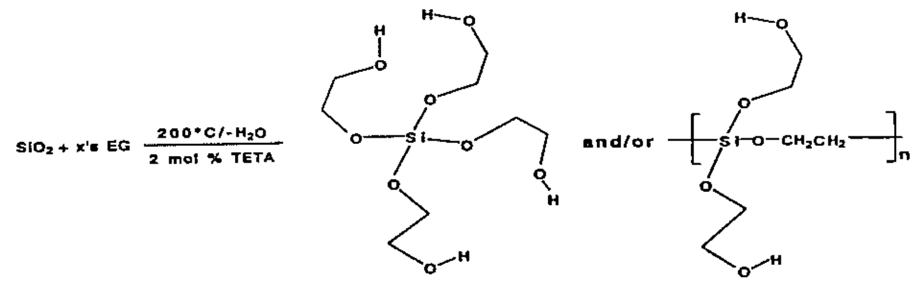
Spinnable?

Characterization

TETA Product: No fragmentation pattern in FABS Mass Spec.

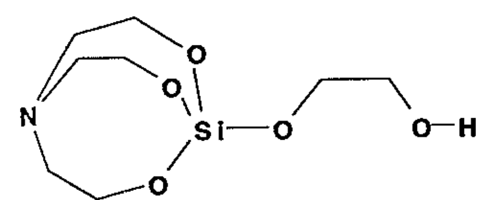
Polymeric material?

^{29}Si NMR, single peak at -82 ppm likely:



Soluble in EG only!!!

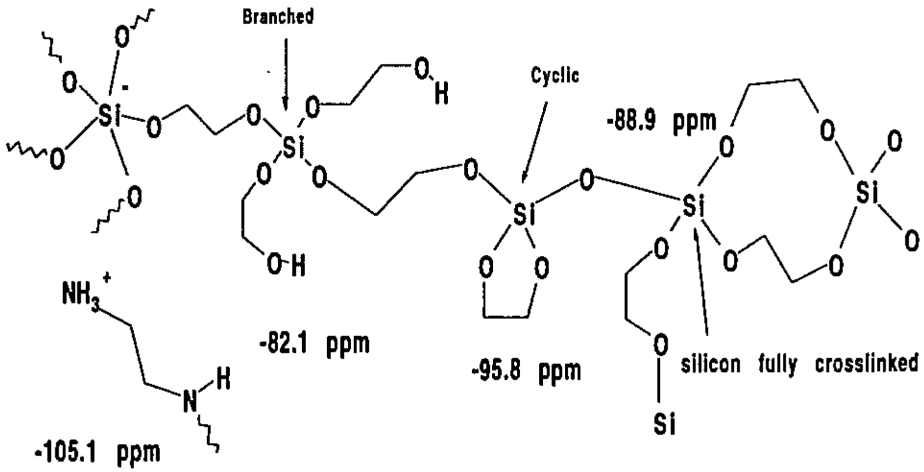
TEA Product: FABS suggests:

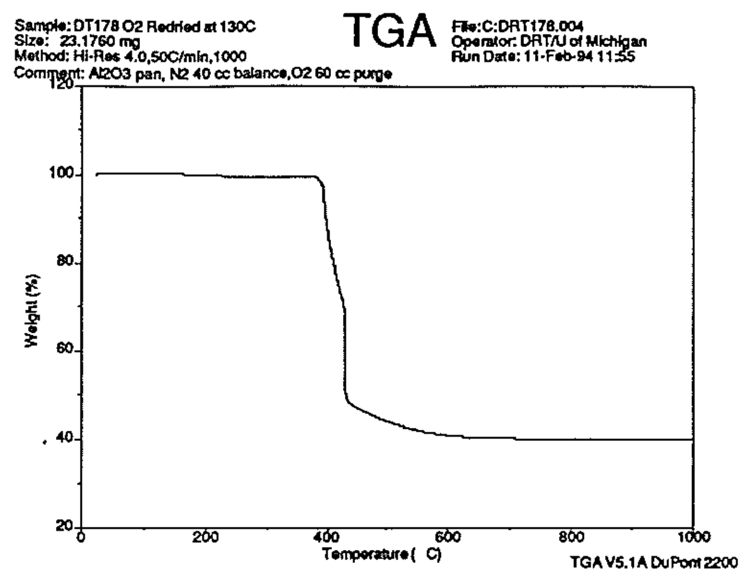


^{29}Si NMR, Single peak at -96.7 ppm (vs TMS)

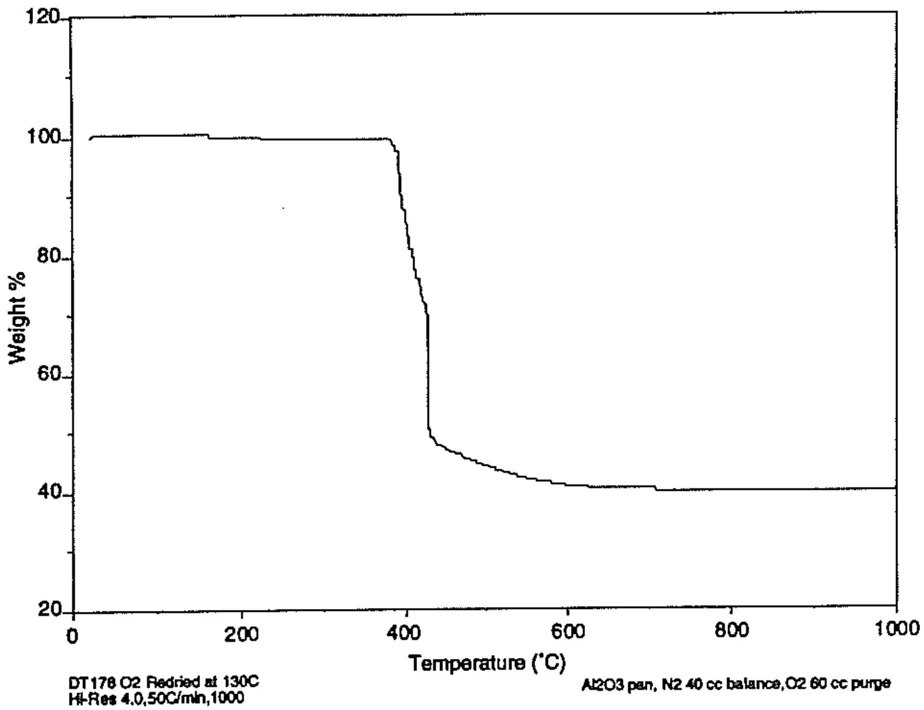
Indicates tetra-alkoxysilanes, no pentacoordinate Si!!!

Solid State ^{29}Si, Idealized Structure:





TGA of $Si(eg)_2$



$Al(OH)_3$ + x's $HOCH_2CH_2OH$ + TEA $\xrightarrow{200°C}$?

<u>Solution clears in 2-4 h</u>:

- When all $Al(OH)_3$ reacts, recover polymer that

  Crosslinks on vacuum drying with heat

  Gives clear, hard plastic

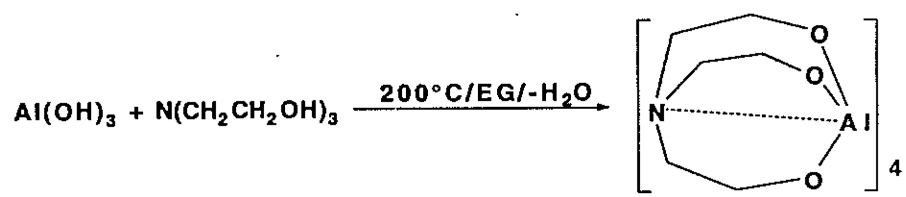
  Soluble in alcohols, CH_2Cl_2

  Melt spinnable?

Will not work with TETA.

<u>Characterization of the Product</u>

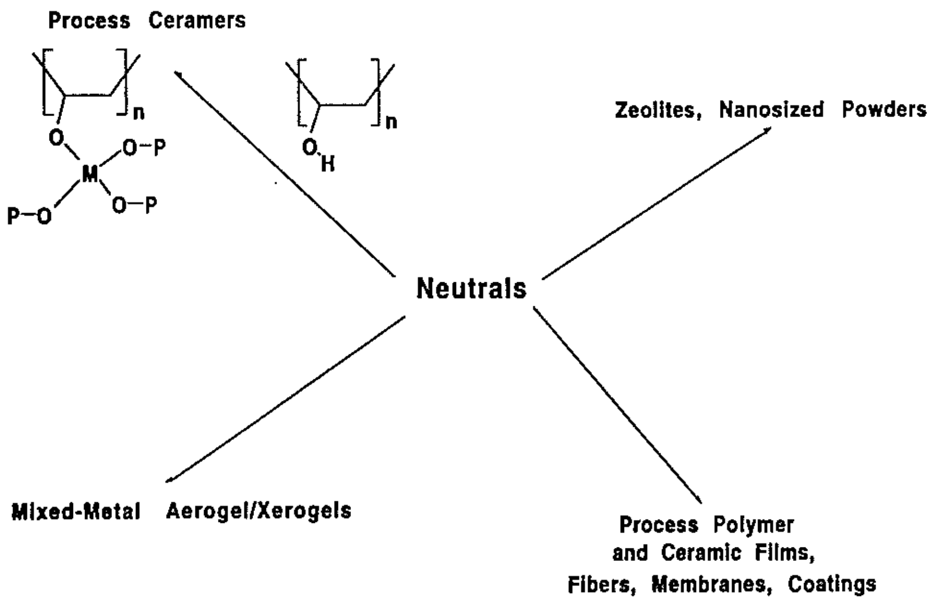
FABS of TEA·Al shows fragmentation patterns that suggest:



^{27}Al (CH_2Cl_2) = 4 ppm (hexacoord.), -60 ppm (tetracoord.)

What Can You Do with Neutral Alkoxides?

What Can You Do with Neutral Alkoxide Complexes?



What Can You Do with Neutral Alkoxide Complexes?

OOPS Process Works for:

Mullite [$2SiO_2 \cdot 3Al_2O_3$]

Spinnable polymer prepared from a mixture of $6Al(OH)_3$ and $2SiO_2$.

Gives phase pure mullite on pyrolysis to 1100-1200°C

Cordierite [$2MgO \cdot 5SiO_2 \cdot 2Al_2O_3$]

Spinnable polymer prepared from a mixture of $4Al(OH)_3$ and $5SiO_2$ and 2MgO.

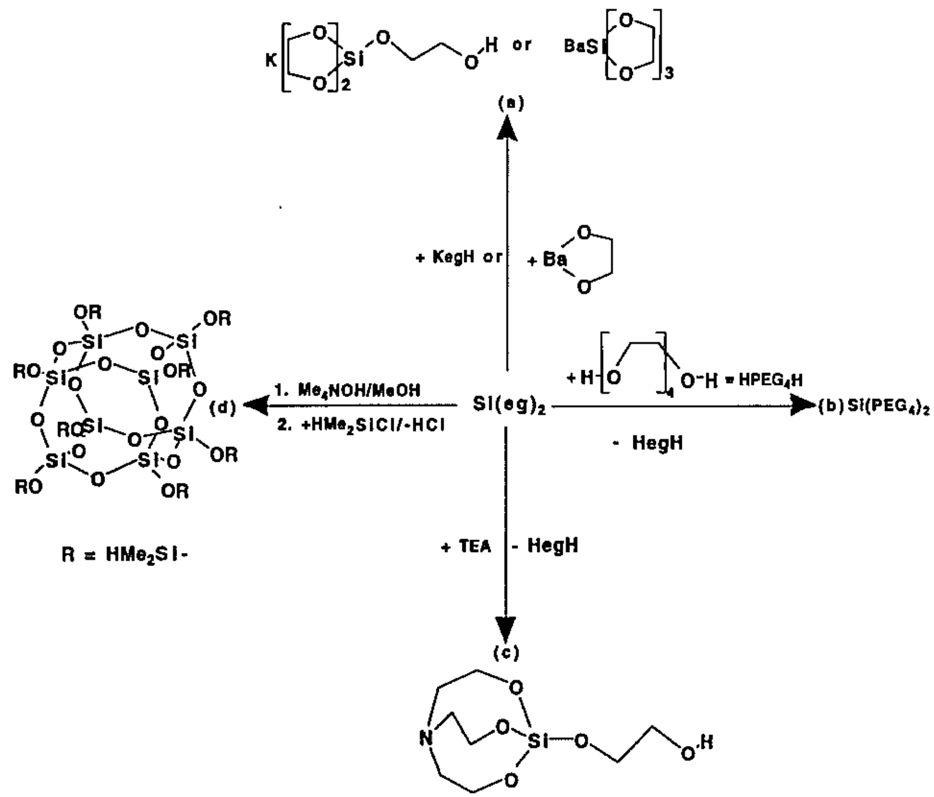
Gives phase pure μ-cordierite at 900°C and ß-cordierite above 1100°C.

Spinel [$MgO \cdot Al_2O_3$]

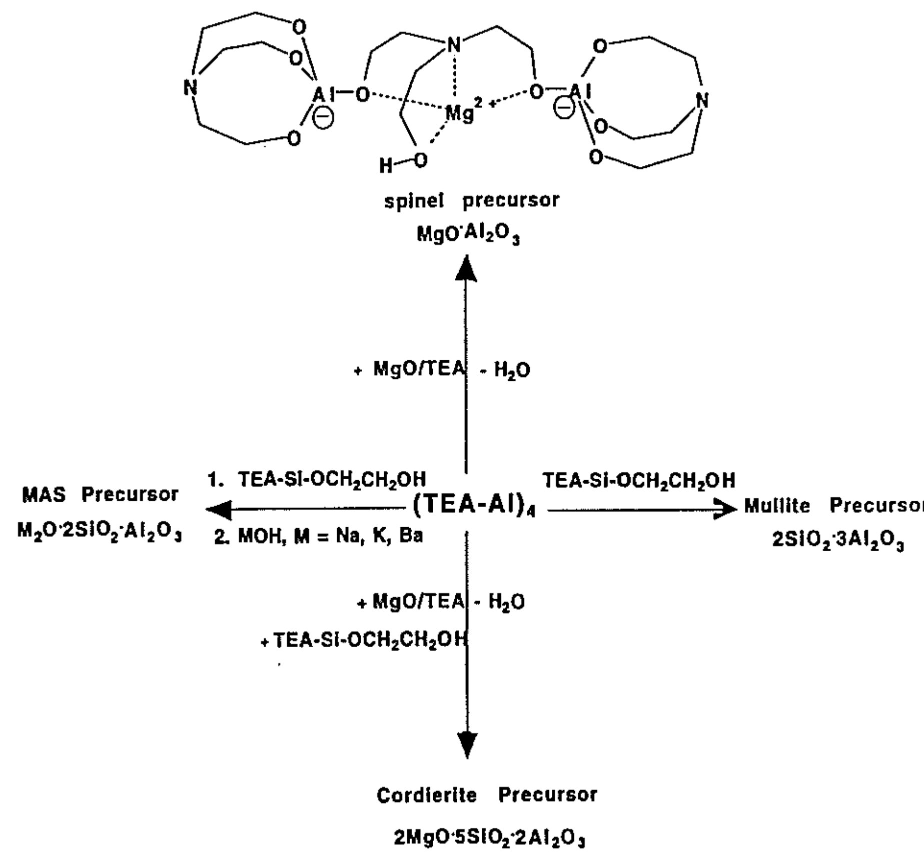
Rheologically useful polymer prepared from a mixture of $2Al(OH)_3$ and MgO.

Gives phase pure Spinel at 1000°C

What Can You Do With It?

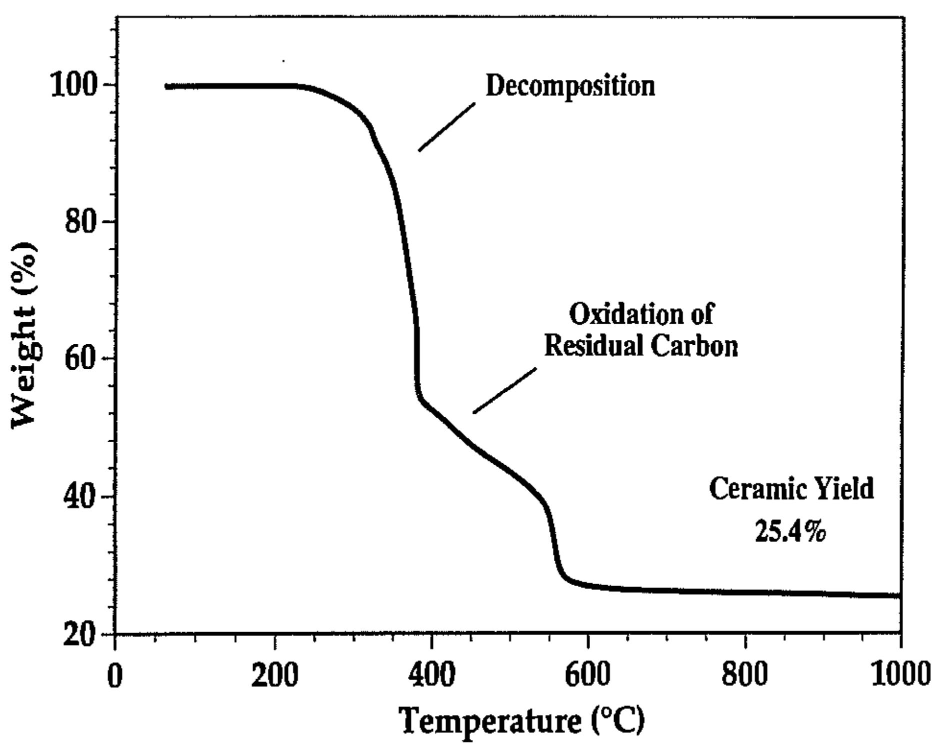


Neutral Oxide Precursors

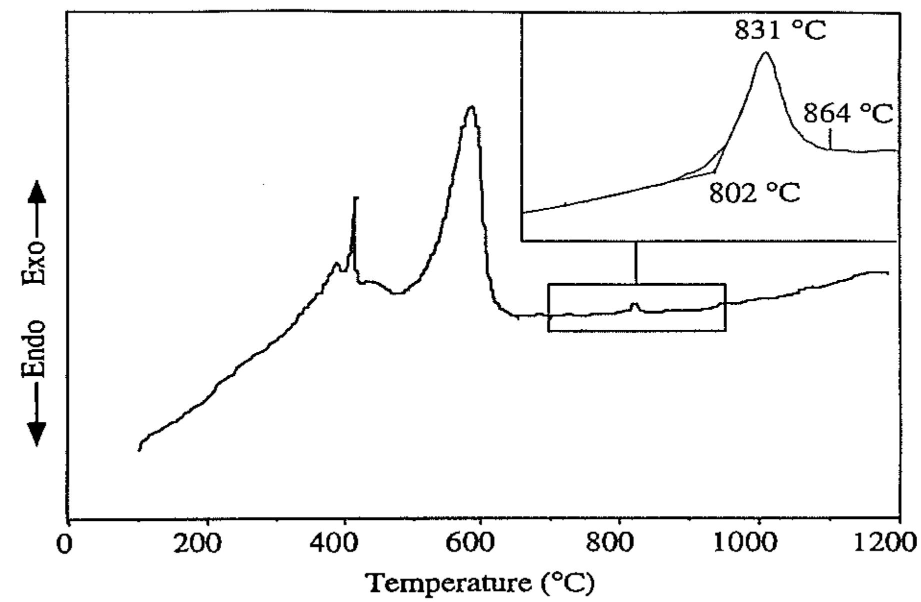


TGA Profile of Spinel Precursor

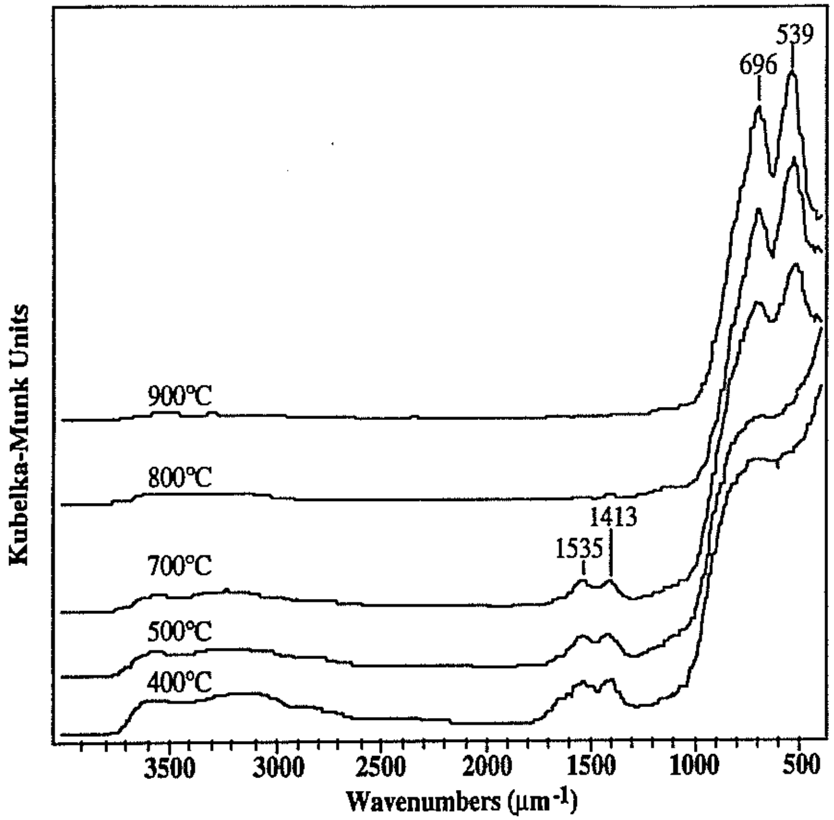
Spinel = $MgAl_2O_4$



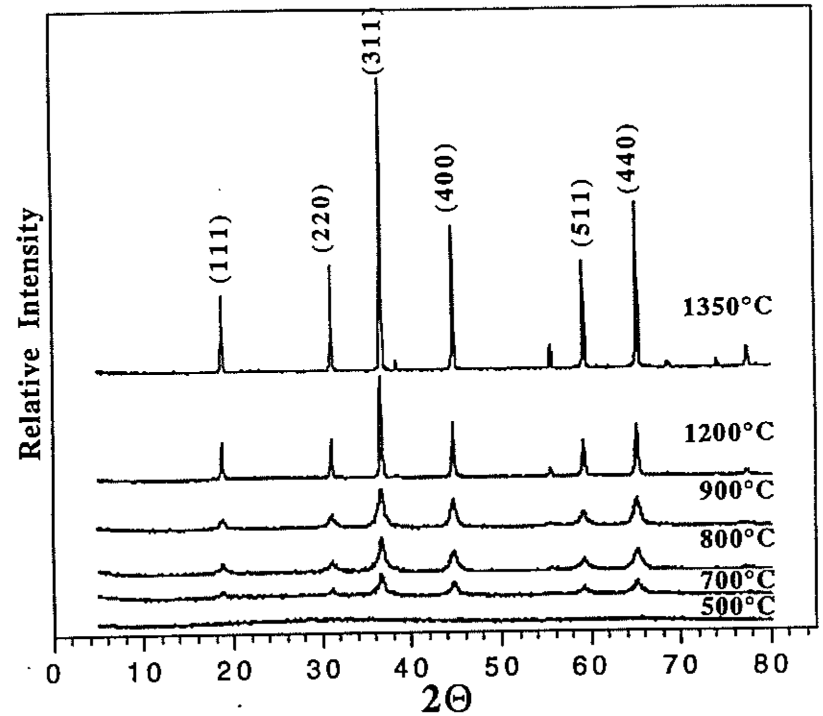
DSC Profile of Spinel Precursor Heated.



DRIFT Spectra of Spinel Precursor Heated to Selected Temps.

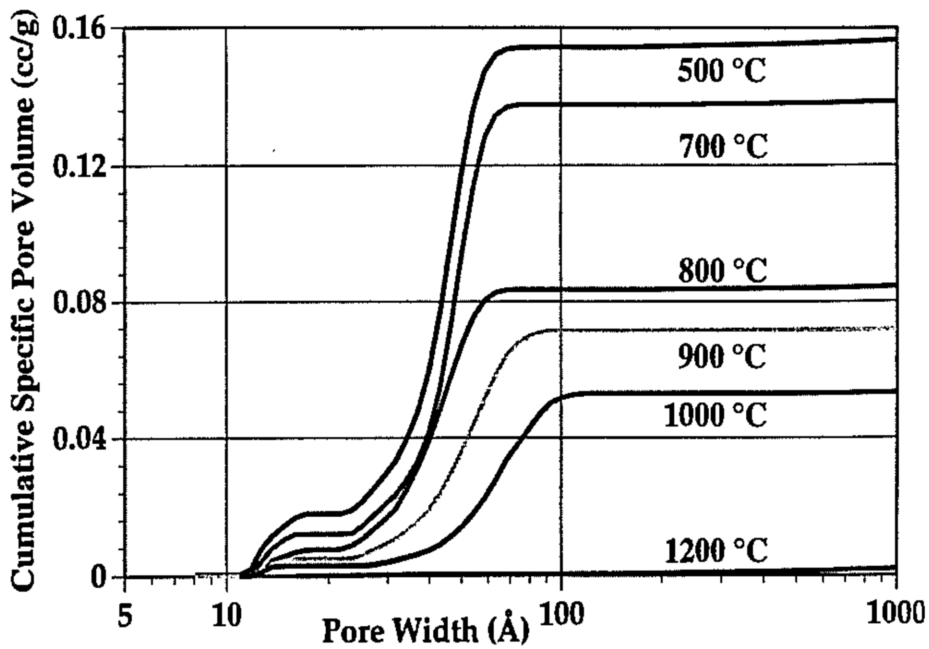


XRD Pattern of Spinel Precursor Heated to Selected



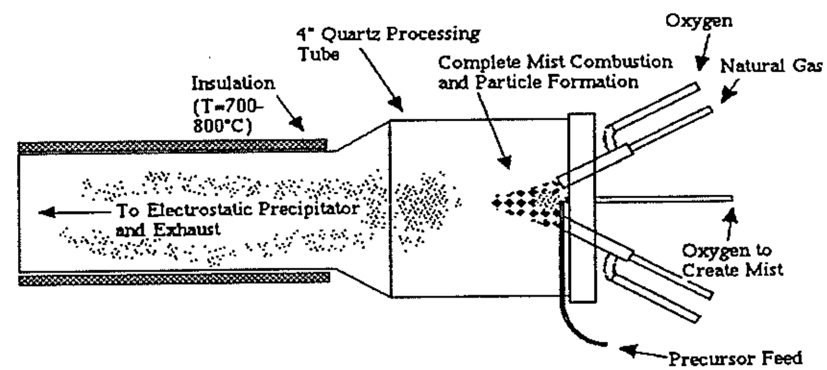
Cumulative Pore Volume for Samples Heated to Selected Temps.

500°C ≈ 200 m^2/g

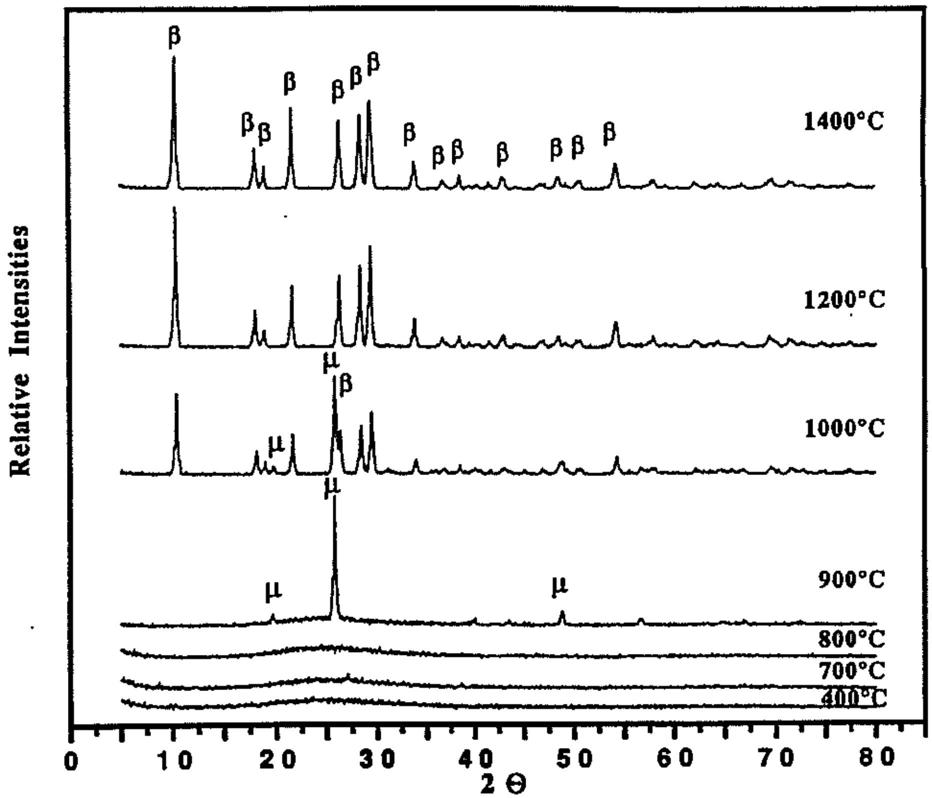


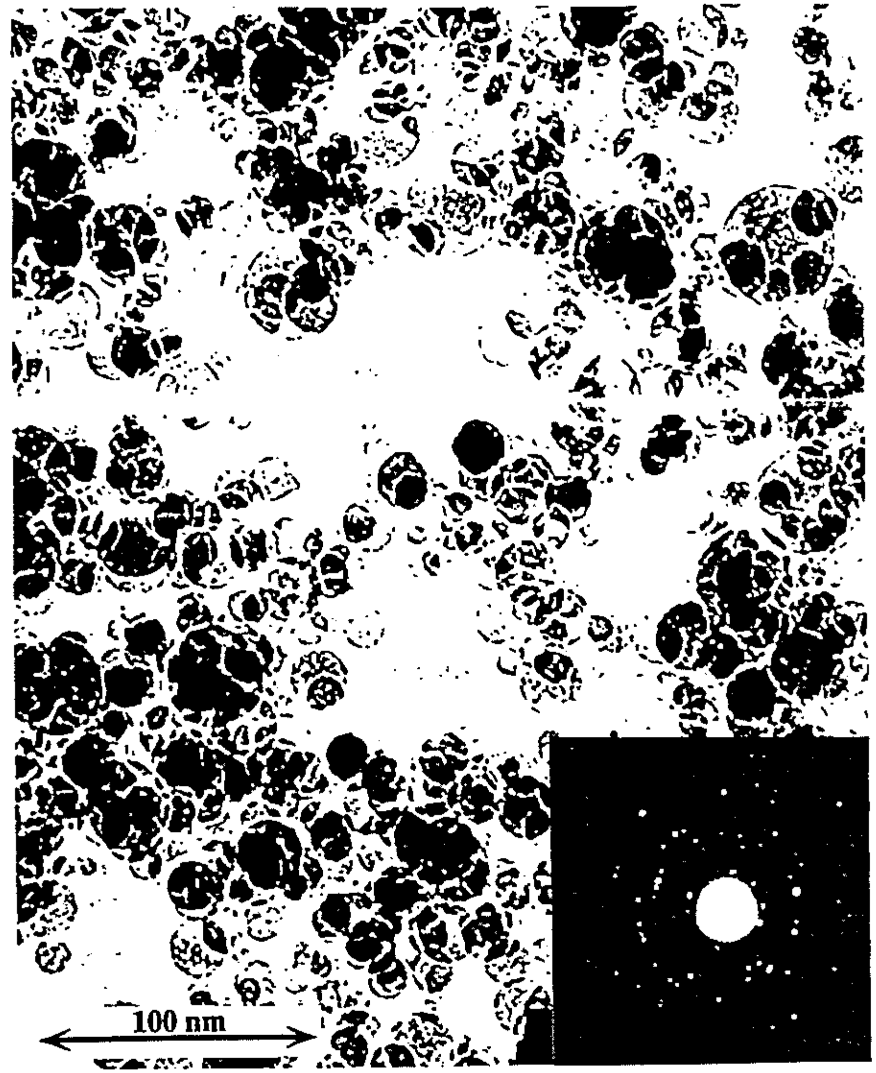
Spray Pyrolysis Unit:

Flame Pyrolysis Combustion Chamber



Powder X-Ray Diffraction of Cordierite Precursor
Pyrolyzed for 4 Hours in Flowing Air





Conclusions

Directly from SiO_2 synthesize:

- tetra-alkoxysilane monomers and oligomers
- penta-alkoxy, aryloxy silicate monomers and oligomers
- hexa-alkoxy, aryloxy silicate monomers

Directly from $Al(OH)_3$ synthesize:

- trialkoxyaluminane monomers and oligomers

From mixtures of SiO_2, $Al(OH)_3$ + other MO_X synthesize:

- Wide variety of aluminosilicate polymer precursors

Can make materials with following properties:

NLO

High Temperature LCs

Ion Conducting polymers

Preceramic Polymers

Ceramic powders, films, fibers

Composites

Paul Calvert	Polymer/Inorganic Composites via Biomimetic Processing
Emanuel Giannelis	Design, Synthesis and Properties of Polymer Matrix Nanocomposites
Bruce Novak	Mutually Interpenetrating Organic-Inorganic Networks: Synthesis, Structure and Properties

BIO-MIMETIC COMPOSITES

Paul Calvert
University of Arizona

Bone Compared to Synthetic Short Fiber Composites
Microstructure and Properties

Organic-Inorganic Hybrids

In situ Precipitation of Elongated Particles

In situ Precipitation in Crystalline Polymers

Biomimetic Composites

Summary

Bone is a composite material with good strength, stiffness and toughness. An equivalent synthetic material could have many applications as a replacement for metal in structures.

Various approaches to organic-inorganic hybrids let us replicate the morphological characteristics of bone: very fine particles, high volume fractions, elongated particles, tough matrices and good adhesion. Interesting materials can be formed, such as surface hardened polymer sheets. However, the materials always be come brittle as they become stiff, in exactly the same way as do normal composites.

A second look at bone shows that its toughness is due to microcracking which arises from a layered structure at the 10μm level, <u>not</u> from the fine scale structure. The secret is in the hierarchy.

We have recently been working on one of a family of solid freeform fabrication methods. These offer a route to the formation of hierarchical structures. Since, like bone, the material is formed layer by layer, these methods also allow chemical formation of materials as opposed to conventional thermal processing.

Properties of Synthetic and Biological Composites

	Volume Fraction,%	Tensile Modulus, GPa	Tensile Strength MPa	Strain to break, %	Work of Fracture J m^{-2}
Continuous fiber PEEK/AS4, Parallel	61	140	2200	1.5	1900
Continuous fiber PEEK/AS4, Perpendicular	61	8.3	73		
Sheet Molding compound (resin + filler + fiber)	50, 15-30% fiber	15	86-230	1.3-1.7	
Polybutyleneterephthalate/ glass beads	25	4.9	95		
Polyethyleneterephthalate + short glass fiber	35	20	165	1	3200
Bone (bovine femur)	41	20	220	10	1700
Collagen (tendon)	0	3	100		
Hydroxyapatite	100	110	100		
Polyethyleneterephthalate	0	3.3	60	275	7300
E glass	100	70	3000		

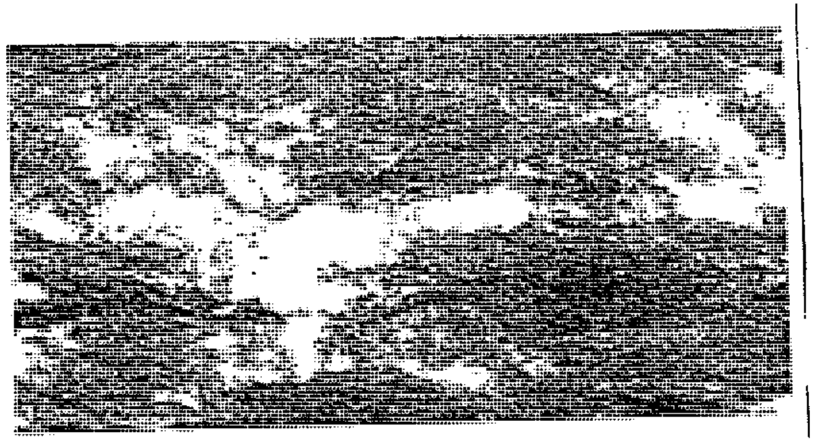
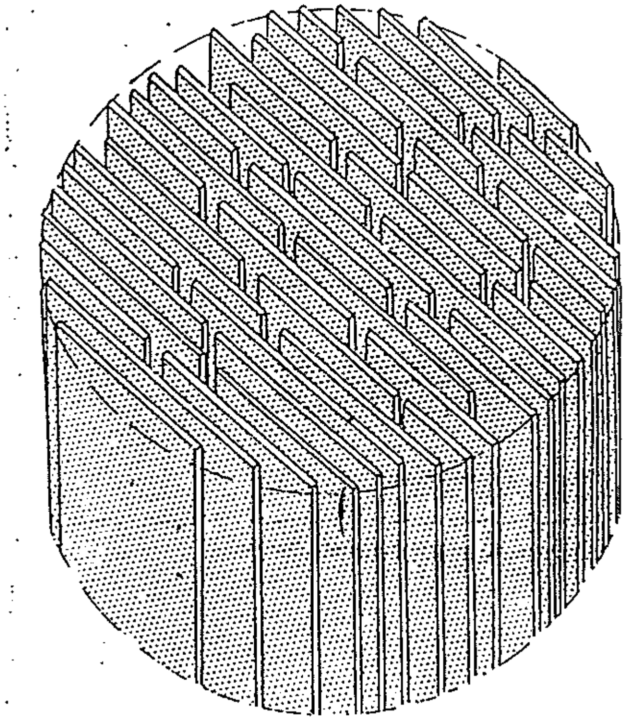
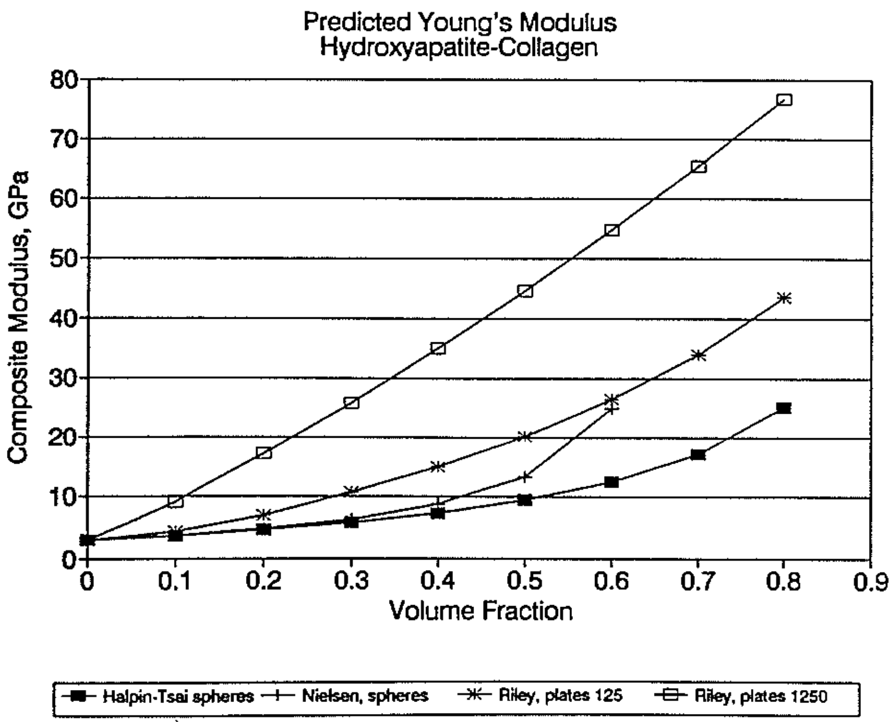


FIGURE 3. Area of advanced calcification in osteonic bone: needle- and filament-like crystals partially mask the inorganic substance in bands (compare with Figure 2). Unstained, original magnification × 80,000.

E Bonucci



Bone : Hydroxyapatite plates in collagen fibril



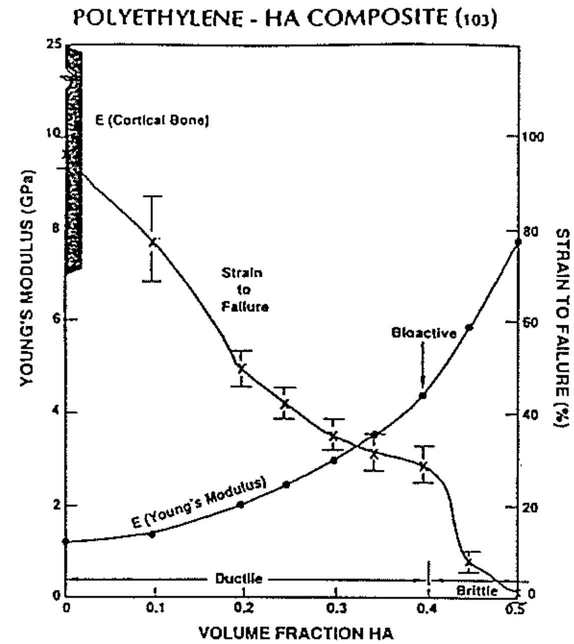


Figure 11. Effect of HA on Young's modulus and strain to failure of a polyethylene-HA composite. (Based on data of Reference 102.)

Bone as a Composite

Nanosized reinforcing particles

Ribbon-like reinforcement

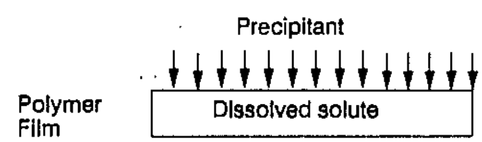
High Volume fraction, oriented packing

Tough matrix

Good Interfacial Bonding

Hierarchical Structure
  Fracture toughness by microcracking ?

IN-SITU PRECIPITATION



SOLUTE	PRECIPITANT	PRECIPITATE
Iron (III) chloride	Base	Haematite, Magnetite
Titanium Isopropoxide	Water	Titania (amorphous)
Titanium Isopropoxide/ Barium Isopropoxide	Water	Barium titanate
Water	Silicon tetraethoxide	Silica --> Silicon carbide
Iron (III) Chloride	Reducing agents	Iron
Zirconium Isopropoxide	Water	Zirconia
Cadmium chloride	Di(trimethylsilyl)sulfur	Cadmium sulfide

Polymers: PMMA, PBuMA, PVF2, Polyethersulfone, Cellulose

Size Control in Titania Mineralization

Phase separation:

Scale about 1 μm in polymer

Diffusion controlled growth

$$r^2 = D(C-C_s)t$$

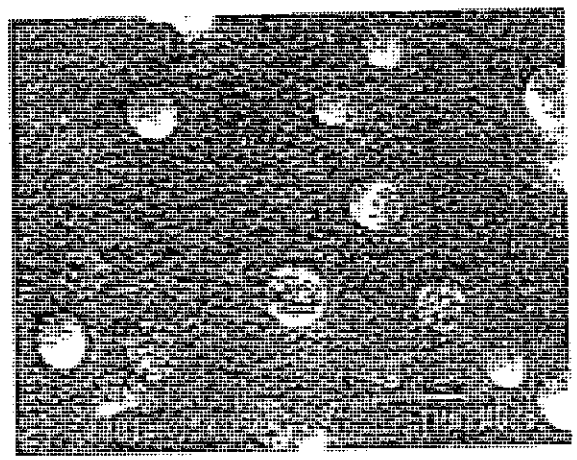
$D=10^{-5}$-10^{-8} cm^2s^{-1}, c=1-10% and t=100 sec..

Precipitation by reaction:

Homogeneous system, followed by reaction
A nucleation concentration must be reached
The growth concentration is then close to this:

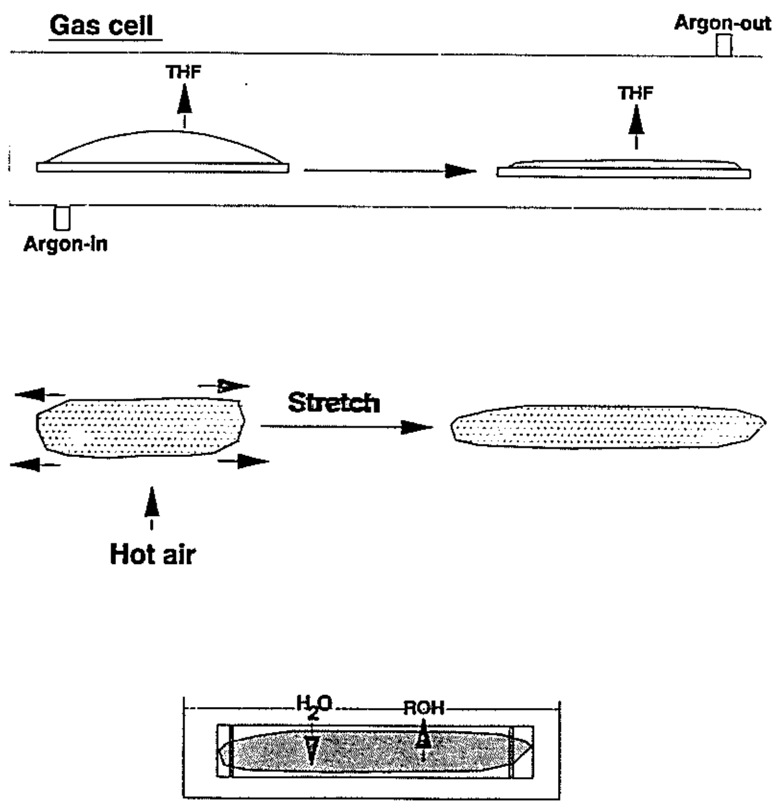
$$r^2 = D(C-C_s)t$$

Now $D=10^{-8}$-10^{-12} cm^2s^{-1}, C is low: 10^{-3}-10^{-5}, and $t=10^4$s.
The resulting r is 0.1 μm or less.

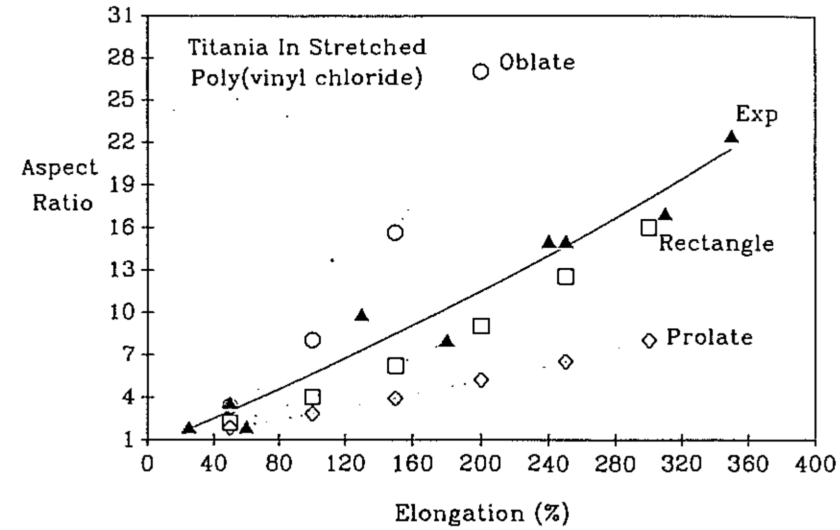


Spherical Barium Titanate particles in an Acrylate matrix

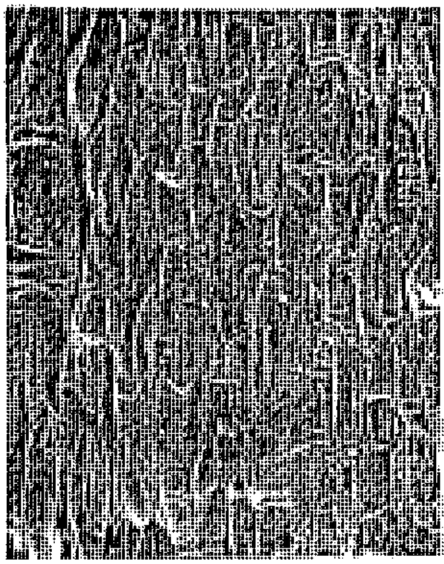
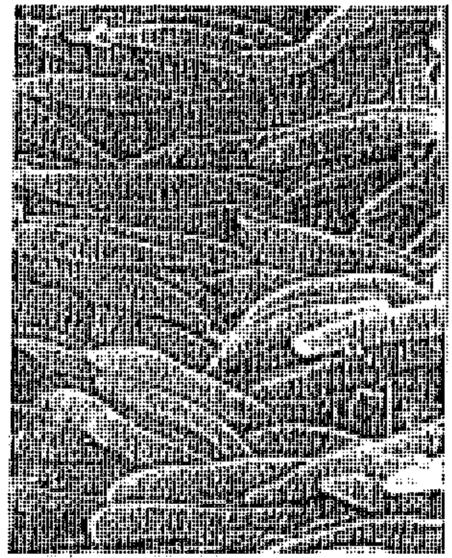
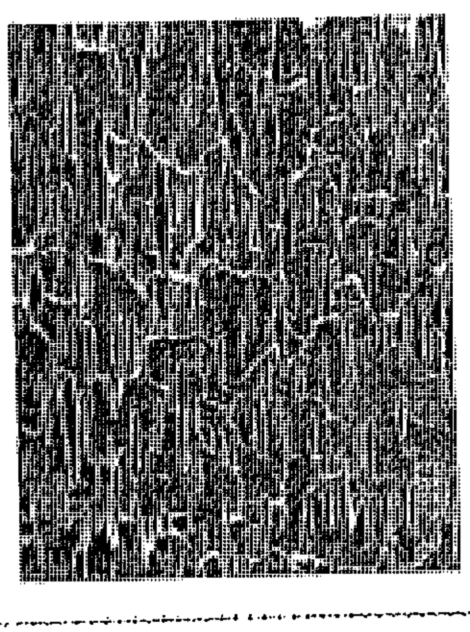
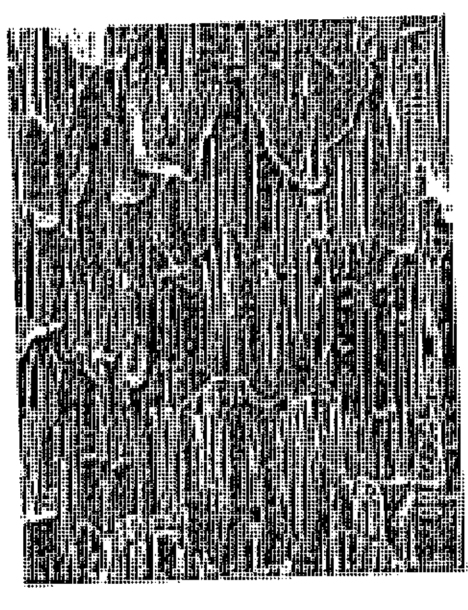
Preparation of Oriented Samples



Clamp sample and hydrolyse.



- Prolate Ellipsoid formation ?
- Selective axis constriction during draw process in film
- Close to rectangular A.R pattern

MELT PROCESSING

Polypropylene + 0-60 wt% Titanium butoxide
+ Potassium Benzoate (Nucleating Agent)
+ Tristearyl titanium isoproxide (coupling agent)

Extrude 180°C, hydrolyze 12 hours 100°C.

PROCESSING

Miscibility in Melt
- Can be achieved by match of solubility parameters

Extrusion
- Titanium Alkoxide reduces melt viscosity

Crystallization
- Nucleation
- Delayed Crystallization
- Rejection

Reaction time
- D (100°C) 10^{-6}-10^{-7} $cm^2.s^{-1}$, Diffusion time(100 μm)=100-1000 sec.

Particle Size & Shape

Coupling Agent

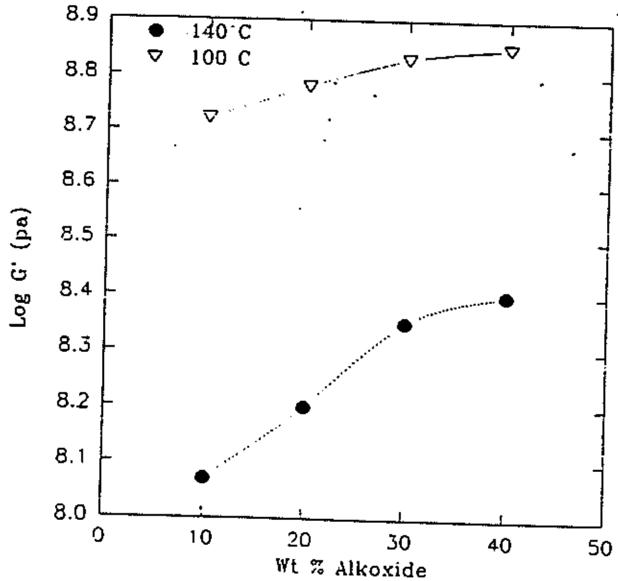


Figure 11 : Effect of temperature on modulus

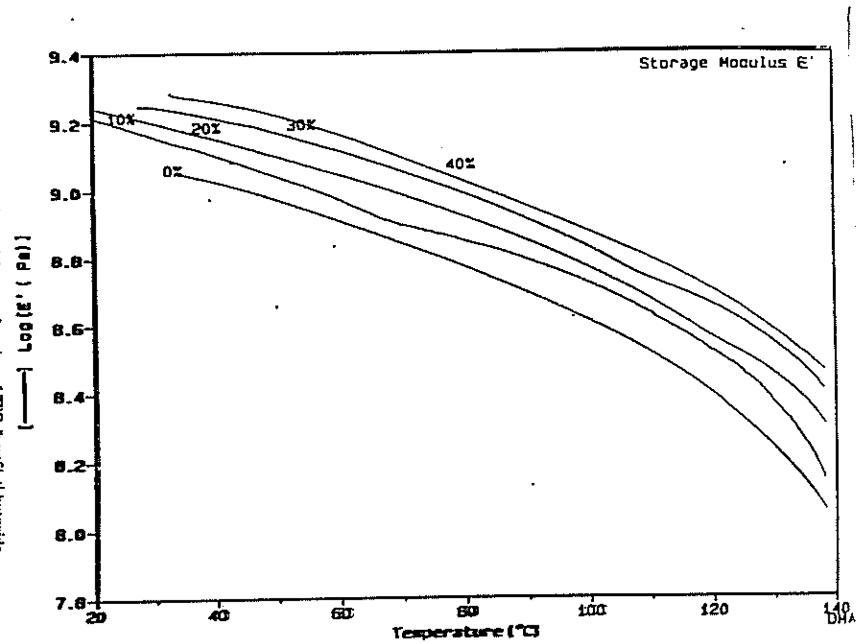


Figure 9 : Dynamic modulus as a function of T°C & wt% ti-butoxide

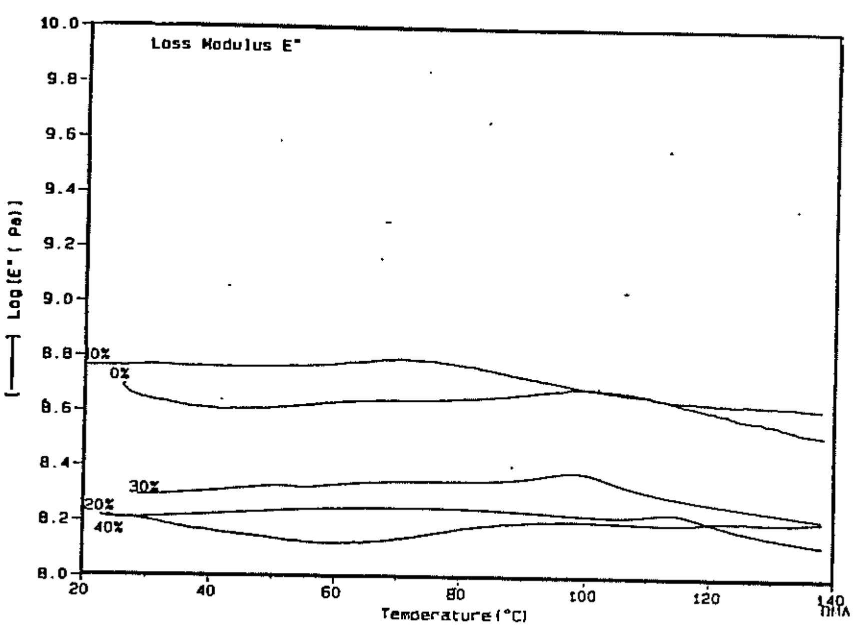


Figure 12 : Loss modulus as a function of T°C & wt% ti-butoxide

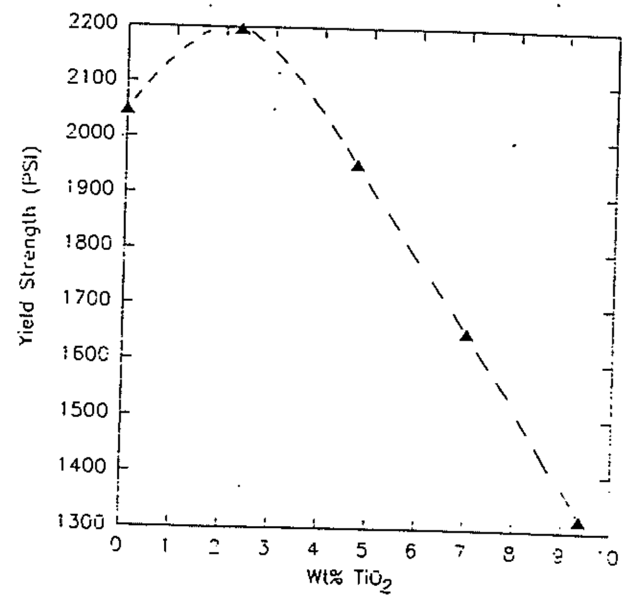


Figure 14 : PP/TiO_2 Composite Strip Yield Strength

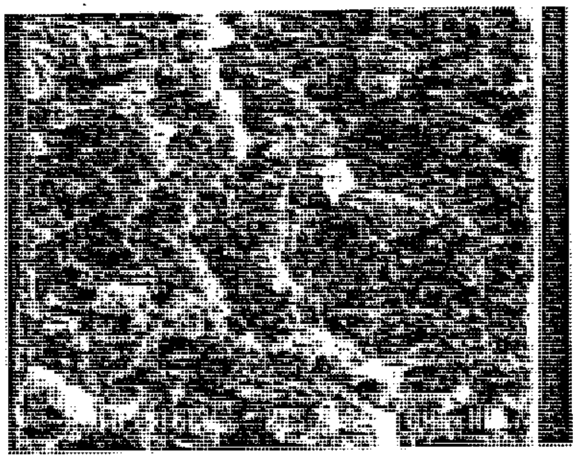


Figure 28 : Tensile specimen fracture - 9.38% TiO_2 composite

Figure 29 : Tensile fracture surface closeup - 9.38% TiO_2 composite

CONCLUSIONS

Suppression of Segregation

Interspherulitic Fracture vs Uniform Yield

Microstructural Control

Interfacial Strength

$Si(NCO)_4$

bp 185.6 °C
mp 26 °C

$$Si(NCO)_4 + 4\,H_2O \rightarrow Si(OH)_4 + 4\,HNCO$$

$$4\,HNCO + 4\,H_2O \rightarrow 4\,NH_3 + 4\,CO_2$$

Sorption Results

140 °C, 1 hr.	Film mass before imm. (g)	Film mass after imm. (g)	% Change
Biaxially Oriented	0.1183	0.1236	4.5
	0.1687	0.1781	5.6
	0.1491	0.1814	5.4
Amorphous A-150	0.1512	0.1814	20.0
	0.1798	0.2138	18.9
	0.1488	0.1771	19.0

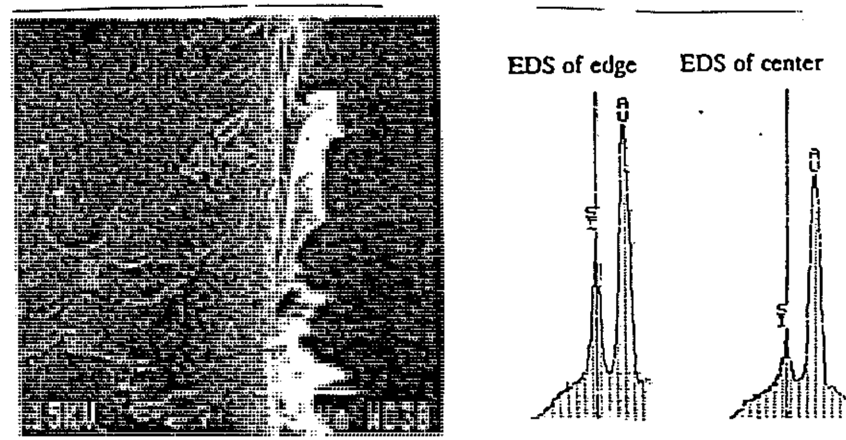


Fig. 2. SEM micrograph/EDS spectra of cross section of $Si(NCO)_4$ treated film. Edge & bulk regions of film are denoted by 1 & 2 respectively.

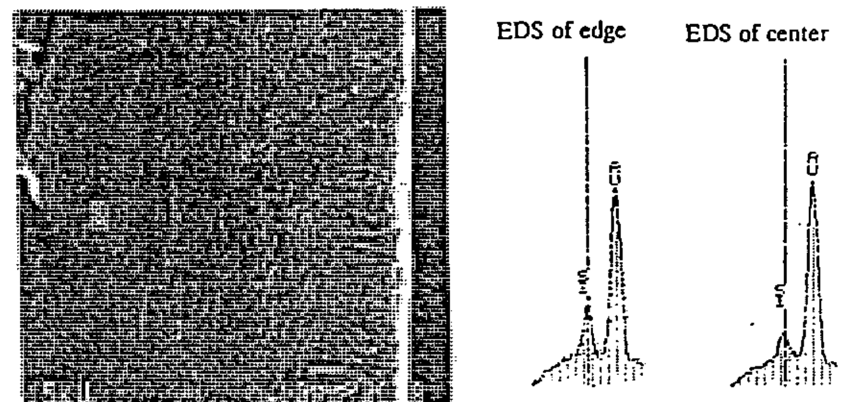


Fig. 3. SEM micrograph/EDS spectra of cross section of $Si(NCO)_4$ treated film washed in $CHCl_3$. Edge & bulk film regions denoted by 1 & 2 respectively

Table I
Hildebrand solubility parameter values for selected organosilanes

Silane	δ (cal/cc)$^{1/2}$
$SiCl_4$	7.82
$Si(OMe)_4$	8.51
$Si(OEt)_4$	6.83
$(MeO)_2Si(O\text{-}Ph\text{-}Me)_2$	9.21
$(EtO)_2Si(O\text{-}Ph)_2$	9.20
$Si(NCO)_4$	9.41

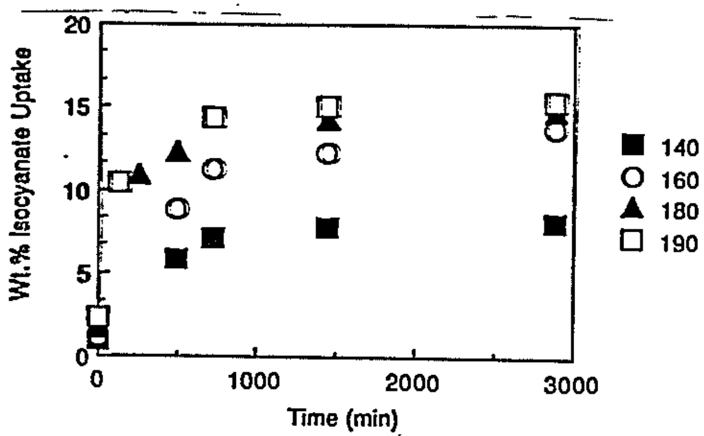


Fig. 1. Sorption isotherms of $Si(NCO)_4$ vapor in Melinex 442 PET film

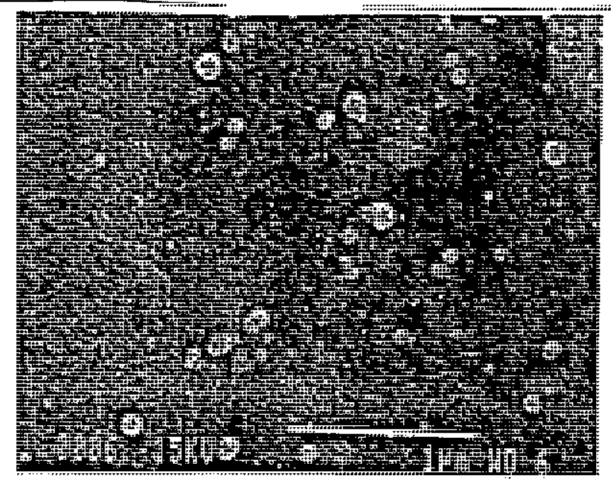
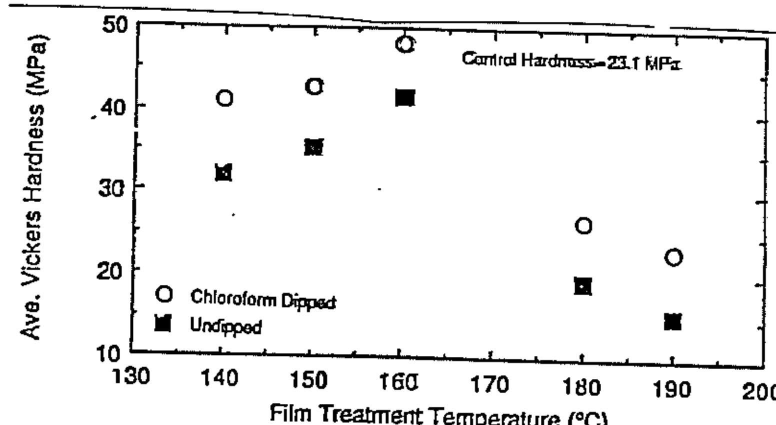
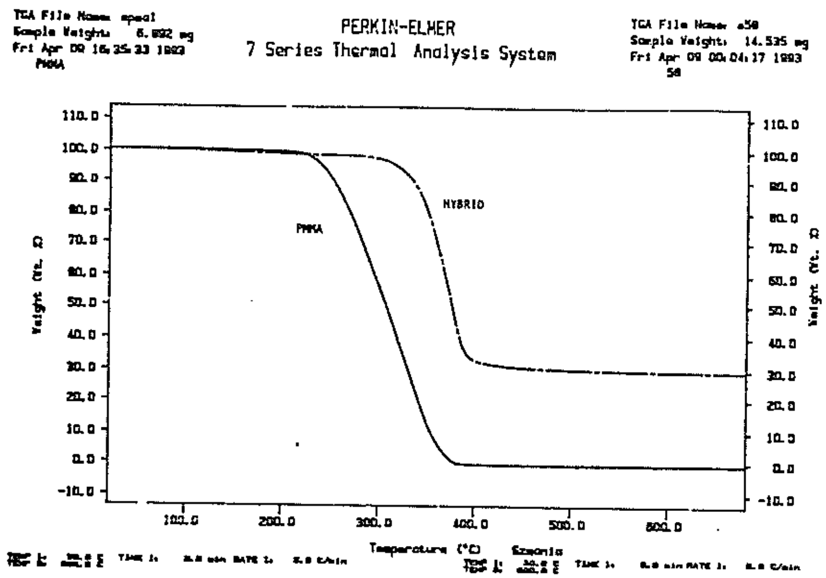


Fig. 5. SEM micrograph of $Si(NCO)_4$/steam treated film cross section
Note white spheres are silica particulates.



ig. 4. Hardnesses of $CHCl_3$ washed & unwashed $Si(NCO)_4$/steam treated PET films



ORGANIC-INORGANIC HYBRIDS

Moldable, high stiffness composites

In Situ Precipitation: Small Particles, no agglomeration
Silica + Various Polymers:
- Amorphous and Crystalline
- Polar and Non-Polar
- Glasses and Rubbers

Volume Fractions 10-50%
Particle Size nm-μm
Spherical (except for intercalated clays)
Interfacial coupling is important

Modulus behaves as expected, but still embrittles at high volume fraction.

Figure 9.4. Scanning electron micrograph of a broken section through the end of the tibia of a young rat. The upper bulbous portion is the epiphysis and below that is the metaphysis. The zone bordering the two is the epiphyseal growth plate. Scale bar: 1 mm.

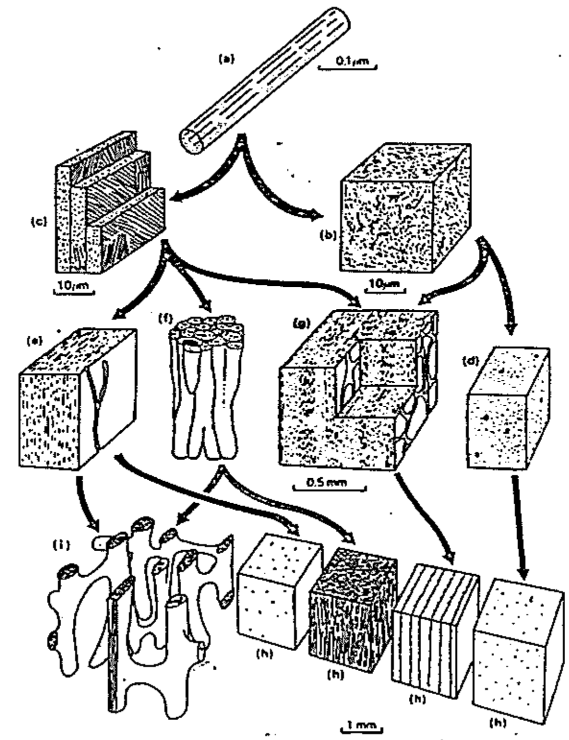


Fig. 5.14 Diagram showing the structure of mammalian bone at different levels. Bone at the same level is drawn at the same magnification. The arrows show what types may contribute to structures at higher levels.
(a) Collagen fibril with associated mineral crystals.
(b) Woven bone. The collagen fibrils are arranged more or less randomly. Osteocytes are not shown.
(c) Lamellar bone. There are separate lamellae, and the collagen fibrils are arranged in 'domains' of preferred fibrillar orientation in each lamella. Osteocytes are not shown.
(d) Woven bone. Blood channels are shown as large black spots. At this level woven bone is indicated by light dotting.

Hierarchical Structures

Bone

Control at nanometer level
- Composition
- Size
- Orientation

Control at micron level
- Phase separation
- Crystallization

Control at Millimeter Level
- SFF: Solid Freeform Fabrication

Functional Gradient Materials

SOLID FREEBODY FORMING OF COMPOSITES AND CERAMICS

Kevin Stuffle and Tony Mulligan
Advanced Ceramics Research Inc, Tucson

John Lombardi, Brian Fabes and Paul Calvert
University of Arizona

Solid Freebody Forming Methods

System and Products

Advantages of Layerwise Processing

Limitations of *In Situ* Polymerization

Solid Freebody Fabrication Methods
Layerwise Processing

Stereolithography
- 3D Systems Inc.
- Prototypes & some usable parts

3D Printing
- Sachs, Cima et al., MIT, E-systems
- Molds

Selective Laser Sintering
- Marcus, Barlow et al., U. of T. Austin, DTM (B.F. Goodrich)

Fused Deposition Modelling
- Stratasys Inc.

Laser Cut and Weld

CNC Machining

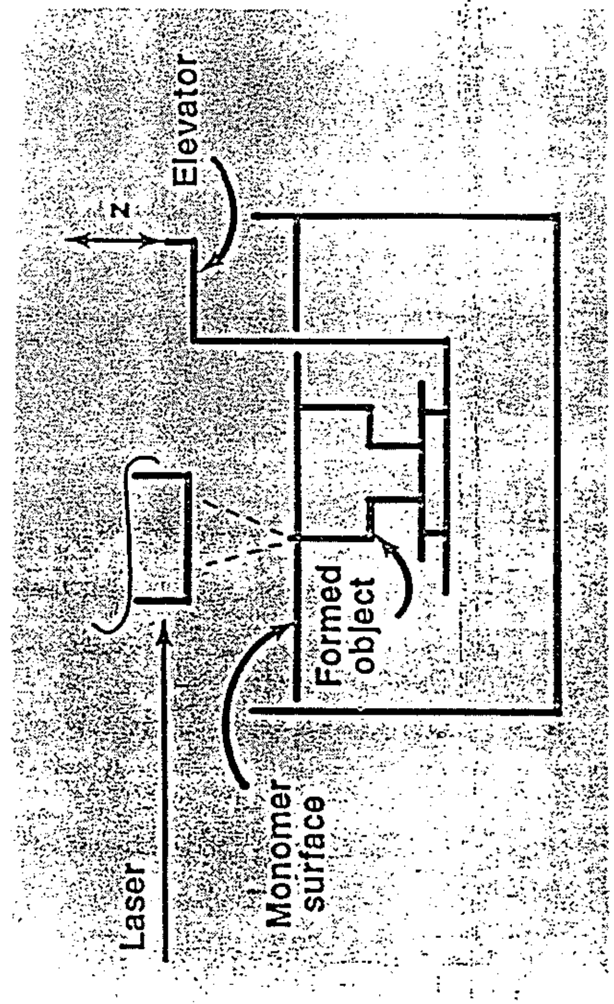
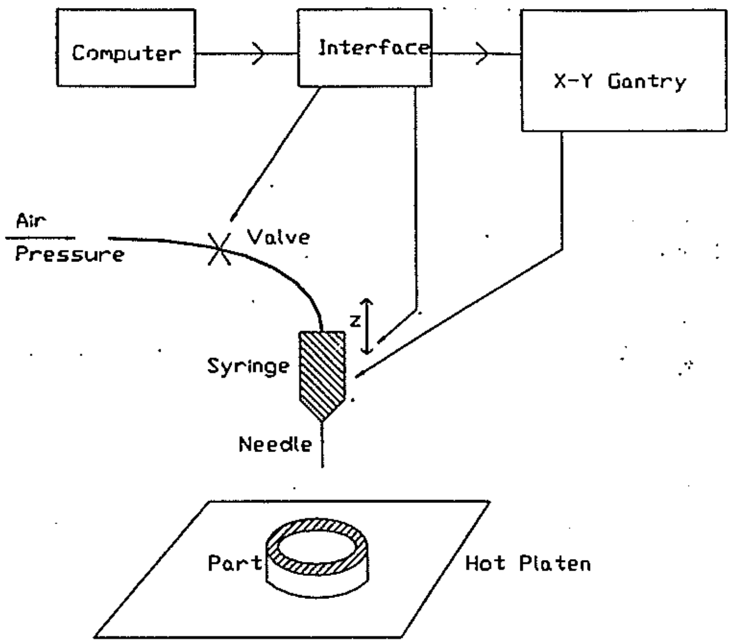
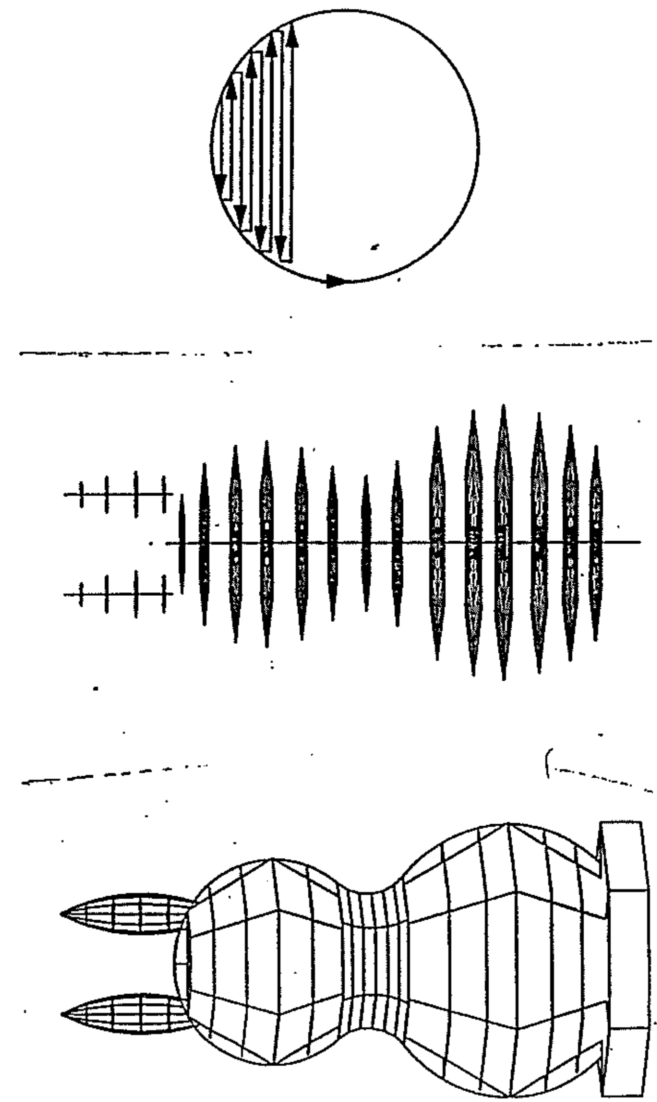


Figure 1. The stereolithography apparatus





Filling Pattern

Table 1: Composition of Acrylic Monomer Formulations

Alumina, wt%	26.2	34.0	39.5	42.5	45.1	47.7	48.9
Triton X-100, wt%	7.8	10.1	10.3	9.8	9.3	10.8	10.5
TMPTA, wt%	3.4	4.4	4.0	3.8	3.6	3.6	3.2
HODA, wt%	29.6	38.3	34.5	32.8	31.3	28.2	27.9
DBE, wt%	32.9	13.1	39.5	11.2	10.7	9.7	9.5
Mill time, hr	24	24	21	21	41	49	49
Density, g/ml	1.54	1.75	2.01	2.00	2.16	2.19	2.23
Viscosity, P	6	12	29	50	112	127	146

HODA: Hexanedioldiacrylate, TMPTA: Trimethylolpropanetriacrylate, DBE: Dibasic ester, plasticizer (dimethylglutarate + dimethylsuccinate).

Properties:
Green Density 60%
Fired Density 90-99%
Flexural Modulus 358 GPa
Flexural Strength 430-600 MPa

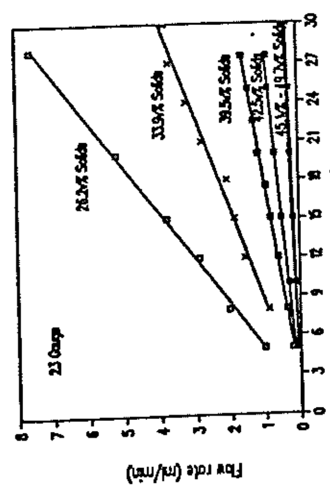
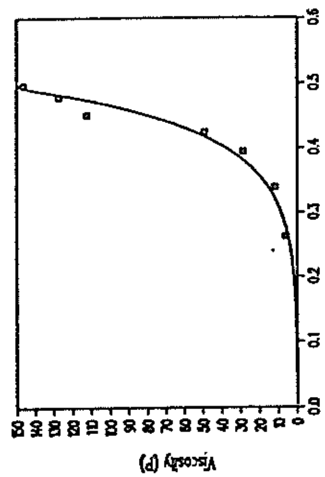
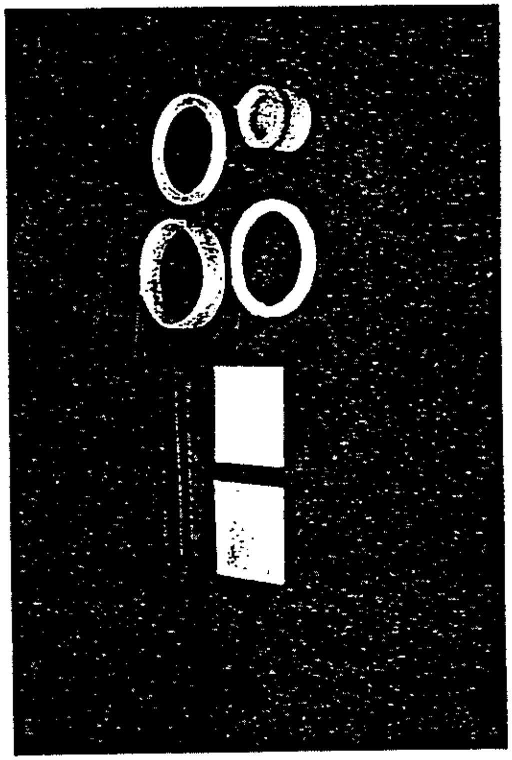


Figure . Flow Rate vs. Pressure Profiles for Al_2O_3 -(HODA-TMPTA) Slurries



3D Bodies Prepared by ACR SFF Process



Rings, Plates and Bar

TABLE III
Summary of Flexure Testing Results

Composition	Max Displacement (MPa)	Max Stress (MPa)	Flexure Modulus (GPa)
0 vt% Silica - Resin I	2.57	38.3	0.96
3.75vt% Silica - Resin I	3.05	42.8	1.03
7.5 vt% Silica - Resin I	3.12	48.8	1.15
11.23vt% Silica - Resin I	3.16	54.9	1.39
15.0 vt% Silica - Resin I	2.99	58.2	1.56
22.5 vt% Silica - Resin I	2.34	75.1	2.56
30.0 vt% Silica - Resin I	1.64	61.5	2.89
7vt% Silica- Resin II (TEOS)	1.75	50.4	2.10
7 vt% C_f - Resin I	1.73	27.0	1.24

ACR Work

Thermoplastic Extrusion
- Use high pressure extruder on polymer slug

Cantilevered Parts
- Toy soldier

Functional Gradient Materials
- Layer a syringe beforehand
- Use double feed

Tungsten-alumina
Silicon Carbide Aluminum?

Zirconia, Silicon Carbide, Silicon Nitride
- Aqueous dispersion?
- Organic liquid?
- Polymer preform?

Semiconductor Packages

Fundamental Issues

Chemical Solidification
No Shrinkage Constraints
Rapid Reactions
Non-Isothermal

Curling
Speed
Precision
Multiple heads
Curing methods
Layer filling patterns

Applications of Freeforming

Functional Gradient Materials

Reinforce Materials by in situ Reaction

Hierarchical Composites

Custom Materials

Form directly from CAD or Tomography data.

ACKNOWLEDGEMENTS

In Situ Precipitation : Jeremy Burdon

Mineralization: Mualla Oner, Jeremy Burdon

Surface Hardening: John Lombardi

SFF: John Lombardi, John O'Kelly, Robert Crockett, Kevin Stuffle

Support: Army Research Office, Elf Atochem, Courtaulds Plc, Sandia National Labs., Battelle Pacific Northwest Labs.

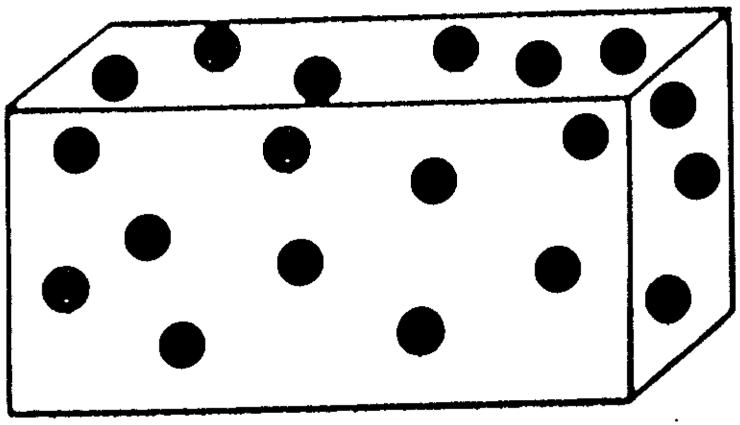
DESIGN, SYNTHESIS AND PROPERTIES OF POLYMER NANOCOMPOSITES

Emmanuel P. Giannelis
Materials Science and Engineering
Cornell University

February 1995

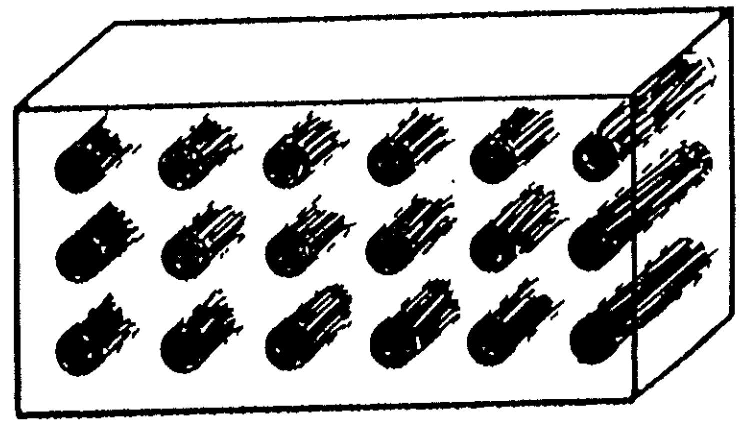
COMPOSITES

PARTICOLATES

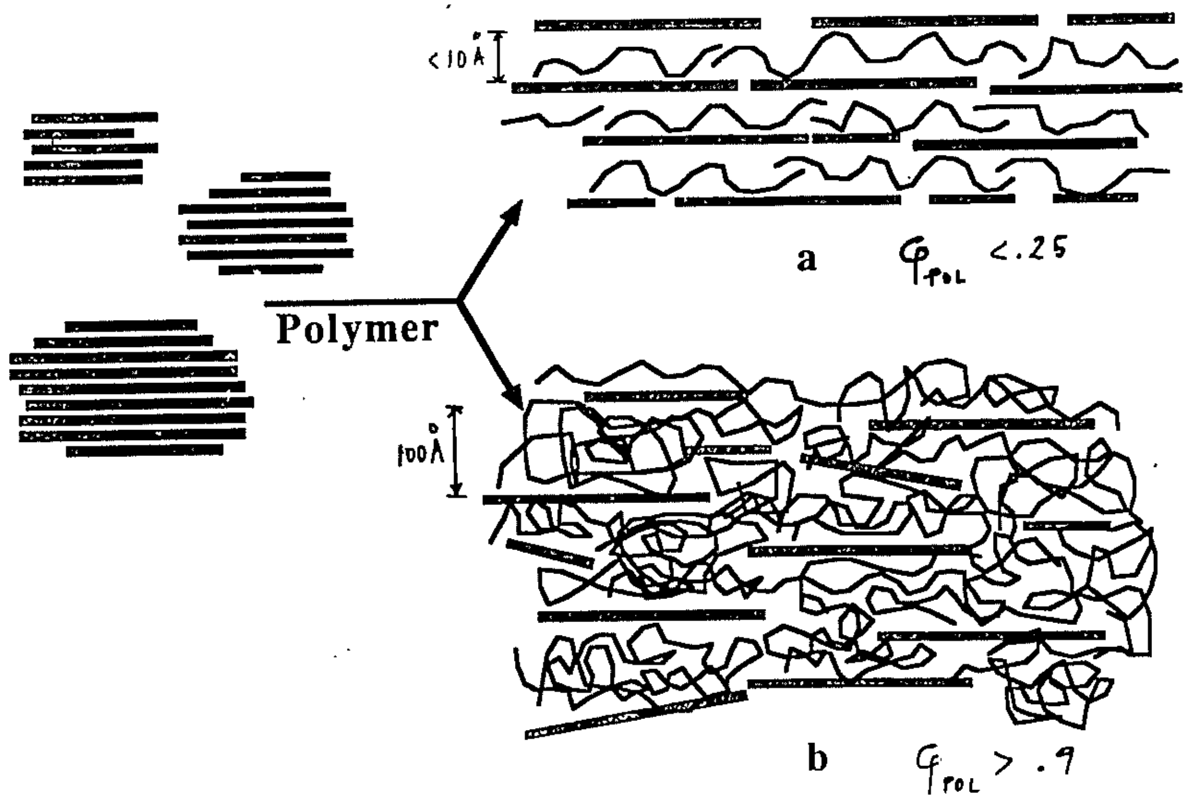


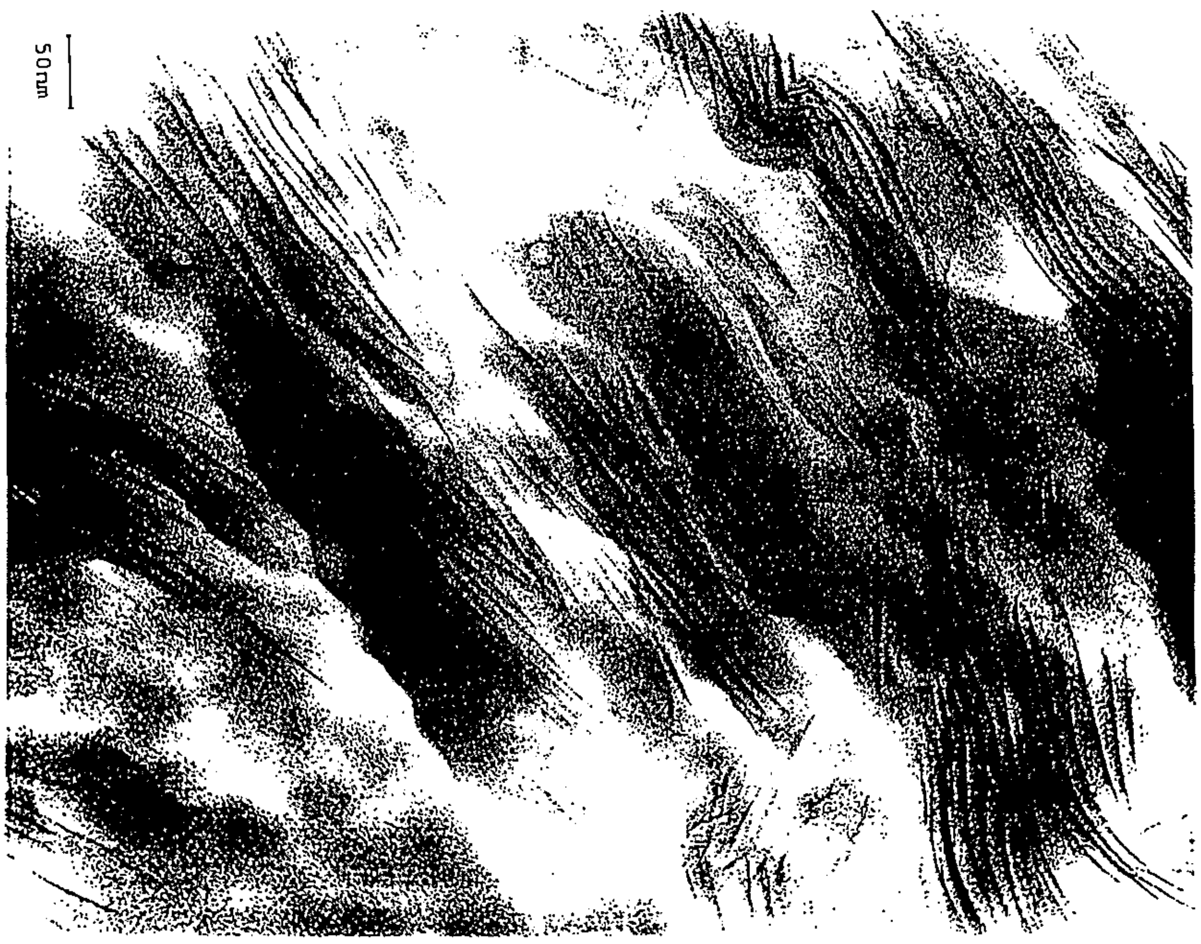
(a)

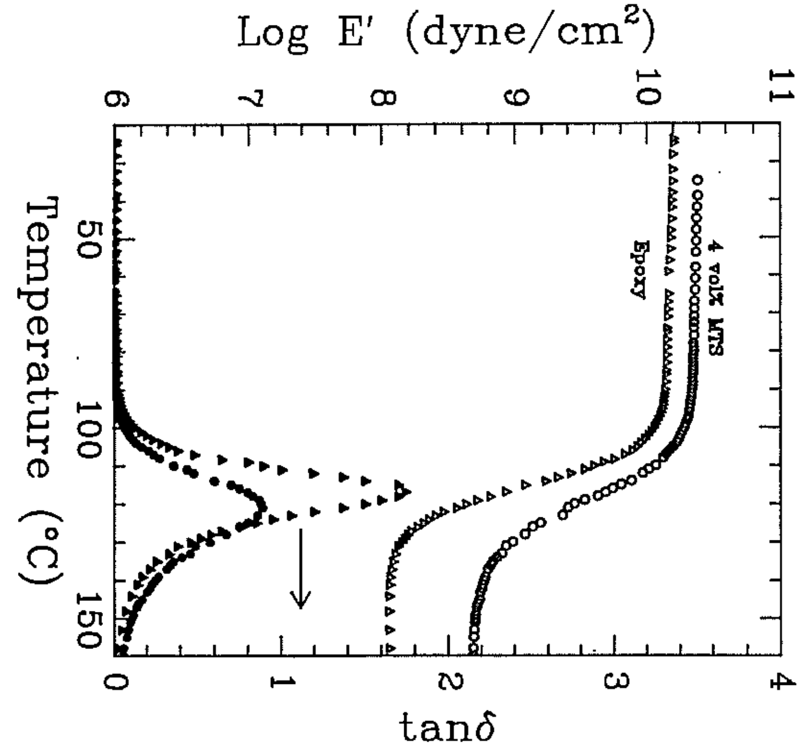
FIBERS



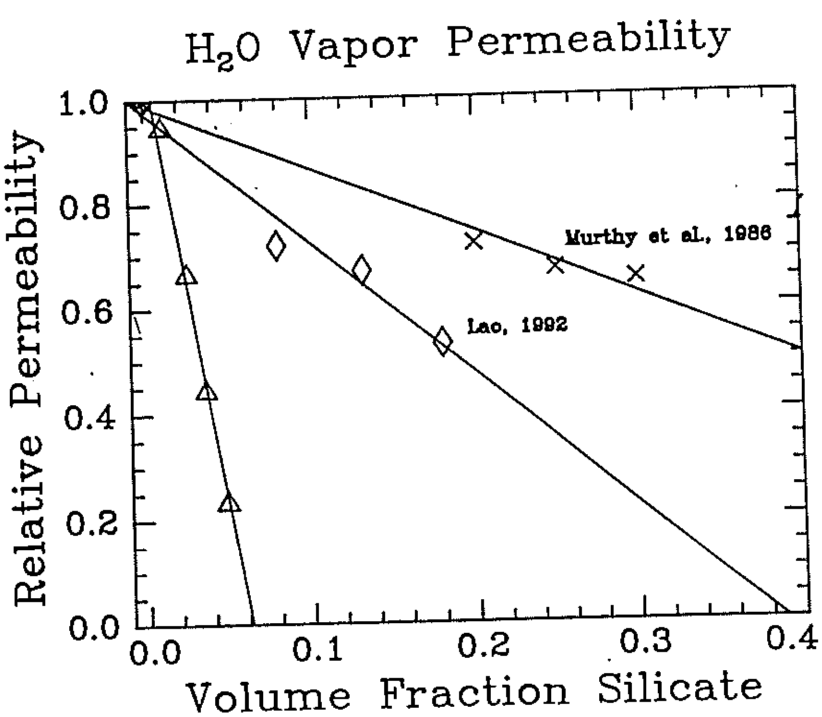
(b)


<10Å
Polymer
a
φ_POL <.25
100Å
b
φ_POL > .9


50nm

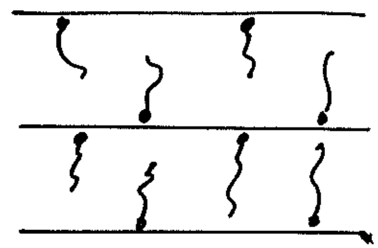


Log E′ (dyne/cm²)
6
7
8
9
10
11
4 vol% MTS
Epoxy
Temperature (°C)
50
100
150
0
1
2
3
4
tanδ



H_2O Vapor Permeability
Relative Permeability
1.0
0.8
0.6
0.4
0.2
0.0
Murthy et al., 1986
Lao, 1992
0.0
0.1
0.2
0.3
0.4
Volume Fraction Silicate

ORGANICALLY MODIFIED SILICATES



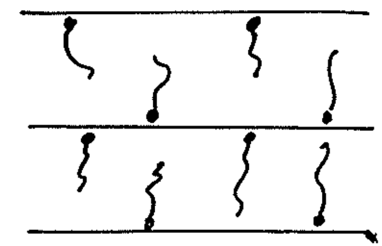
 ALKYL AMMONIUM CATI

EXAMPLES

$H_3\overset{+}{N}(CH_2)_nCH_3$

$H_3\overset{+}{N}(CH_2)_nCOOH$

ORGANICALLY MODIFIED SILICATES



 ALKYL AMMONIUM CATI

EXAMPLES

$H_3\overset{+}{N}(CH_2)_nCH_3$

$H_3\overset{+}{N}(CH_2)_nCOOH$

INTERCALATIVE POLYMERIZATION

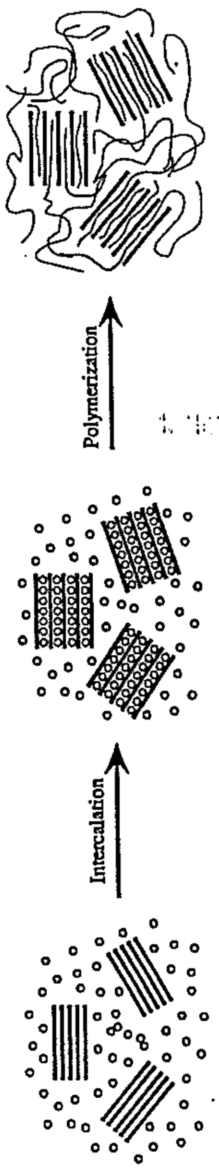
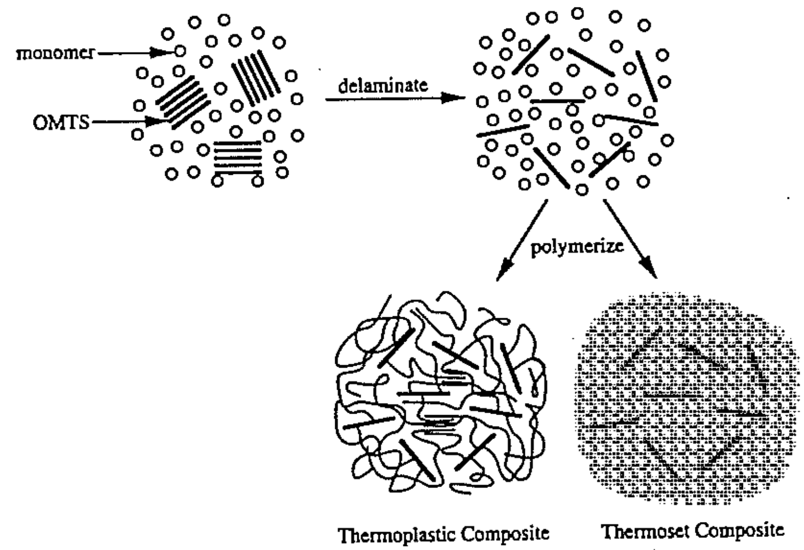
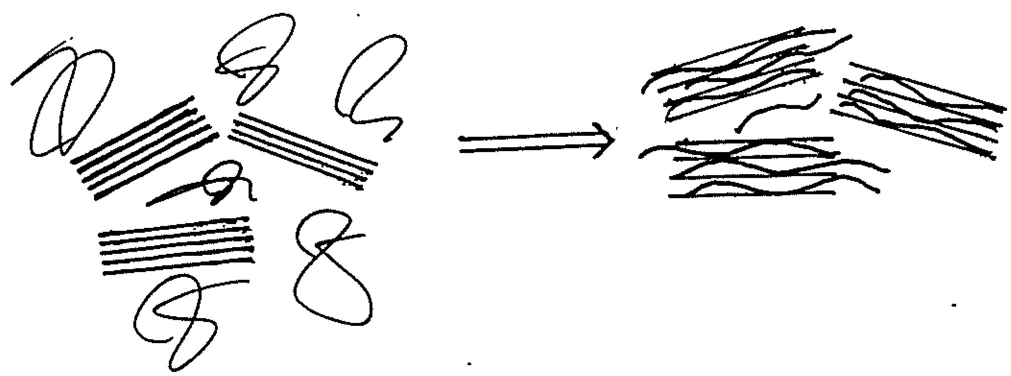


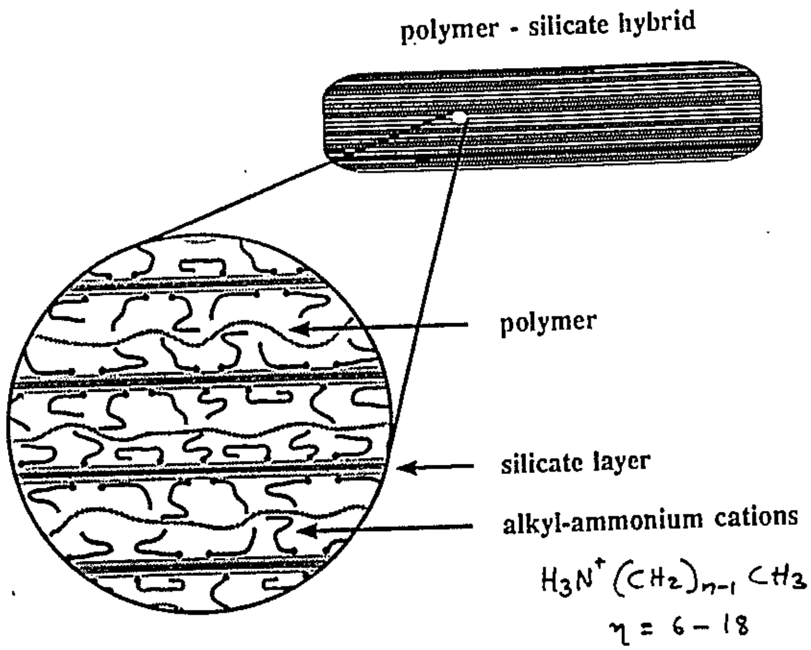
Fig. 1

Schematic of Synthetic Approach



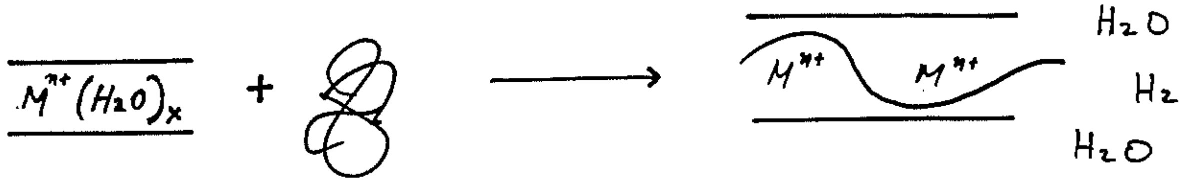


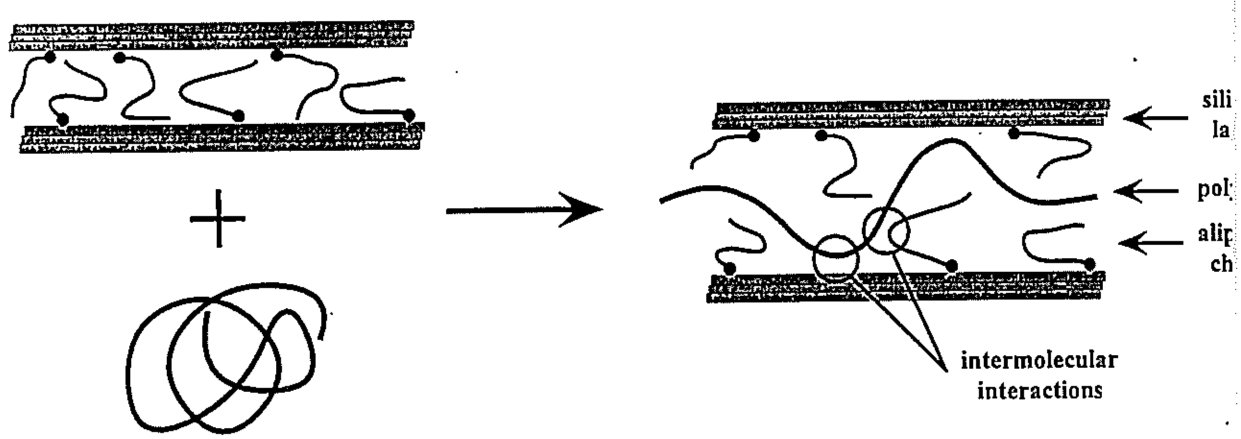
INTERCALATION OF POLYSTYRENE IN ORGANICALLY MODIFIED SILICATES



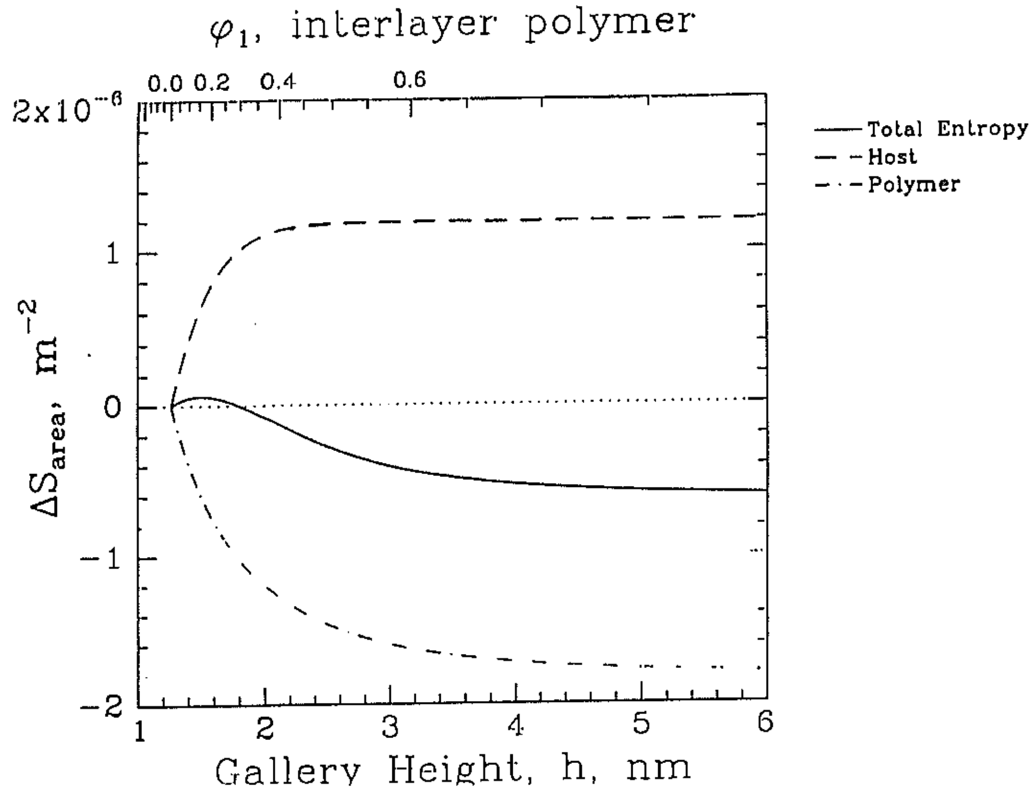
DRIVING FORCE FOR INTERCALATION

- PRISTINE HOST -

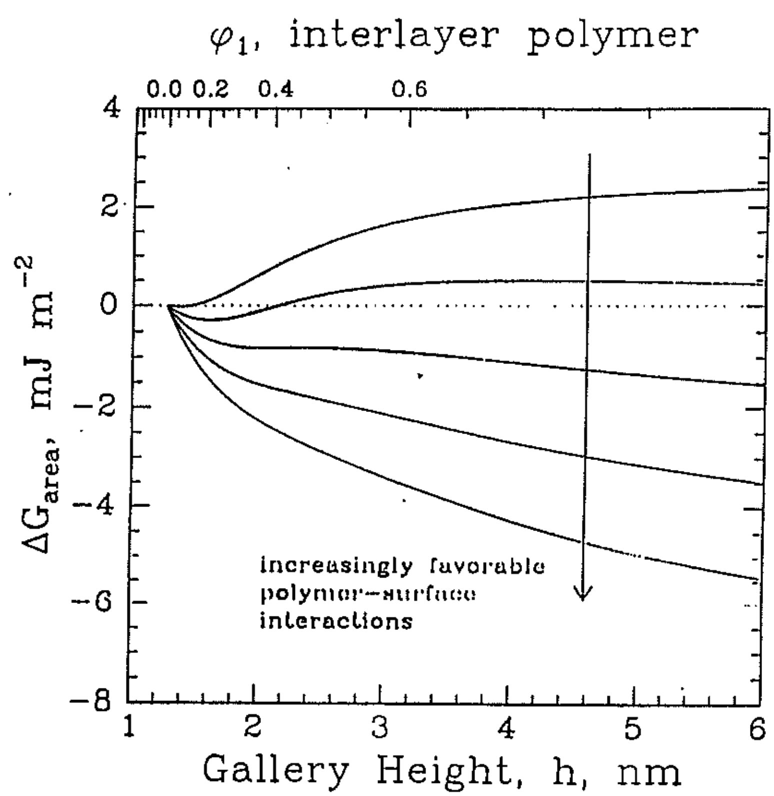




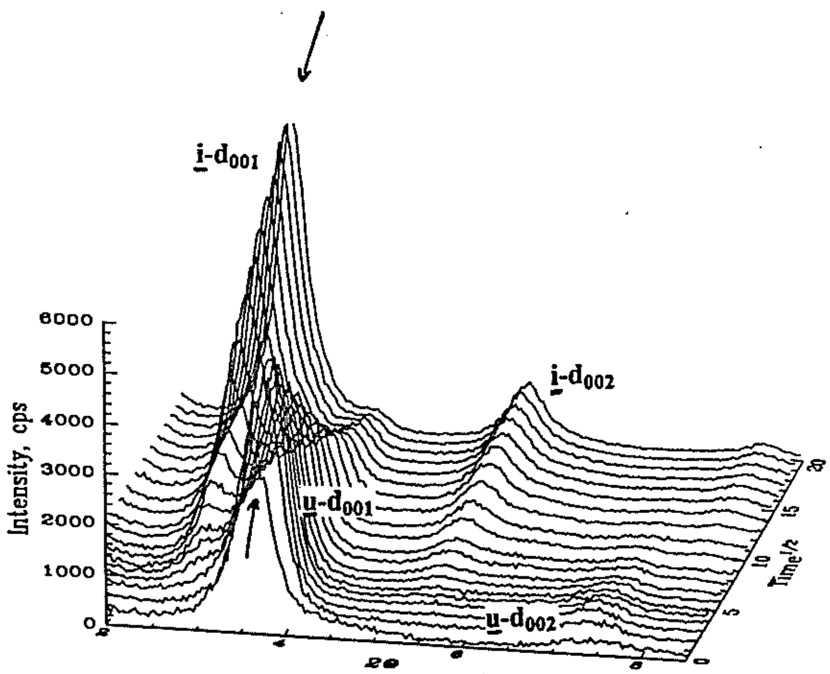
Entropic Factors



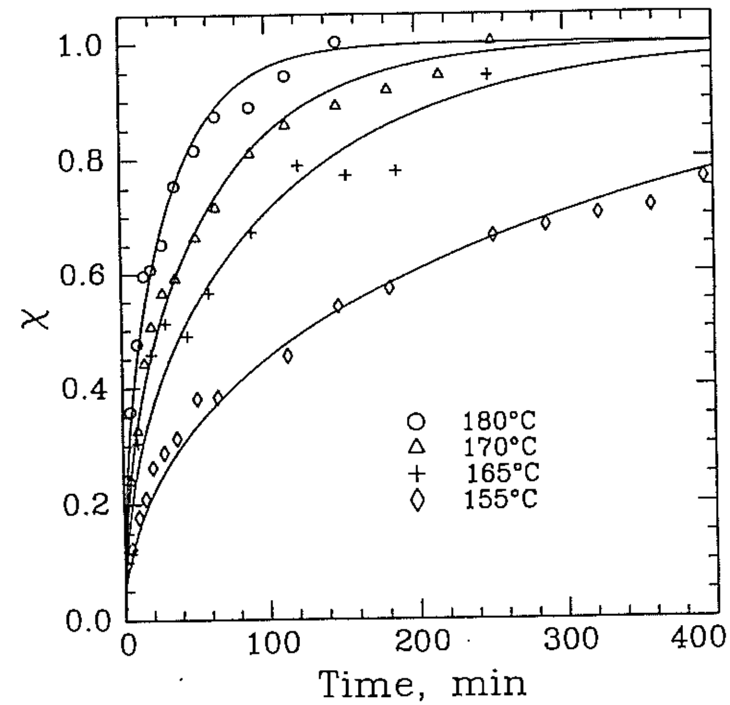
Free Energy Change



Evolution of PS Melt Intercalation

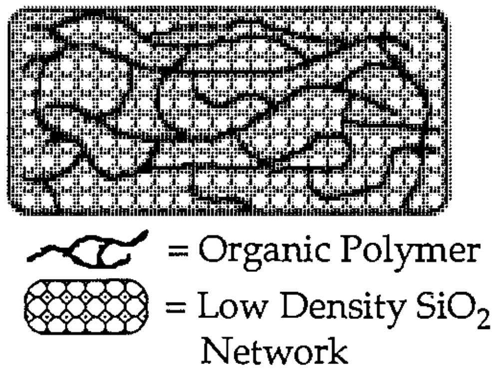


Kinetic Considerations



- Fickian Behavior
- Activation Energy ~ 150 kJ/mol, 35 kcal/mol
- $D_{exp} \sim D_{poly}$
- $T \geq 200$ °C, $t_{intercalation} \sim$ minutes

Optically Transparent Composite Materials



Modified Inorganic Glasses ⟺ **Modified Organic Polymers**

Modified Inorganic Glasses

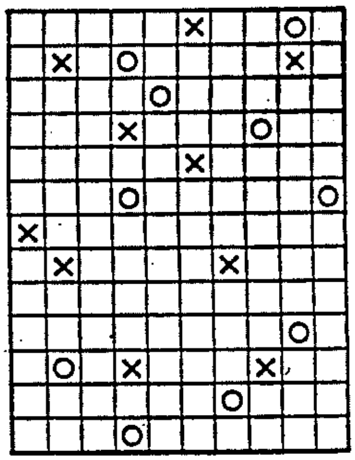
- Fiber Optics
- Wave Guides
- Nonlinear Optical Materials
- Impact Resistant Glasses
- Low Density, Strong Materials
- Inorganic Adhesives
- Safety Glass

Modified Organic Polymers

- Toughness
- Strength
- Modulus
- Modify Adhesive Properties
- Scratch Resistant Coatings

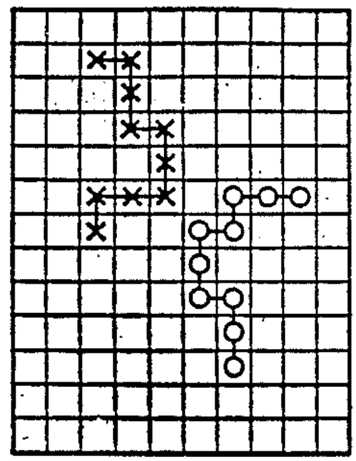
The Thermodynamics of Polymer Blends

Small Molecules



ΔS_{mix} = **Large**

Two Polymers



ΔS_{mix} = Small

Important Synthetic Considerations

1. Thermodynamic Factors

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

2. Kinetic Factors

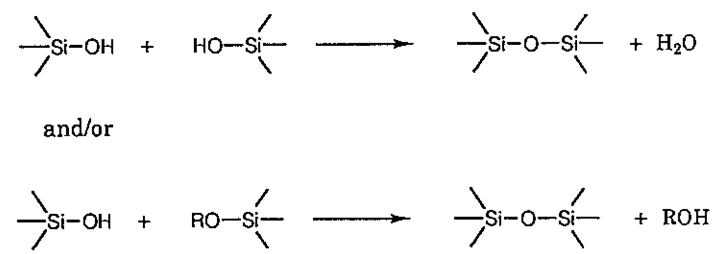
Thermo vs. Kinetics 6/27/94 3:10 PM

The Sol-Gel Process

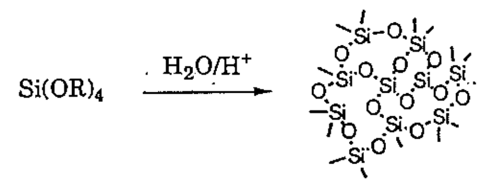
Hydrolysis

$$Si(OR)_4 + H_2O \xrightarrow[\text{Co-solvent}]{H^+} (RO)_3Si\text{-}OH + ROH$$

Condensation



Net Reaction



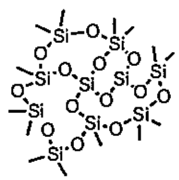
≡ Solvent-Swollen SiO_2 Matrix

- Excess Water
- Alcohol
- Cosolvent

Re Talk Sol-Gel 1 3/26/93 1:22 PM

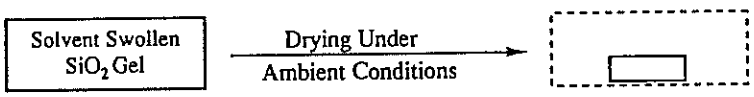
Shrinkage in Sol-Gel Glasses

$Si(OR)_4$ $\xrightarrow[\text{Cosolvents}]{H_2O/H^+}$



- Excess Water
- Alcohol
- Cosolvent

Solvent Swollen Gel



Xerogel

Shrinkages of 75-80% are Routine

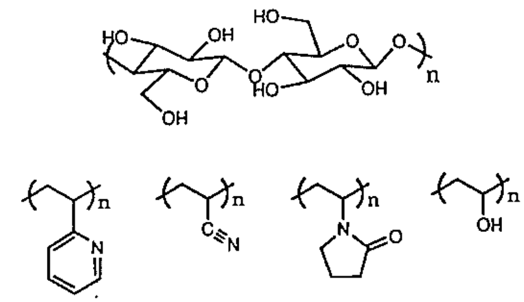
Organic-Inorganic Polymer Composites

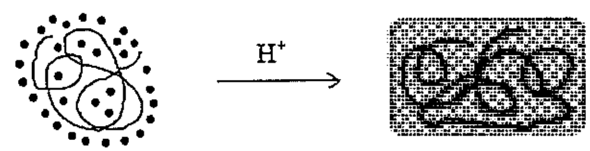
$Si(OR)_4 + 2\,H_2O \longrightarrow SiO_{2(s)}$

Nonpolar Polar

Co-Solvent

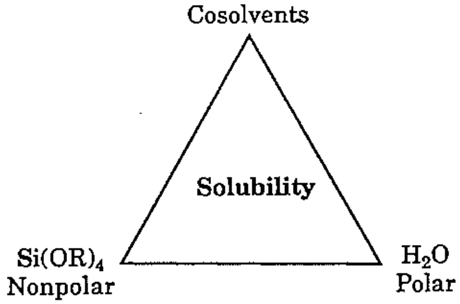
Alcohols
Acetone
THF
Formic Acid





Optically Transparent
Monolithic Composite Glasses

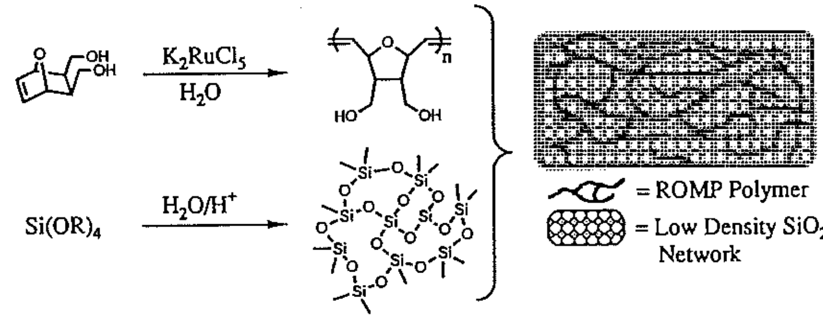
Candidate Composite Polymers

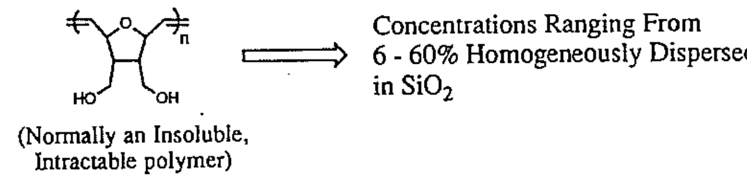


Important Issues

1. Solubility of Polymer in Sol-Gel Solution.
2. Require functionalized polymers in order to control the compatibility between the inorganic and organic phases.
3. Require the ability to adjust the polymer's T_g in order to control the composite's mechanical properties.

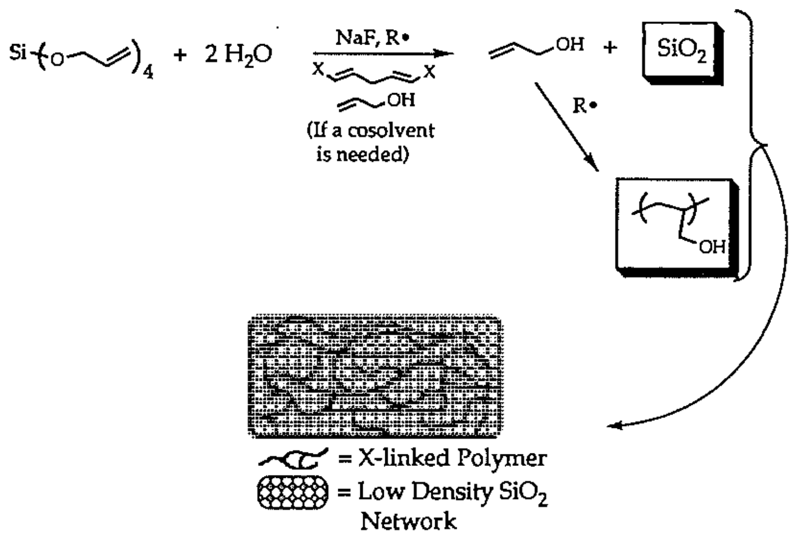
The Formation of Simultaneous Interpenetrating Networks (Organic-Inorganic SIPN's)



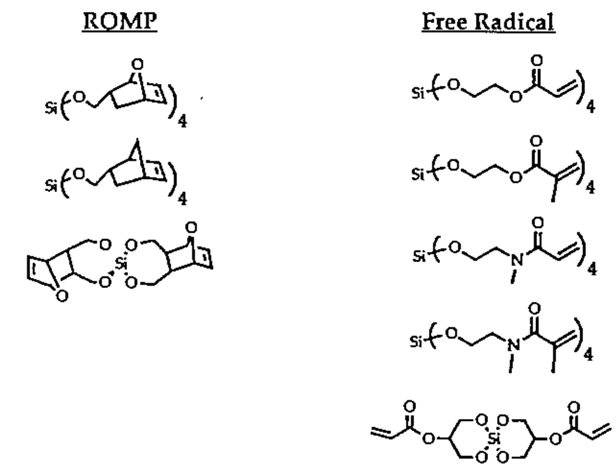


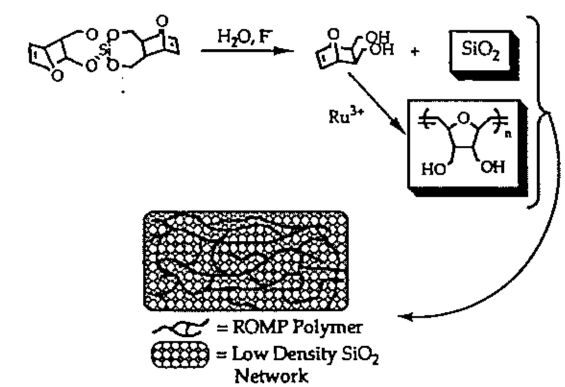
Ellsworth, Novak, *J. Am. Chem. Soc.* 1991, *113*, 2756

The Design of Nonshrinking Sol-Gel Composites

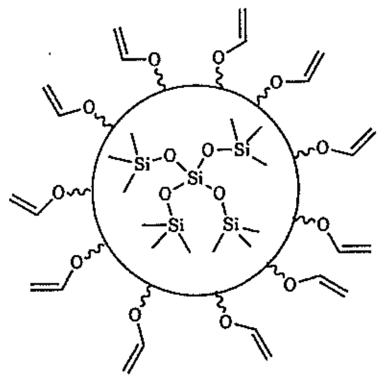


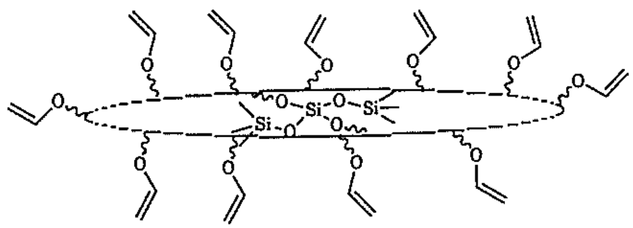
Nonshrinking Sol-Gel Composites: Free Radical and ROMP Systems

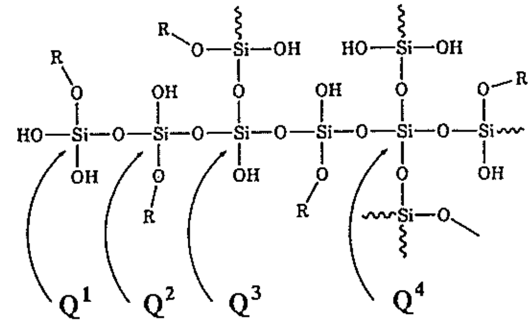




High Glass Composite Strategy: Soluble, Preformed Glass Particles with Controlled Morphologies







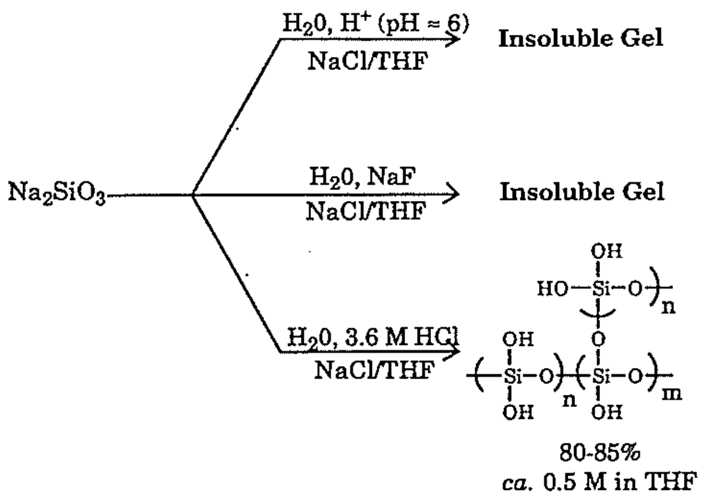
$$\% \text{ Glass} = \left[\frac{1}{n}\left(1 + x\left(\frac{2MW}{60.1}\right)\right)\right]^{-1} + \left[\frac{1}{m}\left(1 + x\left(\frac{MW}{60.1}\right)\right)\right]^{-1} + P$$

Where:

$n = \% Q^2$
$m = \% Q^3$
$p = \% Q^4$
MW = Molecular Weight of Alkoxide
X,X' = Degree of Substitution on Q^2 and Q^3 Centers

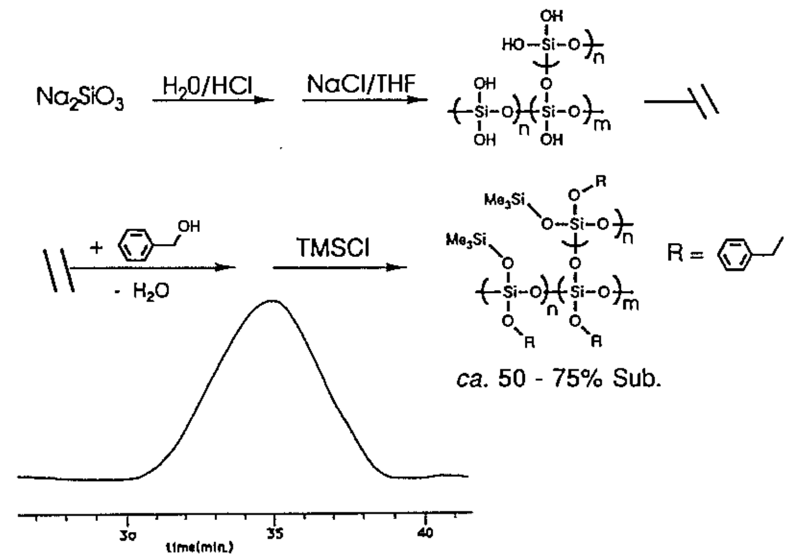
% Glass = ca. 20 - 100%

Branching Ratios in Soluble Poly(silicic acid)



M_n	[HCl]	Q1	Q2	Q3	Q4
8,100	3.6 M	0.7 %	11 %	49 %	39 %
44,700	3.6 M	< 0.1 %	10 %	55 %	35 %
183,000	3.6 M	< 0.1 %	10 %	44 %	46 %
4,000	6.0 M	< 0.1 %	5 %	33 %	62 %
15,000	8.0 M	< 0.1 %	3 %	26 %	71 %

Variation in the Molecular Weight (Particle Size)



Time(Hrs)	M_w	M_n	PDI	Yield
1	8,100	5,000	1.6	80-90%
24	44,700	19,700	2.3	80-85%
48	183,000	26,300	6.9	75-80%
72	7,770,000	1,880,000	4.4	50-60%
72+		- Insoluble Particles -		

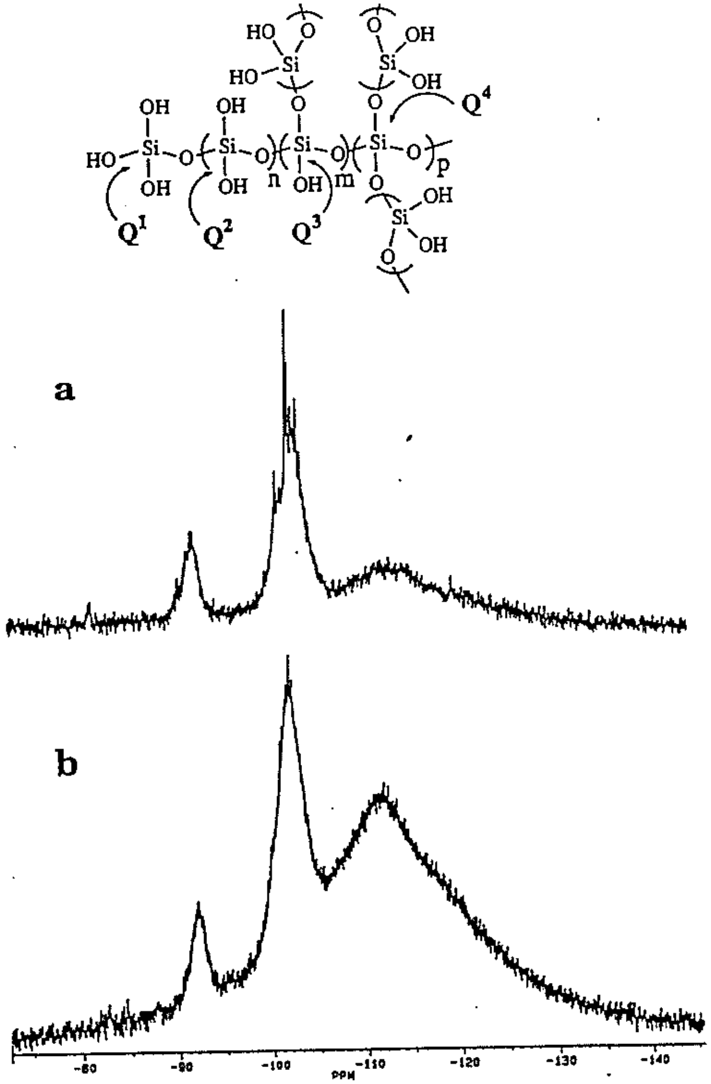
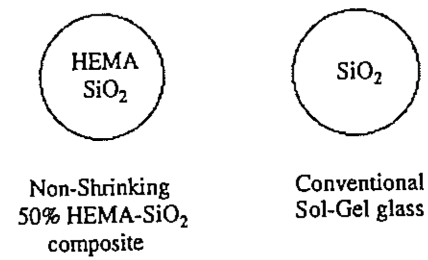


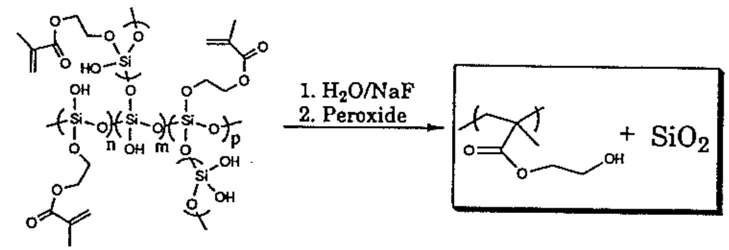
Figure 1. ^{29}Si NMR spectra of poly(silicic acid): a) 3M HCl, one hour reaction; b) 6M HCl, one hour reaction. Assignments: δ -81, Q^1; δ -92, Q^2; δ -103, Q^3; δ -112, Q^4.

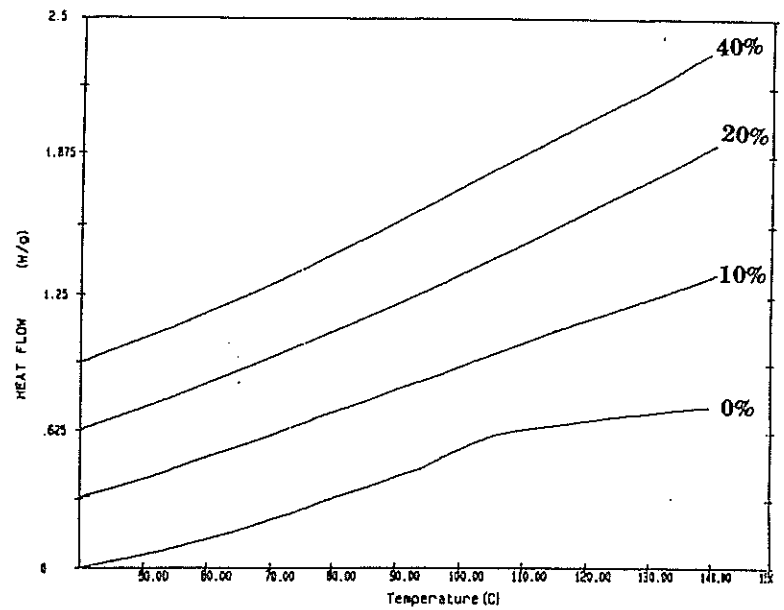


Organic-Inorganic SIPNs: Structural Characterization

1. Solid State CP-MAS 13C, and 29Si NMR
2. Thermal-Mechanical Analysis
   a. Differential Scanning Calorimetry
   b. Dynamic Mechanical Analysis
3. Scattering Techniques
   a. Light Scattering
   b. Small Angle X-Ray Scattering

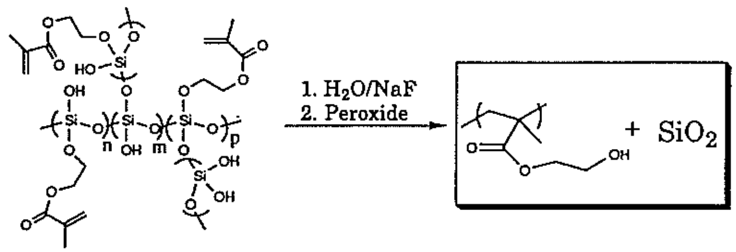
Thermal Analysis of IPN Composites

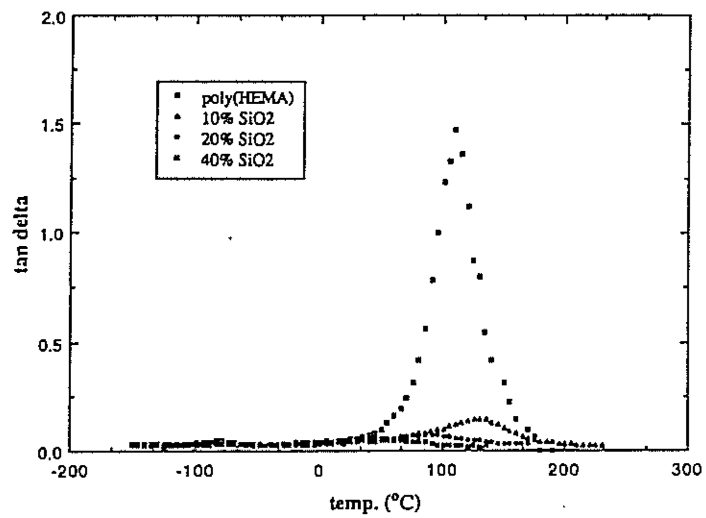




'herm Stability 10/23/93 11:39 AM

Dynamic Mechanical Analysis of IPNs: Loss Tangent (tan δ)





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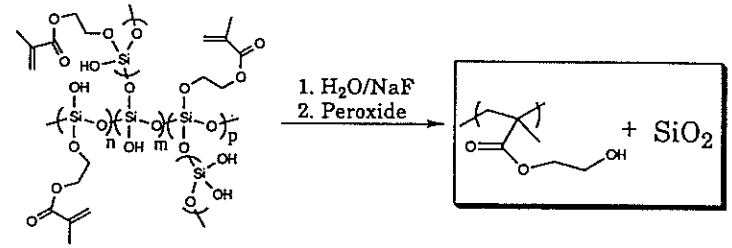
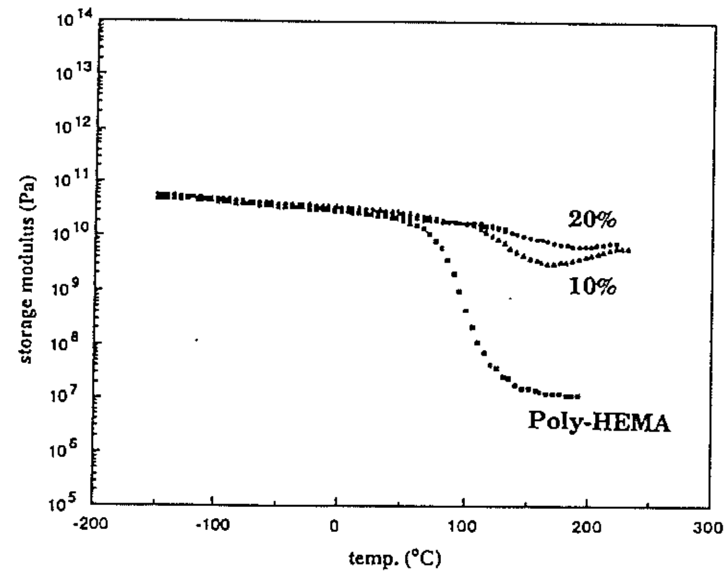
Dynamic Mechanical Analysis of IPNs: Storage Modulus





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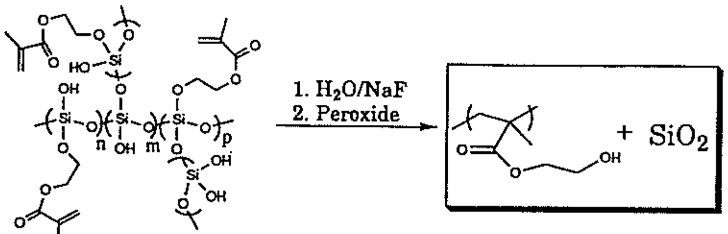
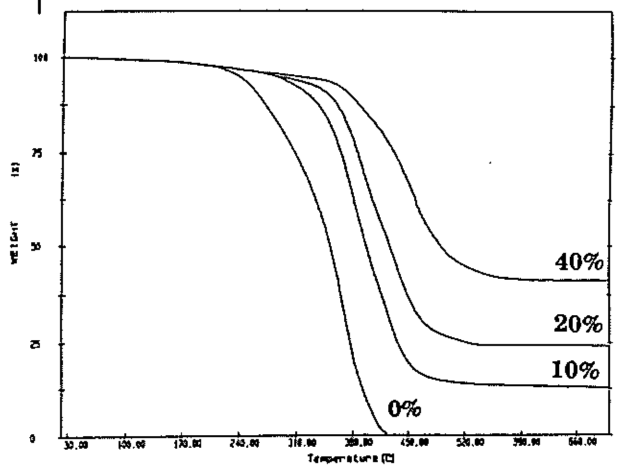
Thermal Stability of IPN Composites





Sample	%SiO_2	T_d (°C)
a	0	260
b	10	322
c	20	340
d	40	356

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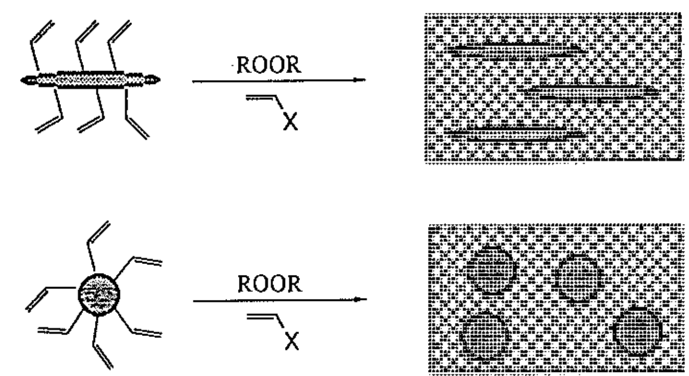
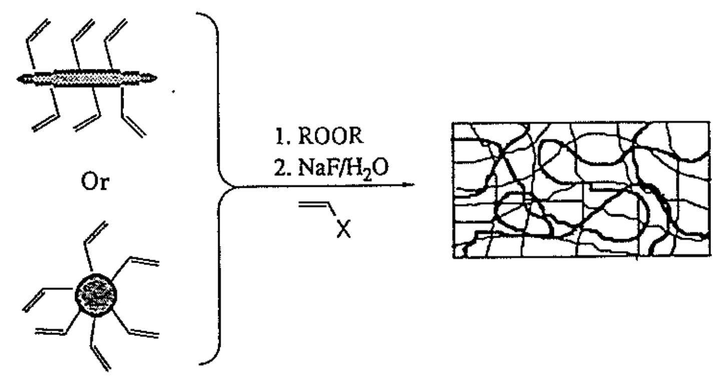
Synthetic Control over Composite Morphology

Organic Polymerization

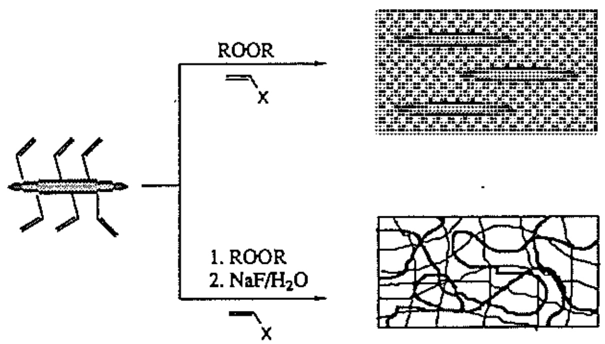


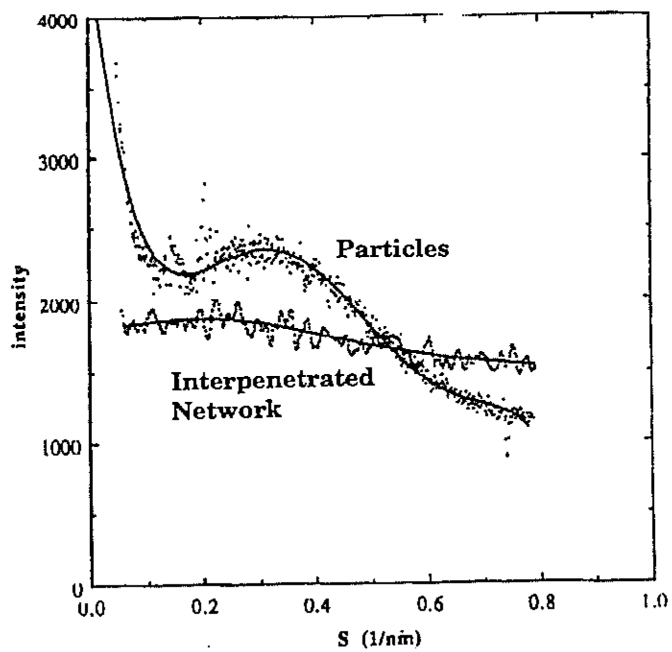
Simultaneous Organic-Inorganic Polymerizations



High Glass Morphology 1/8/93 12:55 PM

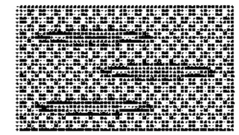
Organic-Inorganic Hybrid Materials: Synthetic Control Over Morphology





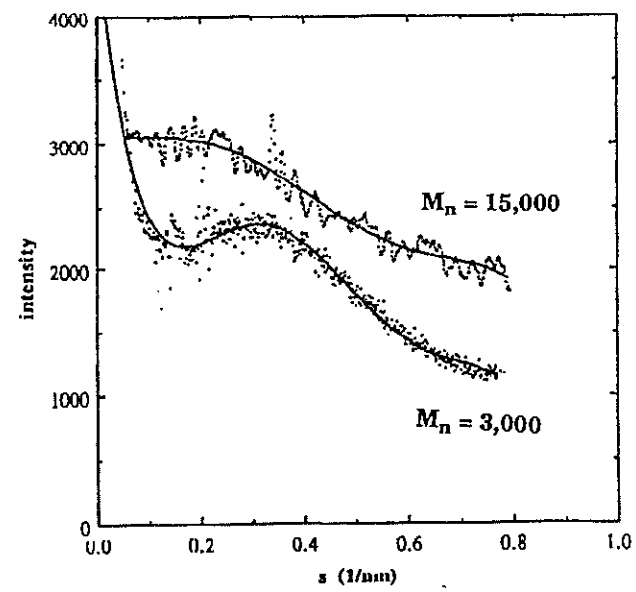
Untitled 10/25/93 12:02 PM

Organic-Inorganic Hybrid Composites: Synthetic Control over Particle Size



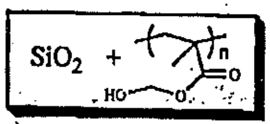
40% SiO_2

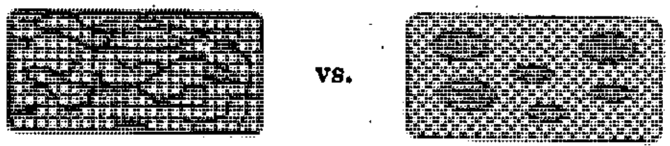
M_n = 3,000 vs. M_n = 15,000

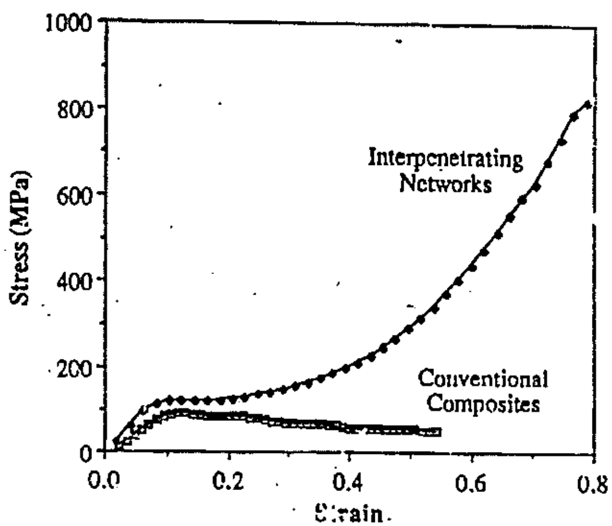


Syn Particle Size 10/25/93 12:18 PM

Conventional Composites
vs.
Mutually Interpenetrating Networks

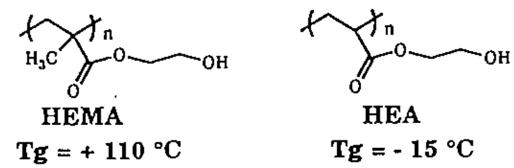


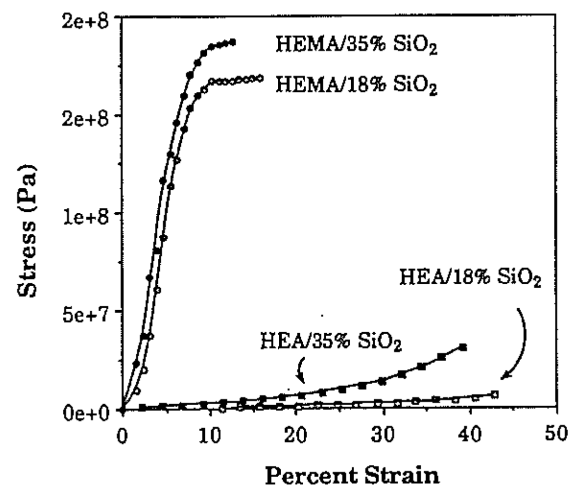




Conventional vs. SIPNs 1/8/93 6:21 AM

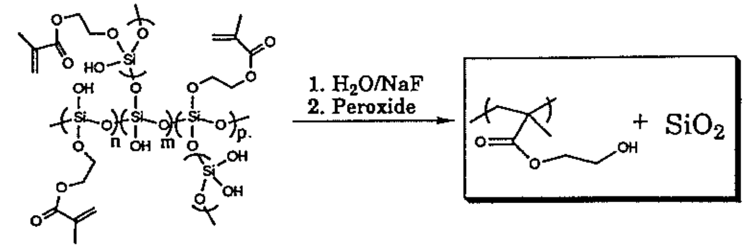
Stress - Strain Curve (Elastic Regime)
Effect of Polymer's Tg

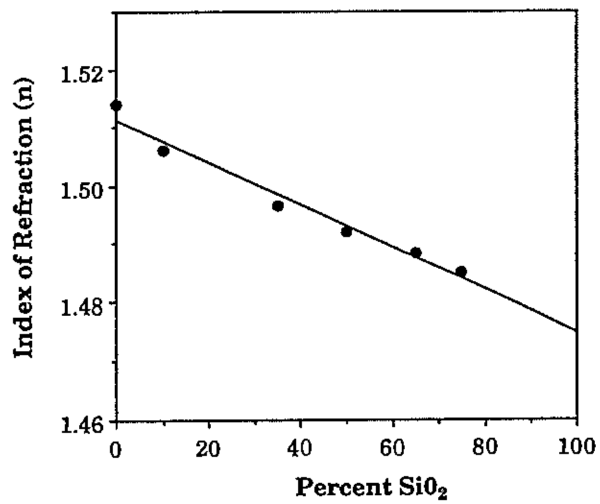




Stress-Strain Tg dep 3/26/93 1:49 PM

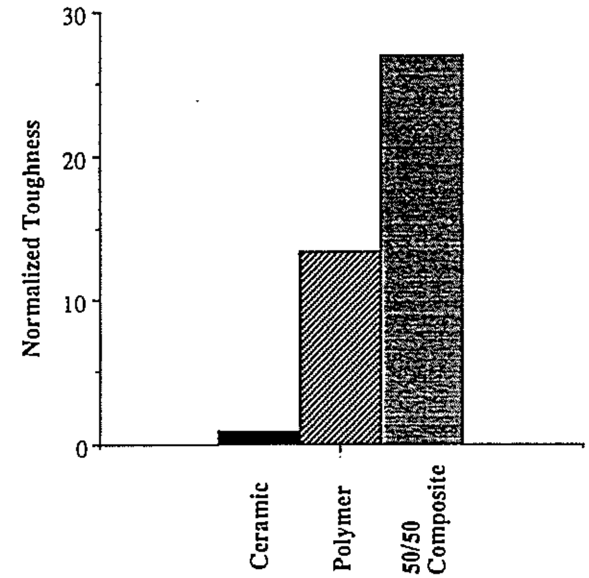
Varying Index of Refraction In Organic - Inorganic Composites





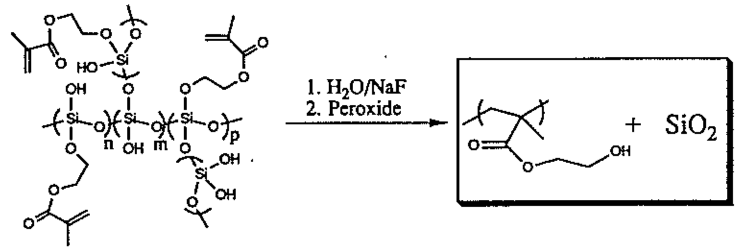
Index of Refraction 2 1/4/93 5:36 AM

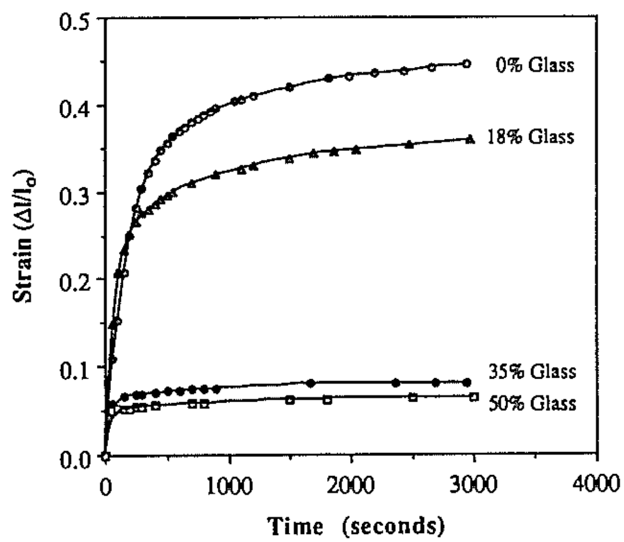
Composite Materials: Toughness



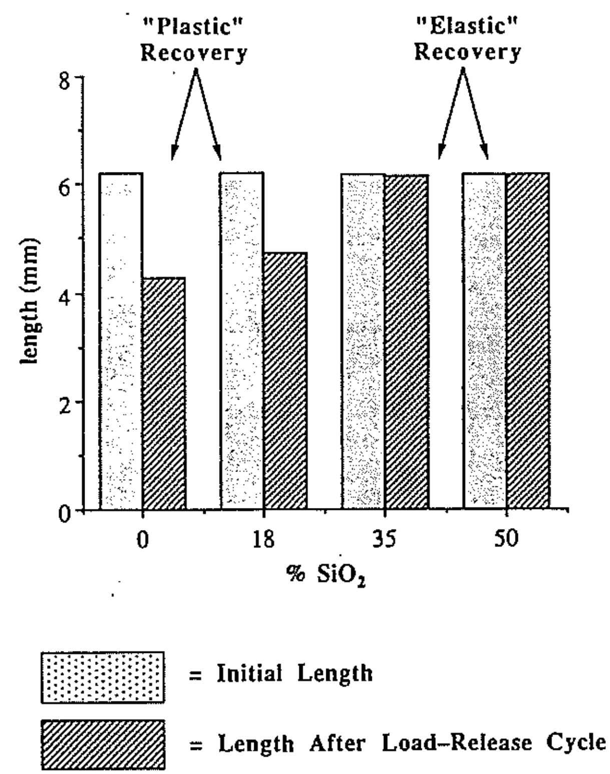
Synergistic Toughness 1/4/93 9:11 AM

Creep at Constant Load

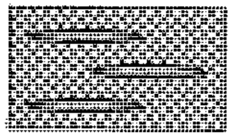




Creep Recovery
Plastic vs. Elastic Materials

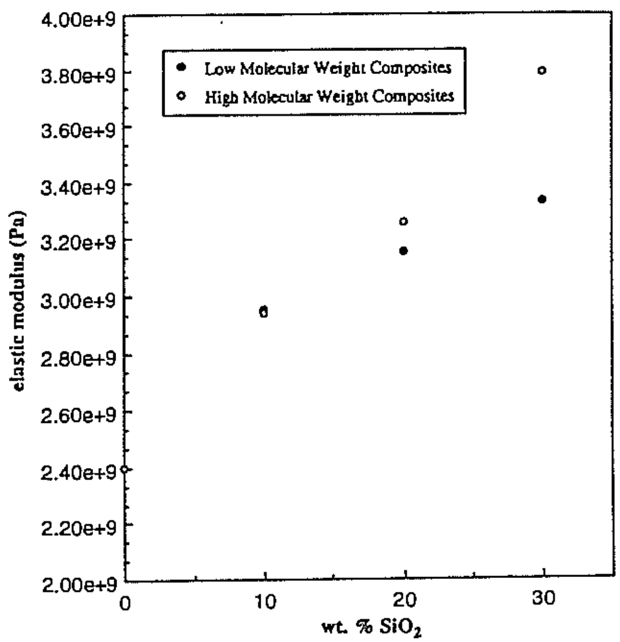


Organic-Inorganic Hybrid Composites: Dependence of Modulus on Particle Size



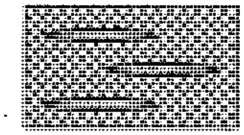
40% SiO_2

$M_n = 3,000$ vs. $M_n = 15,000$



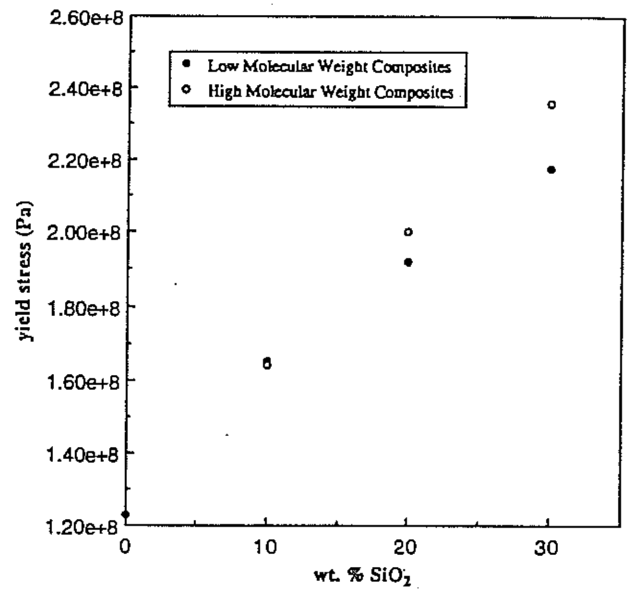
Syn Particle Size 10/25/93 12:25 PM

Organic-Inorganic Hybrid Composites: Dependence of Yield Strength on Particle Size



40% SiO_2

$M_n = 3,000$ vs. $M_n = 15,000$



ʼyn Particle Size 10/25/93 12:26 PM

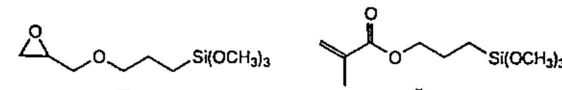
Mutually Interpenetrating Organic-Inorganic Networks

Current Issues

1. Ultra-Low Density Composites
2. Highly Ordered Organic Phases
3. Porous Glasses with Controlled Pore Sizes and Connectivities
4. Alternative Matrices for Conventional Glass Fiber Composites
5. Photo-Curable Inorganic Coatings

Mediating the Matrix - Fiber Interface

Silane Coupling Agents



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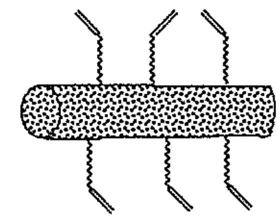
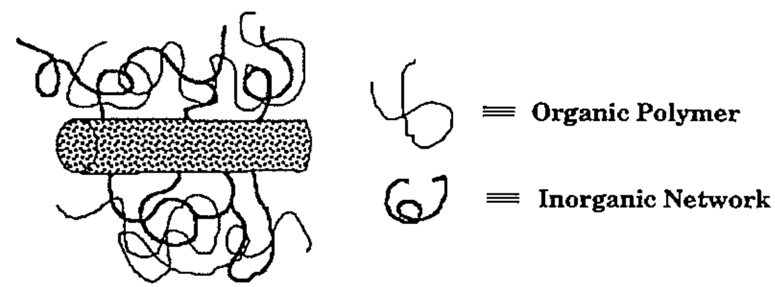
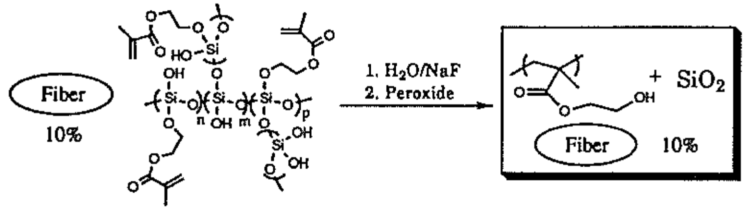


Can Improve Fiber Bonding by Making the Organic Matrix More "Inorganic Like"?

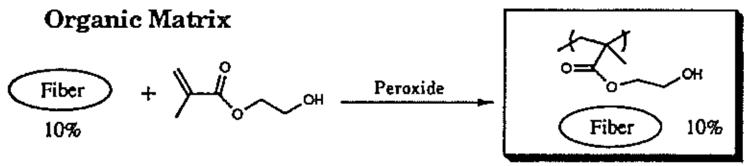


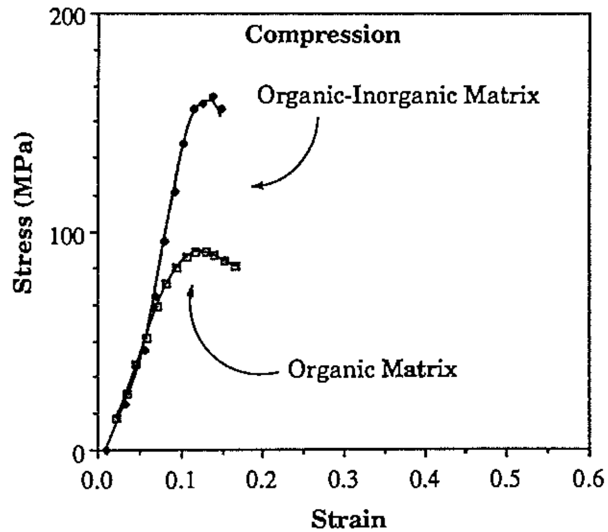
Fiber Reinforced, Composite Materials: Organic Matrix vs. Organic-Inorganic Matrix

Organic-Inorganic Marix



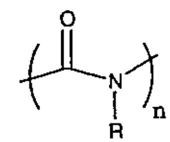
Organic Matrix





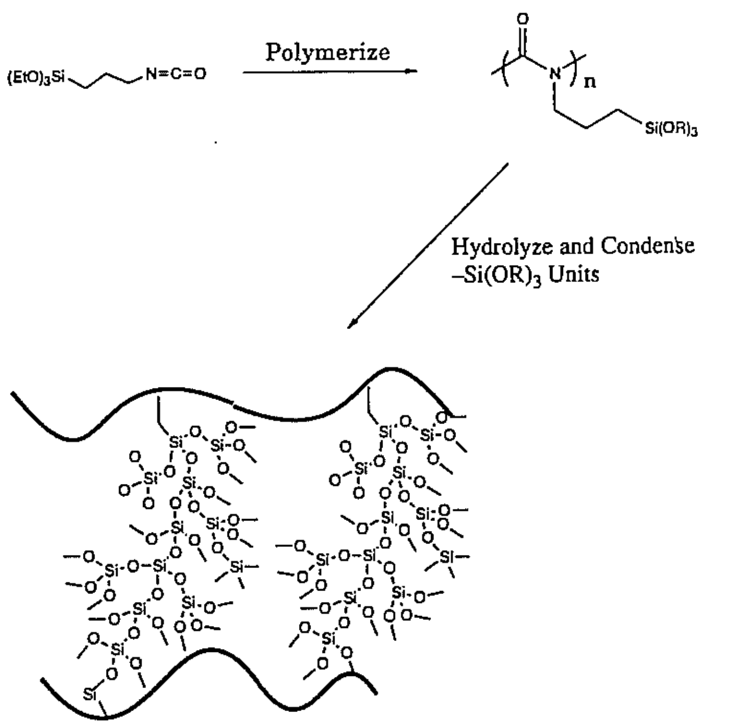
Fiber-Matrix Org vs. Org/Inorg 6/27/94 3:50 PM

Polyisocyanates: A Class of Synthetic, Helical Polymers

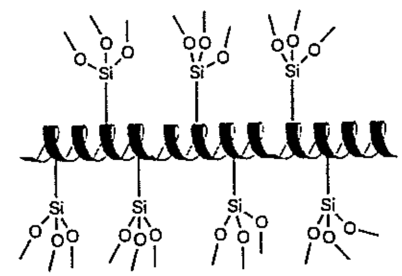


- Helical Conformation (8/3 Helix) in Both the Solid State and Solution.
- Chirality Associated with Helical Backbone Structure
- Stiff-Chain Polymer Properties (Persistence Length ≈ 600 Å)
- Cellulosic Mechanical Properties
- Liquid Crystalline Phases in Solution and Melt

Routes into Polyisocyanate / Inorganic Composite Materials



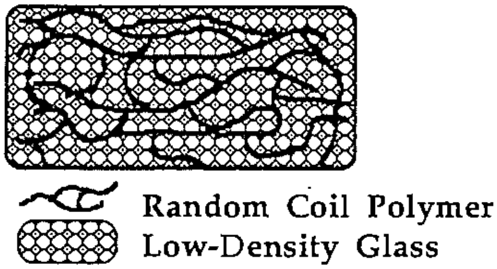
Biomimetic Composite Materials Based on Helical, Synthetic Polymers

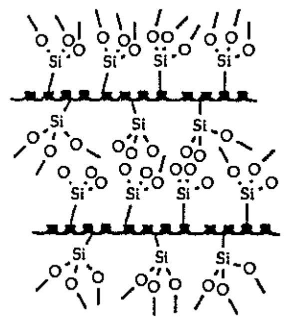


Helical Organic Polymers

- Act as Spatial Templates
- Provide Extended Chain / Liquid Crystalline Properties
- Improve Toughness, Strength, etc.

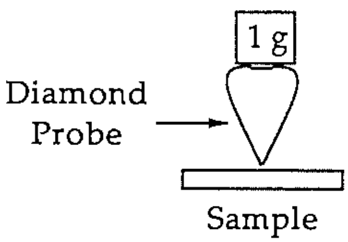
Vicker's Hardness:
Random Coil vs. Ordered Polymer Composites

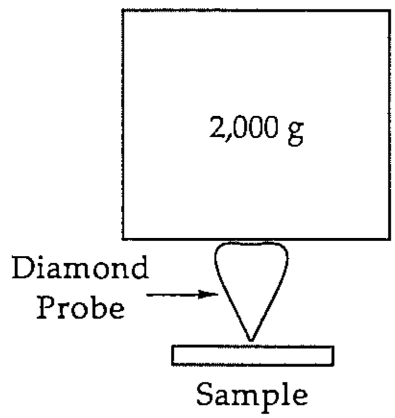


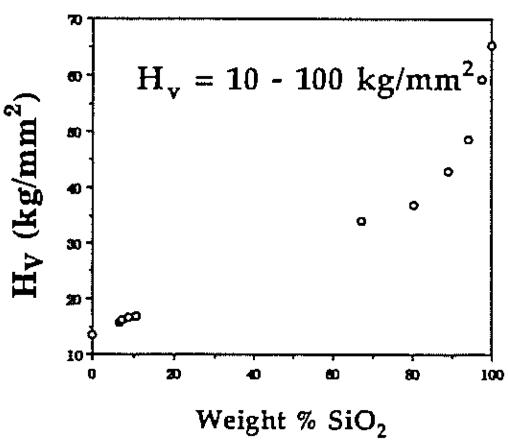


Random Coil Composites

Ordered Polymer Composites







$H_v > 10,000$ kg/mm^2

Poster Abstracts

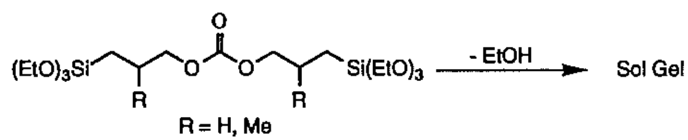
Synthesis and Characterization of Carbonate-bridged Polysilsesquioxane Sol-Gels

James V. Beach, Douglas A. Loy*, Roger A. Assink
Sandia National Laboratories, Properties of Organic Materials Dept. Albuquerque, NM 87185
and
Joe Tran, Ken J. Shea*
Department of Chemistry, University of California, Irvine
Irvine, CA 92717

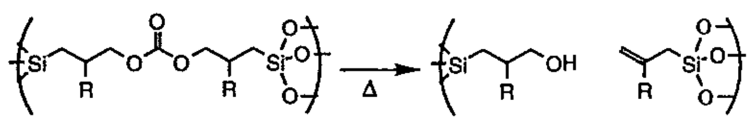
Sol-gels formed from the condensation of alkoxysilanes can serve as precursors to high purity glasses, ceramics, coatings and specialty fibers. While manipulation of the condensation and processing conditions of sol-gels are useful in controlling the materials' physical properties, hybrid organic sol-gels have allowed for systematic modification of the physical and chemical properties of the gels through the introduction of organic functionality.

Of particular interest to our group is the study of organic-bridged polysilsesquioxane gels. The condensation of bis(triethoxysilyl) monomers with various organic spacers has lead to a series of interesting materials. Most of the organic spacers explored so far have been simple hydrocarbons. We are now examining the use of more complex functionalities in the bridge in order to broaden the scope of hybrid organic sol-gels and to generate handles for secondary chemical modification of the materials.

Two new polysilsesquioxanes are examined here incorporating a carbonate bridge into the network architecture.



Characterization of these carbonate gels is presented. Though the gels are interesting materials in their own right, thermal treatment leads to the elimination of carbon dioxide to form a vacant site within the gel with both an alcohol and an olefin functionality present.



Such chemical handles may allow for the attachment of various catalysts or other interesting chemistry.

Acknowledgments

This research is supported by the United States Department of Energy under Contract No. DE-A C04-AL85000.

Annealing Effects on Solid State Properties of Transition-Metal Coordination Complexes and Networks based on Diene Polymers with Palladium Chloride.

Francis Bossé, Pronab Das and Laurence A. Belfiore*

Polymer Physics and Engineering Laboratory

Department of Chemical Engineering

Colorado State University, Fort Collins, Colorado, USA 80523.

Abstract

This study focuses on the thermal and mechanical properties of polybutadiene and/or polyisoprene, with an inorganic salt, bis(acetonitrile) dichloropalladium (*II*). Upon mixing, effective crosslinks are formed, because the acetonitrile ligands of the palladium salt are displaced by olefinic pendant groups of the polymers. Glass transition temperatures (T_g) determined by dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) increase with palladium content, annealing (heat treatment) time, and annealing temperature. Hence, T_g values obtained via differential scanning calorimetry (DSC) on films of transition-metal complex between diene polymers and $PdCl_2$ showed similar trends. Using a customary *n*-th order kinetic rate model, the Heck-like reaction which is catalyzed by palladium was characterized via isothermal and non-isothermal DSC. Relevant kinetic parameters such as the order of the reaction, the characteristic time constant for the chemical reaction, and the activation energy have been determined. Transition-metal compatibilization of atactic 1,2-polybutadiene and 3,4-polyisprene via $PdCl_2$ is demonstrated by monitoring the glass transition obtained from the DMTA tan δ profiles. The effect of annealing this ternary reactive "blend" produces a homogeneous glassy material exhibiting an elevated Tg and synergistic mechanical properties.

* Author to whom correspondence should be addressed.

Reactive Blending via Metal-Olefin Coordination in Diene Polymers---Solid State Properties that Support the Concept of a Network Structure

Francis Bossé, Pronab Das, and Laurence A. Belfiore*
Polymer Physics and Engineering Laboratory
Department of Chemical Engineering
Colorado State University, Fort Collins, Colorado, USA 80523.

Abstract

This study focuses on the properties of solid films formed from tetrahydrofuran solutions containing diene polymers, polybutadiene or polyisoprene, and an inorganic salt, bis(acetonitrile) dichloropalladium (*II*). Upon mixing, effective crosslinks are formed, because the acetonitrile ligands of the palladium salt are displaced by olefinic pendant groups of the polymers. Infrared data measured herein and previous studies of the chemistry of palladium compounds suggest that a Heck-like mechanism is operative to generate chemical crosslinks via palladium-catalyzed reactions. The swelling behavior of polybutadiene and polyisoprene was studied in various solvents. In both cases, equilibrium swelling ratios decrease with an increase in salt content, indirectly supporting the concept of a network structure. Using the Flory-Rehner relation, the number average molecular weight between crosslink junction points (M_c) was calculated from the swelling data. The mechanical properties of polybutadiene and polyisoprene solid films show a dramatic increase of 3 orders of magnitude in Young's modulus of elasticity (0.2 vs. ≅ 200 Kpsi) when the palladium salt content is 4 mole %. The Mooney-Rivlin coefficients C_1 and C_2, which describe the elastic behavior of rubbery materials in simple extension, were determined for films containing up to 2 mole % palladium chloride. Good agreement was found between the M_c values determined by both experimental techniques (equilibrium swelling and stress-strain data). Thermogravimetric measurements show that an increase in the transition-metal salt ($PdCl_2$) content, as well as annealing at 80°C, enhances the thermal stability of solid films. The glass transition temperatures (Tg) of solid films determined by differential scanning calorimetry increase with $PdCl_2$ content until the thermal plateau is achieved between 1 and 3 mole % palladium salt, where the increase in Tg (i.e., ΔTg) is approximately 100°C.

* Author to whom correspondence should be addressed.

Densification Behavior in Organically Modified Silica Systems as a Function of Heat Treatment: A Comparative Study of Bulk Gels and Thin Films Prepared Using Pendant and Bridged Organic Ligands

Narayan K. Raman[1] and C. Jeffrey Brinker[1, 2]

[1]UNM/NSF Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87106; [2]Ceramic Synthesis and Inorganic Chemistry (1846), Sandia National Laboratories, Albuquerque, NM 87185.

We have used pendant and bridged organic ligands to prepare bulk gels, thin films on silicon wafers, and membranes on porous tubular alumina supports. In the pendant case, we have used $R-Si-(OC_2H_5)_3/Si(OC_2H_5)_4$ where R= methyl, ethyl, phenyl, and in the bridged case, we have used $(C_2H_5O)_3Si-R'-Si(OC_2H_5)_3$ where R'= biphenyl, phenyl, ethylene.

We have studied the evolution of porosity in bulk gels as a function of heat treatment using isothermal gas adsorption measurements. We observe the collapse of the pore structure after the organic groups are pyrolyzed. The extent of collapse is determined by the connectivity of the gel network which we control by varying the loading of the organic ligands and reaction conditions (acid versus base catalyzed). We show using dilatometry, TGA/DTA, and ^{29}Si NMR that the disruption of the gel network caused by the pyrolysis of organic ligands causes a dramatic reduction in the viscosity of the network and is primarily responsible for the collapse of the pore structure.

Unlike bulk gels that can shrink isotropically, thin films are constrained in two dimensions causing them to shrink in one dimension only. Consequently, thin films do not show the densification behavior of gels under similar heat treatment conditions. The onset of densification in thin films and membranes depends on the loading of the organic ligands and occurs at 50-100°C above that of bulk gels. We have used ellipsometry and gas transport measurements respectively to study the evolution of porosity in thin films and membranes.

Submitted for consideration as a poster presentation at the Organic/Inorganic Polymer Systems Workshop, Napa Valley, CA, Feb 12-15, 1995.

Aluminosilicate-Poly(ethyleneglycol) Copolymer Electrolytes and Vanadium Oxide Oxymethylene Bridged Polyethylene Oxide Nanocomposite Electrode Materials

Glen Rawsky, Grant Kloster, and Du Shriver
Department of Chemistry and Materials Research Center
Northwestern University, Evanston IL

Solvent-free polyelectrolytes: The low basicity of many natural and synthetic aluminosilicates prompted us to incorporate an aluminosilicate into the backbone of polyethylene oxide with the thought that the anionic aluminosilicate anions would have a reduced tendency to ion pair with alkali metal cations. This reduced ion pairing should lead to increased mobility of the cation and therefore superior electrolyte behavior in a material with only one type of mobile ion. The observed conductivities $>10^{-6}$ S cm^{-1} bear out this expectation.

Redox active vanadium oxide/polymer composites: Alkali metal oxovanadate composites with polyethylene oxide have been prepared previously in Owen's and Kanazadia' groups. Our materials were prepared by a sol-gel method to obtain nano-composites. The electronic conductivity has been measured and ionic conductivity measurements are under way. An interesting scientific issue with these potential electrode materials is the mutual influence of ion and electron transport.

ALUMINOSILICATE-POLYMER ELECTROLYTES

Glenn C. Rawsky, Tatsuo Fujinami, John C. Hutchison and D. F. Shriver
Department of Chemistry, Northwestern University, Evanston, IL.

I. **Aluminosilicate/poly(ethylene glycol) Copolymers. A New Class of Polyelectrolytes.** Novel sodium ion-conducting polyelectrolytes incorporating aluminosilicate anions have been synthesized in order to reduce the strong ion pairing observed in other polyelectrolytes. The conductivity increases in the series $Al(OR)_4^- < Al(OR)_2(OSi)_2^- < Al(OSi)_4^-$ indicating reduced ion pairing by the weakly basic, sterically hindered aluminosilicate anions. The addition of cryptand [2.2.2] increases conductivity 1-2 orders of magnitude through further reduction of ion pairing.

II. **MEEP-Na-Montmorillonite Intercalates as Polyelectrolytes.** Following a report by Giannelis on a PEO-clay intercalation compounds, we are currently exploring the effects of a constrained environment on the ionic-conductivities of poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazine](MEEP-salt complexes. Toward this end, we have synthesized a new clay-polymer intercalation compound by dissolving MEEP in a suspension of Na-montmorillonite(SWy-2). The resulting product can be cast into thin, pliable films and has mechanical properties distinct from either starting material. Evidence of intercalation is provided by an increase in d-layer spacing from 12Å to 19Å, and a narrowing of peak widths in the P-N stretching region of the FTR spectrum. Results of AC-impedance spectroscopy, multi-nuclear NASNMR, and TGA/DSC studies, will be reported.

Ambient Pressure Aerogels via Organosilyl Derivatization of Polysiloxanes

Sai S. Prakash[a], C. Jeffrey Brinker[a,b], Alan J. Hurd[c], and Sudeep M. Rao[a]

[a] University of New Mexico/Sandia National Laboratories Advanced Materials Lab, Albuquerque, NBM 87106

[b] Ceramic Synthesis and Inorganic Chemistry Department, Sandia National Laboratories, Albuquerque, NM, 87185

[c] Ceramic Processing Science Department, Sandia National Laboratories, Albuquerque, NM, 87185

Abstract

Aerogels are highly porous solids normally prepared by the supercritical extraction of pore fluid from a wet gel. Under supercritical conditions liquid-vapor interfaces and therefore capillary stresses are absent so drying occurs with little or no shrinkage. This poster describes an ambient pressure process to prepare aerogels in bulk or thin film form. This process is based on organosilyl-derivatization of an inorganic gel that allows drying shrinkage to be reversible. As prepared gels are hydrophobic, comprise variable porosity, depending on the extent of surface derivatization, and can exhibit reversible capillary induced strains ($\Delta V/V$) of over 6! Pyrolyzed samples exhibit refractive indices as low as 1.006 corresponoding to 98.5% porosity. In general, it is anticipated that organic modification of inorganic networks can be exploited to make a wide range of porous materials with tailored microstructures.

Proposed for presentation at Organic/Inorganic Polymer Systems
February 12-15, 1995, Napa CA

NOVEL, FUNCTIONALIZED HYBRID MATERIALS FROM POLYHEDRAL SILSESQUIOXANES AND PROPARGYLOXY DERIVATIVES,

Alan Sellinger and Richard M. Laine, Macromolecular Science and Engineering Center, and Depts. of Chemistry and Materials Science and Engineering, University of Michigan, Ann Arbor, MI, 48109-1055

Novel hybrid materials have been prepared by Pt catalyzed hydrosilylation of propargyloxy derivatives, $HC{\equiv}CCH_2OR$ with cubic hydridosilsesquioxanes, $(HSiO_{1.5})_8$ and $[H(CH_3)_2SiOSiO_{1.5}]_8$. Reaction stoichiometry was chosen to retain Si-H functionality in the products for further curing at higher temperatures. For example the products obtained by reacting 4 equiv. 4-(4-propargyloxybenzoyl-oxy)biphenyl with either $(HSiO_{1.5})_8$ or $[H(CH_3)_2SiOSiO_{1.5}]_8$ can be cured at temperatures < 180°C to produce clear, hard, thermoset plastics. The DSC traces show multiple transitions before curing indicating potential liquid crystalline (LC) behavior.

Lower temperature curing can be realized using methacrylate chemistry. For example the products obtained by reacting 4 equiv. propargyl methacrylate with either $(HSiO_{3/2})_8$ or $[H(CH_3)_2SiOSiO_{1.5}]_8$ can be thermally cured at temperatures < 90°C or by radical polymerization at 21°C as hydrosilylation occurs at the propargyloxy site, retaining the methacrylate functionality. Thermal stability in air of the materials based on $(ROCH_2CH{=}CH)_4[H_{10.5}SiO_{1.5})_8$ and $(ROCH_2CH{=}CH)_4[H_{0.5}(CH_3)_2SiOSiO_{1.5}]_8$ are 340°C and 250°C respectively. The products were characterized using TGA, DSC, size exclusion chromatography (SEC), and NMR (^1H, ^{13}C, ^{29}Si).

AMERICAN CHEMICAL SOCIETY
ORGANIC/INORGANIC POLYMER SYSTEMS

ABSTRACT

POLYPHOSPHAZENE SOLUTION PROPERTIES

Wendel J. Shuely, Dept. Army, Aberdeen Proving Ground, MD

Polyphosphazenes have unique low temperature properties that provide a highly flexible sealing and gasket material for environmental applications. New applications require additional chemical resistance performance. In order to characterize the solvent-solute interaction behavior of polyphosphazenes in a more general manner, the determination of polymer solubility phase diagrams was conducted. Several sets of solvent parameters for dispersion, polarity, and hydrogen bond acceptor strength were employed and compared. Correlations between the liquid-in-polymer volume fraction results from phase diagram studies were attempted with polymer-in-liquid sorption-desorption measurements.

Preparation and Properties of Inorganic-Organic Composite Materials Containing $R_3SiO_{1/2}$, SiO_2 and TiO_2 Units

Toshio Suzuki*, Youko Sakae, Nobuo Kushibiki and Itaru Mita
Research Center, Dow Corning Asia Ltd.
603 Kishi, Yamakita, Kanagawa, 258-01 Japan
* Central R&D, Dow Corning Corporation
Midland, Michigan 48686-0994

Abstract

A new class of inorganic-organic composite materials containing $RMe_2SiO_{1/2}$ (R=vinyl or methyl), SiO_2 and TiO_2 units, namely organically modified polytitanosiloxane, have been synthesized. The synthetic procedure is as follows; (1) partial hydrolysis of a tetraalkyl titanate in THF at -78 °C, (2) addition of a tetraalkyl silicate and partial hydrolysis under the same conditions, (3) addition of dimethylvinylsilanol and optionally trimethylsilanol and reaction at room temperature, (4) addition of excess water, and (5) removal of volatile components. The resulting polytitanosiloxanes are either viscous liquid or solid materials with good solubility in common organic solvents. The polytitanosiloxane can be cured with an SiH-functional polyorganosiloxane and a Pt catalyst via hydrosilylation to form a transparent hard material. While the cured polytitanosiloxane showed remarkable stability toward hydrolysis, uncured material tends to increase their molecular weight upon exposure to moisture.

MOLECULAR COMPOSITES FROM VINYL AND HYDRIDO FUNCTIONALIZED POLYHEDRAL SILSESQUIOXANES

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The Pt catalyzed co-polymerization, by hydrosilylation, of the vinyl and hydrido functionalized silsesquioxanes: [vinylSi$(CH_3)_2$-O-$SiO_{1.5}$]$_8$, [vinyl$SiO_{1.5}$]$_8$, [HMe_2Si-O-$SiO_{1.5}$]$_8$ and [$HSiO_{1.5}$]$_8$ is currently under investigation with the intent of synthesizing molecular composites that can act as porous, high surface area, low density materials. Copolymerization of the above compounds in common organic solvents provides high surface area (>400 m^2/g) materials with very narrow pore size distributions (10-20 Å). These molecular composites are characterized by TGA, DSC, ^1H-, ^{13}C-, ^{29}Si-NMR, and porosimetry.

Speakers

Speakers	Lecture Topic
Sol-Gel Processing	
1. Clement Sanchez Université Pierre et Marie Curie Laboratoire de la Matiere Condensée Tour 54, 5ème etage, 4 place Jussieu 75252 Paris Cédex 05 France	Hybrid Inorganic/Organic Systems with Electrochromic, Photochromic.. Properties FAX 011-33-1-44-27-47-69 Phone 1-33-14-427-5545
2. Professor Dr. Helmut Schmidt, Institut für Neue Materialien gem. Gmbh Universität des Saarlandes Gebäude 43, Im Stadtwald D-6600 Saarbrücken, Fed. Republic of Germany	Inorganic/Organometallic Hybrid Polymers: Routes to Industrial Applications 49-681-302-5000 or 5005 FAX No. 49-681-302-5223
3. Michael J. Michalczyk Du Pont Central Research and Development Experimental Station E356/327 Wilmington, DE 19880-0356	Star Gels: New Single Component Organic/Inorganic Network Materials (302) 695-9565 FAX 695-1664
4. Douglas A. Loy Advanced Materials Laboratory Sandia National Lab 844-4445 Albuquerque, NM 87185	Silsesquioxane Derived Porous Materials (505) FAX 846-8077
5. Frank J. Feher Frameworks" Dept. of Chemistry University of California, Irvine Irvine, CA 92717	Rational Synthesis of Si/O and Si/O/M (714) 856-4682 FAX 856-8571
6. Professor Bruce Dunn Dept of Materials Science and Eng. 531 Boelter Hall UCLA Los Angeles, CA 90024	Optical Applications of Inorganic/Organic Hybrids (310) 825-1519 FAX 206-7353
7. Richard W. Pekala Lawrence Livermore National Laboratories Chemistry and Materials Science Dept. P.O. Box 808, L-322 7000 E Ave. Livermore, CA 94550	Organic/Inorganic Aerogels: Controlling Structure at the Nanometer Scale (510) 422-0152 FAX 423-4897
Inorganic/Organometallic Polymers	
8. Harry Allcock Evan Hugh Professor Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802	Polyphosphazenes, Properties and Application Phone (814) 865-3527 FAX 814-865-3314

9. James E. Mark — Properties of Inorganic Polymers with Bimodal Chain Distributions
Dept. of Chemistry
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10. Richard M. Laine — Chemicals and Polymers from Silica and Alumina
Depts. of MSE and Chemistry
2300 Hayward St.
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Ann Arbor, MI 48109-2136
(313) 764-6203
FAX 763-4788

11. Barry Arkles — Commercial Production of Inorganic/Organometallic Hybrids
President of Gelest, Gelest
612 William Leigh Dr.
Tullytown, PA 19007-6308
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12. Len Interrante — Preceramics Polymers
Dept of Chemistry
Cogswell Laboratory
Rensselaer Polytechnic University
Troy, N. Y. 12180-3590
(518) 276-8752
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Composites

13. Professor Bruce Novak — Mutually Interpenetrating Organic-Inorganic Networks: Synthesis, Structure and Properties
Polymer Science and Engineering
University of Massachusetts at Amherst
Room 701, Lederle Graduate Res. Center
Amherst, MA 01003
Phone (413) 545-2160
FAX 413-545-0764

14. Paul D. Calvert — Polymer/Inorganic Composites via Biomimetic Processing
Arizona Materials Laboratory
4715 East Fort Lowell Rd.
Tucson, AZ 85712
(602) 322-2994
FAX 322-2993

15. Emanuel Giannelis — Design, Synthesis and Properties of Polymer Matrix Nanocomposites
Dept. of MSE
Cornell University
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Attendees