$^{19}$F DOSY DIFFUSION-NMR SPECTROSCOPY OF FLUOROPOLYMERS

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NMR studies of fluoropolymers is a very exciting and useful field. The presence of three NMR active nuclei, the high natural abundance of both $^1$H and $^{19}$F, and the unique NMR properties of $^{19}$F produce NMR spectra with an amazing amount of information. $^{19}$F detected diffusion ordered spectroscopy (DOSY) NMR experiments have been shown to be useful for distinguishing between the resonances of main-chain and chain-end polymer units. The performance of $^{19}$F DOSY NMR experiments (and in general any type of NMR experiments) on fluoropolymers creates some unique complications that very often prevent detection of important signals. Factors that create these complications include: 1) the presence of many scalar couplings among $^1$H, $^{19}$F and $^{13}$C nuclei; 2) the large magnitudes of many $^{19}$F homonuclear couplings (especially $^{2}$J$_{FF}$); 3) the large $^{19}$F NMR chemical shift range; and 4) the low solubility of these materials (which requires that experiments be performed at high temperature). Many methods for performing $^1$H detected DOSY experiments have been reported in the literature. Very often, these methods fail to produce detectable signals in $^{19}$F detected DOSY experiment, especially for the weak signals from fluoropolymer chain-ends and branch structures, which are often the most important components to characterize.

A systematic study of the various methods for obtaining DOSY NMR data, and the adaptation of these methods to obtain $^{19}$F detected DOSY data has been performed using a mixture of low
molecular weight, fluorinated model compounds. The best pulse sequences and optimal experimental conditions have been determined for obtaining good quality $^{19}$F DOSY spectra. The optimum pulse sequences for acquiring $^{19}$F DOSY NMR data have been determined for various circumstances taking into account the spectral dispersion, number and magnitude of couplings present, and experimental temperature. Pulse sequences and experimental parameters for optimizing these sequences for the study of fluoropolymers have been determined.

The utility of these optimized experiments is illustrated with various fluoropolymers including poly(vinylidene fluoride-co-hexafluoropropylene) copolymer, poly(vinylidene fluoride-ter-tetrafluoroethylene-ter)hexafluoropropylene terpolymer, and poly(chlorotrifluoroethylene-co-vinylidene chloride) copolymer. Using these new experimental conditions, it is possible to study the diffusion of polymeric structure elements whose weak NMR signals were previously undetectable in DOSY experiments.

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