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Progress Summary: Solid-state NMR experiments have been developed to probe crystallization behavior fluoropolymers

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Disclaimer

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Progress Summary: Solid-state NMR experiments have been developed to probe crystallization behavior fluoropolymers (H. Mason, mason42@llnl.gov)

Motivation: The FK-800 fluoropolymer elastomer is being developed as a replacement material for the Kel-F 800 binder in the plastic bonded explosive PBX-9502. These polymers are a random co-polymer of poly-vinylidene fluoride (PVDF) and poly-chlorotrifluoroetheylene (PCTFE) in nominal 1:3 ratio. Initial characterizations of the FK-800 replacement show similar characteristics as the legacy Kel-F 800. However, differences in bulk crystallinity and crystallization kinetics have been observed. These differences may be driven by small differences in the distribution of the monomers on the polymer backbone (sequence distribution).

Significance: Solid-state NMR spectroscopy can access detailed information about the development of crystallinity in semi-crystalline polymers. Information about crystallite abundance, morphology, and size can be obtained using NMR spin diffusion measurements. The rates of spin diffusion are well known for protonated polymers such as HDPE and polystyrene, but ^{19}F spin diffusion rates in polymers are still unknown. We are using careful measurements of ^{19}F spin diffusion of model fluoropolymers to determine these rates.

Progress: We have successfully implemented a spin diffusion sequence that utilizes a dipolar filter to obtain phase contrast between crystalline and amorphous domains in a partially crystalline sample of PCTFE. Using Fast Magic Angle Spinning (MAS) we can collect well resolved ^{19}F NMR spectra that show that peaks associated with crystalline phases are suppressed effectively (Figure 1 bottom spectrum) but that intensity is recovered through spin diffusion transfer at longer recovery delays (Figure 1 top spectrum). A corresponding decrease in the signal intensity is also observed for the amorphous peaks as well. Measuring this intensity decline as a function of the

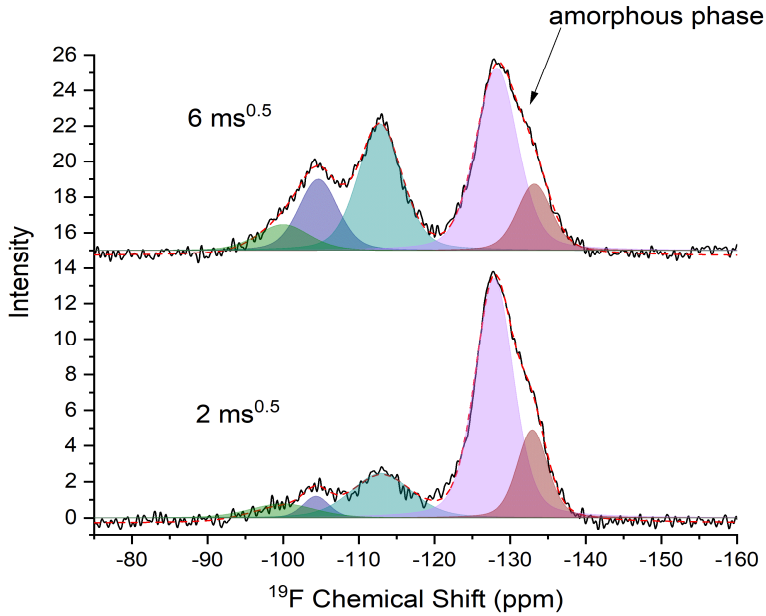

Figure 1. Individual results for dipole filtered ^{19}F spectra. The bottom spectrum shows that the left most peaks are suppressed at short delay but recover at longer delay periods (top spectrum).

recovery delay, we can measure the spin diffusion of the system (Figure 2). The initial slope of the first linear portion of the curve depends on the size of the crystalline domain. We have also observed that as the percent crystallinity (as determined by density measurements) increases we see a corresponding change in the initial slope of the data (Figure 2). This result indicates that we are seeing discrete changes in the crystalline domain size as the crystallinity increases. Combining these results with those from small angle x-ray scattering (SAXS), we can develop a method to determine crystalline domain sizes in more complex fluoropolymer formulations such as Kel-F or FK 800.

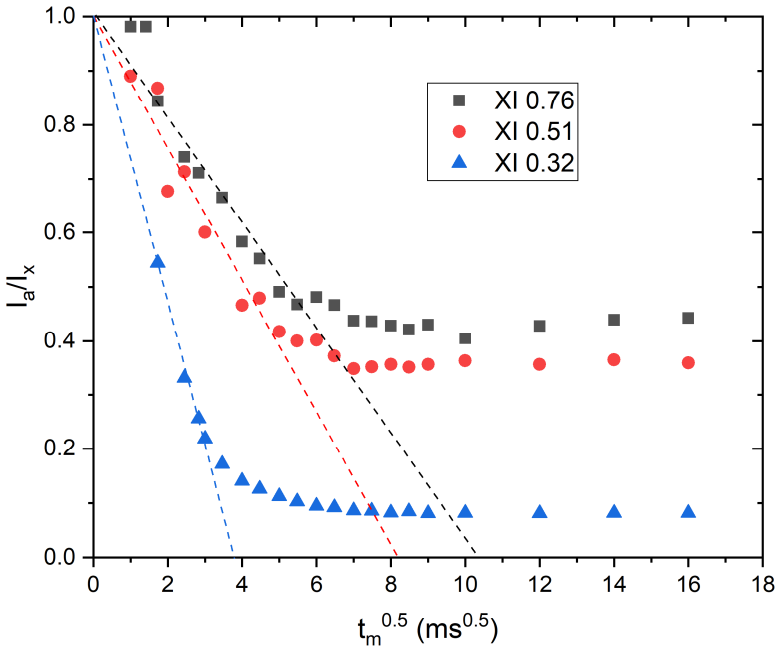

Figure 2. Intensity changes for the amorphous peaks as a function of spin diffusion time and crystallinity. The crystallinity ratio for each sample is provided in the Figure legend

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