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Chromophore Motion in Polymers for Nonlinear Optics by Solid-State NMR

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There is much current interest in polymer materials for nonlinear optical (NLO) applications. These materials are commonly prepared by either dissolving (doping) a suitable NLO chromophore into a glassy[1,2] or liquid crystalline polymer[3] or by covalently attaching the chromophore to the polymer host either by direct synthesis[4,5] or radiative cross-linking.[6] Regardless of the method of preparation, macroscopic orientation of the chromophore must be induced and maintained for efficient second-harmonic generation (SHG) in frequency-doubling applications. For the most common use of a glassy polymer host, chromophore orientation is achieved by the process of poling. Briefly, the material is heated above T_g, a strong electric field is applied to orient the chromophores, and the material is cooled below T_g to lock in the orientation before the field is removed. A major problem in polymeric NLO materials is loss of SHG properties over time. For example, in a study of 4-(dimethylamino)-4′-nitrostilbene in PMMA, Hampsch and co-workers reported that up to 80% of the SHG efficiency was lost after 12 h at 298 K.[1]

Improvements in NLO polymers will require long-term retention of chromophore orientation. Loss of orientation is (at least in part) related to the mobility of the chromophore in the polymeric host. Our laboratory is undertaking an investigation of orientation and dynamics in NLO polymers using suitable solid-state NMR experiments. In the first contribution from these investigations, we report an ^{15}N study of the molecular motion of a representative NLO chromophore, 4-nitroaniline, in two commonly used host polymers, poly(methyl methacrylate) (PMMA) and poly(vinyl cinnamate) (PVCN). This is the first report of an NMR study of the dynamics of an NLO chromophore in a polymer. Most previous NMR studies of small molecules dissolved in polymers have concentrated on changes induced in the polymer (plasticization or antiplasticization effects)[7-11] as opposed to the dynamics of the dissolved molecule itself.[12-15]

PMMA and PVCN were obtained from Aldrich, and 4-nitroaniline-$^{15}N_2$ was prepared by Cambridge Isotope Laboratories. The ^{15}N-labeled chromophore was doped (10% by weight) into the host polymer by casting films from either chloroform (PMMA) or toluene (PVCN). The films were air dried at room temperature and showed no evidence of phase separation. DSC curves were obtained for both polymers before and after doping. Glass transition temperatures were determined from the second heating ramp (20 K/min). Before doping, the T_g's for PVCN and PMMA were 357 and 390 K, respectively. Doping with 10% 4-nitroaniline-$^{15}N_2$ lowered these values to 336 and 357 K, respectively.

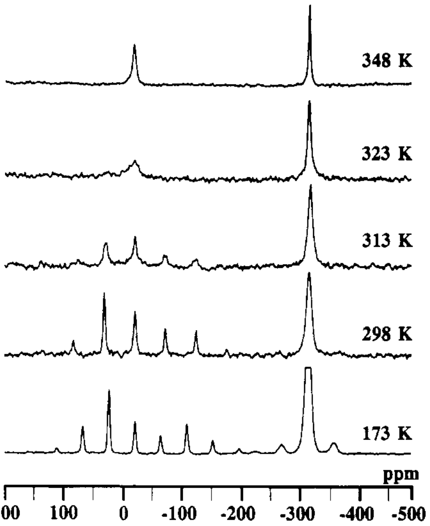

Figure 1. Variable-temperature ^{15}N MAS NMR spectra of 10% 4-nitroaniline-$^{15}N_2$ in poly(vinyl cinnamate) (T_g = 336 K).

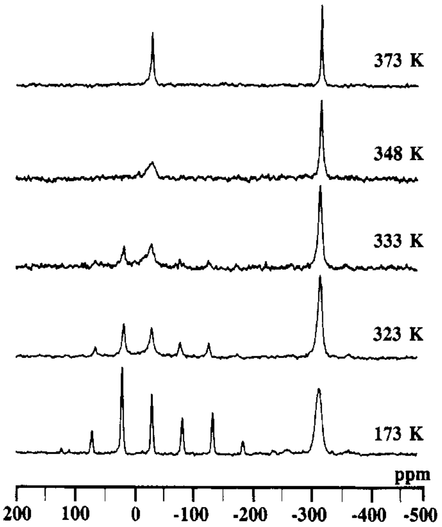

Figure 2. Variable-temperature ^{15}N MAS NMR spectra of 10% 4-nitroaniline-$^{15}N_2$ in poly(methyl methacrylate) (T_g = 357 K).

NMR interactions suitable for probing chromophore orientation and dynamics include chemical shift anisotropy (CSA), dipolar couplings, and quadrupolar coupling (e.g., ^{2}H spectroscopy). We selected the ^{15}N CSA for our first experiments because of the ubiquitous presence of nitrogen in the chromophores used in polymeric NLO materials, the absence of background signals from the polymeric hosts, and the possibility of obtaining site-specific orientation and dynamics information in future studies of large NLO chromophores such as azo dye derivatives. Variable-temperature ^{15}N spectra were acquired at 36.5 MHz on a Chemagnetics CMX-360. Spectra were obtained using both cross polarization (CP) and direct excitation with an ^{15}N 90° pulse (Bloch decay). CP gave better results below T_g, whereas Bloch decay provided higher sensitivity above T_g. All spectra were acquired at a spinning speed of a ca. 2 kHz.

CSA powder patterns are most conveniently characterized without sample rotation, but this straightforward approach suffers from lack of sensitivity and (in the case of multiple resonances) spectral overlap. We therefore obtained all NLO polymer spectra using slow-speed magic-angle spinning (MAS) and used the side-band intensities to calculate the chemical shift parameters by the method of Herzfeld and Berger.[16]

Selected ^{15}N MAS spectra of doped PVCN and PMMA are shown in Figures 1 and 2, respectively. The amino group nitrogen (−323 ppm) has a CSA that is too small for probing motion or orientation, and no further mention

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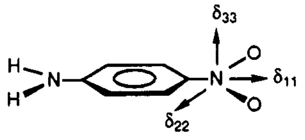
will be made of it. The ^{15}N on the nitro group, in contrast, has a large CSA which is very sensitive to motional averaging or orientation. The samples studied here were prepared without poling and are therefore unoriented. CSA patterns determined from spectra like those in Figures 1 and 2 thus reflect only motional averaging. The principal components of the ^{15}N chemical shift tensor, δ_{11}, δ_{22}, and δ_{33}, were determined by a Herzfeld–Berger analysis. The



CSA and asymmetry parameter, η, were calculated from the principal components using standard formulas.[17] The orientation of the tensor in the molecular frame was selected by analogy to previous studies of nitrobenzene[18] and benzoic acid.[19] For comparison, the chemical shift parameters for the chromophore were determined in the pure crystalline phase as $\delta_{11} = 200$ ppm, $\delta_{22} = -41$ ppm, $\delta_{33} = -91$ ppm, CSA = 266 ppm, and $\eta = 0.28$. A potential complication with the use of the nitro group as a probe of chromophore dynamics is the possibility of unrestricted rotation of that group about the C–N axis, which in the limit of continuous rotational diffusion would reduce η to 0 without changing the CSA. π-flips would have no detectable effect on CSA or η, and, as we will show, continuous rotation of the NO_2 group does not occur in the doped polymers below T_g, in spite of a low barrier in the gas phase.[20,21]

Chemical shift parameters for 4-nitroaniline doped in the polymers were essentially identical to those in the crystalline phase, provided that the temperature was more than ca. 40 K below T_g. At 20 K below T_g, the CSA was ca. 20% smaller than the rigid lattice value, but η was still near 0.28. The latter observation rules out continuous rotational diffusion about any single axis prior to the onset of large-amplitude isotropic motion.

The increase in chromophore motion as the sample temperature is raised is clearly reflected in the representative spectra in Figures 1 and 2. The spinning side bands noticeably broaden at ca. 30 K below T_g and coalesce to a single broad line at ca. 10 K below T_g. The resonance sharpens as the temperature is raised above T_g and narrows to a width comparable to that of the NH_2 resonance at ca. 20 K above T_g. This behavior closely resembles magnetic site exchange in liquids and was first described in detail for rotating solids by Waugh and co-workers.[22] The broadening in Figures 1 and 2 is due to the coherent averaging of the CSA by MAS encountering interference with the incoherent averaging by molecular motion on the same time scale. Waugh and co-workers showed that the maximum line width was achieved for isotropic rotational diffusion with a correlation time equal to the inverse of the spinning speed. We conclude that the 4-nitroaniline chromophore is tumbling isotropically on a time scale of ca. 0.06 ms at a temperature of ca. 10 K below T_g in either polymeric host. This observation is consistent with the observation of rapid loss of SHG properties in poled NLO polymer even at temperatures well below T_g.

This study demonstrates that ^{15}N NMR provides detailed information about chromophore dynamics on NLO polymers. Current studies are moving in three directions: measuring very slow motions at temperatures well below T_g using methods described by Spiess,[23] studying NLO polymers with azo dye chromophores, and developing NMR methods for measuring orientation in NLO polymers.

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