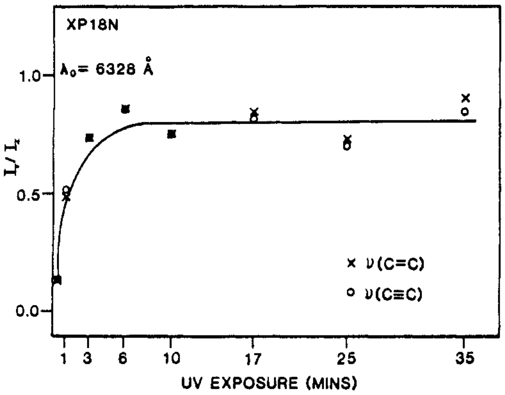

Figure 4. Fractional decrease in resonance Raman intensity for cross-polymerized poly(1,8-nonadiyne) after thermal treatment, as a function of UV exposure. I_T refers to the intensity after thermal treatment, I_I refers to the intensity before thermal treatment.

chromic transition is partially reversible, especially at higher (>17 min) UV exposures. In a future publication, this reversibility will be discussed along with a full study of the conversion and chromic behavior of XP18N using RR spectroscopy (employing various incident laser frequencies) and optical spectroscopy.

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Proton Magic-Angle-Spinning NMR Method for Determining Intimate Mixing in Polymer Blends

A knowledge of the intimacy of mixing is important for understanding the properties of polymer blends. A solid-state ^{13}C NMR method[1] is available to test for mixing on a molecular scale in systems where one of the two polymers is perdeuteriated and the other is fully protonated. This method relies on the short effective range (<0.5 nm) of the dipolar interaction between carbons and protons. When this dipolar interaction is strong enough, i.e., carbons on deuteriated chains are close enough to protons on the protonated chains, then cross-polarization[2] (CP) can take place between these two kinds of spins. Under circumstances where carbons on the deuteriated chains can be distinguished spectrally from those carbons on protonated chains, observation of a cross-polarized signal from carbons on the deuteriated chains provides strong evidence for intimate mixing. This method is semiquantitative and suffers from a rather low, but usually manageable, sensitivity. Moreover, in using this method, one must be cautious that residual proton-containing impurities do not cause any observed CP of the carbons on the deuteriated chains.

In this communication, we present an alternate method for identifying intimate mixing in a blend in which one polymer is deuteriated and the other is protonated. This method relies on the dipolar interactions among protons and involves direct proton observation in the presence of magic angle spinning (MAS).[3]

This method focuses on the proton signals arising from the residual protons (usually 1–2%) in a perdeuteriated solid polymer. In the presence of MAS, these signals behave very differently[4,5] depending on whether the immediate environment of the deuteriated molecules contains only deuterons or possesses some protons, e.g., protons belonging to a protonated molecule.

Consider the resonance of these residual protons in the perdeuteriated homopolymer. The protons are generally scattered statistically throughout a sample. As such, the most probable distance between first nearest-neighbor protons will fall into the 0.5–0.7-nm range. For a pair of protons separated by 0.5 nm, the maximum excursion of the dipolar interaction (which depends on the inverse cube of the internuclear separation) from its mean value over a rotor cycle is 1.44 kHz. Therefore, many protons in the deuteriated homopolymer will experience individual dipolar interactions with other protons no stronger than 1.5 kHz. Therefore, since MAS averages to zero dipolar interactions between pairs of spins,[3] the onset of this averaging will take place at very low spinning frequencies, ν_r. The evidence for this averaging is the breaking up of the nonspinning dipolar line shape into centerbands as well as sidebands which are displaced from the centerbands by multiples of ν_r.

The influence of the proton–deuteron dipolar interactions must also be considered since this effect will generally dominate the nonspinning line shape for the residual protons in the perdeuteriated homopolymer. MAS also averages these interactions because the lifetime of the I_z states of the deuterons tends to be longer than ν_r^{-1} since spin exchange between deuterons is not very facile.[6] Thus, the signal from the residual protons in a deuteriated matrix is typified by substantial sidebands and centerbands in the presence of low-frequency (1–2 kHz) MAS. In Figure 1 is compared the 200-MHz nonspinning proton spectrum (A) of a deuteriated (nominally 98%) atactic polystyrene, a-PS-D, to the MAS spectrum (B) of the same material with ν_r = 2.22 kHz. In spectrum B, about half of the total

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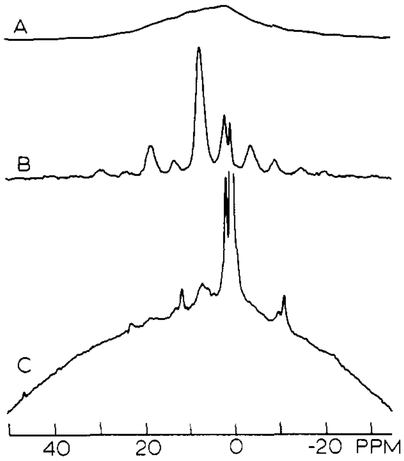

Figure 1. 200-MHz proton spectra of atactic polystyrenes: (A) 98% deuteriated (a-PS-D) nonspinning, 200 scans; (B) a-PS-D, ν_r = 2.2 kHz, 200 scans; (C) blend of 30% a-PS-D and 70% protonated (a-PS-H), ν_r = 2.2 kHz, 2000 scans. All spectra are normalized to the same weight of a-PS-D and the same number of scans. The substantial attenuation of the aromatic proton centerband at 7 ppm in C relative to B indicates that the protonated chains are in very close proximity to the deuteriated chains in this blend. The large resonances in the 0–2.5 ppm range in C arise from mobile proton-containing impurities; these impurities are present to a lesser extent in a-PS-D. The centerband of the aliphatic protons of polystyrene lies beneath these impurity peaks. Spectrum C displays base-line curvature because the broad and intense proton resonance of the a-PS-H chains lies underneath the resonance structure arising from the impurities and the more isolated residual protons in a-PS-D.

intensity resides in the centerbands and sidebands. The strong centerband at 7 ppm is assigned to the five aromatic protons. The three aliphatic protons give rise to a signal in the 1–2 ppm region. There are impurity peaks at about 0.4 and 1.7 ppm which overlap the aliphatic centerband. These impurity protons belong to one or more unidentified mobile species. The signal from these protons is also responsible for the resonance maximum in spectrum A. The sidebands of the aliphatic PS resonance are easily identified in spectrum B. These sidebands have only a small contribution from the impurity protons because of the weak dipolar interactions experienced by these spins. Note that the nonspinning line width for the residual protons in the deuteriated homopolymer is about 5 kHz. It is also important to recognize that, from a statistical point of view, the protons which contribute most strongly to the MAS centerbands are those which are most isolated from the other protons and deuterons. Thus the centerband is the spectral feature having the greatest sensitivity to the introduction of protonated chains in any blend involving the a-PS-D. This selection and sensitivity increases as ν_r decreases.

To test for intimate mixing in a blend of a-PS-D (30% by weight) and a protonated atactic PS (a-PS-H), we simply adjusted ν_r to the same value as in spectrum B and looked for evidence of the aromatic centerband and sidebands. Spectrum C is an expansion of the region of the broad resonance maximum for this blend. The underlying broad and intense a-PS-H line shape has a 35-kHz line width. Spectra B and C are normalized to the same mass of a-PS-D and the same number of scans. The amplitude of the aromatic centerband is attenuated in spectrum C to 15 ± 3% relative to this centerband amplitude in spectrum B. If phase separation into large domains had occurred, the amplitudes of the aromatic peaks in spectra B and C would be equal. The attenuation is proof that there is a high probability that protons on a protonated chain lie at a distance less than, say, 0.8 nm from the protons on the a-PS-D chains. That is to say, mixing is quite intimate. Intimate mixing in this blend is expected since both materials are a-PS. The only reasons for any phase separation would be an isotope effect or the 10-fold difference in molecular weights (1×10^5 for a-PS-D and 1×10^6 for a-PS-H).

The weakening of the aromatic centerband in spectrum C follows not only from the increase in static line width for those protons on the a-PS-D chains when protonated chains are introduced as neighbors but also because the protons on the a-PS-H chains are undergoing facile spin exchange[7] with one another over times shorter than ν_r^{-1}. This exchange interferes with the ability of MAS to average each dipolar interaction, especially between proton pairs on the a-PS-H chains but also between pairs where one proton is on an a-PS-D chain and the other is on a a-PS-H chain. (Although not shown here, the spectrum of the a-PS-H homopolymer exhibited no aromatic centerband at ν_r = 2.2 kHz.)

We regard this method to be a semiquantitative test for intimate mixing. At a fixed ν_r, one can compare spectra of the deuteriated homopolymer with spectra of its blends with protonated homopolymers having mobility and proton density similar to one another. By examining the intensity of the aromatic centerband in appropriately normalized spectra, one can thereby obtain a ranking of the intimacy of mixing in these blends. We have used this method along with the CP method to investigate intimacy of mixing in blends of atactic and isotactic PS. Substantial differences in centerband intensities are observed depending on the kind of blend and the thermal history of the sample. These results are now being written.

The method presented here has the following advantages over the CP method: (a) higher sensitivity, (b) simplicity of experiment, and (c) use of very modest spinning speeds. With respect to the problem of variable levels of residual proton impurities, the use of MAS enabled us to make our measurement in spite of the impurities because the aromatic resonance at 7 ppm is separate from the impurity resonances at 0–2.5 ppm. This method and the CP method share the liability that proton-containing impurities which are relatively rigid will create confusion for both methods. The near liquidlike mobility of the impurity in this case means that CP contributions from these impurity protons will be very weak and that contributions to the attenuation of the proton centerband will also be negligible.

Possibilities exist, in principle, for obtaining information about distributions of nearest-neighbor distances between the two kinds of polymer chains via the centerband attenuation behavior (relative to the deuteriated homopolymer) as a function of ν_r. The range of ν_r that one will have available will generally be determined at the low end by the resolution desired in the proton spectra, i.e., the minimum separation between sidebands that one can tolerate (about 1.8–2.0 kHz in our case). At the higher end, one wants to choose ν_r so that the protonated homopolymer gives no discernible centerbands which would interfere with the weak centerbands arising from the residual protons on the deuteriated chains.

Finally, it is clear that this method is not limited to polymeric systems. Mixing in any diamagnetic systems possessing similar proton densities could be probed in this way.

Registry No. a-PS-H, 9003-53-6; a-PS-D, 27732-42-9.

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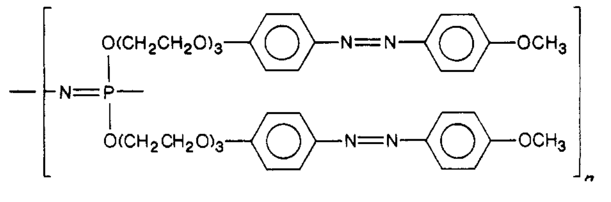
A Liquid Crystalline Poly(organophosphazene)

Polyphosphazenes comprise a broad class of macromolecules with the general formula $(NPR_2)_n$.[1-4] The physical properties of polyphosphazenes can be understood in terms of a highly flexible backbone, with specific physical or chemical characteristics imposed by the side groups. This side-group influence depends on the size, shape, polarity, and flexibility of the side units.[4]

In earlier work, we have explored the influence on the polymer properties exerted by flexible aliphatic side groups[4-6] or rigid units such as phthalocyanine,[7] TCNQ,[8] steroidal,[9] and other planar or rigid structures, both linked directly to the chain and separated from it by flexible spacer groups. One objective of these studies was to identify those molecular structural features that might lead to side-chain liquid crystalline behavior.[10,11] A conclusion reached from these studies was that liquid crystalline behavior was probably accessible provided the appropriate mesogenic groups could be linked to the polyphosphazene chain through a sufficiently flexible spacer unit.

Thus, our recent studies have focused on the synthesis of polymer 1, a species in which the mesogenic aromatic azo unit is linked to the polymer chain through tri(ethylene oxide) spacer groups.



Species 1 was synthesized by the reaction of poly(dichlorophosphazene) with $NaO(CH_2CH_2O)_3C_6H_4N{=}NC_6H_4OCH_3$. Poly(dichlorophosphazene) was prepared by the well-known polymerization of the cyclic trimer $(NPCl_2)_3$.[1-3] *p*-(Methoxyphenyl)azophenol was prepared by a diazo coupling reaction between *p*-anisidine and phenol. The hydroxyl group of 2-[2-(2-chloroethoxy)ethoxy]ethanol was protected by dihydropyran in methylene chloride with the use of pyridinium *p*-toluenesulfonate as a catalyst at 25 °C for 5 h.[12] The protected spacer unit was allowed to react with *p*-(methoxyphenyl)azophenol and sodium hydroxide in dimethyl sulfoxide in the presence of tetra-*n*-butylammonium bromide at 100 °C for 10 h. The coupled product was then deprotected in ethanol with pyridinium *p*-toluenesulfonate. The resultant alcohol was recrystallized from ethanol.[13]

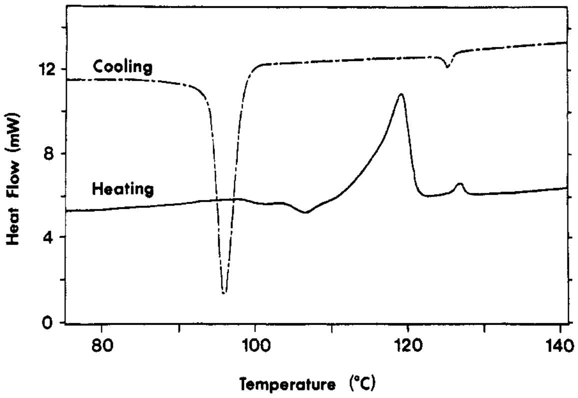


Figure 1. DSC thermograms of polymer 1 at a scanning rate of 10 °C/min.

Polymer 1 was then prepared by the reaction of poly(dichlorophosphazene) with the sodium salt of this alcohol in tetrahydrofuran at reflux temperature for 6 h. The final polymer was purified by precipitation from warm tetrahydrofuran into water, ethanol, and 50 vol % acetone in hexane.[14] On the basis of gel permeation chromatography data in THF solvent, $M_w = 6.8 \times 10^6$ and $M_n = 3.3 \times 10^5$.

The synthesis of 1 was preceded by trial reactions carried out with the cyclic trimeric chlorophosphazene $(NPCl_2)_3$ (**2**). Reaction of **2** with $NaO(CH_2CH_2O)_3C_6H_4N{=}NC_6H_4OCH_3$ yielded the corresponding organophosphazene trimer, $[NP(O(CH_2CH_2O)_3C_6H_4N{=}NC_6H_4OCH_3)_2]_3$ (**3**). This compound was characterized by NMR and infrared techniques.[15]

Polymer 1 was isolated as a pale yellow material that shows typical microcrystalline, thermoplastic properties at temperatures below 118 °C. Above 118 °C a mesophase is formed, detectable by optical microscopy with crossed polarizers and by differential scanning calorimetry (Figure 1). Melting of the mesophase occurs above 127 °C during the heating cycle to give the isotropic melt. Formation of the mesophase during the cooling cycle occurs at 126 °C. In the cooling cycle, supercooling is detected for the mesophase–crystalline phase transition (94 °C). Several cycles of heating and cooling within the temperature range of −100 to +200 °C showed that the phenomenon could be recycled. No evidence of thermal decomposition was detected.

Polymer 1 is the first polyphosphazene synthesized in our laboratory that shows definite thermotropic liquid crystalline character. A wide range of related derivatives have been prepared and studied, including examples in which aromatic Schiff's base units, aromatic ester groups, and aromatic amide groups have been linked to the backbone or ring through oxygen atoms in mixed-substituent polymers.[6] None of these was liquid crystalline. The analogue of 1 that lacks the terminal methoxy groups has been synthesized but has not yet shown evidence of liquid crystalline character

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