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Communications to the Editor

Conversion and Chromic Behavior of Cross-Polymerized Poly(1,8-nonadiyne)

Although most poly(diacetylenes) (PDA's) are insoluble, there is a growing class of these materials which are soluble in normal organic solvents. Most of these soluble poly(diacetylenes) can undergo a chromic transition in solution. The transition can be induced either by thermal treatment of the solution[1] or by reducing the solvent quality by addition of a nonsolvent.[2-4] Although the mechanistic details of this transition are still under debate,[5-7] it is generally agreed that the solvatochromic behavior is caused by a change in conjugation length in going from one phase to the other. In a good solvent, the chain forms a coiled structure. This coiled structure necessarily leads to a decrease in conjugation length compared to the crystalline form. This causes a blue-shift in the optical spectrum from approximately 600 nm in the crystal to about 450 nm in solution. Upon addition of a nonsolvent, the yellow solution will turn red or blue, and the optical spectrum shows a considerable red-shift. This is caused by an increase in the conjugation length of the PDA chain in the poor solvent.

Similarly, one would expect a decrease in order and, therefore, conjugation length upon melting of PDA chains. This behavior has also been observed.[15]

Our studies have dealt with chromic transitions in a unique PDA system. Instead of using conventional diacetylene monomers, we have been investigating the diacetylene macromonomer poly(1,8-nonadiyne) [P18N], which has the repeat unit

$$-[(CH_2)_5C{\equiv}CC{\equiv}C]_x-$$

Upon exposure to high-energy radiation, thermal annealing, or strain, this material reacts through the diacetylene units (via 1,4 addition) to form a two-dimensional network containing poly(diacetylene) chains (Figure 1).[9,10] This reaction has been shown to occur mainly in the crystalline regions of the material.[11] Although this network structure renders cross-polymerized P18N (XP18N) insoluble and infusible, the material shows distinct solvatochromic and thermochromic behavior. As mentioned earlier, this type of chromic change in PDA's is generally induced by dissolving or melting the polymer, and the transition is attributed to an introduction of disorder into the chain backbone, which causes a decrease in the effective conjugation length. Since XP18N is insoluble and infusible, it is not immediately apparent how this type of transition can take place.

This communication reports preliminary work which indicates that the chromic transition in XP18N is an order–disorder transition that is fundamentally similar to the chromic transition observed in other PDA systems. We have previously reported optical spectroscopic studies[9] (some of which will also be discussed here) which allowed a qualitative explanation of the chromic behavior in XP18N. Resonance Raman (RR) spectroscopy has also been used to help get more specific information about the changes that take place in XP18N after thermal treatment. The preliminary results from these RR and optical spectroscopic studies are summarized below.

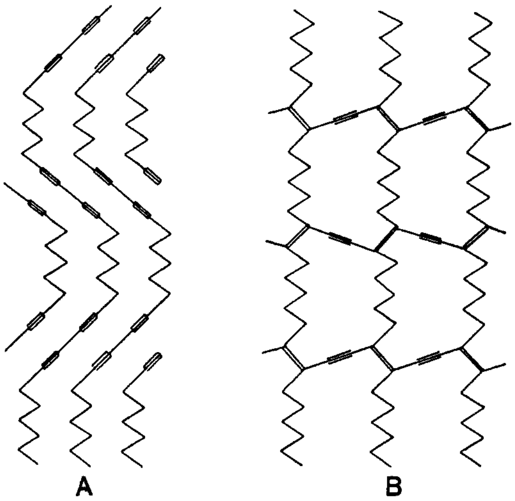

Figure 1. Schematic of poly(1,8-nonadiyne) cross-polymerization reaction: (A) macromonomer; (B) cross-polymerized product. Hydrogen atoms omitted for clarity.

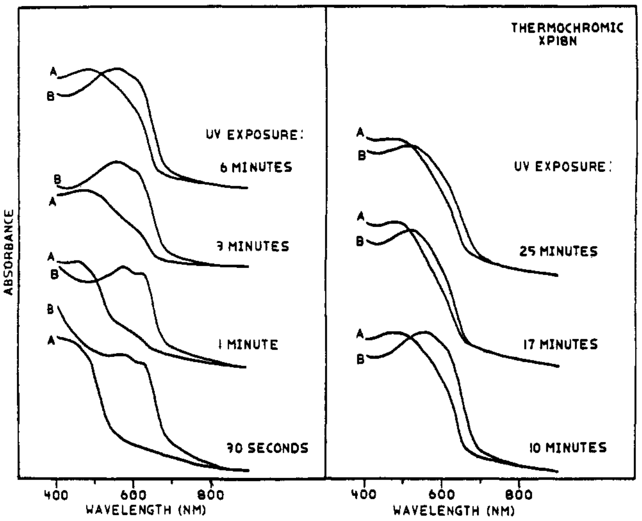

Figure 2. Optical spectra of cross-polymerized poly(1,8-nonadiyne) after various UV exposure times: (A) after thermal treatment (described in text); (B) before thermal treatment.

The poly(1,8-nonadiyne) used for these experiments was synthesized by the method of White.[8] Optical spectra were recorded on a Perkin-Elmer Lambda-4 spectrometer. RR spectra were recorded with a Spex double monochrometer using the 6328-Å line of a He–Ne laser with incident intensity of less than 1 mW. Thin films of P18N cast from a 1% methylene chloride solution were used for all spectroscopic studies. Cross-polymerization was induced by exposing the films to UV light (1600 $\mu W/cm^2$ at 254 nm) for various amounts of time under an argon purge. The films were mounted on a sample spinner to prevent sample heating due to the laser beam during the Raman experiments.

P18N films that are exposed to UV light for short time intervals (0.25–1 min) are light greyish-blue. As the UV exposure time is increased, the films become increasingly darker blue and eventually turn dark purple. Figure 2 shows that after 30-s UV exposure there are two absorbance maxima in the optical spectrum—one at 630 nm and one at 575 nm. As UV exposure is increased, the spectra

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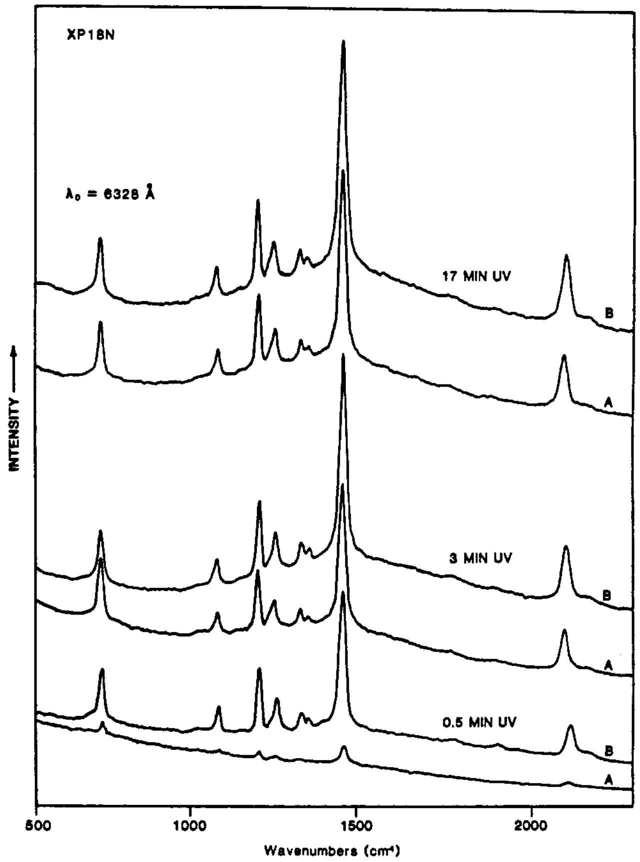

Figure 3. Resonance Raman spectra of cross-polymerized poly(1,8-nonadiyne) after various UV exposure times: (A) after thermal treatment (described in text); (B) before thermal treatment.

are blue-shifted and broadened, consistent with the observed color change. After the films are heated at 115 °C for 4 min and then cooled to room temperature, the spectra labeled A in Figure 2 are obtained. The sample with 30-s UV exposure is bright yellow after thermal treatment. Thermally treated samples with about 1 min of UV exposure are dark yellow, samples given about 3–10 min of UV exposure are orange, and samples with more than 10 min of UV exposure appear red to purple. The optical spectra illustrate the visual observations in a more quantitative way. The spectra show that at low conversions a large blue-shift is observed after thermal treatment and that as conversion is increased the blue-shift is less pronounced.

It should be noted that the thermochromic transition can be induced in this material only at temperatures above the melting point of the macromonomer (approximately 90 °C). We have also observed that solvatochromic behavior can be effected by soaking the cross-polymerized material in solvents that are capable of dissolving the macromonomer. Liquids that do not dissolve the macromonomer will not cause the chromic transition.

The optical spectra are able to give general information about the cross-polymerization reaction and the chromic transitions. To get more specfific information, studies using RR spectroscopy are now being performed. With various incident laser frequencies, the specific conjugation lengths in the sample can be isolated and studied.[12]

Our initial RR studies were performed with the 6328-Å line of a He–Ne laser, which closely corresponds to one absorption maximum (630 nm) of XP18N at low UV exposures. Figure 3 shows RR spectra of XP18N before and after thermal treatment (5 min at 120 °C and then cooled to room temperature) after three different UV exposure times. Before thermal treatment, the C=C stretching band is at 1463 cm^{-1} and the C≡C stretching band is at 2107 cm^{-1}. The other bands present in the spectrum are likely due to coupled modes between the PDA backbone and the aliphatic chains.[13]

As expected, the 30-s sample shows an almost complete loss of Raman intensity after thermal treatment. This is consistent with the blue-shift observed for the optical spectrum of the 30-s sample in Figure 2. As UV exposure is increased, the RR spectra after thermal treatment more closely resemble the spectra before treatment. This behavior is summarized in Figure 4 which shows the fractional decrease in Raman intensity after thermal treatment for $\nu_{\mathrm{C=C}}$ and $\nu_{\mathrm{C\equiv C}}$ plotted against UV exposure time. (It should be noted that the RR line widths do not change appreciably after thermal treatment so, therefore, it is possible to use the analysis shown in Figure 4. Full details of the method used to generate Figure 4 will be discussed in a future publication.) The figure shows that after about 3–6 min of UV exposure the intensity ratio reaches a plateau.

From the above results, one can get a general understanding of the processes causing the chromic transitions. As mentioned earlier, the degree of chromic response is directly related to the amount of UV exposure the sample has received—the longer the exposure time, the less drastic the change. This indicates that at low conversions, the PDA chains can become more disordered and, therefore, have shorter average conjugation lengths than at higher conversions. If the cross-polymerization is a homogeneous type of solid-state reaction (as are most diacetylene polymerizations[14]), the material will consist of isolated PDA chains in a macromonomer matrix (i.e., the network structure will not be very well developed) after short UV exposures. As the macromonomer is heated above 90 °C (or solvent treated), the remaining macromonomer can melt (or dissolve), forcing the isolated PDA chains to disorder, introducing large conformational changes and thereby decreasing the average conjugation length. As conversion is increased, the network structure becomes more developed and, therefore, less disorder can be induced after thermal (or solvent) treatment. When the conversion is high enough so that the network approaches full development (as in the schematic of Figure 1), disorder in the PDA chains after thermal (or solvent) treatment will be limited to bond angle deformations or small rotations about the single bonds. This will prevent the average conjugation length from decreasing much from the original value (the value before treatment). This explanation is consistent with the observation that there is more chromic change at low conversion than at high conversion.

The RR spectra obtained with 6328-Å light allow us to monitor changes in the portions of the sample that have PDA chains with long conjugation lengths. RR spectra obtained after thermal treatment show that at low conversions there is very little material with long conjugation lengths, but at slightly higher conversions (3-min UV exposure) there is a considerable amount of material in resonance after thermal treatment. The plot of I_T/I_I shows that, in regions where long conjugation lengths can form, large-scale disorder is limited after about 6 min of UV exposure. This would indicate that in these regions (probably the more perfect crystalline material in the sample) network formation is nearly complete after 6 min of UV exposure.

Although in situ thermal studies have not yet been performed, visual observations indicate that the thermo-

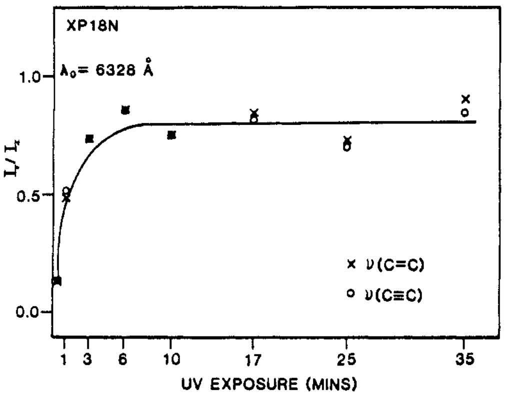

Figure 4. Fractional decrease in resonance Raman intensity for cross-polymerized poly(1,8-nonadiyne) after thermal treatment, as a function of UV exposure. I_T refers to the intensity after thermal treatment, I_I refers to the intensity before thermal treatment.

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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