Chromic Transitions in Cross-Polymerized Poly(α,ω-alkyldiyne) Macromonomers[1]

R. J. Butera,* B. Simic-Glavaski,† and J. B. Lando

Department of Macromolecular Science and Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.
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ABSTRACT: Chromic transitions have been observed in poly(α,ω-alkyldiyne) macromonomers that have been cross-polymerized by exposure to UV light. A solvatochromic transition can be induced by exposing the cross-polymerized material to liquids that are good solvents for the virgin macromonomer; similarly, a thermochromic transition can be induced by exposing the cross-polymerized material to temperatures greater than the melting point of the macromonomer. These transitions occur despite the fact that the cross-polymerized material is insoluble and infusible. The degree of chromic change has been found to be dependent upon the degree of conversion to the poly(diacetylene) form. Resonance Raman and UV–vis spectroscopic studies as well as X-ray diffractometry studies have shown that these chromic changes are due to order–disorder transitions. A study of the chromic behavior as a function of conversion for the macromonomer poly(1,8-nonadiyne) revealed that the cross-polymerization reaction is homogeneous and that the cross-polymerization process in the most highly ordered regions in the sample is virtually complete after about 3–6 min of UV exposure.

1. Introduction

It is now well-known that certain classes of poly(diacetylenes) (PDA's) are soluble in common organic solvents and that solutions of these PDA's can undergo dramatic color changes when the solvent composition is varied (see ref 2–5, for example). Yellow solutions are formed when a PDA is dissolved in a good solvent; in this case the chain backbone has a coil-like structure. If the solvent is made poorer, either by adding a nonsolvent or by decreasing the temperature, the solution undergoes a reversible yellow-to-blue or yellow-to-red transition. This transition is accompanied by a change in conformation from the coil-like structure to a rod-like structure and an associated increase in the conjugation length.

Likewise, some PDA's can undergo thermochromic transitions in the bulk state. When the proper temperature is reached, a reversible blue-to-red transition will take place. This color change is caused either by the thermal disruption of hydrogen bonding of the sidegroups or by a disordering of the methylene chains in the side groups, both of which induce a less planar backbone conformation.[6–10] For those PDA's that are capable of melting, a further red-to-yellow transition can take place, the yellow color being caused by a decrease in average conjugation length resulting from the large-scale disordering of the PDA chains, similar to the case of a PDA dissolved in a good solvent. The thermally induced red-to-yellow transition is generally not reversible.

It should also be noted that a blue-to-yellow thermochromic transition has been observed in a polyurethane–diacetylene system.[17] However, the yellow phase of this material can be induced without a substantial loss of crystallographic order. It appears that the flexibility of the side groups allows enough conformational disorder in the PDA backbone to form the yellow phase without disruption of the crystallites.

As the above examples indicate, the key to both the solvatochromic and thermochromic behaviors lies in the ability to cause conformational disorder along the PDA backbone.

Both solvatochromic and thermochromic behavior has been observed for the cross-polymerized poly(α,ω-alkyldiyne) macromonomers, despite the fact that the cross-polymerized material is insoluble and infusible. If the cross-polymerized material is exposed to a solvent that can dissolve the virgin macromonomer, a solvatochromic transition is observed. A thermochromic transition can be induced by exposing the material to temperatures above the melting point of the macromonomer. In addition, it has been found that the extent of the transition depends upon the degree of conversion: at low conversions, the originally blue material turns yellow, at moderate conversions turns orange, and at high conversions turns red. It is somewhat surprising that this type of chromic behavior can take place, considering the apparently rigid structure of the cross-polymerized macromonomers. One would expect that there would not be enough flexibility in the structure to permit a substantial decrease in the conjugation length, especially the kind of decrease needed for transition to the yellow phase. Since the yellow phase is usually associated with a coil-like structure, it is not immediately apparent how the cross-polymerized material can undergo the blue-to-yellow transition.

The goal of this paper is to describe the molecular mechanism of the chromic transition observed for the cross-polymerized macromonomers. In this context, visible spectroscopy has provided information that has allowed a general picture of the transition mechanism to emerge. Resonance Raman (RR) spectroscopy has been used to obtain more specific information about the transition process. It will also be shown that information about the nature of the solid-state cross-polymerization reaction can be obtained by studying the change in the chromic behavior as function of conversion.

Most of our studies to date have dealt with poly(1,8-nonadiyne) (P18N), and so most of the results presented here will pertain to P18N. Preliminary data on the chromic behavior of poly(1,6-heptadiyne) (P16H) and poly(1,11-dodecadiyne) (P111D) also will be presented. We will see that, although the cross-polymerized macromonomers are insoluble and infusible, useful analogies can be drawn between the chromic behavior of PDA solutions and the chromic behavior of the cross-polymerized materials.

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* To whom correspondence should be addressed at Exxon Research and Engineering Co., Corporate Research, Annandale, NJ 08801.

† Department of Chemistry.

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2. Experimental Details

Materials. All macromonomers used in this study were synthesized as described previously.[11,12]

Cross-Polymerization. Cross-polymerization of the macromonomer films was induced by exposing thin films of the macromonomers to UV light (1600 μW/cm^2 at 254 nm) under an argon purge. All films were cast from 1 wt % methylene chloride solution as described previously.[11,12] After the solvent was allowed to evaporate, the films were dried under vacuum for about 30 min in the dark prior to use.

Visible Spectroscopy. Spectra were recorded on either a Perkin-Elmer Lambda-4 spectrometer or a Perkin-Elmer Lambda Array 3480 spectrometer. Samples used for visible spectroscopy were thin films (0.01–0.05 mm thick) cast directly onto quartz plates (190-nm cutoff). High-temperature spectra were obtained by using an aluminum heating cell that was heated by four cartridge heaters. Temperature control was maintained by a Cole-Parmer temperature controller. The cell was continually supplied with a slow flow of argon to minimize sample degradation at elevated temperatures. Temperatures reported are +4 °C. Samples were allowed to equilibrate for 1 min after being placed in the temperature cell. (It was found that thermal equilibrium was reached after 30–45 s).

Resonance Raman Spectroscopy. RR spectra were recorded with a Spex double monochrometer using a 90° scattering arrangement. Thin films of 0.01–0.05 mm thickness were used. The films were mounted on a sample spinner to prevent sample heating due to the laser beam. The incident wavelengths used were the 6328-Å line of a Spectra Physics Model 124B He-Ne laser (incident intensity at sample less than 1 mW) and the 5145-Å line of a Coherent Radiation Model 52 argon ion laser (incident intensity at sample less than 15 mW).

X-ray Diffraction. X-ray diffraction patterns were recorded with a Phillips Model PN-3550/10 diffractometer using Cu Kα radiation. Thin films of 0.01–0.05 mm thickness were used.

3. Results and Discussion

3.1. General Observations of Chromic Behavior.

Upon exposure to UV light, the initially white P18N films turn blue, even at low UV doses. After 30 s of UV exposure, the sample is light blue in color. As the UV exposure is increased, the sample becomes darker blue and will eventually turn dark purple at long UV exposure times. If these irradiated samples are then heated above approximately 90 °C, a color change will occur, and the samples will not regain their original color, regardless of how much their temperature is lowered. Samples given short UV exposures (i.e. 30 s or less) turn bright yellow after thermal treatment. Samples with 1 min of UV exposure turn light orange, samples with 3–10 min UV exposure turn orange, and samples with more than 10 min of UV exposure turn red after thermal treatment.

Visual examination of the transition process shows evidence of partial reversibility at higher UV exposures. Samples given more than about 1-min UV exposure are lighter in color above 90 °C than at lower temperatures.

Similar chromic behavior is observed when XP18N is immersed in solvents that can dissolve the macromonomer. Solvents that will cause the transition include methylene chloride, chloroform, and tetrahydrofuran. Liquids that are not good solvents for the macromonomer will not cause the chromic transition. Samples with low conversions undergo the transition immediately upon exposure to the solvent. As UV exposure is increased, it takes longer for the sample to change color after being immersed in the solvent. Partial reversibility similar to that observed for the thermochromic transition is also observed for the solvatochromic transition; i.e. the samples were darker in color after drying than while immersed in the solvent. The principal difference between the solvatochromic and thermochromic responses is that, in general, the color change after thermal treatment is more dramatic than the color change after solvent treatment.

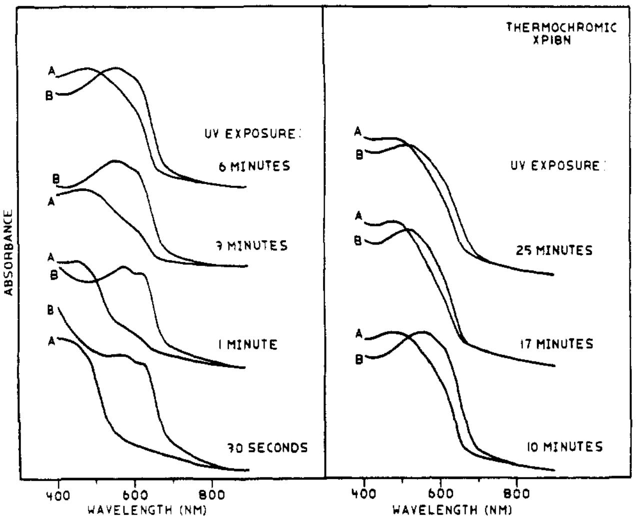

Figure 1. Visible spectra of cross-polymerized poly(1,8-nonadiyne) films. Spectra labeled (A) were recorded after the samples were heated to 115 °C for 4 min and then returned to room temperature. Spectra labeled (B) were recorded before thermal treatment. Sets of spectra have been arbitrarily offset for clarity.

3.2. Visible Spectroscopy.

Figure 1 shows the visible spectra of several P18N samples, each given a different UV dosage. Spectra B are from the irradiated macromonomer before thermal treatment. These spectra show the expected features.[12] The low conversion spectra show two maxima, one at about 645 nm and one at about 590 nm. These peaks shift to about 620 and 575 nm as conversion is increased.

It should be noted that none of the visible spectra shown have been corrected for scattering background,[12] since the heat and solvent treatment used to induce the chromic transitions would likely disrupt the crystallites in the sample (as discussed later) and thereby change the scattering profile from that observed before the heat and solvent treatment.

Spectra A in Figure 1 were obtained from the same samples as used for spectra B after they were heated to 115 °C for 4 min (under vacuum) and then quenched to room temperature. For the sample given 30 s of UV exposure, heat treatment results in a dramatic blue shift and broadening of the visible spectrum, similar to that observed for the spectrum of a PDA in a good solvent. The absorption maxima at 645 and 590 nm have disappeared, and the new maximum is at about 450 nm. As conversion is increased, there is less overall blue shifting of the spectrum after thermal treatment, and the absorption at 620 nm makes more of a contribution to the spectra of the thermally treated samples. After about 17–25 min of UV exposure, the spectra recorded after thermal treatment are nearly identical in character with the spectra recorded before thermal treatment.

The changes that take place in the visible spectra of XP18N after solvent treatment are fundamentally similar to those observed in the thermochromic case. Figure 2 shows the visible spectra of several XP18N samples both before (spectra B) and after (spectra A) solvent treatment. The solvatochromic transition was induced by immersing the XP18N sample (on a quartz plate) into methylene chloride for 5 min. The samples were removed from the solvent and vacuum dried for 30 min before the spectra were recorded.

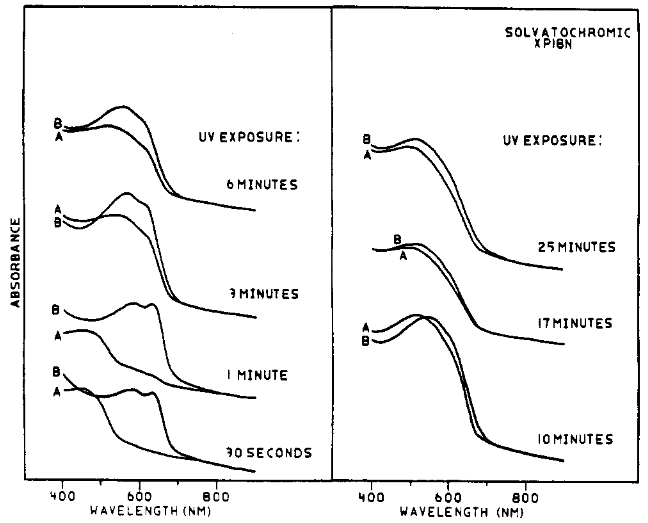

Figure 2. Visible spectra of cross-polymerized poly(1,8-nonadiyne) films. Spectra labeled (A) were recorded after the samples were soaked in methylene chloride for 5 min and then dried. Spectra labeled (B) were recorded before solvent treatment. Sets of spectra have been arbitrarily offset for clarity.

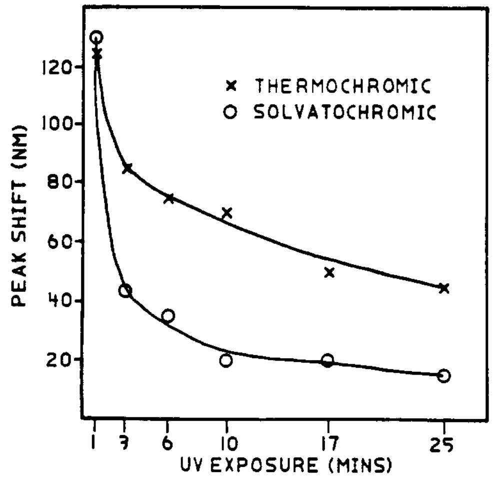

Figure 3. Change in absorbance maximum position for XP18N after thermal and solvent treatment, as a function of UV exposure.

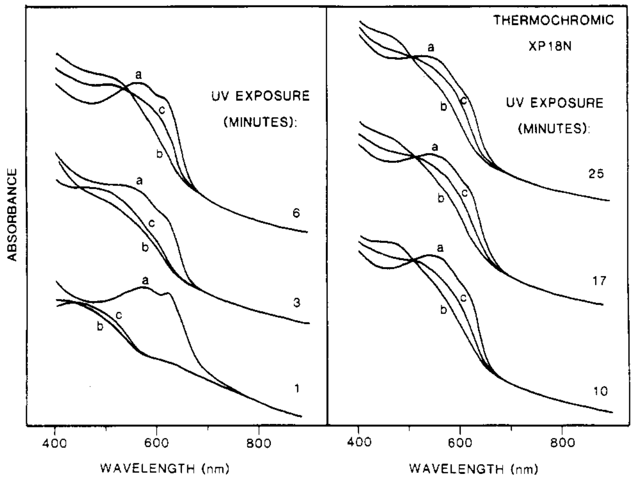

Figure 4. Visible spectra of cross-polymerized poly(1,8-nonadiyne) films. Spectra labeled (A) were recorded at room temperature. Spectra labeled (B) were recorded at 120 °C. Spectra labeled (C) were recorded after the samples were cooled from (B) back to room temperature. Sets of spectra have been arbitrarily offset for clarity.

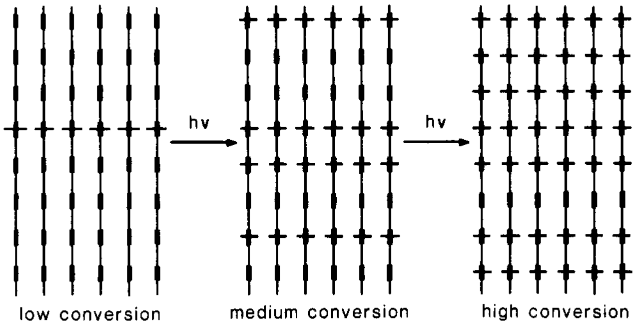

Figure 5. Schematic of the progressive development of network structure in poly(1,8-nonadiyne). The vertical lines represent the macromonomer chains, and the dashed horizontal lines represent the PDA chains formed upon cross-polymerization.

Figure 2 shows that the sample with 30-s UV exposure shows a very large blue shift after solvent treatment. As conversion is increased, there is less overall blue shifting and more contribution from the 620-nm band after solvent treatment. At high conversions, the shape of the absorption envelope for the solvent treated sample is nearly identical with that before solvent treatment.

Comparison of Figures 1 and 2 shows that the spectral changes that take place after thermal and solvent treatment are very similar. The main difference is that there is more blue shifting of the spectra of the thermally treated samples. This is demonstrated in Figure 3. In this figure, the peak shift after thermal or solvent treatment is plotted as a function of UV exposure time. For UV exposures of 1 min or less, the peak shift is effectively identical for the two cases. At longer UV exposures, the thermochromic transition shows a greater shift than the solvatochromic transitions.

As mentioned in the previous section, there is a small degree of reversibility in the chromic transitions that can be observed visually. Figure 4 shows the visible spectra of several XP18N samples before thermal treatment (A), at 120 °C (B), and after the samples are returned to room temperature (C). These spectra show that for the samples given less than 1-min UV exposure, the optical properties above the transition temperature are identical with the optical properties after it is returned to room temperature. At higher conversions, however, the high-temperature spectrum is shifted to shorter wavelengths than the spectrum that was recorded after the sample was cooled to room temperature.

3.3. General Mechanism of the Chromic Transition. As shown in Figures 1 and 2, the visible spectrum of a P18N sample with 30-s UV exposure shows a blue shift of over 150 nm after heat or solvent treatment. A blue shift of this magnitude indicates that the average conjugation length of the PDA chains is reduced to about five to six repeat units after the chromic transition, which is about the same conjugation length as found for PDA's dissolved in a good solvent or in the melt.[3,5,6] This, in turn, indicates that a large degree of conformational disorder, probably involving rotations about the PDA single bonds, must be induced in the PDA chains of the cross-polymerized material.

In order to achieve this kind of long-range disorder, the cross-polymerized structure at low conversions must consist of isolated PDA chains within a macromonomer matrix, as shown schematically in Figure 5. When the sample is exposed to heat (or solvent), the long segments of macromonomer chains that separate the isolated PDA chains will "melt" (or "solubilize"). As they disorder, these macromonomer segments will force the

PDA chains to disorder, causing a large decrease in the average conjugation length, which gives rise to the blue shift observed in the visible spectrum. In this respect, the unreacted macromonomer segments act like the "solubilizing side groups" found in soluble PDA's, in that these macromonomer segments are responsible for the induced conformational disorder of the PDA chains.[3,4,13,14] Thus, it appears that at low conversions the network structure is "loose" enough to allow considerable disorder to be induced in the PDA chains upon "melting" (or swelling) the unreacted macromonomer regions. The transition is irreversible, since the only way for the average conjugation length to be restored to the value observed before the transition would be for the PDA chains to regain their all trans-planar conformation. This is unlikely because it would essentially require the unreacted macromonomer segments to resume exactly the same positions they had before the transition.

As the degree of conversion increases, more PDA chains will start to "fill-in" the network structure. That is, the average length of the unreacted macromonomer segments separating the PDA chains will be reduced. This causes the structure to be more rigid and makes it more difficult for long-range conformational disorder to be introduced into the PDA chains. In energetic terms, the disordering of the unreacted macromonomer segments will become less of an entropic driving force as the unreacted macromonomer segments become shorter. The structure will become more constrained as to the possible conformations that can be accessed. This leads to less blue shifting in the visible spectrum after thermal or solvent treatment.

The increased reversibility of the chromic transition that is observed with increasing UV exposure is consistent with the above model. As discussed earlier, the long-range disordering of the long macromonomer segments that occurs in low conversion samples after heat or solvent treatment is permanent, since the segments are free to assume nearly any conformation. But at higher conversions, as the network structure becomes more complete, the remaining macromonomer segments are more constrained and do not have as many conformations available to them. These constraints not only limit the amount of disorder that can be developed while the sample is at temperatures above the transition temperature (or while the sample is immersed in solvent) but also make it more likely that the PDA chains will regain more of their original all trans-planar structure after cooling (or removing from the solvent).

This explanation of the mechanism of the chromic transition implies that the solid-state cross-polymerization is a homogeneous reaction, as opposed to a heterogeneous reaction where phase separation of the product occurs. The spectroscopic results are consistent only with a homogeneous cross-polymerization. If phase separation were to occur during the reaction, it would be virtually impossible to cause the large blue shifts observed after the thermal and solvent treatments, since the local environment around any given PDA chain would be very rigid (even at low conversions). This would prohibit the large-scale disordering needed to cause the decrease in the average conjugation length that gives rise to the blue shifts observed in the spectra of the low-conversion samples.

The differences between the thermochromic and solvatochromic behavior can also be understood in terms of the above discussion. The solvatochromic response depends upon the ability of the solvent to diffuse into the sample. At low conversions, this should not be difficult since the sample is mostly unreacted macromonomer, which the solvent can easily penetrate. But, as the conversion increases, there will be regions of the material that are composed primarily of cross-polymerized material. It will be more difficult for the solvent to diffuse into these particular regions and solvate the material. In addition, the amount of disorder induced will be dependent upon how effectively the solvent can solubilize the material once it has diffused into the sample. In the case of thermochromism, there will be no such limitations. Therefore, one would expect that the thermochromic response would be of greater magnitude than the solvatochromic response, at least at high conversions. At low conversions, where diffusion of solvent into the sample is not restricted, the solvatochromic and thermochromic responses would be expected to be nearly identical (as is observed).

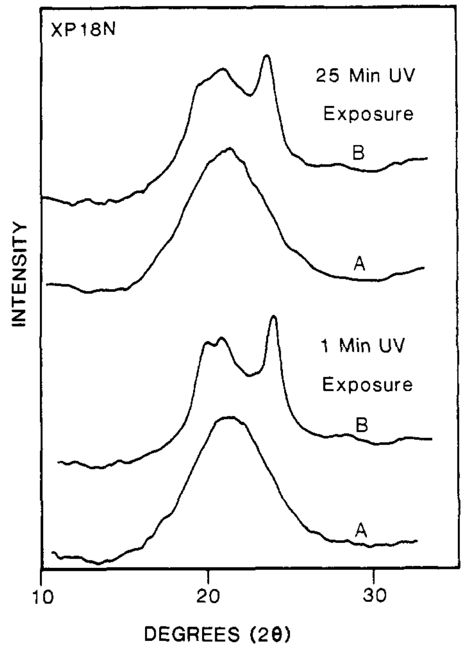

Figure 6. Wide-angle X-ray diffractometer patterns of cross-polymerized poly(1,8-nonadiyne): (A) after heating to 120 °C for 2 min and then returning to room temperature; (B) before thermal treatment.

On the basis of the spectroscopic evidence, we can conclude that the chromic transitions observed in XP18N are of the order–disorder type. The originally crystalline cross-polymerized material is disordered through exposure to heat or solvent. The order–disorder model is supported by the fact that the thermochromic transition occurs only at or above the melting temperature of the macromonomer, and the solvatochromic transition occurs only when the cross-polymerized material is exposed to solvents that will dissolve the macromonomer. These facts point to the important role played by the residual macromonomer in inducing the chromic transitions.

If these transitions are in fact order–disorder processes, we should observe a decrease in the amount of crystallinity of the samples after the transition takes place. The expected loss of crystallinity is observed, as demonstrated in the wide-angle X-ray diffractometer patterns shown in Figure 6. The patterns labeled B were obtained from XP18N films given the indicated UV dosage, and the patterns labeled A were obtained after the same samples were heated to 120 °C for 2 min (under argon purge) and returned to room temperature. Figure 6 shows that the behavior for the 1-min sample is almost exactly the

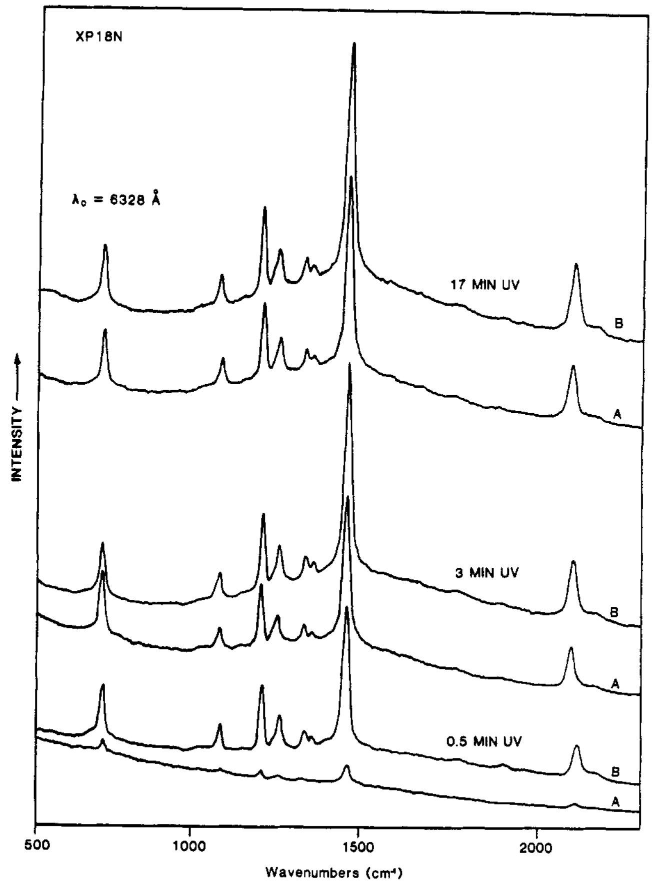

Figure 7. Resonance Raman spectra of cross-polymerized poly(1,8-nonadiyne) after various UV exposure times; (A) after heating to 120 °C for 5 min and then returning to room temperature; (B) before thermal treatment. Incident wavelength = 6328 Å. Sets of spectra have been arbitrarily offset for clarity.

same as that for the 25-min sample; the samples with intermediate UV doses showed the same behavior as the 1-min and 25-min examples. Thus, regardless of the degree of conversion, the chromic transition is accompanied by a loss of crystallographic order, which is consistent with the order–disorder mechanism proposed above.

3.4. Resonance Raman Spectroscopy. The previous sections of this paper have described a general mechanism for the thermochromic and solvatochromic transitions observed in XP18N. This section will show how resonance Raman spectroscopy can be used to obtain more specific information regarding the chromic transitions and about the progress of the cross-polymerization reaction. Most of the data to be presented was obtained by using 6328-Å incident light, since this wavelength presented the fewest experimental difficulties. Limited data obtained by using 5145-Å incident light will also be discussed.

Figure 7 shows RR spectra of XP18N before (spectra B) and after (spectra A) thermal treatment (5 min at 120 °C under argon purge and then cooled to room temperature). The two main features of these spectra are the C=C stretching band and the C≡C stretching band, occurring at 1464 and 2107 cm^{-1}, respectively, before thermal treatment. The other bands present in the spectra are due to coupled modes between the PDA backbone and the aliphatic spacers.[15] Since 6328-Å incident light was used to obtain these spectra, Raman scattering from regions having the longest conjugation lengths will be preferentially enhanced, and the vibrational information obtained will pertain to these PDA chains. Accordingly, the RR spectrum from the sample with 30-s UV exposure shows an almost complete loss of intensity after thermal treatment. This is expected on the basis of the drastic blue shift observed in the visible spectrum after thermal treatment (see Figure 1). As the UV exposure is increased, the RR spectra obtained after thermal treatment more closely resemble the spectra obtained before thermal treatment.

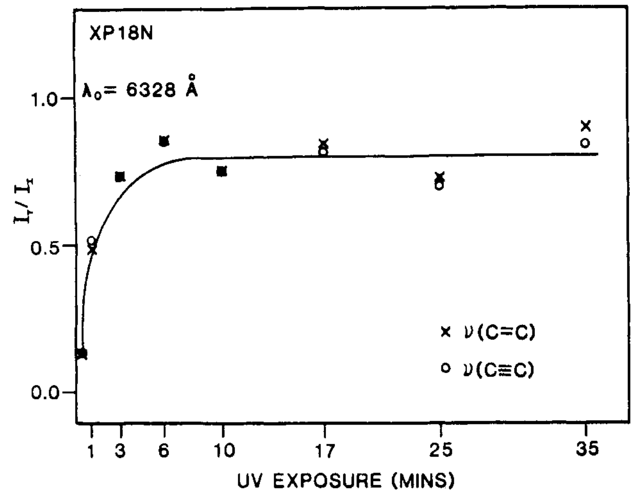

Figure 8. Fractional decrease in resonance Raman intensity for cross-polymerized poly(1,8-nonadiyne) after thermal treatment, as a function of UV exposure. I_T refers to the intensity after thermal treatment; I_I refers to the intensity before thermal treatment.

The observed intensity behavior of ν(C=C) and ν(C≡C) has been summarized in Figure 8, where the intensity after thermal treatment (I_T) divided by the intensity before thermal treatment (I_I) is plotted as a function of UV exposure time. Peak heights were used as intensities (peak heights and peak areas gave the same results, within experimental error, for several test peaks). The full widths at half-height are about 20 cm^{-1} for ν(C=C) and 23 cm^{-1} for ν(C≡C); these values stay constant (within experimental error) over the whole range of conversion, both before and after thermal treatment. Figure 8 shows that I_T/I_I for both ν(C=C) and ν(C≡C) increases sharply at short UV exposures and then reaches a plateau after about 3–6 min of UV exposure.

As mentioned earlier, since an incident wavelength (IW) of 6328 Å was used for the above RR experiments, the information obtained will pertain to those portions of the sample where long conjugation lengths can form, i.e. the most perfect crystalline regions of the sample. At low conversions, the results show that very little material with long conjugation lengths remains after thermal treatment, as evidenced by the very low RR intensity. This decrease in average conjugation length results because the network structure has not developed enough to prevent long-range disordering of the PDA chains after thermal treatment (as discussed earlier). However, after about 3–6-min UV exposure, the intensity ratio I_T/I_I reaches a plateau. This indicates that after 3–6 min of UV exposure, the network structure within the highly crystalline regions has developed as much as possible. In other words, the cross-polymerization reaction is effectively completed in the most ordered regions of the sample after about 3–6 min of UV exposure. This is in contrast to the behavior of the visible spectroscopic results which show that, overall, the reaction continues well past 6-min UV exposure.[12]

The frequency shift observed for ν(C=C) after thermal treatment parallels the intensity behavior discussed above. Table I shows the C=C stretching frequency both

Table I
Comparison of the Resonance Raman C=C Stretching Frequency of XP18N before and after Thermal Treatment (TC) at 120 °C (λ_0 = 6328 Å)

UV exp time, min	ν(C=C), cm^{-1}	TC, ν(C=C), cm^{-1}	$\Delta[\nu$(C=C)], cm^{-1}
0.5	1463	1470	7
1	1463	1468	5
3	1464	1467	3
6	1464	1466	2
10	1464	1466	2
17	1464	1466	2
25	1464	1466	2
35	1464	1466	2

before and after thermal treatment for various UV exposure times. At 30-s UV exposure there is a 7 cm^{-1} increase after thermal treatment. The frequency difference decreases as the UV exposure is increased, until a plateau is reached at about 6-min UV exposure, where there is a 2 cm^{-1} increase after thermal treatment. This is in contrast to ν(C≡C) which does not shift as a result of thermal treatment.

The reason for the observed increase in ν(C=C) after thermal treatment is probably related to the fact that the sp^2 carbons of the PDA backbone are directly bonded to the aliphatic spacer groups. Although at low conversions most of the PDA chains will be isolated, statistically there will be a few small regions where network development is sufficient to prevent the PDA chains from becoming severely disordered after thermal treatment. (Keep in mind that these "domains" do not have to be very large; as few as two PDA chains next to each other would likely prevent long-range disordering from occurring.) It is these regions that will give rise to the observed RR signal after thermal treatment. However, the macromonomer domains surrounding these regions will disorder after thermal treatment. Since the unreacted macromonomer segments are attached to the cross-polymerized domains via the PDA sp^2 carbon, the double bond could become somewhat strained by the disordered macromonomer after thermal treatment, giving rise to an increase in frequency. As the conversion is increased, there will be less overall disorder after thermal treatment and, consequently, less strain on the double bond and, thus, less frequency shift. The data in Table I suggests that after about 6 min of UV exposure, the network structure has reached its final stage of development; this is in good agreement with the intensity data shown in Figure 8.

In the context of this explanation, a frequency shift of ν(C≡C) would not be expected (since the triple bond is not directly attached to the aliphatic spacer), in agreement with the experimental observations.

It could be suggested that the frequency shift is related to a population effect. In this scenario, instead of observing a RR spectrum of the material that retains long conjugation lengths after thermal treatment, the observed spectrum would be due to a preresonance enhancement of the more plentiful material with short conjugation lengths. This would cause an increase in the Raman frequency. However, this explanation is unlikely since one would expect a much greater frequency shift if this were the case, especially at low conversions where the average conjugation length is about five to six repeat units after thermal treatment. In addition, if the shift was due to this type of conjugation length effect, the triple-bond stretching frequency would also be shifted, contrary to the experimentally observed behavior.

In order to obtain vibrational information about the behavior of the shorter conjugation lengths in the XP18N samples, it is necessary to use shorter incident wavelengths. Although it would be useful to perform an intensity analysis similar to that done for the RR spectra obtained by using 6328-Å light, two problems prevented this type of analysis when shorter incident wavelengths are used. First, RR spectra of thermally treated samples with 30 s and 1 min of UV exposure show an enormous amount of fluorescence, making it difficult to obtain the RR spectrum. At higher conversions, there is still an increase in fluorescence after thermal treatment, although spectra can be obtained. However, the large difference in fluorescence before and after thermal treatment makes accurate intensity comparisons difficult.

Second, more complicated band shapes are obtained by using shorter wavelength incident light than are obtained by using 6328-Å light. When 6328-Å light was used, only one band was obtained, and no changes in bandwidth were caused by thermal treatment or increased conversion. When the higher incident frequencies are used, new bands occur as a function of conversion and thermal treatment, making quantitative comparison of intensities before and after conversion extremely difficult and uncertain.

Although a detailed intensity analysis cannot be performed, other useful information can be obtained from spectra obtained with IW = 5145 Å. Figure 9 shows the RR spectra for several XP18N samples given the indicated UV dosage. The spectra labeled "B" correspond to XP18N samples before thermal treatment, and the spectra labeled "A" to the same samples after thermal treatment (5 min at 120 °C under argon purge and then cooled to room temperature).

The changes that occur in the C=C stretching region of the 5145-Å RR spectra as a function of UV exposure have been discussed.[12] As shown in the "B" spectra of Figure 9, a new peak at about 1515 cm^{-1} starts to develop at UV exposure is increased. It has been suggested[12] that this new peak is due to a "population effect"; i.e., the new peak is caused by an increase in the amount of material with short conjugation lengths as UV exposure is increased. This explanation is supported by the behavior of the RR spectra recorded after the samples are thermally treated. The spectrum of the thermally treated 3-min UV sample shows two peaks—the first is at approximately 1491 cm^{-1} and corresponds to the peak observed before thermal treatment, and the second is a new peak at 1537 cm^{-1}. (The peak positions are approximate since deconvolution of the bands was not performed.) The intensity of the new band is about twice the intensity of the 1491 cm^{-1} band.

It appears that this new band is caused by the increased amount of material with short conjugation lengths which is formed after the thermal treatment. The spectrum for the thermally treated 6-min UV sample shows that the intensity of the new band is only slightly greater than the intensity of the 1491 cm^{-1} band. After thermal treatment of the 10- and 17-min UV samples, the C=C stretching region shows only a broad envelope, and individual bands are not resolved; this indicates that the bands are of about equal intensity. Since the visible spectra show less blue shifting (and thus less material with short conjugation lengths) after thermal treatment as UV exposure is increased, one would expect the behavior described above if the high-frequency C=C band is due to the increase of short conjugation lengths in the sample after thermal treatment. Thus, the behavior of the RR spec-

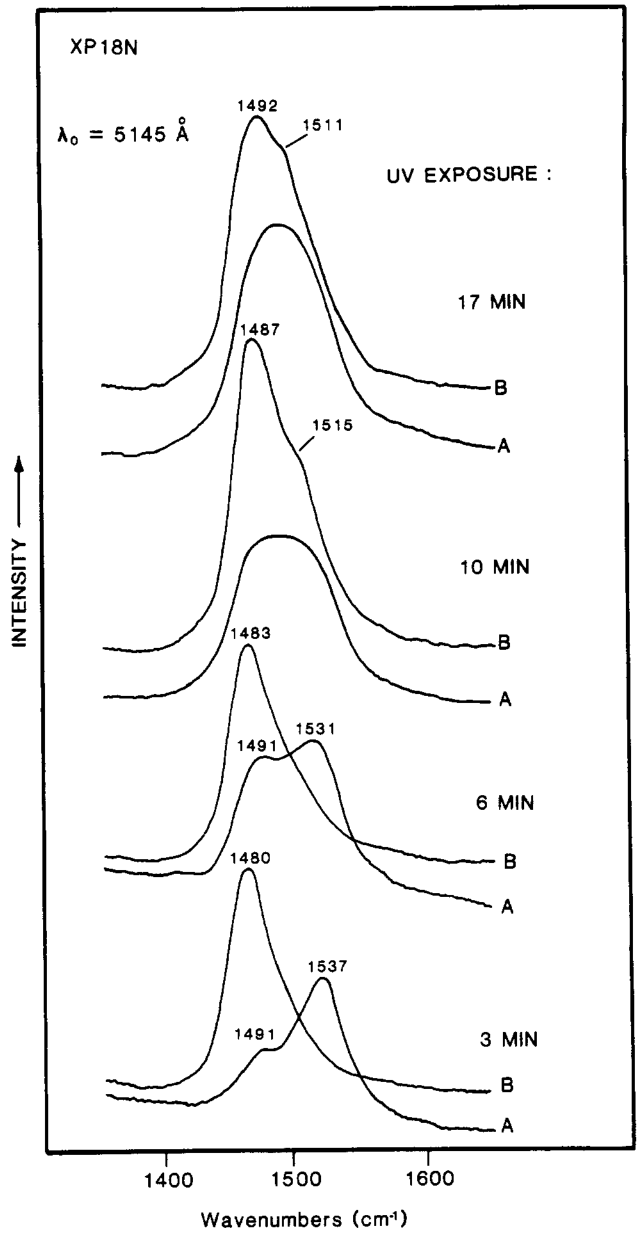

Figure 9. Resonance Raman spectra of cross-polymerized poly(1,8-nonadiyne) after various UV exposure times: (A) after heating to 120 °C for 5 min and then returning to room temperature; (B) before thermal treatment. Incident wavelength = 5145 Å. Sets of spectra have been arbitrarily offset.

tra of the thermally treated samples is consistent with the explanation that the high-frequency band that develops with increased conversion is due to the increased amount of material with short conjugation lengths.

The question remains as to why only one ν(C=C) band is observed when an incident wavelength of 6328 Å is used, and two are observed when IW = 5145 Å. At present we have no explanation for this behavior.

3.5. Chromic Behavior of XP16H and XP111D. XP16H and XP111D show both solvatochromic and thermochromic behavior, similar to that observed for XP18N. This section presents preliminary data that demonstrates the chromic behavior for these materials.

Visual examination of the thermochromic and solvatochromic transitions of XP111D yields results similar to those seen for XP18N—at low conversions, the material transforms from light blue to yellow, at moderate conversions, the material changes from blue to orange, and at high conversions, the change is from purple to red. Also similar to XP18N, the thermochromic transition temperature coincides with the melting point of the macromonomer (about 93 °C), and solvatochromism is caused only by solvents that dissolve the macromonomer (the same solvents that cause the solvatochromic transition in P18N also cause the transition in XP111D.)

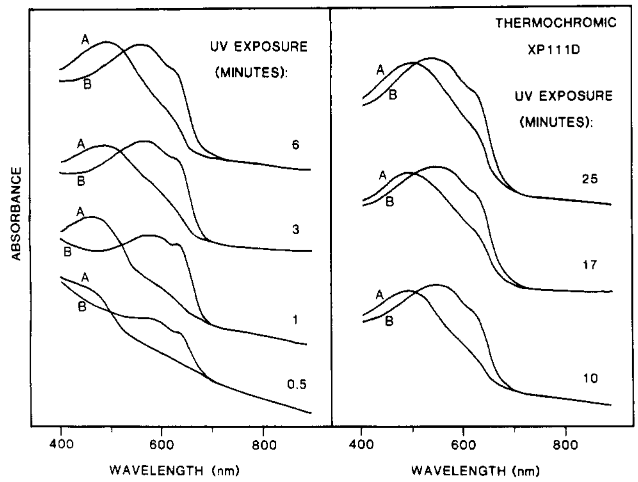

Figure 10. Visible spectra of cross-polymerized poly(1,11-dodecadiyne) films. Spectra labeled (A) were recorded after the samples were heated to 115 °C for 4 min and then returned to room temperature. Spectra labeled (B) were recorded before thermal treatment. Sets of spectra have been arbitrarily offset.

Figure 10 shows the visible spectra of XP111D both before and after thermal treatment (115 °C for 4 min under argon purge and then cooled to room temperature). The changes in the visible spectra of XP111D after thermal treatment are similar to those observed for XP18N. At low conversions, there is a drastic blue shift in the spectrum after thermal treatment; as conversion is increased, there is less drastic blue shifting after thermal treatment.

XP16H has similar solvatochromic behavior to both XP18N and XP111D. Visual examination of XP16H after the solvatochromic transition shows that the color changes that take place for XP16H are similar to those for XP18N and XP111D. However, the thermochromic behavior of P16H is significantly different from that of the other two macromonomer systems. Figure 11 shows the visible spectra of XP16H before and after thermal treatment (4 min at 120 °C under argon purge and then cooled to room temperature) for three different UV exposure times. The visible spectra of the thermally treated samples for UV exposures from 30 s to 25 min look nearly the same—they are very broad and blue shifted. All samples were dark yellow after thermal treatment.

The observed thermochromic behavior of XP16H is probably due to the fact that the material begins to degrade when raised above its melting temperature (even in an inert atmosphere[16]). This degradation would cause a decrease in the PDA chain length and, thus, would decrease the conjugation length, leading to the blue shifting observed for all samples.

If an XP16H sample is briefly held against a hot surface (such as a hot-plate), the thermochromic changes that occur are more similar to those seen for XP18N and XP111D (at high conversions the sample is red after heating rather than yellow). This suggests that a more thorough and careful study of the thermochromic behavior of XP16H will show that if degradation can be prevented, XP16H will show thermochromic behavior similar to that of XP18N and XP111D.

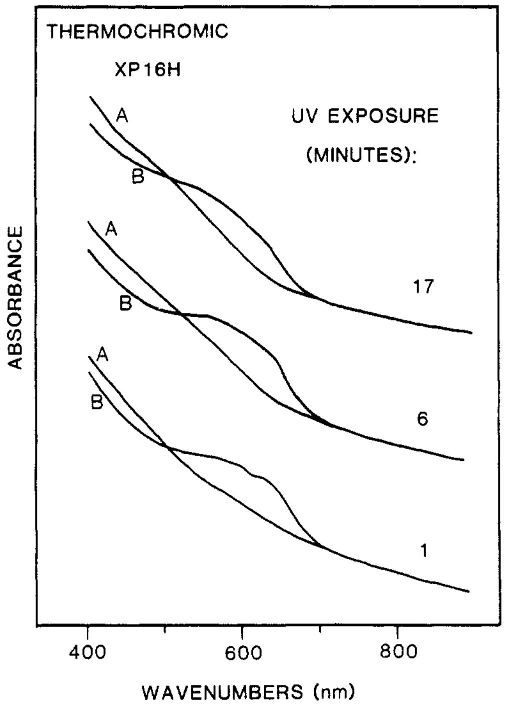

Figure 11. Visible spectra of cross-polymerized poly(1,6-heptadiyne) films. Spectra labeled (A) were recorded after the samples were heated to 120 °C for 4 min and then returned to room temperature. Spectra labeled (B) were recorded before thermal treatment. Sets of spectra have been arbitrarily offset.

4. Conclusions

XP18N can undergo chromic transitions that are surprisingly similar to those observed for conventional PDA's. This chromic behavior is dependent upon the degree of conversion; as conversion is increased, less chromic change is observed. This conversion dependence of the chromic behavior indicates that the cross-polymerization is a homogeneous reaction (at least for the degrees of conversion studied) and reflects the important role played by the unreacted macromonomer in bringing about the chromic transition. Specifically, disordering of the residual macromonomer forces disorder to be introduced into the PDA backbone, leading to a decrease of the average conjugation length in the sample and, thus, the observed color change.

Resonance Raman results (using 6328-Å incident light) have shown that the cross-polymerization reaction within the most highly ordered regions of the sample is virtually complete after about 3–6 min of UV exposure. This is in contrast to the visible spectroscopic results, which showed that, overall, the reaction continues well past 6-min UV exposure. The difference stems from the fact that RR spectroscopy preferentially probes specific regions of conjugation length within the sample, whereas visible spectroscopy gives more general information.

Chromic behavior has been observed for the other macromonomer systems we have investigated. Although a detailed investigation of the chromic transitions of these materials has not been made, the preliminary observations suggest that this chromic response is a general feature of the cross-polymerized macromonomers.

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Registry No. P18N, 30523-90-1; P16H, 30523-92-3; P111D, 77860-27-6.

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