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Cross-Polymerization of Poly(α,ω-alkyldiyne) Macromonomers

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ABSTRACT: The solid-state cross-polymerization reactions of several poly(α,ω-alkyldiyne) macromonomers $[-C{\equiv}CC{\equiv}C(CH_2)_n-]_x$ (where n = 3, 5, and 8) were characterized. UV–vis and resonance Raman spectra were recorded as a function of conversion, and the results show that a broad distribution of conjugation lengths is present in the partially cross-polymerized macromonomers. Results from samples in which the cross-polymerization was initiated with UV light were compared with those obtained by using samples that were thermally initiated. It was found that the distribution of conjugation lengths is probably caused by constraints imposed upon the growing poly(diacetylene) (PDA) chains by the crystallite size distribution and the crystallite defect density distribution of the sample as well as by UV-induced chain degradation (for those samples that were initiated with UV light). Resonance Raman spectra of the three macromonomer systems investigated show that the low-frequency bands are mixed modes that are primarily due to motions of the aliphatic spacer groups. The intensity behavior of the 720 and 1211 cm^{-1} bands indicates that a structural change takes place in the aliphatic side chains after about 1 min of UV exposure.

1. Introduction

Perhaps the most basic characterization parameter for a diacetylene material is the extent of conversion of the diacetylene reaction. The degree of conversion affects virtually all physical properties of the material. This parameter may be even more significant for the class of materials referred to as diacetylene macromonomers than for conventional diacetylenes, since the diacetylene polymerization in the macromonomers results in cross-linking within the crystalline regions.[1,2] Although this "cross-polymerization" reaction differs from conventional polymer cross-linking processes, one would expect many of the same types of physical property modifications to result from cross-polymerization as from more conventional cross-linking. For this reason, it is important to have a full understanding of how the structure of the macromonomer changes as a function of the degree of conversion. The work presented here is specifically concerned with understanding the structural changes which take place upon cross-polymerization of the poly(α,ω-alkyldiyne)'s, whose general structure is

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

Although the degree of conversion is a very basic quantity, it is difficult to measure quantitatively for the macromonomers. The most common technique used to determine the degree of conversion in conventional diacetylene systems is the monomer extraction method. In principle, monomer extraction is a very simple technique. A diacetylene monomer sample of known weight is exposed to high-energy radiation (or thermal annealing) for a given amount of time. The sample is then immersed in a solvent that will dissolve the monomer but leave the polymeric portion of the sample intact. The insoluble portion of the sample is recovered, thoroughly dried, and then weighed. The degree of conversion is determined by the ratio of the weight of recovered insoluble material to the weight of the original sample.

Despite the conceptual simplicity of the monomer extraction method, there are some complicating factors, even in the case of conventional diacetylene systems. At low conversions, the small amount of insoluble material formed may be difficult to fully recover, leading to an underestimation of the degree of conversion. At high conversions it is possible that small "pockets" of unreacted monomer could be trapped within a matrix of insoluble polymer. This effect would lead to an overestimation of the degree of conversion.[3]

The extraction method has even more severe drawbacks when applied to the macromonomers. If any portion of a particular macromonomer chain is incorporated into a cross-polymerized region of the sample, the whole chain will be rendered insoluble, leading to a gross overestimation of the degree of conversion. Clearly then, the monomer extraction technique is not a suitable method for determining the extent of cross-polymerization in the macromonomer systems (although we will see later that other useful information about the macromonomers can be gained from this technique).

Another method that can be used to determine the degree of reaction in conventional diacetylene systems is UV spectroscopy.[4] There is a weak monomer absorption (with associated vibronic peaks) at about 250 nm due to the diacetylene unit. As the polymerization pro-

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ceeds, this absorbance will decrease in intensity. The degree of conversion can then be estimated by the ratio of absorption intensity before reaction to the absorption intensity after reaction.

The UV–visible spectra of the macromonomer systems have curved base lines due to scattering (as will be demonstrated); since we are dealing with a semicrystalline polymer film, scattering of the incident light occurs because of the refractive index difference between the crystalline and amorphous regions. The scattering gets more severe as the wavelength decreases, causing the weak monomer absorption at 250 nm to be obscured. Thus, UV spectroscopy cannot be used to determine the absolute degree of conversion in the macromonomers.

Infrared spectroscopy could conceivably be used to monitor conversion in the macromonomers. Most diacetylenes show infrared bands associated with the C≡C stretch in the 2140–2260 cm^{-1} region. These bands are typically very weak due to the symmetry of the diacetylene unit (in the case of symmetrically substituted diacetylenes) and are quite irregular in shape.

This problem is intensified in the case of the macromonomers because the degree of conversion for the samples is quite low; since only the crystalline regions are able to react, the maximim attainable conversion will be equal to the degree of crystallinity, which is only about 30% for the macromonomers used in this study. This means that small changes in very weak bands would need to be measured.

Resonance Raman (RR) spectroscopy is certainly a sensitive way to monitor the diacetylene polymerization. However, it is difficult to quantify the results from resonance Raman spectroscopy for several reasons. The most significant problem is that the spectrum is representative of PDA chains of one particular conjugation length in the sample rather than the entire sample (see, for example, ref 16). We will see later that the cross-polymerized macromonomers contain a range of conjugation lengths; thus the RR technique would not give an accurate measure of conversion. Conventional Raman spectroscopy could be used to determine the degree of conversion by monitoring the decrease of the diacetylene C≡C stretching band (usually found near 2260 cm^{-1} [3]) as the cross-polymerization proceeds. However, this method will be valid only if an incident laser frequency is used that lies well outside the visible absorption envelope of the material. If an incident frequency that lies within any portion of the absorption band is used, it will result in a resonance Raman spectrum. Thus, in order to eliminate the resonance effect a long wavelength laser (such as an infrared laser) would be needed.

Because unit cell changes take place upon cross-polymerization, X-ray diffraction would seem a viable method to monitor the degree of conversion. Unfortunately, this method suffers from the fact that it is difficult to resolve changes in the diffraction patterns obtained from the macromonomer films. Since the films are of low crystallinity and have a fairly broad distribution of crystallite sizes, the diffraction maxima obtained are broad, making changes in the pattern difficult to identify and almost impossible to quantify. In addition, exposure to the X-ray beam can induce additional cross-polymerization of the sample. Although the X-ray induced reaction is minimal over the time needed to obtain a diffraction pattern, the results at low conversion would be somewhat suspect.

Solid-state ^{13}C-NMR spectroscopy has been used effectively to study structural changes that occur upon cross-polymerization of poly(1,11-dodecadiyne).[6] However, degrees of conversion were not measured in that study. The degree of conversion could be measured by monitoring the decrease in the peaks associated with the diacetylene triple-bond carbons. However, it is difficult to measure changes in nonprotonated carbons, especially ones within crystalline regions, because of their long relaxation times. Cross-polarization (CP) could be used to decrease the associated relaxation times, but it is usually very difficult to quantify information from CP spectra. In addition, sensitivity is a problem since relatively small changes need to be measured.

Differential scanning calorimetry has been used to obtain semiquantitative information about the degree of conversion.[21] Although this information is useful as an estimate, there are certain limitations to this method also. At low conversions, the DSC method underestimates the degree of conversion, and at high conversions the DSC method overestimates the degree of conversion (see ref 21 for details). Despite its disadvantages, the DSC method is the most quantitative way to estimate the degree of conversion for the macromonomers.

The above discussion demonstrates the difficulty in obtaining an accurate determination of the degree of conversion in the macromonomer systems. However, it is possible to obtain other useful structural information by using some of the spectroscopic techniques discussed above. The goal of the work reported here is to characterize the solid-state reactivity of the macromonomer systems. Most of the results presented pertain to one particular macromonomer system, poly(1,8-nonadiyne) (P18N), but preliminary results from two other systems, poly(1,6-heptadiyne) (P16H) and poly(1,11-dodecadiyne) (P111D), will also be discussed.

2. Experimental Details

Materials. The monomers 1,6-heptadiyne and 1,8-nonadiyne were purchased from Farchan Chemical Co. and were distilled once before use (1,6-heptadiyne, 108 °C at atmospheric pressure; 1,8-nonadiyne, 30–31 °C at 3.2 mmHg).

Since 1,11-dodecadiyne was not commercially available, it was synthesized from 1,8-dibromooctane and lithium acetylenide–ethylenediamine complex (LiAc·EDA) by using a literature procedure[24] with some modifications. The reaction can be written as follows:

$$2LiC{\equiv}CH{\cdot}EDA + Br(CH_2)_8Br \rightarrow HC{\equiv}C(CH_2)_8C{\equiv}CH + 2LiBr$$

All glassware used in this reaction was thoroughly dried at 120 °C before use. All chemicals were used as received.

To a three-necked, 500-mL round-bottom flask was attached a drying tube (containing fresh dririte), a 50-mL pressure-equalizing dropping funnel, and an argon purge line. Approximately 135 mL of dimethyl sulfoxide was added to the flask, and the flask was then purged for 0.5 h with argon. The argon flow rate was then increased slightly, and 0.30 mol of LiAc·EDA complex (Aldrich Chemical Co.) was added to the stirring dimethyl sulfoxide (the LiAc·EDA complex was weighed under argon purge). The solution–slurry was then placed in an ice bath and stirred vigorously for approximately 15 min. A solution of 0.1425 mol of 1,8-dibromooctane (Aldrich Chemical Co.) in 15 mL of dimethyl sulfoxide was placed in the dropping funnel and added dropwise to the slurry over a period of approximately 25 min. The reaction was allowed to proceed for 1 h at 0–1 °C. At this point an additional 50 mL of dimethyl sulfoxide and 0.078 mol of LiAc·EDA complex were added, and the reaction mixture was removed from the ice bath and allowed to react for an additional hour. After the reaction period was completed the mixture was placed back in the ice bath and 75 mL of water was slowly added to the mixture (the mixture frothed quite vigorously when the water was added). The mixture was allowed to stir for about 5 min, and then 200 mL of water was again slowly added to the reaction mixture. The hydrolyzed ture was then added to a 1-L separatory funnel, and an additional 200 mL of water was added to the mixture. The mixture was then extracted three times with hexane (200 mL of hexane each time). The combined hexane extracts were placed in a 1-L separatory funnel and washed six times with water (200–250 mL of water for each wash). The washed hexane extract was filtered, and the hexane was removed under reduced pressure, with gentle heating in a water bath. The remaining crude product was light yellow. This yellow liquid should be composed mainly of 1,11-dodecadiyne along with smaller amounts of 10-bromo-1-decyne and unreacted 1,8-dibromooctane.

The crude product was purified by vacuum distilling twice using a microdistillation path; the boiling point was 70–72 °C at 1.0–1.1 mmHg (other workers have reported a boiling point of 104 °C at 15 mmHg[26]). To confirm the purity of the product, an ^{1}H NMR spectrum of the product was obtained. The spectrum showed that the reaction product has no measurable amount of brominated material remaining, as evidenced by the absence of resonances at 3.40 and 1.85 ppm in the product spectrum; resonances in these positions would indicate the presence of 1,8-dibromooctane and/or 10-bromo-1-decyne.[25]

Synthesis of Macromonomers. All macromonomers used in this study were synthesized by using a Glaser coupling reaction.[22] The details of this reaction as used to synthesize poly(1,8-nonadiyne) can be found elsewhere.[21,23] The same procedure has been used to synthesize the macromonomers used in this work. The macromonomers produced by this reaction are white, semicrystalline materials.

Molecular weight averages were obtained by using gel permeation chromatography. The GPC analyses were carried out by using a Perkin-Elmer Series 10LC chromatograph (equipped with an LC-100 column and a Sigma 15 data station), using a UV detector and tetrahydrofuran as solvent (1 mL/min, 40 °C). All molecular weights reported are with respect to polystyrene standards. The molecular weights for the macromonomers are listed in Table I.

Table I
Macromonomer Characteristics

sample	M_w[a]	M_w/M_n[a]	mp,[b] °C
P16H	30 000	2.10	113
P18N	33 500	1.90	90
P111D	38 500	2.05	93

[a] Determined by GPC. [b] Determined by DSC.

All three macromonomers are soluble in methylene chloride, chloroform, and tetrahydrofuran at room temperature. More extensive solubility studies were performed on P18N than on the other macromonomers. The results of these studies showed that benzene is also a good solvent for P18N at room temperature; 1,2-dichloroethane and 1,2-dichlorobenzene will dissolve P18N at room temperature, but not as readily as the above solvents. 1,3-Dichlorobenzene and all three isomers of xylene were found to dissolve P18N at elevated temperatures.

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. Thermally cross-polymerized samples were held at room temperature (approximately 20 °C) in the dark for various amounts of time. The films were prepared as described previously.[21] Briefly, the films were formed by casting a 1 wt % methylene chloride solution of the chosen macromonomer onto a glass microscope slide (or quartz plate, for use in UV–vis studies) placed under a petri dish (to control solvent evaporation). This process was carried out on top of a levelled glass plate to ensure film uniformity. Films produced by this method were approximately 30% crystalline (as determined by X-ray diffractometry). The films were dried under vacuum in the dark for about 30 min prior to use.

UV–Visible Spectroscopy. Spectra were recorded on either a Perkin-Elmer Lambda-4 spectrometer or a Perkin-Elmer Lambda Array 3840 spectrometer. Samples used for UV–visible spectroscopy were thin films (0.01–0.05 mm thick) cast directly onto quartz plates (190-nm cutoff).

Resonance Raman Spectroscopy. RR spectra were recorded with a Spex double monochromator using a 90° scattering arrangement. Free-standing thin films (0.01–0.05 mm thick) were used for all RR experiments. These films were mounted on a sample spinner to prevent sample heating due to the laser beam. Various incident wavelengths were used: 6328-Å line of a Spectra Physics Model 124B He–Ne laser (incident intensity at sample less than 1 mW) and 5145, 4965, and 4880 Å lines of a Coherent Radiation Model 52 argon ion laser (incident intensity at sample less than 15 mW).

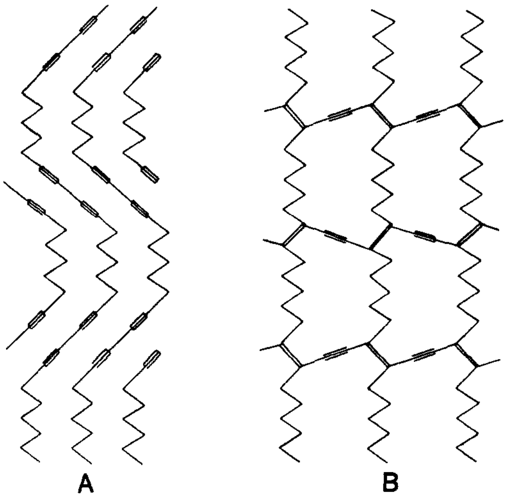

Figure 1. Schematic of poly(1,8-nonadiyne) cross-polymerization reaction: (A) macromonomer; (B) cross-polymerized product. Hydrogen atoms omitted for clarity (from ref 2).

Extraction Studies. Thin films (0.01–0.05 mm thick) were prepared as described above. The films were dried, irradiated, and then weighed on a Perkin-Elmer autobalance. Each sample had a weight of about 4 mg. The samples were placed in a vial containing 20 mL of methylene chloride and were then allowed to soak for 24 h. The samples were removed from the solvent, dried under vacuum for 8 h (constant weight was usually attained after about 2 h), and subsequently weighed. The fractional weight loss was calculated by dividing the weight of the sample after solvent treatment by the sample weight before solvent treatment. Results reported are averages of at least four samples for each UV exposure time.

3. Results and Discussion

3.1. UV–Visible Spectroscopy. Upon exposure to UV light, cross-polymerization takes place in the crystalline regions of P18N to form a structure like that shown schematically in Figure 1. The conjugated PDA backbone gives rise to optical absorption in the visible region of the spectrum, thus causing the cross-polymerized material to be highly colored. Although the monomer absorption usually observed in the UV spectrum cannot be used to investigate the cross-polymerization reaction (as discussed in the Introduction), changes in the visible region of the spectrum can give clues about the structural changes that occur as a function of conversion.

Before discussing the changes that occur in the visible spectrum as conversion is increased, it will be useful to discuss some general features of the UV–visible spectrum of a semicrystalline, as-cast P18N film that has not been exposed to radiation. As expected, the white macromonomer film shows no absorbance in the visible region (Figure 2, spectrum A). However, it does show a base line that becomes more curved as the wavelength is decreased. This type of base line is usually caused by scattering of incident light by the sample. As indicated in the Introduction, in a semicrystalline polymer film, this scattering can be caused by the difference in refractive index between the crystalline and amorphous portions of the sample. It is also possible that scattering

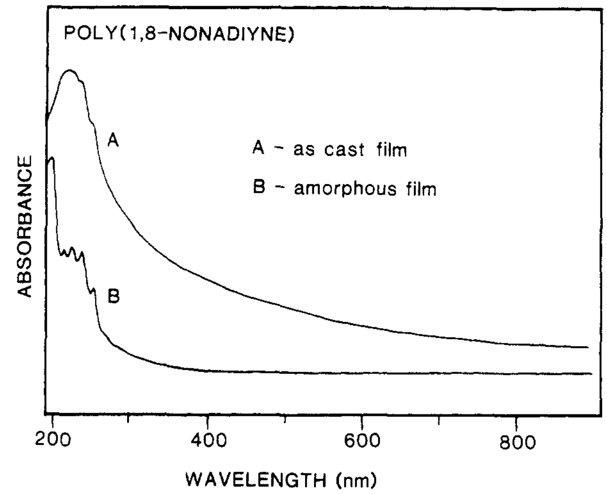

Figure 2. UV-visible absorption spectra of a poly(1,8-nonadiyne) film: (A) solution cast film; (B) same film as in (A) except heated to 120 °C, annealed for 5 min, and quenched to room temperature.

from the air-film interface could contribute to this behavior.[4] To determine if surface scattering were contributing to the base-line curvature, a drop of distilled water was placed on the top of the film so that a quartz–P18N–water–quartz sandwich was formed. The same procedure was repeated with various other liquids with different refractive indices. It was found that the base line was virtually unaffected by this procedure. Thus, it seems that surface scattering is not contributing significantly to the base-line curvature.

To confirm that the base-line curvature is caused by scattering due to the semicrystalline nature of the sample, the film used to produce spectrum A in Figure 2 was heated to 120 °C and held there for 5 min. The film was then quenched to room temperature to yield a clear, amorphous (as determined by X-ray diffractometry) P18N film. The UV-visible spectrum of the film is shown in Figure 2 (spectrum B). The base line of the amorphous sample is flat over the visible region of the spectrum. The absence of the strong base-line curvature in the amorphous sample indicates that the curvature was due to the semicrystalline nature of the P18N film. The same behavior was noted with the other macromonomers studied.

In addition, a progression of peaks caused by the diacetylene group is observed between 210 and 260 nm in the amorphous film. These peaks show a spacing of about 2200 cm^{-1}, which is near the triple bond stretching frequency expected for a diacetylene linkage.[4,5,7] There is also an intense peak centered at about 198 nm. The origin of this peak is not known with certainty, but it appears in all macromonomer systems investigated. Although we have not performed studies specifically to determine the origin of this peak, it is likely that it is due to hyperconjugation of the single bond joining the diacetylene group to the alkyl chain.

As expected, the scattering observed in the P18N spectrum is also observed in the visible spectra of the cross-polymerized films (cross-polymerized P18N will be referred to as XP18N). Figure 3A shows a P18N film that has been exposed to UV light for 2 min. Figure 3B shows the same spectrum after correcting for scattering by subtracting the spectrum of the same film recorded before UV irradiation. The validity of this subtraction procedure is based upon the assumption that the scattering from the sample is unaffected by the UV irradiation process. The background scattering could be altered by effects such as volume changes in the crystallites during cross-polymerization; however, the change in background scattering is probably negligible compared to the overall scattering magnitude. Thus, all visible spectra of the cross-polymerized macromonomers shown here have been corrected for scattering background in this way.

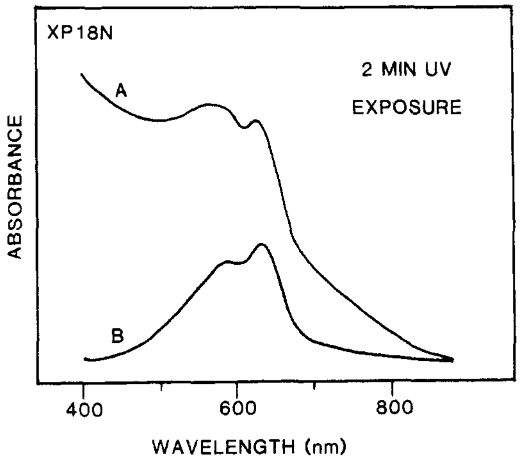

Figure 3. (A) Visible absorption spectra of a poly(1,8-nonadiyne) film exposed to UV light for 2 min. (B) Same film as (A) except corrected for scattering.

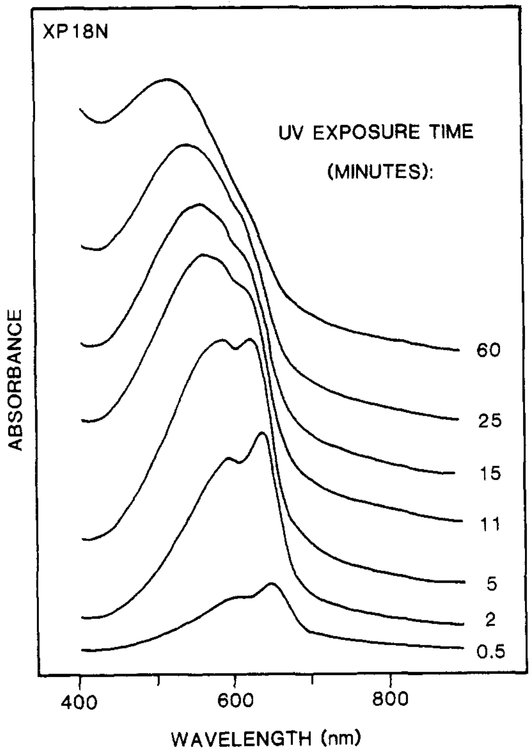

Figure 4. Visible absorption spectra of a poly(1,8-nonadiyne) film recorded after various UV exposure times. All spectra have been corrected for scattering and have been arbitrarily offset for clarity.

Figure 4 shows visible spectra for a P18N sample which has been given increasing amounts of UV exposure. The main features of the XP18N spectra are similar to the visible spectra of conventional PDA's. At low conversions, two maxima are clearly visible—one at about 645 nm and one at about 590 nm. As the UV exposure is increased, the relative intensities of the two maxima change until, at about 5 min of UV exposure, the relative intensities are the same. Also, at this point the two maxima have shifted to about 620 and 575 nm. Further irradiation increases the intensity of the 575-nm band more than that of the 620-nm band. Until about 5 min of exposure, both peaks gain overall intensity, but at higher exposure times the 620-nm peak actually starts to lose intensity (this will be discussed at greater length in the next section). There is a continual broadening and blue shifting of the absorption envelope and an increase in the intensity of the high-energy tail as UV exposure is increased. After about 25 min of UV exposure, a broad, nearly featureless envelope is obtained.

The changes that take place in the visible spectrum can be identified by the changes in color observed with increasing UV exposure. At low UV doses (from the start of irradiation to about 1-min UV exposure) the samples are light grayish blue. As exposure time is increased, the sample color progresses to blue, dark blue, purple, and, at very high irradiation times (i.e. greater than about 25 min), dark purple.

When interpreting the XP18N visible spectra, it is important to remember that the macromonomers are relatively poorly ordered semicrystalline materials (recall that the films used in this study are only about 30% crystalline). The films will contain some amorphous regions, some crystalline regions with varying degrees of defect density, and some nearly perfect crystalline regions. This is in contrast to conventional diacetylenes that are usually nearly 100% crystalline and are often studied in the form of macroscopic single crystals. The breadth of the visible absorption peaks for XP18N is greater than is generally observed for PDA single crystals but is similar to the breadth of spectra obtained from polycrystalline PDA films. The broad peaks are caused by the fact that a wide distribution of PDA chain lengths (and, thus, conjugation lengths) is present in the sample (the existence of various conjugation lengths will be confirmed by resonance Raman spectroscopy in a later section). Because cross-polymerization is a topochemical reaction, the growth of a PDA chain will stop when a defect is encountered. The defect could be in the form of a crystallite boundary or a lattice mismatch within the crystallite. In small crystallites, the PDA chain length will be short since the chain can grow no longer than the crystallite dimension that lies along the direction of chain growth. In regions where the defect density is high, the PDA chain length will be governed by the distance between defect sites. It is therefore likely that chains initiated in the less perfect crystalline regions, or in small crystallites, contribute to the low wavelength absorption observed in Figure 4. This effect will also add to the breadth of the absorption envelope. As noted, the breadth of the XP18N spectra is similar to that of spectra obtained from polycrystalline films of conventional PDA's.[4] The spectra of those films also would be expected to be broad since in that case as well there will be a distribution of crystallite sizes and perfection.

In the visible spectra of some conventional PDA's there is often observed a pair of absorption maxima in the 500–600 nm region, in addition to the primary, lowest energy absorption in the 600–650 nm region. These higher energy absorptions are vibrational sidebands. The lower energy sideband is separated from the primary absorption by about 1450 cm^{-1}, the frequency of the PDA C=C stretching vibration, and the higher energy sideband is separated from the primary peak by about 2100 cm^{-1}, the frequency of the PDA C≡C stretching vibration. In the XP18N spectra there is only one broad maximum in the 500–600 nm region. This broad band probably results because the broad range of conjugation lengths in the sample causes a range of sideband wavelengths to be observed, preventing the resolution of two separate sidebands.

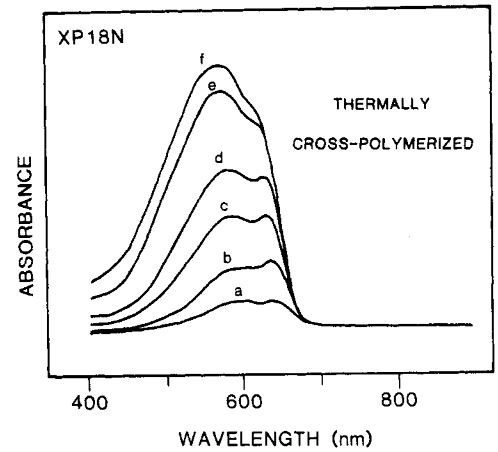

Figure 5. Visible absorption spectra of a poly(1,8-nonadiyne) film thermally polymerized in the dark at 20 °C for the following amount of time: (a) 10 days, (b) 15 days, (c) 20 days, (d) 25 days, (e) 35 days, and (f) 45 days. All spectra have been corrected for scattering.

One likely factor contributing to the broadening and blue shifting of the spectra with increasing UV exposure is UV-induced degradation of the PDA chains. This degradation has been observed in PDA solutions[8–10] and could also reasonably be expected to occur in solid PDA's.[14] This type of degradation would obviously decrease the intensity of the 620-nm absorption and would contribute to the broadening and blue shifting of the spectra through the production of an array of shorter conjugation lengths from chains that originally had long conjugation lengths.

Other results support this suggestion. Figure 5 shows a sequence of visible spectra obtained from a thermally cross-polymerized XP18N film. The sample used to generate these spectra was a solution cast P18N film that was stored in the dark at about 20 °C. Spectra were taken at the indicated time intervals.

In contrast to the spectra obtained for UV-initiated XP18N, the spectra in Figure 5 show no decrease in the intensity of the high wavelength absorption as conversion increases. The 45-day sample in Figure 5 corresponds in shape and relative intensity of the two absorption maxima to the 15-min UV-initiated sample. Whereas the 620-nm band starts to decrease after about 5 min of UV exposure, the same band in the 45-day sample is still increasing in intensity, although there is some blue shifting of this band. Other differences in the thermally cross-polymerized sample are the relative lack of absorption around 400 nm compared to the UV-initiated sample, and the fact that the intensity of absorbance at 575 nm does not seem to level off as it does for the UV-initiated sample. These observations are all consistent with the suggestion that UV-induced chain degradation occurs in the UV-irradiated sample. In the thermally cross-polymerized sample, no chain degradation occurs, so an increase in intensity of the absorption maxima is observed at longer reaction times. In the UV-initiated sample, the absorption at 620 nm decreases in intensity while the lower wavelength region (where absorption is caused by shorter conjugation lengths) increases in intensity.

Another process that could possibly contribute to the observed broadening and blue shifting is accumulation of lattice strain as the cross-polymerization proceeds. This is a reasonable suggestion since a unit-cell contraction has been observed for P18N upon cross-polymerization.[2] Also, it should be remembered that each diacetylene unit is directly connected to many other diacetylene units via the aliphatic spacer in the macromonomer chain (see Figure 1). When one diacetylene group reacts, any movement of the aliphatic segment will acutely affect the next diacetylene group along the macromonomer chain. This could introduce more defects into the lattice of the unreacted macromonomer by causing diacetylene units to move out of register or could place strain on already existing poly(diacetylene) chains (this type of process has been suggested for some amphiphilic diacetylenes containing two diacetylene groups per monomer[12]). It has recently been shown that strain on the PDA backbone induced by side-group movement can cause substantial blue-shifting of the visible spectrum.[13]

In this context it should be noted that electron diffraction results for XP18N[2] seem to rule out an explanation that suggests that the material disorders during the course of the cross-polymerization reaction. The diffraction analysis, performed on microscopic single crystals, indicates that the final cross-polymerized product is as ordered as the original macromonomer crystals. It seems unlikely, then, that there is any large scale disordering of the crystallites in the film. However, the diffraction results do not rule out the possibility that the PDA backbones formed early in the reaction could become more strained as the reaction continues. This type of distortion of the backbone induced by the side groups does not necessarily lead to a loss of crystallinity but could cause a blue shift in the visible spectrum.[13]

One other plausible contributing factor to the increase in intensity in the lower wavelength region as the cross-polymerization proceeds is that proportionately more chains with short conjugation lengths are being formed later in the reaction. It is reasonable to expect that macromonomer segments in crystallites that have a higher defect density would tend to react later, since the probability of initiation will be lower in these regions. Once the reaction *is* initiated in these regions, it is more likely that the chain growth will be halted by a lattice mismatch or other defect, resulting in a shorter conjugation length. This effect has been suggested to help explain an increase of the short chain lengths at longer irradiation exposures in one study of poly-3BCMU.[14] This type of process may also account for the small increase in absorption in the 400-nm region that occurs at longer reaction times in the spectra of thermally cross-polymerized XP18N.

3.2. Resonance Raman Spectroscopy. Resonance Raman spectroscopy has proven to be a useful technique for studying many different types of conjugated molecules. Resonant enhancement of the Raman scattering process occurs when the energy of the incident laser light is equal (or nearly equal) to the energy of an electronic transition in the species being investigated. When the incident frequency is "tuned" to the electronic absorption of the sample in this way, an enhancement of as much as 10^6 times the normal Raman intensity may occur.[15] However, the vibrational information contained in the RR spectrum pertains only to the particular chromophore to which the incident frequency is tuned. In a sample that has several chromophoric components, one may get specific vibrational information about each particular chromophore by using several different incident frequencies, each frequency corresponding to the electronic transition energy of one of the various chromophores.

In the specific case of PDA's, the chain backbone is the chromophore in which we are interested. When the incident laser frequency is chosen to lie within the visible absorption profile of the sample, resonance enhancement of the backbone scattering, relative to the side-group scattering, will occur. The observed RR spectrum will contain vibrational information about pure backbone modes and coupled backbone–side-group modes, but no information about pure side-group modes.

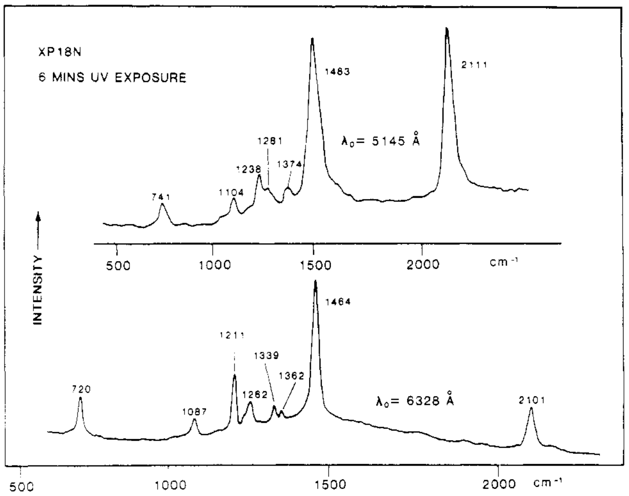

Figure 6. Resonance Raman spectra of poly(1,8-nonadiyne) films exposed to UV light for 6 min. Spectra were obtained by using 6328 and 5145 Å incident wavelengths.

If several conjugation lengths are present in a PDA sample, each conjugation length will contribute to a different portion of the visible absorption spectrum. If the incident laser frequency is varied through the PDA absorption band, the various conjugation lengths in the sample can be isolated, and the observed vibrational frequencies obtained from each incident frequency will correspond to one particular conjugation length (or narrow range of conjugation lengths). This method has been used to demonstrate the existence of a distribution of conjugation lengths in PDA solutions.[16,19]

The reason why different vibrational frequencies are obtained for the PDA backbone vibrations as the conjugation length is changed is because the effective force constants for the backbone bonds change with electron delocalization. As conjugation length increases, the electron delocalization is increased, and the effective force constants for $\nu(C{=}C)$ and $\nu(C{\equiv}C)$ decrease; hence, the observed frequencies decrease.[16,17]

An illustration of this behavior is shown in Figure 6, where representative RR spectra, recorded by using the 5145-Å line of an argon ion laser and the 6328-Å line of a He–Ne laser, are shown for XP18N samples that have been given 6-min UV exposure. These spectra have the same general features as the RR spectra of conventional PDA's. In the spectrum obtained with an incident wavelength (IW) of 6328 Å, $\nu(C{\equiv}C)$ is located at 2101 cm^{-1} and $\nu(C{=}C)$ is located at 1464 cm^{-1}. The various lower frequency bands correspond to mixed modes that contain side-group character (this will be discussed in more detail later). The spectrum obtained with IW = 5145 Å is, in general, similar to that obtained with IW = 6328 Å. However, as illustrated in Table II, the observed frequencies from the spectrum obtained by using IW = 5145 Å are all higher than the corresponding frequencies obtained by using IW = 6328 Å. This is a clear indication that the breadth of the bands observed in the visible absorption spectrum of XP18N is caused by the presence of a distribution of conjugation lengths in the sample. Although other line-broadening mechanisms may also contribute, conjugation length dispersion is undoubt-

Table II
Comparison of Observed Resonance Raman Frequencies Using Incident Wavelengths of 6328 and 5145 Å for XP18N (6-Min UV Exposure)

obsd freq, cm^{-1}		
λ_0 = 6328 Å	λ_0 = 5145 Å	band assignmts
2101	2111	$\nu(C\equiv C)$
1464	1483	$\nu(C=C)$
1362 1339	1374 (br)	
1262	1281	
1211	1238	
1087	1104	
720	741	

edly the main cause of the breadth of the visible absorption bands. When IW = 5145 Å, shorter conjugation lengths (on the order of nine to ten repeat units) are probed, whereas when IW = 6328 Å, PDA chains with nearly infinite conjugation lengths are photoselected. If only one conjugation length were present in the sample, the observed frequencies would not be dependent upon the incident wavelength.

When IW = 6328 Å, the spectra obtained from XP18N as a function of UV exposure do not show any change in the number of observed bands (although there are some interesting intensity changes that will be discussed later). However, spectra obtained with IW = 5145 Å show significant changes as a function of UV exposure. Figure 7 shows the C=C stretching region, recorded by using IW = 5145 Å, obtained for XP18N after various UV exposure times.

It was found that XP18N will continue to slowly cross-polymerize when exposed to 5145-Å laser light or any of the other incident wavelengths produced by the argon ion laser (the 6328-Å line from the He-Ne laser does not produce cross-polymerization because it is not of high enough energy). Low laser powers (less than 15 mW at sample) were used to prevent significant cross-polymerization from being induced during the recording of the spectra. In addition, a different sample was used for each of the spectra shown in Figure 7, so that inadvertent cross-polymerization would not be accumulated from spectrum to spectrum. Because different samples were used for each spectrum, the intensities of the spectra in Figure 7 should not be directly compared.

At 1- and 3-min UV irradiations, the C=C stretching band has only one maximum (located at 1480 cm^{-1}) but has a broad high-frequency tail. At 6-min UV exposure, the high-frequency tail becomes more prominent, and for the 10-min UV sample the tail has become a shoulder with about two-thirds the intensity of the lower frequency band. The intensity of this shoulder in the 17-min sample is nearly the same as that of the lower frequency band.

This change in the double bond stretching region appears to be due to a population effect; as UV dosage is increased, there is an increase in short conjugation lengths, as demonstrated by the increased absorption at short wavelengths and blue shifting in the visible spectrum. It is these shorter conjugation lengths that give rise to the high-frequency band (more evidence for this explanation will be presented in the following paper in this issue). This behavior is reminiscent of the RR spectra of blue PDA solutions.[16] At long incident wavelengths there is only one $\nu(C=C)$ band observed for the solutions (as there is only one $\nu(C=C)$ band for XP18N when IW = 6328 Å), but when short incident wavelengths are used, two bands appear.[16]

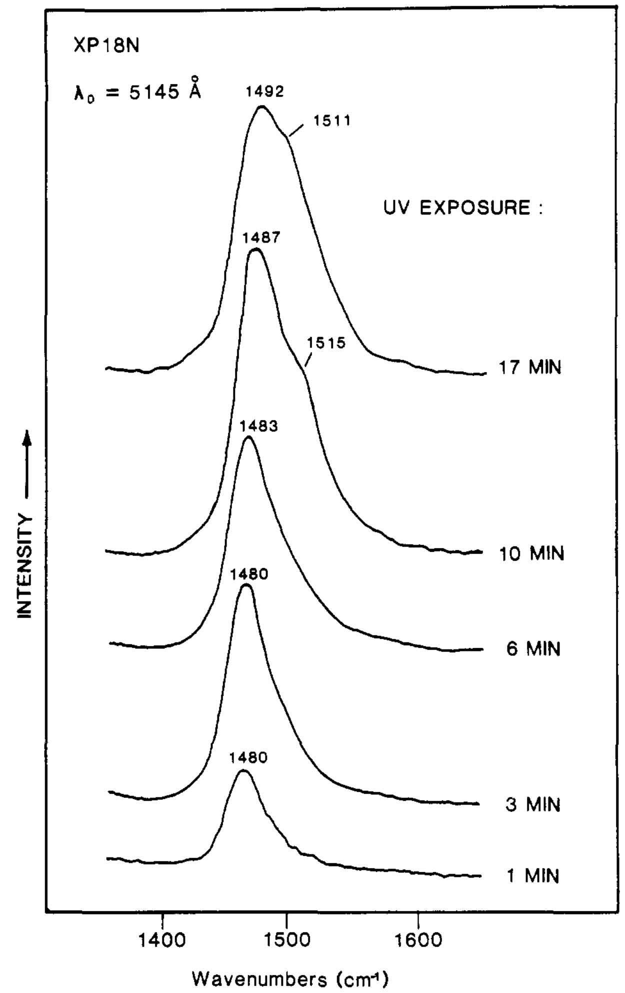

Figure 7. Resonance Raman spectra (IW = 5145 Å) of poly(1,8-nonadiyne) films exposed to UV radiation for the indicated amount of time. (A different sample was used for each spectrum.) The spectra have been arbitrarily offset for clarity.

The same type of effect is encountered when samples with a given UV exposure are examined by using different incident wavelengths. Figure 8 shows the C=C stretching region for four different XP18N samples, each exposed to 6-min UV irradiation.

As mentioned earlier, the $\nu(C=C)$ band obtained by using IW = 6328 Å has only one maximum. When the incident wavelength is decreased, a high-frequency band becomes visible. This occurs because as the incident wavelength is decreased, the spectrum becomes more sensitive to shorter conjugation lengths, thereby increasing the intensity of the high-frequency band. In addition, note that the frequencies of the C=C stretch increase as incident wavelength is decreased, consistent with the fact that there is a range of conjugation lengths in the sample and that shorter conjugations lengths are probed with shorter incident wavelengths. Analogous behavior is observed with samples given various amounts of UV exposure.

The $\nu(C\equiv C)$ bands for the samples used to obtain spectra in Figure 7 have only one maximum but become broader as UV exposure is increased. The broadening is slightly asymmetric with a high-frequency tail. The full width at half-height values (fwhh) for the $\nu(C\equiv C)$ bands are plotted as a function of UV exposure in Figure 9. This plot shows that the peak widths are virtually identical for 1- and 3-min UV exposures, consistent with the similarity of the $\nu(C\equiv C)$ regions at those exposures. After 3-min UV exposure, there is a linear increase in fwhm as

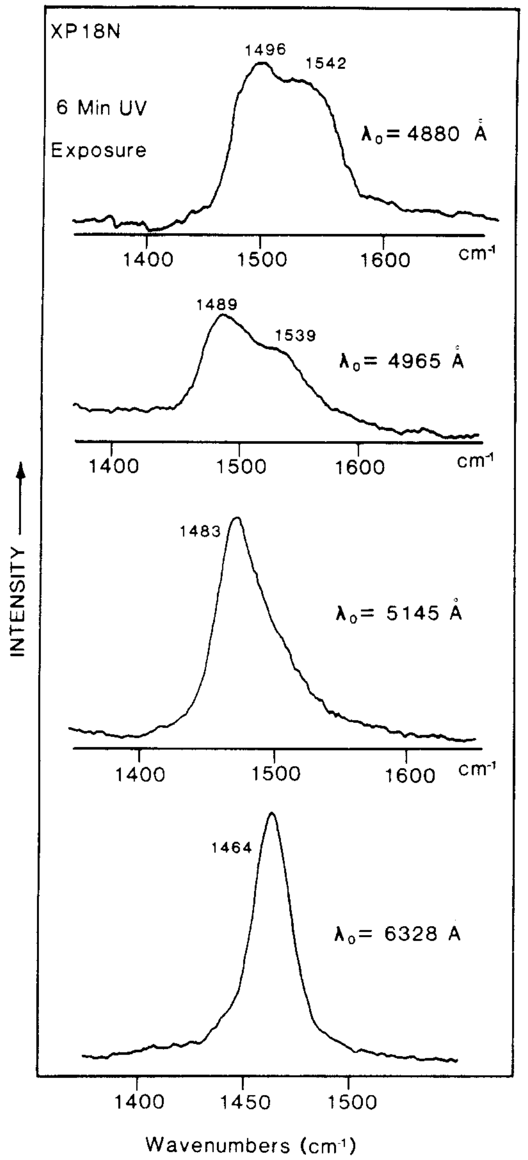

Figure 8. Resonance Raman spectra of the ν(C=C) region for poly(1,8-nonadiyne) films exposed to UV radiation for 6 min. Spectra were obtained by using 6328, 5145, 4965, and 4880 Å incident wavelengths.

a function of UV dose. This indicates that, although two maxima are not observed for the ν(C≡C) bands, the increase in the range of conjugation lengths produced upon increased UV exposure affects the ν(C≡C) region as well as the ν(C=C) region.

In general, the RR spectrum of a PDA will have significantly fewer observed frequencies than the infrared spectrum of the same material. This occurs because most of the side-group modes will be infrared active, whereas only those side-group motions that are coupled to the backbone modes are observed in the RR spectrum. Although the simplicity of the RR spectrum can sometimes be advantageous, it makes a detailed vibrational analysis quite difficult. For example, it is difficult to perform normal coordinate calculations for PDA's since there are many more internal coordinates than experimentally observed vibrational frequencies. A set of force constants can still be obtained in this case, but it is not unique. Infrared frequencies could be used in addition to the RR frequencies, but the large side groups usually found on PDA's make the problem computationally difficult, leading to large uncertainties in the resultant force constants.[15]

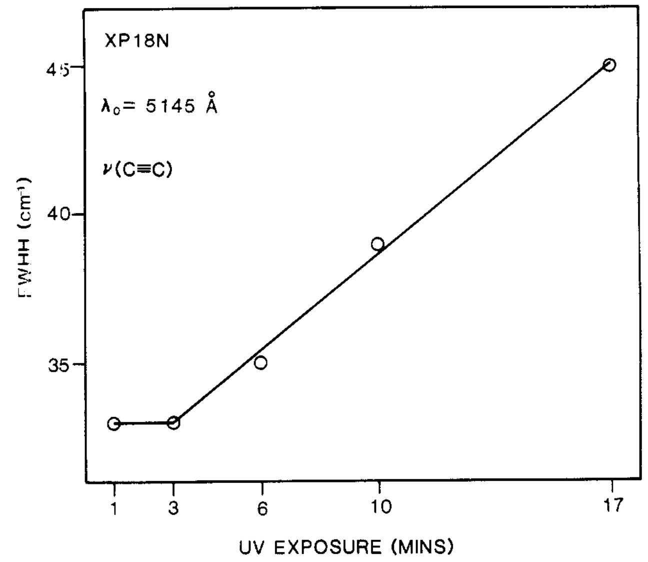

Figure 9. Full width at half-height for the ν(C≡C) band (IW = 5145 Å) as a function UV exposure.

Table III
Comparison of Observed RR Frequencies for XP18N and PUDD (IW = 6328 Å)

obsd freq, cm^{-1}		
XP18N	PUDD[a]	band assignmts
2101	2072	ν(C≡C)
1464	1460	ν(C=C)
1362		
1339	1345	
1262		
1211	1215	ν(C—C)
1087	1050	
720	700	

[a] PUDD frequencies taken from ref 18.

Despite these problems, Lewis and Batchelder have performed normal coordinate calculations for several PDA's (using certain assumptions and approximations that will be discussed later) and have calculated the forms of the normal modes.[18] One of the PDA's chosen, the polymer of bis(phenylurethane) of 4,6-decadiyne-1,10-diol (abbreviated as PUDD, R = $(\text{-CH}_2\text{-})_3\text{CONHC}_6\text{H}_5$), is reasonably similar to the cross-polymerized macromonomers in that it has an aliphatic chain directly bonded to the PDA backbone. The following paragraphs will show that the results for PUDD can be used to help understand the RR spectrum of XP18N.

Most of the observed frequencies for PUDD match closely those observed for XP18N (Table III). (The frequencies for PUDD were obtained from RR spectra of single crystals[15] and, therefore, represent frequencies for chains with long conjugation lengths; thus, the frequencies from the 6328-Å spectra of XP18N should be used for comparison.) Of particular interest is the 1215 cm^{-1} band of PUDD. This mode has been calculated to be due to the C-C stretching of the PDA backbone.[18] This suggests that the 1211 cm^{-1} band observed for XP18N corresponds to the PDA backbone C-C stretch. The atomic displacement vectors calculated for the other low-frequency modes indicate that they are highly mixed modes, containing significant displacement of the side-group atoms.[18] The low-frequency modes of XP18N probably have similar motions.

Proof that the low-frequency modes of XP18N have a substantial side-group contribution is provided by a comparison of the 1000–1400 cm^{-1} region of the RR spectra

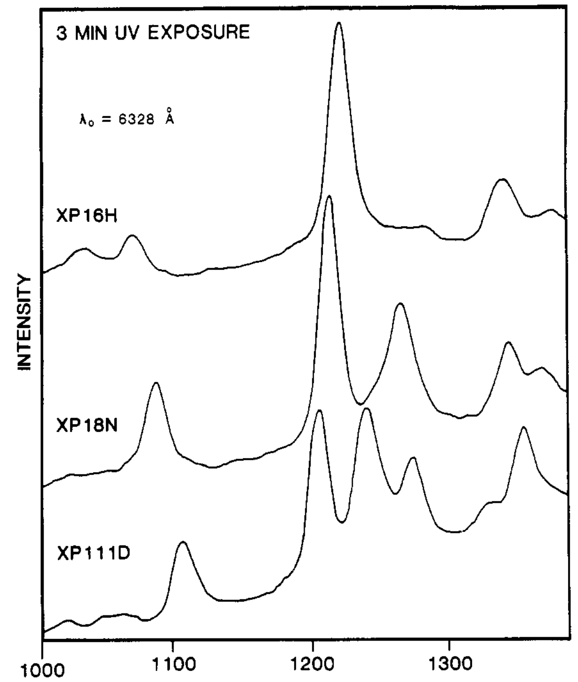

Figure 10. Resonance Raman spectra of poly(1,11-dodecadiyne), poly(1,8-nonadiyne), and poly(1,6-heptadiyne) all exposed to UV light for 3 min. Spectra have been arbitrarily offset for clarity.

Table IV
Observed RR Frequencies for XP16H, XP18N, and XP111D Obtained by Using IW = 6328 Å

obsd freq, cm^{-1}			
XP16H	XP18N	XP111D	band assignmts
2100	2101	2099	ν(C≡C)
1460	1464	1464	ν(C=C)
1374	1362	1352	
1341	1339	1328	
1285	1262	1241	
(weak)		1274	
1221	1211	1209	ν(C—C)
1071	1087	1107	
726	720	714	

of cross-polymerized P16H (P16H) and cross-polymerized P111D (XP111D), with the spectrum of XP18N (Figure 10). The XP16H spectrum has the same number of bands as the XP18N spectrum, but some of the intensities in the XP16H spectrum are relatively low compared to those for XP18N. The XP111D spectrum differs from those of the other two materials in that it has a new band at 1241 cm^{-1} that is not present in the other spectra (although there is a hint of this band on the low-frequency side of the 1262 cm^{-1} band of XP18N). In addition to the differences in the number and intensities of the bands in the 1000–1400 cm^{-1} region, the frequencies of the corresponding bands are also different for the three materials. This is in contrast to the bands assigned to ν(C=C) and ν(C≡C) that are nearly identical for all three materials (see Table IV). These results indicate that the low-frequency bands have a substantial contribution due to the side-group motions.

The behavior of the cross-polymerized macromonomers is consistent with that expected on the basis of Lewis and Batchelder's work. They assumed that the PDA side group could be adequately modelled by using only the number of carbon atoms between the PDA backbone and the first heavier structural unit (for instance SO_2 or CO) in the side group (PUDD's side group was modelled with an alphatic chain of three CH_2 units). It was felt that the heavier atoms in the side group would act as decouplers for the atomic vibrations.[18] The other PDA's investigated by Lewis and Batchelder had either just one carbon atom connected to the PDA backbone or an aromatic ring directly attached to the backbone. Therefore, PUDD was structurally the most similar to the cross-polymerized macromonomers. Consequently, only PUDD has observed (and calculated) frequencies that compare closely to those observed for the cross-polymerized macromonomers; this indicates that the side group can adequately be modelled by using only the atoms closest to the PDA backbone. Furthermore, it is obvious from the macromonomer results that the influence of the aliphatic side group extends past the first few carbon atoms, consistent with the computational result that when additional atoms are included in the model side group, more Raman bands are predicted.[15,18] (This also helps explain why there are more frequencies observed for XP18N than for PUDD.)

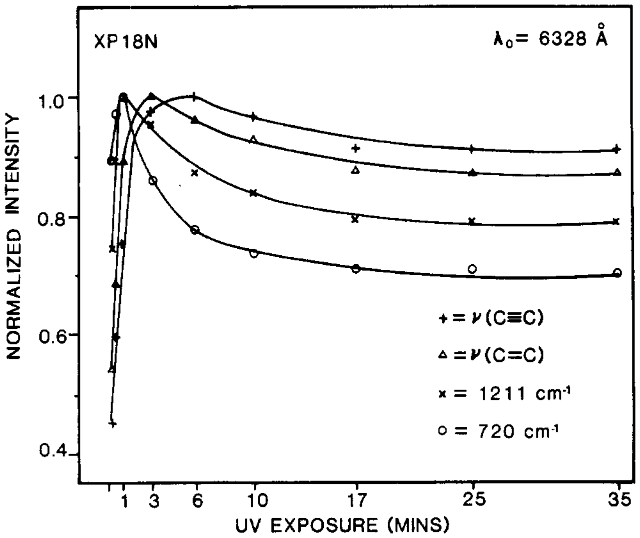

Figure 11. Normalized intensity of ν(C≡C) (+), ν(C=C) (▵), the 1211 cm^{-1} band (×), and the 720 cm^{-1} band (○) as a function of UV exposure time (IW = 6328 Å).

From the above discussion, it is clear that the lower frequency bands are related to mixed backbone-side-group motions. Even the band that is assigned to the C–C stretch of the PDA backbone is shifted in frequency from one macromonomer system to the next, indicating that this mode also has considerable side-group character. Given these results, it seems likely that if there are any changes in the side-group packing or conformation, these changes may be reflected by changes in the lower frequency bands.

As mentioned earlier, there is very little change in the spectra of XP18N as a function of UV exposure when an incident wavelength of 6328 Å is used. New bands do not appear as they do when shorter incident wavelengths are used, and the peak width for any given band stays constant over the entire UV exposure range investigated (fwhh for ν(C=C) is about 20 cm^{-1}; fwhh for ν(C≡C) is about 23 cm^{-1}). However, there are some interesting differences in the intensity behavior of the observed bands. Figure 11 shows the normalized intensity changes as a function of UV exposure for the ν(C≡C), ν(C=C), ν(C—C), and 720 cm^{-1} bands of the XP18N RR spectrum obtained with IW = 6328 Å. The intensities have been normalized by dividing the observed intensity of a given band at each UV exposure by the highest intensity

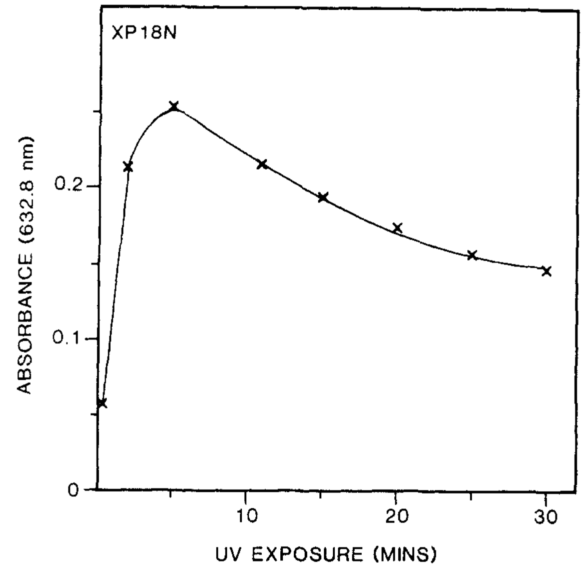

Figure 12. Absorption intensity (arbitrary units) at 632.8 nm as a function of UV exposure for XP18N.

observed for that particular band over the UV exposure range.

The intensity data for $\nu(C\equiv C)$ show a very broad maximum at about 6-min UV exposure. The $\nu(C=C)$ intensity also has a very broad maximum, but it has its highest value at 3-min UV exposure. For both the $\nu(C=C)$ and $\nu(C\equiv C)$ bands, the intensity drops off slightly after the maximum and then plateaus after about 17 min of UV exposure. The behavior of these two curves mimics the behavior of the visible spectrum intensity at 632.8 nm, which shows a maximum at about 5 min of UV exposure (Figure 12). This is the expected behavior for the intensity of a resonance Raman band. As the amount of the chromophore being observed decreases, so should the intensity of the observed resonance Raman spectrum. In this case, after about 5 min of UV exposure, the amount of material contributing to the resonance effect decreases, thereby causing a decrease in the $\nu(C\equiv C)$ and $\nu(C=C)$ intensities.

The intensities of the 720 and 1211 cm^{-1} bands show a different behavior from the $\nu(C\equiv C)$ and $\nu(C=C)$ intensities. The 720 cm^{-1} band intensity has its maximum at about 1-min UV exposure, followed by a sharp drop in intensity for higher UV exposures. The 1211 cm^{-1} band shows similar behavior, but the intensity drop is not as sharp as for the 720 cm^{-1} band.

As mentioned earlier, the $\nu(C\equiv C)$ and $\nu(C=C)$ bands are fairly pure modes, whereas the 1211 cm^{-1} band and especially the 720 cm^{-1} band have significant contributions from side-group vibrations.[18] The fact that the intensity behavior of the 1211 and 720 cm^{-1} bands differs from that of the double- and triple-bond stretching modes (and the visible absorption intensity data at 632.8 nm) suggests that there is some perturbation of the side-group conformation or packing after 1 min of UV exposure. A possible explanation for this type of perturbation is that at approximately 1 min of UV exposure, there occurs a change from the macromonomer crystal structure to the cross-polymerized crystal structure. This is a reasonable possibility since there is a significant difference in unit cell volume between the two structures.[2] For most PDA's at very low conversions, the isolated polymer chains are formed under the constraints of the monomer unit cell. When the conversion reaches a high enough value, there is a transformation from the monomer unit cell to the polymer unit cell.[20] It is possible that the observed decrease in the intensity of the 1211 and 720 cm^{-1} bands could be caused by this type of phase change.

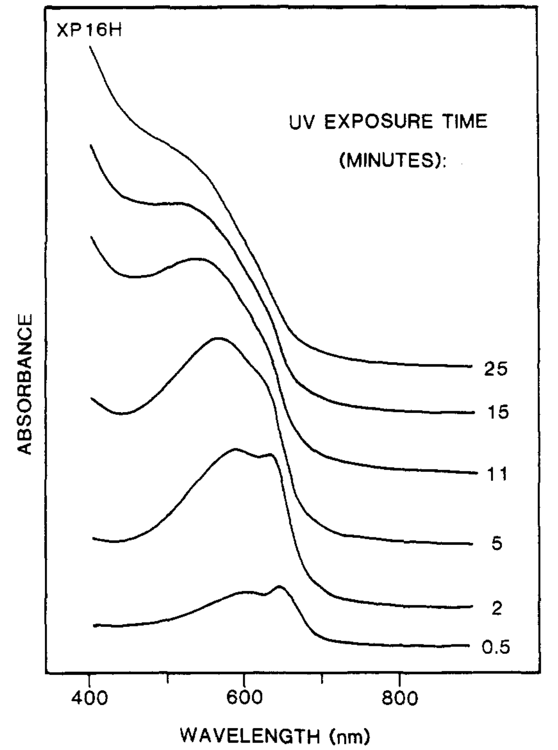

Figure 13. Visible absorption spectra of a poly(1,6-heptadiyne) film recorded after various UV exposure times. All spectra have been corrected for scattering and have been arbitrarily offset.

It should be noted that even if this explanation is correct, it applies only to the regions of the sample where the largest conjugation lengths can form. Since the spectra were obtained by using IW = 6328 Å, we are probing only the largest conjugation lengths in the sample. Because the longest conjugation lengths would be expected to form in the most perfect crystallites in the sample, the conclusions reached would strictly correspond only to the reaction process in those regions.

We cannot at this time be certain about the nature of the structural change that is causing the observed intensity behavior. However, it is obvious that some change in the side group must be taking place that serves to decouple the mixed side-group modes from the backbone electronic structure, thereby causing relatively less resonance enhancement for these modes and, thus, producing the observed relative intensity decrease. Further structural studies are needed to specify the precise changes that occur.

3.3. Comparison of the Cross-Polymerization Behavior of P16H, P18N, and P111D. This section presents preliminary results on the photoreactivity of P16H and P111D and compares these results to those obtained earlier for P18N. Visible spectroscopy and extraction experiments have been used to obtain information about the relative reactivities of the three macromonomer systems.

The visible absorption spectra of P16H and P111D as a function of UV exposure are shown in Figures 13 and 14, respectively. Each set of spectra was obtained in a similar fashion as those for P18N in Figure 4; a single sample was used for each set so that intensities within each set can be directly compared, and the base-line curvature was corrected in the same manner as described earlier. Sample thicknesses for all three macromonomer

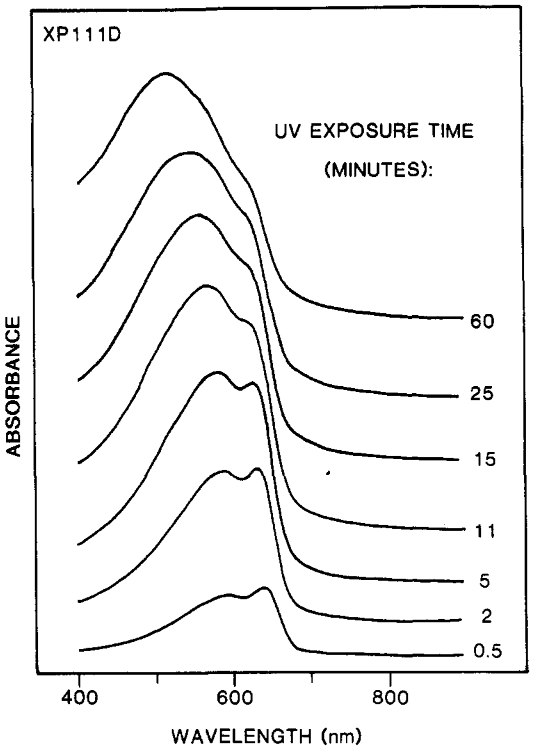

Figure 14. Visible absorption spectra of poly(1,11-dodecadiyne) film recorded after various UV exposure times. All spectra have been corrected for scattering and have been arbitrarily offset.

samples were similar so as to minimize any differences between the samples due to nonuniformity of the UV-induced cross-polymerization reaction across the thickness of the film. Film thicknesses were controlled by casting identical amounts of 1 wt % solutions (in methylene chloride) onto quartz slides with identical surface areas. As noted earlier, the degree of crystallinity was also similar for all three materials.

The spectral features of all three cross-polymerized macromonomers are similar at low conversions. All three systems show two absorption maxima occurring near 590 and 640 nm. The degree of broadening and blue-shifting is nearly the same for XP18N and XP111D. In contrast, XP16H shows much more drastic broadening at any given UV exposure than the other two materials. In addition, the absorption scale for the XP16H plots shown is about half that used for XP18N and XP111D. Since all three films are nearly the same thickness, this would indicate that XP16H contains roughly half the amount of PDA chains as XP18N or XP111D, for any given UV exposure.

One factor that affects the amount of PDA formed is the degree of crystallinity. The higher the crystallinity, the more PDA chains that can form (since the cross-polymerization takes place only in crystalline regions). Recall, however, that the three samples have approximately the same degree of crystallinity. Thus, a difference in crystallinity cannot be the reason for the differences seen in the visible spectra. Consequently, it appears that P16H is somewhat less reactive than P18N or P111D.

An effect that could be responsible for both the reduced reactivity and the increased broadening observed for XP16H compared to the other macromonomers is that more accumulated lattice disruption occurs in the P16H system during cross-polymerization than in the other two systems. As mentioned earlier, the macromonomers should be more sensitive than conventional diacetylene systems to disruption of the lattice during reaction, since each diacetylene unit is connected to many other diacetylene units in the macromonomer chain via the aliphatic spacer. Since the spacer in P16H is shorter than the spacers in the other two systems (three methylenes for P16H, five for P18N, and eight for P111D), less of the lattice strain occurring during cross-polymerization can be dissipated by the spacer in P16H. This effect would lower the reactivity and cause shorter conjugation lengths, since accumulated lattice mismatch would eventually lead to a defect large enough to stop chain growth.

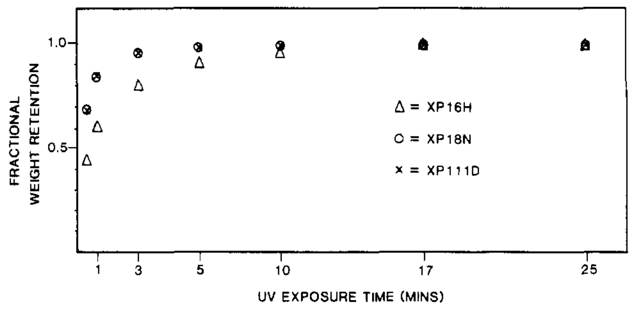

Figure 15. Fractional weight retention as a function of UV exposure time for poly(1,6-heptadiyne) (Δ), poly(1,8-nonadiyne) (O), and poly(1,11-dodecadiyne) (×).

To compare further the reactivity of the macromonomer systems, extraction experiments were performed. As discussed in the Introduction, extraction experiments cannot be used to determine absolute degrees of conversion in the macromonomer systems. However, other useful information about the progress of the cross-polymerization can be obtained from these experiments.

Figure 15 shows plots of fractional weight retention as a function of UV exposure time for all three macromonomer systems. XP18N and XP111D again show nearly identical behavior. XP16H shows less fractional weight retention than XP18N or XP111D at UV exposures of less than 10 min.

It is obvious from these plots that the degree of conversion cannot be determined by this method. The most conversion possible in these samples is about 30% (since the samples are about 30% crystalline), but these plots indicate that the "conversion" is higher than that value after only 30 s of UV exposure. Furthermore, no diacetylene system yet investigated has been reacted to 100% conversion by using UV initiation,[4] yet the extraction data indicate that the "apparent conversion" reaches 100%. Thus, it is safe to conclude that this method cannot give reliable estimates for the degree of conversion in the macromonomer systems.

However, these plots give an estimation of the amount of UV exposure needed to insolubilize all of the macromonomer chains in the sample. This point occurs at about 6-min UV exposure for P18N and P111D, but not until 10-min UV exposure for P16H. So again, it appears that P16H is less reactive than the other two systems.

It should be noted that the measured point at which the entire sample becomes insolubilized will be dependent upon several factors: (1) inherent molecular reactivity, (2) degree of crystallinity, (3) molecular weight of macromonomer, and (4) solvent quality. The first two factors have been discussed earlier in conjunction with the visible spectroscopic results. The last two factors are unique to the extraction experiments and will be discussed below.

Since the macromonomer segments in the amorphous regions of the sample cannot cross-polymerize (at least, not to a significant extent), the only way for these chains to become insolublized is for part of the chain to be incorporated into a crystalline region. If the macromonomer molecular weight is increased, the likelihood is increased that a given chain in the amorphous region will also be part of a crystalline region. It could be suggested that this effect may be contributing to the results shown in Figure 15 since P16H has the lowest molecular weight of the macromonomers used (P16H, M_w = 30 000; P18N, M_w = 33 500; P111D, M_w = 38 000). However, the molecular weights of the three macromonomers are quite similar to each other and would not be expected to have a major influence on the extraction results.

The effect of solvent quality is important, since if the solvent used for the extraction experiments was preferentially better for one macromonomer system than for the others, the results would obviously be affected. But, all three macromonomers had nearly identical solubility characteristics in methylene chloride (the solvent used for extraction), so this effect should not be a factor.

Thus, the results from visible spectroscopy and the extraction experiments indicate that P18N and P111D possess similar photoreactivity, whereas P16H seems to be considerably less photoreactive than either P18N or P111D.

4. Conclusions

Although an accurate determination of the degree of conversion is difficult to obtain for the macromonomer systems, it is possible to gain an understanding of the cross-polymerization process by studying changes in the optical properties of the materials as a function of conversion. The visible and resonance Raman spectra are consistent with the existence of a broad distribution of conjugation lengths in the cross-polymerized material. The breadth of the visible absorption maxima is due to the constraints placed on PDA chain growth by the crystallite size distribution and crystallite defect density distribution in the materials. In addition, it was found that UV-induced chain degradation takes place during the UV initiated cross-polymerization reaction, adding to the breadth of the visible absorption maxima.

Through use of resonance Raman spectroscopy with various incident wavelengths, the behavior of the various conjugation lengths that comprise the macromonomer sample was studied. Comparative studies of XP16H, XP18N, and XP111D using 6328-Å incident light have shown conclusively that the lower frequency RR bands are mixed modes that contain a large contribution from side-group motions. These studies also provide experimental justification of assumptions used by Lewis and Batchelder[18] to calculate the normal modes of PDA chains. Comparison of the RR intensity behavior of the 720 and 1211 cm^{-1} bands with that of the $\nu(C\equiv C)$ and $\nu(C=C)$ bands indicates that a structural change takes place in the aliphatic side chains after about 1-min UV exposure. This change could be related to a phase change from the macromonomer crystal structure to the cross-polymerized crystal structure.

Finally, a preliminary comparison of the reactivity of P16H, P18N, and P111D showed that P18N and P111D seem to have nearly identical reactivity but that P16H is considerably less reactive than P18N or P111D.

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Registry No. P18N, 30523-90-1; P16H, 30523-92-3; P111D, 77860-27-6; LiAc·EDA, 6867-30-7; 1,11-dodecadiyne, 20521-44-2; 1,8-dibromooctane, 4549-32-0.

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