

I, to 100-mL stirred glass flasks thermostated at 50 °C. Polymers were coagulated with acidified methanol and worked out as usual. Polymer samples were fractionated with boiling acetone in Kumagawa-type extractors. The extraction residues of polymers obtained in runs 1-5 are highly syndiotactic (fraction of rr triads, determined by  $^{13}\text{C}$  NMR, >98%) and melt at 260 °C. The extraction residue of the polymer produced in run 7 has a content of rr triads of 88% and melt at 220 °C.

Molecular weights were determined on the raw polymers by GPC in 1,2-dichlorobenzene at 135 °C using a Waters 150-C apparatus.

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**Registry No.** Ti(bz)<sub>4</sub>, 17520-19-3; Ti(O-bu)<sub>4</sub>, 5593-70-4; TiCpCl<sub>3</sub>, 1270-98-0; Ti(acac)<sub>3</sub>, 14284-96-9; Ti(ph)<sub>2</sub>, 14724-88-0; Zr(bz)<sub>4</sub>, 24356-01-2; syndiotactic polystyrene, 28325-75-9.

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## Synthesis and Optical Properties of a New Class of Polyamides Containing Reactive Diacetylene Groups

H. W. Beckham and M. F. Rubner\*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received August 22, 1988;  
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**ABSTRACT:** New polyamides containing reactive diacetylene groups in their repeat structures were synthesized from a diacetylene diacid chloride and two different diamines by using interfacial polymerization techniques. Thermal analysis and  $^{13}\text{C}$  NMR spectroscopy were used to estimate the extent of conversion of the diacetylene groups to polydiacetylene network chains upon exposure to electron beam radiation in the solid state. The diacetylene groups contained in a polyamide based on an aliphatic diamine were found to be more reactable than those incorporated in a polyamide based on an aromatic diamine. The cross-polymerized polyamide-diacetylenes were found to exhibit reversible thermochromic behavior during temperature cycling which occurs with complete retention of hydrogen bonds and without any hysteresis effects. The thermochromic reversibility of these materials was attributed to the strongly hydrogen-bonded chain segments pendent to the newly formed polydiacetylene chains.

## I. Introduction

This paper describes the preparation and properties of several new polyamides that contain the reactive diacetylene group as part of their repeat structure. The goal of this research is to identify new types of chemistry that can be utilized to modify and enhance selected properties of fiber-forming polymers after they have been processed into highly anisotropic forms. In order to accomplish this goal, it is necessary to introduce reactive groups into the polymer chain that remain dormant during processing but that can also be readily activated in the solid state to produce the desired changes in properties. We are currently focusing on the chemistry of the diacetylene group, which, as indicated below, provides a novel way to dramatically modify the mechanical and optical properties of the host polymer system.

The solid-state polymerization of diacetylene monomers,  $\text{RC}\equiv\text{CC}\equiv\text{CR}$ , has been well documented in the literature.<sup>1</sup> A unique feature of this polymerization is that it often proceeds as a homogeneous single-phase process taking place without destruction of the crystalline order of the original monomer lattice. The resultant fully extended polydiacetylene chains,  $[\text{-(R)C}\equiv\text{C(R)C}\equiv\text{C-}]_x$ ,

exhibit many novel linear<sup>2</sup> and nonlinear<sup>3</sup> optical properties, all of which are a direct consequence of the one-dimensional nature of the polydiacetylene conjugated backbone and its highly delocalized electronic states. This chemistry can be initiated using actinic radiation, ionizing radiation, or, in some cases, simple thermal treatment, making it ideal for postprocessing modification schemes.

As has been previously demonstrated,<sup>4-10</sup> the reactive diacetylene group can be readily incorporated into many different polymeric structures,  $[\text{-C}\equiv\text{CC}\equiv\text{CR-}]_x$ , making it possible to synthesize a wide variety of fiber- and film-forming polymers with tunable mechanical and optical properties. The controlled solid-state cross-polymerization of polymers containing diacetylene groups is therefore an extremely attractive method for the systematic postsynthesis modification of the mechanical and optical properties of polymeric materials. This chemistry provides a novel way to introduce well-defined, nonrandom cross-links into a polymeric material often times without disruption of the packing and order of the polymer chains. In addition, since the resultant cross-links are actually conjugated polydiacetylene chains, the material develops all of the novel optical properties characteristic of the polydi-

acetylenes such as thermochromism,<sup>2,5</sup> mechanochromism,<sup>5</sup> and nonlinear optical behavior.<sup>3</sup> Thus, it is possible to dramatically modify the mechanical properties of the material and, at the same time, introduce conjugated segments that can be exploited for their unusual linear and nonlinear optical properties. Since the polymerization generally proceeds as a diffusionless, lattice-controlled process, it is possible to selectively modify the cohesiveness and thermal stability of the polymer chains without drastically changing their packing or molecular organization. This means that it is possible to obtain highly anisotropic structures when oriented extended polymers are used as the host polymer.

Clearly, the true utility of this chemistry can only be realized when the diacetylene groups have been properly engineered into the molecular structure of the polymer. Simply placing diacetylene groups into polymer chains without consideration of the consequence of the structural changes introduced upon their polymerization could easily produce highly cross-linked, excessively brittle materials with vastly compromised mechanical properties. In addition, if the molecular environment of the diacetylene group is too rigid, then cross-polymerization of the diacetylene groups could be completely prevented, again limiting the usefulness of this approach. Thus, it is essential that the molecular structure, and ultimately the molecular organization, of the polymer chains be engineered so as to produce materials that benefit from this novel chemistry. In fact, only very recently with our work on diacetylene-containing segmented copolymers<sup>11</sup> has it been demonstrated that this chemistry, when properly engineered into a macromolecule, can be utilized to significantly enhance the mechanical properties of polymers. For example, it was found that the ultimate tensile strength of select members of this family of reactive polyurethanes could be essentially doubled by the solid-state polymerization of diacetylene groups contained within the phase-separated hard domains of these two-phase copolymers.

In the case of the polyamides, we are systematically varying the nature of the polymer chain from flexible to semiflexible to rigid by controlling the length of the spacer group separating the diacetylene functionality from the amide linkage and the type of diamine (aromatic or aliphatic) used to synthesize the polymer. Each of these different polymers will provide information about diacetylene reactivity, processing characteristics, and the influence of the diacetylene cross-polymerization on the mechanical and optical properties of these new materials. In this paper, we present a comparison of the optical properties of two types of diacetylene-containing polyamides with flexible spacer groups of similar length prepared with either an aliphatic diamine or with an aromatic diamine. Techniques that can be utilized to estimate the extent of diacetylene polymerization as a function of radiation dosage are also presented.

## II. Experimental Section

### A. Synthesis of Polyamide-Diacetylenes. 1. Materials.

1,6-Hexanediamine (Polysciences) was vacuum distilled at 40 °C (50  $\mu$ m) and stored under dry nitrogen. 1,4-Phenylenediamine (Aldrich) was recrystallized from warm chloroform and sublimed at 130 °C. Thionyl chloride (Fluka) was distilled at 75 °C immediately prior to use. Chloroform and carbon tetrachloride were washed with water, dried over calcium chloride, and finally distilled over phosphorus pentoxide under dry nitrogen. Water used was purified with a Millipore reverse-osmosis system coupled with a Millipore Milli-Q purification system. 10,12-Docosadiyn-1,22-dioic acid (8,8-diacid) was synthesized by oxidative coupling of 10-undecynoic acid (Farchan Laboratories) according to the

procedure of Hay.<sup>12</sup> The sodium salt of 10-undecynoic acid in water was slowly added to the catalyst mixture of copper(I) chloride (Aldrich) and *N,N,N',N'*-tetramethylethylenediamine (Aldrich) stirred in a solvent mixture of water and tetrahydrofuran (2:1) into which oxygen was bubbled for 12 h. The 8,8-diacid was recrystallized from methanol at 0 °C and vacuum dried for 8 h prior to use, giving a white solid with mp 112–114 °C. Refluxing in thionyl chloride for 5 h followed by removal of the excess reagent under high vacuum for 4 h afforded the 8,8-diacid chloride which was used immediately.

**2. Polymerization.** The diacetylene-containing polyamides were prepared by a low-temperature interfacial polycondensation method common for condensation polymers such as nylon.<sup>13</sup> The 8,8-diacid chloride was reacted with 1,6-hexanediamine to form a completely aliphatic polyamide-diacetylene (PADA, 6,22), and with 1,4-phenylenediamine to form a partly aromatic polyamide-diacetylene (PADA PPD,22).

a. PADA 6,22 was synthesized as follows: a three-neck, round-bottom flask containing 2.77 mmol of vacuum-dried (made from 1.0 g of 8,8-diacid) 8,8-diacid chloride was rinsed with 23.5 mL of dry chloroform into a 200-mL beaker, giving a 0.12 M solution. In a separate beaker, 0.2216 g (5.54 mmol) of sodium hydroxide and 0.3213 g (2.77 mmol) of 1,6-hexanediamine were dissolved in 14 mL of water, giving a solution concentration of 0.2 M diamine. This aqueous solution was carefully poured over the organic phase, and the resulting polymer film formed at the interface (area = 3 in<sup>2</sup>) was removed from the center at a constant speed as a coherent fiber by a homemade wind-up device. After thorough washing with water and then acetone, the dried polymer weighed 0.337 g (34%).

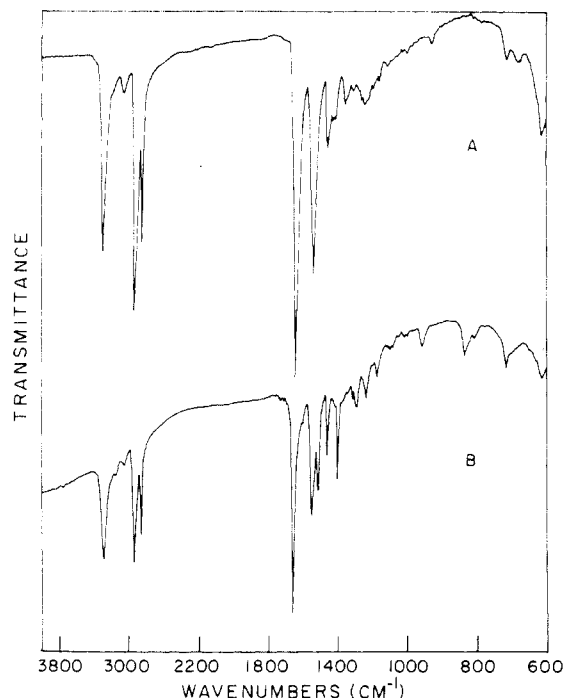
b. PADA PPD,22 was prepared as follows: to the newly formed 2.77 mmol of 8,8-diacid chloride was added 45 mL of dry carbon tetrachloride, giving a 0.062 M solution which was transferred to a high-speed blender. The aqueous solution was made to 0.13 M diamine with 0.35 g (3.24 mmol) of 1,4-phenylenediamine and 0.16 g (4 mmol) of sodium hydroxide in 25 mL of water. To the rapidly stirring diacid chloride solution the aqueous solution was poured over a period of about 15 s. After an additional 5 min of stirring, the polymer was collected and washed with water, acetone, and then chloroform before finally vacuum drying.

Besides interfacial polycondensation, attempts were made to synthesize these polymers in a homogeneous medium from diisocyanates and diacids,<sup>14</sup> a method which precludes the intermediate synthesis and purification of the diacid chlorides. The reaction involves the initial formation of a *N*-carboxy anhydride, which decomposes to species such as ureas and carbamic acids, all of which decompose at elevated temperatures to give the amide. Because of the high temperature required, initial trials have produced only the insoluble cross-polymerized polymer, but in quite high yields. Use of lower temperatures prevents cross-polymerization but results only in low molecular weight polymers. It is interesting to note that these low molecular weight polymers are highly reactive to UV radiation, turning deep blue with only limited exposure to this radiation. The materials discussed in this paper will be only those made via the traditional interfacial route.

### B. Characterization of the Polyamide-Diacetylenes.

Inherent viscosities of 1.05 dL/g for PADA 6,22 and 0.55 dL/g for PADA PPD,22 were measured with a Ubbelohde viscometer on 0.5 g/dL *m*-cresol solutions at 30 °C. These results indicate that the aliphatic-based polymer is of higher molecular weight than the aromatic-based polymer. The value obtained for the aliphatic-based polyamide is consistent with what has been reported in the literature for traditional aliphatic polyamides made via interfacial techniques.<sup>13</sup> It should be noted that the polymers synthesized were insoluble in most solvents commonly used for polyamides with the exception of *m*-cresol.

Infrared spectra were recorded on a Nicolet 20 DX Fourier transform infrared spectrophotometer (FTIR) using thin films cast from solution onto a nonabsorbing substrate. Figure 1 shows the spectra of the aromatic-based and aliphatic-based polyamide-diacetylene polymers. These spectra clearly demonstrate that we have synthesized the desired products as peaks attributed to the amide bands<sup>15</sup> in the region between 1800 and 1400 cm<sup>-1</sup> are clearly discernible. Also note that these polymers are fully hydrogen bonded as indicated by the position and intensity<sup>15</sup> of



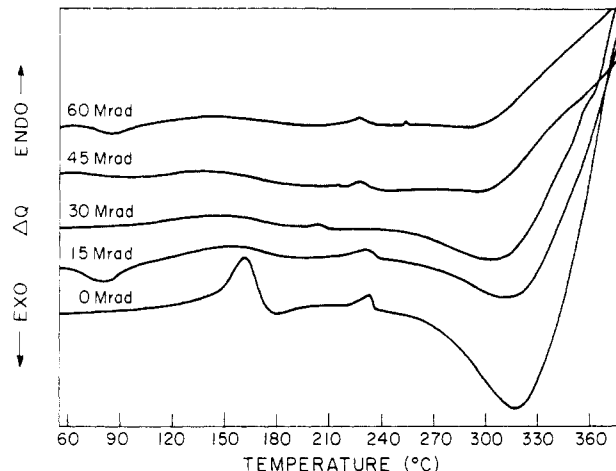
**Figure 1.** FTIR spectra of PADA 6,22 (curve A) and PADA PPD,22 (curve B).

the N-H stretching band found around  $3300\text{ cm}^{-1}$ . The major differences in the spectra of these two new polymers are due to the different diamine residues (aromatic or aliphatic) that were incorporated in the polymer during synthesis. Verification of the expected polymer structure was also found by NMR as will be discussed in detail in the section on NMR.

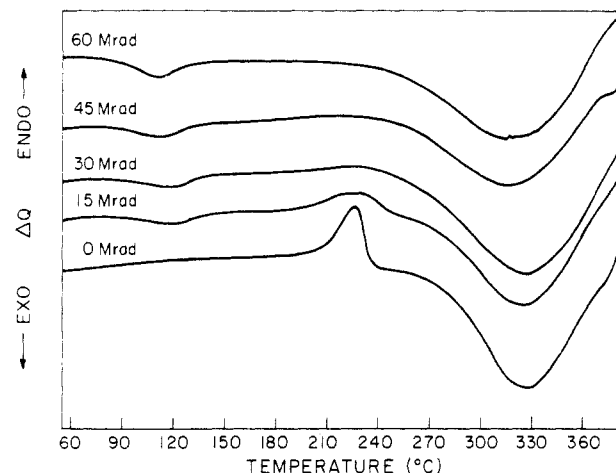
Visible absorption spectra were recorded with a Cary 17 spectrophotometer. Temperature studies were conducted on the cross-polymerized polymer thin films by using a heated precision cell equipped with a Fenwal Model 550 temperature controller (temperature range,  $25\text{--}200\text{ }^{\circ}\text{C}$ ). Spectra and peak areas were recorded at each temperature after a 10-min equilibration period. For the FTIR and visible absorption temperature studies, the polymer thin films were cross-polymerized by exposure to UV light of  $5\text{ mW/cm}^2$  power density for 30 min. Thermal analysis of the polymers was performed by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-4 operated at a scan rate of  $10\text{ }^{\circ}\text{C/min}$  from  $30$  to  $400\text{ }^{\circ}\text{C}$ . Solid-state  $^{13}\text{C}$  nuclear magnetic resonance spectra were recorded on an IBM NR/200 AF (4.7 T) spectrometer operating at  $50.3\text{ MHz}$  using a cross-polarization (CP) pulse sequence and dipolar decoupling (DD) in conjunction with magic angle spinning (MAS). The polyamide-diacetylenes in powder form were packed into an aluminum oxide rotor with Kel-F [poly(chlorotrifluoroethylene)] caps and spun at ca.  $3.8\text{ kHz}$  with a Doty Scientific probe. A cross-polarization contact time of  $2\text{ ms}$  was employed with a  $5.0\text{-}\mu\text{s}$   $90^{\circ}$  proton pulse and a  $3.0\text{-s}$  recycle time. All spectra were referenced to the methyl resonance of *p*-di-*tert*-butylbenzene ( $31.0\text{ ppm}$  from TMS). For the DSC and NMR studies, the powdered polymers were cross-polymerized by exposure to varying dosages ( $15, 30, 45$ , and  $60\text{ Mrad}$ ) of high-energy electrons ( $\beta$  radiation) generated with a Van de Graff accelerator operated at  $2.6\text{ MeV}$ .

### III. Results and Discussion

**A. Cross-Polymerization.** The reactive diacetylene groups contained along the backbone of the polyamides may be activated by UV radiation or by ionizing radiation to give a network structure in which the newly formed cross-links are actually conjugated polydiacetylene chains. Clearly, a knowledge of the extent of diacetylene conversion to polydiacetylene chains is of critical importance for gaining an understanding of how this chemistry influences the final properties of these materials. In order to estimate what percentage of the diacetylene groups were actually involved in the solid-state polymerization, we explored two



**Figure 2.** DSC scans of PADA 6,22 with increasing radiation dosage.



**Figure 3.** DSC scans of PADA PPD,22 with increasing radiation dosage.

separate analysis techniques; thermal analysis (DSC) and NMR spectroscopy.

**1. Thermal Analysis.** The DSC scans for as-prepared PADA 6,22 after exposure levels of  $0, 15, 30, 45$ , and  $60\text{ Mrad}$  of high-energy electrons ( $\beta$  radiation) are shown in Figure 2. Before cross-polymerization, the aliphatic polyamide-diacetylene displays an endothermic transition at about  $160\text{ }^{\circ}\text{C}$  and a broad exothermic peak beginning around  $275\text{ }^{\circ}\text{C}$ . The endotherm is a melting transition resulting from the thermal disruption of localized crystalline segments of the polymer. As the extent of cross-polymerization is increased, the melting endotherm flattens and disappears, indicative of the formation of a network-like structure that renders the crystalline regions infusible. The broad exotherm, which also decreases with increasing radiation dosage, has been attributed to a combination of diacetylene polymerization and degradation<sup>4,7,16</sup> and is therefore related to the number of diacetylene groups in the polymer. Thus, integration of this peak could, in principle, provide a means to determine how many diacetylene groups have reacted on cross-polymerization. The limitations of this approach will be discussed shortly. The origin of the small endotherm at about  $230\text{ }^{\circ}\text{C}$ , which is not significantly influenced by cross-polymerization, is yet to be determined.

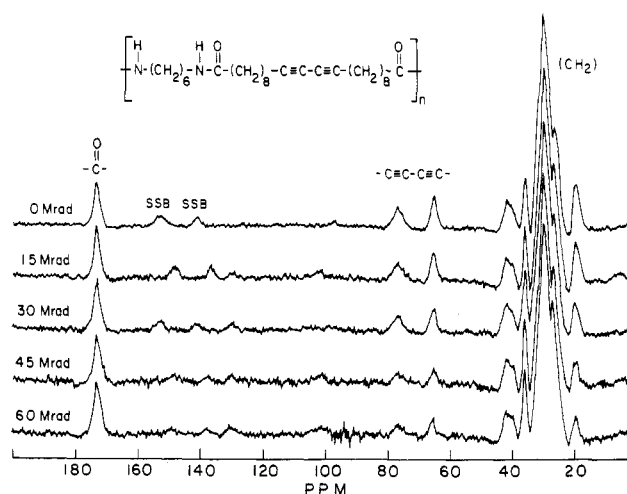
The DSC scans of PADA PPD,22 are shown in Figure 3 for varying dosages of  $\beta$  radiation. These curves reveal the same essential features as the aliphatic-based polyamide except that the endothermic transition appears at higher temperatures. This is to be expected, as the phenyl

ring renders the polymer more rigid, thereby decreasing its entropy content and hence increasing its melting point. The onsets of the exothermic peaks are the same for both polymers, reflecting the fact that the sequence of atoms nearest to the diacetylene units is identical.<sup>4</sup> To determine the origin of this exothermic activity in the polyamide-diacetylene polymers, <sup>13</sup>C NMR spectra of PADA PPD,22 were measured before and after a thermal treatment involving ramping the sample at 10 °C/min to 300 °C followed by quenching. The <sup>13</sup>C solid-state NMR data (not shown) reveal complete disappearance of the acetylenic carbons (see NMR section for information about the location of these peaks) after this treatment while additional peaks do not appear in the spectrum. It was also found that significant broadening of the methylene and aromatic carbon resonances resulted from the thermal treatment. Thus, although we have yet to establish the exact fate of the diacetylene groups, it is clear that this exotherm is related to a reaction of the diacetylene groups at elevated temperatures. Thermal gravimetric analysis (TGA), however, revealed a weight loss at about 380 °C for both polymers before and after cross-polymerization, indicating that degradation, which is clearly dominated by the amide portion of the chain, is also taking place at the higher temperature range of the exotherm. Previous workers have also found that the primary thermal decomposition process in polyamides involves cleavage of the amide bond.<sup>17</sup> Thus, although integration of the exotherm should provide quantitative information on the degree of cross-polymerization at various radiation dosages, it is not feasible in practice due to the overlap of degradation onto the tail of the exothermic peak, as can be seen most clearly in the DSC scans of PADA 6,22 in Figure 2. Because of this overlap, the exothermic feature cannot be unambiguously integrated to yield quantitative data, especially as the radiation dosage is increased. As indicated in Figure 3, a deconvolution of the diacetylene exotherm from the high-temperature degradation processes seems more plausible for the aromatic-based polyamide; however, a quantitative estimation of diacetylene conversion is still highly questionable.

With the above limitations in mind, it can be seen by comparing DSC results for the two polymers, that the aliphatic polyamide-diacetylene provides a more favorable environment for diacetylene polymerization, as indicated by a more significant reduction in the intensity of its exotherm with increasing radiation dosage. Integration of the exothermic peak reveals about a 90% conversion after a 60-Mrad dosage. The partly aromatic polyamide-diacetylene, on the other hand, contains a fairly large amount (50% by DSC exotherm integration) of unreacted diacetylene groups even after a radiation dose of 60 Mrad. Again it is to be recognized that the actual numbers obtained with this technique are most useful for comparison purposes only.

**2. NMR Analysis.** An alternative method for studying the cross-polymerization of these materials is solid-state <sup>13</sup>C NMR. The <sup>13</sup>C NMR spectra of solid PADA 6,22 shown in Figure 4 were obtained with a cross-polarization pulse sequence using a 2-ms contact time and a 3-s recycle time. Two thousand scans were time-averaged and collected under identical conditions for the polymer at varying radiation dosages. Signal-to-noise differences between spectra arise from different sample weights used for data accumulation. Peak assignments were made based on reports in the literature.<sup>18-22</sup>

The highest field resonance at 19.6 ppm is attributed to the  $\alpha$ -methylene carbons bonded to the acetylenic



**Figure 4.** CP MAS/DD <sup>13</sup>C NMR spectra of PADA 6,22 with increasing radiation dosage.

carbons, while the lowest field methylene resonance at 41.5 ppm is due to the methylene carbons next to the nitrogen which are broadened by quadrupolar coupling. The next resolvable methylene resonances are the methylenes  $\alpha$  to the carbonyl at 35.7 ppm, and the remaining methylenes appear as shoulders on the broad peak that encompasses all of the interior methylene carbons. The acetylenic carbons appear at 64.9 and 76.7 ppm, with the interior carbons resonating at higher field due to additional shielding provided by the sp bonds. The spinning sidebands shown around 140 and 152 ppm originate from these acetylenic carbons due to inefficient averaging of the chemical shift anisotropy which is typically greater for multiply bonded carbons.<sup>23</sup> As shown in Figure 4, the resonances due to the acetylenic carbons gradually decrease with increasing radiation dosage. During this process, all other peaks remain constant except for the peak at 19.6 ppm which is due to the methylene groups next to the diacetylene functionality which also decreases as it shifts and becomes lost in the broad absorption due to the interior methylenes. Since this is presumably due to diacetylene polymerization with formation of the polydiacetylene backbone, new resonances should appear for the sp- and sp<sup>2</sup>-hybridized carbons of the conjugated chain. The fact that they are not easily resolved may just be an artifact of the experimental conditions. For example, since cross-polymerization presumably yields more rigid networklike domains, protons in the local environment may have longer  $T_1$ 's and do not efficiently relax in the time allowed by the recycle delay, thereby impeding cross-polarization. Also, since the polydiacetylene chain is non-protonated, the experimental spin-lock contact time may have been too short to allow sufficient cross-polarization.<sup>19</sup> Another explanation, and probably the most reasonable, is simply the large dispersion of chemical shifts observed for conjugated carbon chains of varying length. It has been reported that the chemical shift of sp-hybridized carbon atoms is dependent on the number of conjugated carbon bonds and may vary from 80 to 110 ppm. Wegner et al.<sup>20</sup> have studied the solution and solid-state NMR of polydiacetylenes obtained from crystalline disubstituted diacetylene monomers and suggest that the <sup>13</sup>C NMR signal shift with varying conjugation length may arise from a resonance admixture of the butatrienic and acetylenic structures of the conjugated backbone. Koenig and co-workers<sup>19</sup> have reported the CP MAS/DD spectrum of the macromonomer poly(1,11-dodecadiyne) before and after cross-polymerization, in which they also observed chemical shift fluctuations that they attributed to differing extents

of conjugation. In all cases, however, signals due to the sp carbons resonate around 100 ppm and the sp<sup>2</sup> carbons appear around 130 ppm. Careful examination of the spectrum of nylon 6,22 exposed to 60 Mrad does reveal the appearance of broad absorptions in these two general areas.

Since the peaks due to the diacetylene group decrease relative to the other peaks in the spectrum, it should be possible to at least estimate the degree of cross-polymerization as a function of radiation dosage. In an attempt to circumvent most problems associated with quantitative analysis of <sup>13</sup>C spectra such as nuclear Overhauser effects, the average of the two acetylenic peak areas was taken as a ratio of the carbonyl peak area. Being an isolated resonance, the carbonyl served as an internal reference against which the diacetylene peak intensity/area could be followed. The ratio for the as-prepared material was assumed to be 0% diacetylenes reacted, and the subsequent values calculated for the irradiated samples were scaled appropriately.

It should be noted that nuclear magnetic resonance data obtained with polarization transfer techniques are usually not amenable to quantitative analysis due to nuclei possessing different rates of cross-polarization. Through static dipolar interactions between the carbons and protons, carbon magnetization is built up at a rate depending on the number of adjacent protons and molecular motion. This process may be observed experimentally as the increase in intensity of the carbon peaks as a function of contact time between the carbon and proton spin reservoirs. At longer contact times, the intensity may be observed to slowly decrease due to relaxation effects. Thus, in order to obtain quantitative data, all carbon nuclei should ideally reach maximum intensity at the same experimental contact time. In practice, this is difficult to achieve. However, because relaxation is usually much slower than the cross-polarization buildup, a sufficiently long contact time may be employed such that all carbons in a sample reach full or near-full intensity. This only holds for rigid polymers in which contact times of 1–3 ms have been reported for quantitative studies.<sup>24</sup>

To assess the validity of our technique for estimating the extent of diacetylene conversion, the <sup>13</sup>C NMR spectra of the polyamide-diacetylenes were determined as a function of spin-lock/contact time. For our method to yield reasonable data, we must assume that the rates of cross-polarization of the carbonyl and both diacetylene nuclei remain essentially unchanged after cross-polymerization. If integrated peak intensities are plotted versus contact time for the unreacted and cross-polymerized materials, changes in cross-polarization rates caused by possible local molecular environmental changes may be detected. PADA PPD,22 was subjected to this treatment at contact times of 62.5 to 2000 μs for both the as-prepared polymer and after exposure to 60 Mrad of radiation. As expected, the carbonyl carbon and outer acetylenic carbons cross-polarized at essentially identical rates in the unexposed polymer, while the inner acetylenic carbons cross-polarized at a much slower rate due to the lack of adjacent protons. By comparison with the polymer exposed to 60 Mrad of radiation, the three nuclei examined displayed no significant changes in cross-polarization rates upon the formation of the polydiacetylene network structure. More specifically, the carbonyl carbon showed no variation in CP rate, while the diacetylenic carbons did display subtle differences which proved to be insignificant because of the breadth of the maximum in the intensity versus contact time curves. Due to the breadth of these curves, and the sufficiently long contact time (2 ms) em-

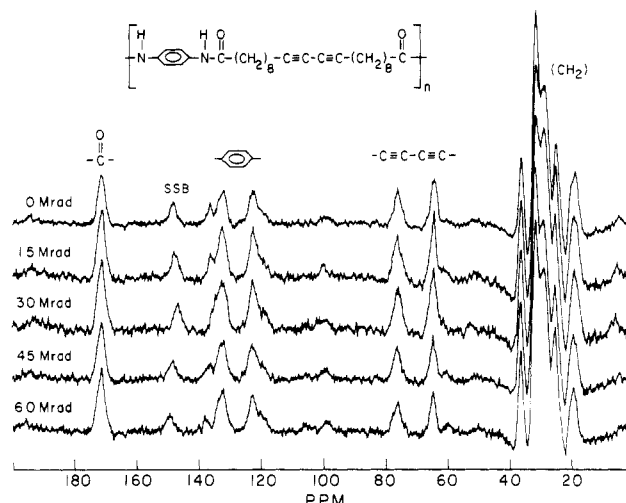


Figure 5. CP MAS/DD <sup>13</sup>C NMR spectra of PADA PPD,22 with increasing radiation dosage.

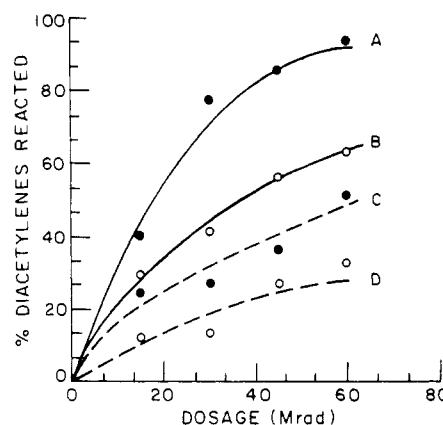


Figure 6. Percentage of diacetylenes reacted as a function of radiation dosage as determined by NMR and DSC. Open circles represent NMR data; closed circles represent DSC data. Curves C and D (dashed lines) are for PADA PPD,22; curves A and B (solid lines) are for PADA 6,22.

ployed, all three signals had reached near-full intensity, and error associated with this type of analysis, although present, was minimized. Thus, these data further support the use of the carbonyl resonance as an internal reference unperturbed by the solid-state chemistry and its utilization to monitor the reaction of the diacetylene carbons by the relative ratio method outlined in this paper.

Figure 5 displays the same <sup>13</sup>C NMR data for the partly aromatic polyamide-diacetylene in which the peak assignments are essentially the same with the exception of the protonated aromatic resonances at 123.0 ppm and the quaternary aromatic resonance at 132.5 ppm. Following the same procedure of comparing the acetylenic peak areas with their respective carbonyl peak areas, the degree of cross-polymerization was plotted as a function of radiation dosage for both polymers and is presented in Figure 6. The results obtained by DSC analysis are also plotted on this curve for comparison.

As indicated in Figure 6, the diacetylene groups present in the aliphatic-based polyamide are significantly more reactive than those present in the aromatic system. It can be seen that after a 60-Mrad dosage, about 60% of the diacetylenes has reacted compared with about 35% in the aromatic-based system. The trend of these results is consistent with what was observed by DSC. In fact, for the case of PADA PPD,22, in which the DSC exotherms are more easily resolved in the high-temperature region,

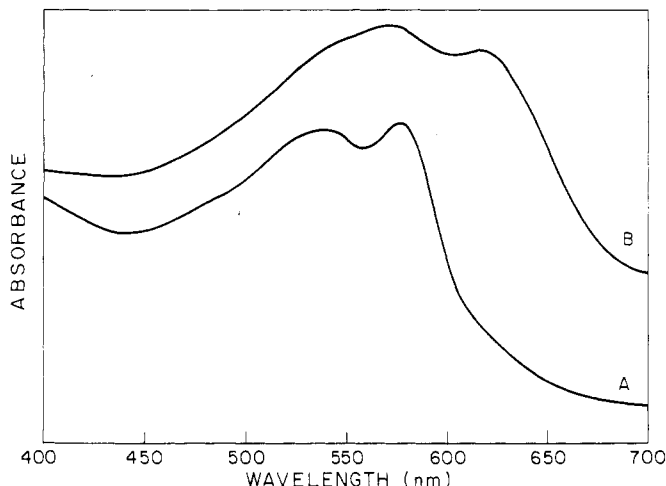
the degree of cross-polymerization obtained by solid-state NMR is in closer agreement with the DSC results than for the aliphatic-based polyamide. It is clear, however, that for both polymers the DSC technique grossly overestimates the number of diacetylene groups that have reacted. It is interesting to note that our findings on the relative reactivity of the two macromonomers thus far synthesized agree with the results reported by Patil et al.<sup>7</sup> on polyester macromonomers. For their polyesters of the general formula  $[\text{OCH}_2\text{C}\equiv\text{CC}\equiv\text{CCH}_2\text{O}(\text{C}=\text{O})\text{R}(\text{C}=\text{O})]_n$ , those in which  $\text{R} = (\text{CH}_2)_{n=2-8}$  were consistently more photo-reactive than the polymers that contained  $\text{R} = p$ - and  $m$ -phenylene.

In short, both the DSC technique and the NMR technique reveal that the aliphatic-based system is more reactive than its aromatic analogue. A more realistic estimate of the actual degree of conversion is clearly better provided by the NMR technique. However, the obtainment of quantitative numbers by the polarization transfer method used here is complicated by the fact that polymers contain a wide distribution of molecular motions some of which may be too rapid to experience any static dipolar interaction and therefore not contribute to the total intensity of observed peaks. If this were the case in the polyamide-diacetylenes, and if cross-polymerization yielded more rigid structures in which these highly mobile carbons could subsequently cross-polarize, then our analysis technique would underestimate the extent of diacetylene conversion. It seems reasonable to assume in this case, where extensive chain mobility is limited by the molecular environment provided by the hydrogen-bonded network and the rigid diacetylene groups, that such effects would be minimal. They cannot, however, be completely ruled out.

To gain an understanding of how local molecular mobility may be influencing the reactivity of these polymers, preliminary  $^{13}\text{C}$  spin-lattice relaxation measurements were accumulated with a modified Torchia's pulse sequence<sup>25</sup> in which cross-polarization is utilized for signal/noise enhancement. For the PADA PPD,22 it was found that the  $T_1$  measured for the carbonyl signal remains essentially constant from the uncross-linked samples to the cross-polymerized samples, thereby supporting the use of the carbonyl signal as an internal reference not affected by the radiation. Comparisons of the  $T_1$  relaxation times for the aromatic and aliphatic polyamides revealed that there were no significant differences between the relaxation times of the acetylenic carbons found in either of these two polymers. This would imply that the origin of the different reactivities of these two polymers is to be found in variations in the level of crystallinity or the type of molecular packing existing in each sample and not in differences associated with chain segment mobility in the vicinity of the diacetylene groups. Further information on the relaxation times of these and other carbons obtained through additional experiments of this nature will allow a better understanding of the influence of polymer structure and amorphous versus crystalline organization on diacetylene reactivity in the polyamides. These experiments coupled with measurements of the percent crystallinity of the these polymers are currently under way.

#### IV. Optical Properties: Thermochromism

Cross-polymerization and the formation of conjugated polydiacetylene chains transverse to the host polyamide chain direction produce highly colored materials, with electronic transitions occurring in the visible portion of the spectrum. The exact excitation energies of these newly formed absorption bands are highly dependent upon the

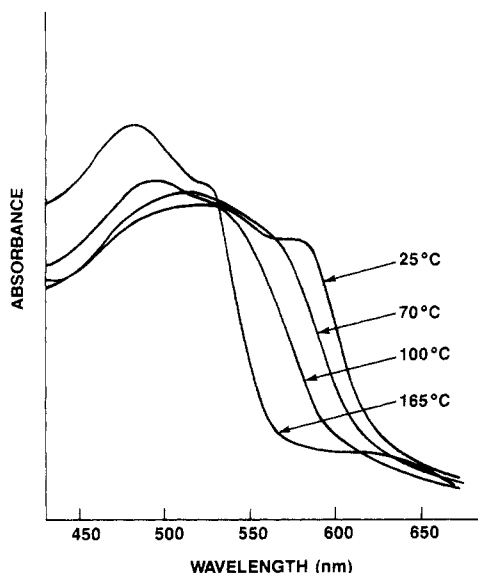


**Figure 7.** Visible absorption spectra of cross-polymerized PADA 6,22 recorded (A) from a sample cast onto a water surface and (B) from a sample cast onto a glass slide (spectra have been arbitrarily offset along the absorbance axis for clarity).

molecular environment and torsional mobility of the polydiacetylene chains which, in turn, are determined by the chemical structure and organization of the host polymer chain atoms (which now can be thought of as side groups pendent to the polydiacetylene backbone). The different constraints placed on the torsional mobility of the backbone through variations in the local molecular organization of the side-chain atoms, such as would occur by variations in their conformational states and intra- or interchain packing, can result in a wide variety of excitation energies, as is well documented in the literature.<sup>5,26</sup> The ability to vary the side-group organization (via temperature, stress, or solvent quality changes), and, hence, its influence on the torsional freedom of the polydiacetylene backbone, gives rise to the many different types of chromism observed in these materials. The dramatic color changes associated with these organizational changes directly reflect the unusually strong coupling that exists between the electronic states of the polydiacetylene backbone and its conformational state. Although the kinds of backbone conformations or distortions responsible for the different electronic states have not been unambiguously determined, it is clear that any disruption in the effective overlap of the  $\pi$  orbitals of the conjugated backbone will shift the absorption band to higher energies as the electronic states become more localized.

Figure 7 shows the visible absorption spectra of thin films of PADA 6,22 that were cast from *m*-cresol solutions onto different surfaces and then cross-polymerized by exposure to UV radiation. Sample B was cast onto a glass substrate at a sufficiently high temperature that the *m*-cresol evaporated in about 15 min, while sample A was cast under milder conditions onto the surface of a water bath which allowed the *m*-cresol to quickly disperse, thereby leaving a thin polymer film at the air-water interface which could be readily transferred onto a glass slide. The sample prepared directly on the glass slide is purple, whereas the sample cast onto the water surface is blue. The difference in excitation energies between these two samples clearly illustrates how molecular organization can influence their optical properties. Both samples display broad absorption bands with significantly developed high-energy shoulders characteristic of a collection of polydiacetylene chains with a wide range of effective conjugation lengths. The blue sample, however, has its lowest energy optical transition at about 620 nm, whereas for the purple sample it occurs at about 570 nm. Clearly, the different casting environ-



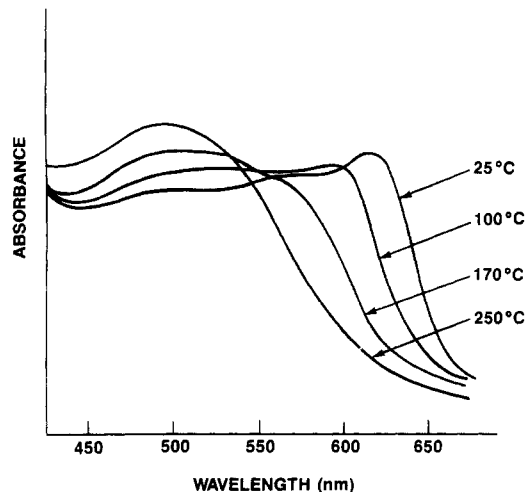


**Figure 8.** Visible absorption spectra of cross-polymerized PADA 6,22 recorded as a function of temperature.

ments have produced polymers with quite different side-group molecular organizations which, although we can only speculate at this point, most likely reflect differences in the conformations and packing of the side-chain methylene groups adjacent to the conjugated backbone. The high-energy tail ( $<450$  nm) displayed by both of these films is due to a large amount of scattering present in the polymer due to its semicrystalline nature. By controlling the processing conditions in a manner that creates much smaller crystallites, however, it is possible to largely eliminate the scattering observed in these thin films.

It is worth noting that the breadth of the above absorption bands indicates that for solution cast films the newly formed polydiacetylene chains are contained within a fairly disordered matrix. It is to be expected that the diacetylene groups of the host polyamide chain will be located in both the crystalline and amorphous regions of the polymer. Clearly, the diacetylenes residing in the most ordered regions of the host polymer are best arranged for topochemical polymerization and will quickly react to form polydiacetylene chains within their ordered environment. It has been previously found,<sup>4,8</sup> however, that cross-polymerization can also occur in much less ordered domains as evidenced by a substantial conversion of diacetylene groups to polydiacetylene chains in host polymers that show no indication of crystallinity by diffraction or thermal techniques. Thus, cross-polymerization takes place in both the crystalline regions, and, to a lesser extent, in more disordered paracrystalline regions.<sup>8</sup> The chains formed in these paracrystalline regions will be shorter and more disordered (nonplanar), whereas the chains formed within well-defined crystallites will have a higher degree of polymerization and remain more ordered (planar). The presence of a wide range of polydiacetylene chains with different effective conjugation lengths and levels of order is therefore responsible for the broad absorption bands exhibited by this material. Although this seems like a rather undesirable state, it should be pointed out that the development of relatively short polydiacetylene cross-links within a fiber-forming host polymer may in fact produce materials with better overall mechanical properties.

Figure 8 shows the visible absorption spectra of a cross-polymerized thin film of PADA 6,22 as a function of temperature. Similar curves are shown in Figure 9 for a sample of PADA PPD,22. Both films were cast from



**Figure 9.** Visible absorption spectra of cross-polymerized PADA PPD,22 recorded as a function of temperature.

*m*-cresol solutions of the appropriate host polymer and cross-polymerized with UV radiation at 254 nm with an intensity of 5 mW/cm<sup>2</sup>. As can be seen in the figures, both materials exhibit thermochromic behavior. The PADA 6,22 polymer changes from purple to red with increasing temperature, whereas the PADA PPD,22 polymer changes from blue to red. Both of these dramatic color changes reflect significant shifts in the absorption bands to higher energies. Perhaps the most striking observation about the thermochromic transitions of these polymers is the fact that they are completely reversible as long as an upper temperature characteristic of the particular polymer is not exceeded. In the case of the aliphatic-based polyamide, that temperature is about 130 °C, and for the aromatic-based polyamide, it is about 160 °C. In addition, no hysteresis was observed during temperature cycling, and no changes in the absorption curves recorded at any temperature between the two temperature extremes were observed in the heating or cooling cycles. This is in sharp contrast to many of the thermochromic polydiacetylenes which typically exhibit poor reversibility after cycling to high temperatures and extensive hysteresis effects.<sup>22,27</sup> It was also found that these materials could be cycled to much higher temperatures with only minor changes in their room-temperature curves. For example, the aromatic-based polyamide could be cycled to temperatures as high as 220 °C without drastically altering its original absorption spectrum. Thus, the thermochromic transitions of the cross-polymerized polyamide-diacetylene polymers are remarkably reversible and exhibit essentially no hysteresis effects.

It was originally believed that the thermochromic transitions exhibited by urethane-substituted polydiacetylenes were driven by a thermal disruption of the hydrogen-bonded side groups.<sup>28</sup> It has recently been shown, however, that many of the urethane-substituted polydiacetylenes display thermochromic transitions that occur with complete retention of these highly directional secondary bonds.<sup>4,22,27</sup> In this case, it has been proposed<sup>27</sup> that changes in the torsional mobility and hence planarity of the polymer backbone are brought about by changes in the conformations of the side-group methylene groups connecting the backbone to the urethane linkage. In polydiacetylenes fitted with fairly rigid side groups these changes occur without significant disruption of hydrogen bonds. Evidence for conformational changes in the methylene groups has been provided by FTIR<sup>27</sup> and <sup>13</sup>C NMR<sup>22</sup> spectroscopy.

For the polyamide-diacetylene polymers, the side groups are actually segments of a polymer chain containing two strong amide hydrogen bonds per segment. This results in a side-group organization that is much less flexible or "entropically active" than the urethane-substituted polydiacetylenes synthesized from diacetylene monomers. The amide hydrogen bonds serve as anchors that hold the side groups in place, thereby preventing complete disordering at elevated temperatures and ensuring reversible behavior. Once a significant portion of the hydrogen bonds have been broken as would occur with extensive disordering, the reversibility of the thermochromic transition becomes highly compromised. In this light, the higher temperature capabilities of the aromatic-based polyamide can be seen as a direct consequence of the decreased side-group mobility brought about by the incorporation of a rigid phenyl ring in the side group. We have verified that the hydrogen bonds of the polyamide-diacetylene polymers are not disrupted at elevated temperatures using the FTIR techniques described in our previous publications.<sup>4,27</sup> We find only the expected changes in hydrogen bond strength that occur due to thermal expansion of the polymer<sup>15</sup> and no indication of the presence of nonbonded free N-H groups throughout the entire thermochromic temperature range.

In summary, the thermochromic behavior exhibited by the polyamide-diacetylene polymers reflects the development of increasing torsional mobility of the conjugated backbone which occurs as the side-group methylene segments adjacent to the backbone become thermally activated at elevated temperatures and release their mobility restricting hold on the backbone. Once freed from its rigid environment, the conjugated backbone can readily obtain a less planar conformation with more localized electronic states. Reversible thermochromic behavior is ensured by retention of hydrogen bonds which serve to partially restrict the mobility of the side groups and prevent complete disordering from taking place. In this case, the thermochromic behavior is manifested as a continuous shifting of the absorption band to higher energies with no indication of an abrupt first-order phase transition as has been found in the more highly crystalline thermochromic polydiacetylenes.<sup>27</sup> It is this lack of the coexistence of two well-defined separate phases during the transition that is most likely responsible for the absence of hysteresis in these materials.

## V. Conclusions and Summary

The development of fiber-forming polymers containing reactive groups either along the polymer backbone or pendent to the polymer backbone that can be activated in the solid state after processing requires the utilization of solid-state reactions that must satisfy a number of different requirements. Most importantly, the reactive groups must remain dormant during processing and, at the appropriate time, be highly reactive in the condensed state. Additionally, it is highly desirable to have complete control over the extent of the solid-state reaction and the form and type of structural modifications that are introduced.

In this paper, we have explored the use of diacetylene chemistry as a means to create polyamide polymers with postprocessing capabilities. Key to an understanding of the influence of this chemistry on the relevant properties of the polymer is the development of techniques that provide reliable information on the number of diacetylene groups converted to polydiacetylene network chains upon cross-polymerization. We have found that <sup>13</sup>C NMR techniques and to a lesser extent DSC techniques can be utilized to ascertain relative trends in reactivities. Using these techniques we have found that the diacetylene groups

contained in polyamides based on the 8,8 diacetylene diacid can be more readily cross-polymerized when these materials are synthesized with an aliphatic diamine as opposed to an aromatic diamine. Preliminary relaxation studies indicate that the differences in reactivity are not related to differences in chain segment mobility in the region of the diacetylene groups. We are currently evaluating how this chemistry influences the mechanical properties of these new polymers, and the results of this investigation will be presented in a future publication.

In addition to an ability to systematically modify the mechanical behavior of the polyamides, the creation of a cross-linked network comprised of conjugated polydiacetylene chains introduces optical properties typically not found in nylon-type polymers. For example, as pointed out in this paper, the cross-polymerized polyamide-diacetylene polymers exhibit reversible thermochromic behavior, in some cases, to temperatures as high as 220 °C. These dramatic color changes reflect the sensitivity of the polydiacetylene conjugated backbone to its molecular environment and provide useful information on the kinds or organizational changes that take place at elevated temperatures. For the polyamide-diacetylene polymers, as has been found for certain urethane-based polydiacetylenes, thermochromism occurs without disruption of the hydrogen-bonded structure of the polymer.

In short, the investigation of polyamides containing reactive diacetylene groups could result in a new class of polymers with novel postprocessing capabilities and technologically useful optical properties. This paper describes the first steps toward the obtainment of such materials.

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**Registry No.** (8,8-Diacid chloride)(1,6-hexanediamine) (copolymer), 112651-32-8; (8,8-diacid chloride)(1,6-hexanediamine) (SRU), 112652-16-1; (8,8-diacid chloride)(1,4-phenylenediamine) (copolymer), 112651-33-9; (8,8-diacid chloride)(1,4-phenylenediamine) (SRU), 112652-10-5.

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## Deuterium NMR Analysis of Poly( $\gamma$ -benzyl L-glutamate) in the Lyotropic Liquid-Crystalline State: Orientational Order of the $\alpha$ -Helical Backbone and Conformation of the Pendant Side Chain

Akihiro Abe\* and Toshimasa Yamazaki

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan. Received June 9, 1988;  
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**ABSTRACT:** Deuterium NMR studies have been performed on variously labeled PBLG samples in the lyotropic liquid-crystalline state: PBLG-*N*-*d*,  $\alpha$ -*d*,  $N,\alpha$ -*d*,  $\alpha,\beta$ -*d*,  $\gamma$ -*d*, and *benzyl*-*d*. The orientational order *S* of the  $\alpha$ -helical backbone was estimated from the observed quadrupolar splittings  $\Delta\nu$  of the N-D and C $^\alpha$ -D bonds. The relative orientation of the side chains with respect to the backbone was elucidated by the rotational isomeric-state analysis of the  $\Delta\nu/S$  data observed for the  $\beta$ -,  $\gamma$ -, and  $\zeta$ -methylene and the *p*-benzyl deuterons. The most preferred conformation of the side chain was found to be  $\chi_1\chi_2\chi_3\chi_4\chi_5 = \text{tttt}$  (31%) in 1,4-dioxane,  $\text{tttt}$  (18%) in chloroform, and  $g^{\text{tttt}}$  (20%) in *m*-cresol at 30 °C. The analysis also indicates that the steric overlaps between adjacent side chains play an important role in determining the preference of conformations in the PBLG system. The lateral dimension of the  $\alpha$ -helical PBLG rod, expressed by the radius of gyration, was estimated to be  $6.5 \pm 0.1$  Å, being substantially larger than those (3.5–4.8 Å) reported by Luzzati et al. using the SAXS method.

### Introduction

In our preliminary communication,<sup>1a</sup> we have demonstrated that the deuterium NMR technique is useful in studying the molecular ordering of poly( $\gamma$ -benzyl L-glutamate) (PBLG) in the lyotropic liquid-crystalline state. The orientational order parameter of the  $\alpha$ -helical backbone has been elucidated as a function of concentration by using the PBLG samples deuterated at the amide group. In this treatment, the observed deuterium quadrupolar splitting  $\Delta\nu$  has been related to the order of the uniaxial liquid crystal by the expression

$$S = (2/3)\Delta\nu/q_h \quad (1)$$

where *S* designates the degree of orientation defined as the second-order Legendre polynomial and  $q_h$  is the component of the quadrupolar interaction tensor along the  $\alpha$ -helical axis

$$q_h = \left( \frac{e^2qQ}{h} \right)_{\text{ND}} \left( \frac{3 \cos^2 \theta_N - 1}{2} + \frac{\eta}{2} \sin^2 \theta_N \cos 2\phi_N \right) \quad (2)$$

where  $(e^2qQ/h)_{\text{ND}}$  is the quadrupolar coupling constant of the N-D bond,  $\eta$  is the asymmetry parameter, and  $\theta_N$  and

$\phi_N$  are the angles which define the orientation of the  $\alpha$ -helical axis in the Cartesian coordinate system affixed to the amide group (Figure 1): the *z* axis is taken to be parallel to the N-D bond, the *x* axis defined in the amide plane, and the *y* axis perpendicular to the plane.

The orientational order parameter of the  $\alpha$ -helical backbone can also be deduced by introducing deuterium in the  $\alpha$ -methine group. For the C $^\alpha$ -D bond, the asymmetry parameter is known to be negligibly small, and thus

$$q_h = \left( \frac{e^2qQ}{h} \right)_{\text{CD}} \left( \frac{3 \cos^2 \theta_\alpha - 1}{2} \right) \quad (3)$$

where  $(e^2qQ/h)_{\text{CD}}$  is the quadrupolar coupling constant of the C-D bond and  $\theta_\alpha$  designates the angle between the C $^\alpha$ -D bond and the  $\alpha$ -helical axis. In this paper, determination of the orientational order parameter of the  $\alpha$ -helical axis has been attempted by using samples deuterated at the amide as well as  $\alpha$ -methine group.<sup>1b</sup>

Under the experimental condition employed, PBLG molecules assume a nematic ordering. Samulski et al.<sup>2,3</sup> and Sohma et al.<sup>4</sup> have measured D NMR spectra of PBLG having partially or fully deuterated benzyl groups in the lyotropic liquid-crystalline state. From the observed quadrupolar splittings, they concluded that the orientation