Structural Characterization of the Cross-Polymerization of a Diacetylene-Functionalized Polyamide

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Received July 6, 1992; Revised Manuscript Received April 1, 1993

ABSTRACT: The molecular structural changes caused by the radiation-induced cross-polymerization of diacetylene units across host chains of a diacetylene-functionalized polyamide have been studied by solid-state ^{13}C NMR and wide-angle X-ray diffraction. By measuring ^{13}C NMR spin–lattice relaxation times of poly(hexamethylene-10,12-docosadiyne-1,22-diamide) before and after diacetylene cross-polymerization, it was found that cross-linking occurred primarily within the crystallites, as evidenced by the complete retention of amorphous-phase segmental mobility and constant rigid-component mass fractions. Cross-linking was also found to be accompanied by an increase in the local segmental mobility within the crystallites which was shown to result from a trans to gauche conformational transition of the methylene carbons pendant to the newly formed polydiacetylene chains. Wide-angle X-ray diffraction revealed that the diacetylene-functionalized polyamide crystallizes in a manner similar to that of conventional polyamides. Upon cross-polymerization, the formation of gauche conformers expanded the interplanar spacing between the hydrogen-bonded sheets while the spacing between the hydrogen-bonded chains remained constant, at least adjacent to the amide groups. Thus, the full hydrogen-bonding strength is retained since any lattice strains imposed by polymerization of the diacetylene units to polydiacetylene chains are accommodated by the conformational changes of the methylene segments connecting the amide groups to the polydiacetylene cross-links.

Introduction

Diacetylene functionalization of linear polymers is now recognized as a viable route to creating materials whose physical properties can be dramatically modified in the solid state.[1,2] For example, the diacetylene groups contained along a host polymer backbone can be activated either by thermal means or via radiation (UV, e^-, γ) to cross-link the host polymer via the formation of conjugated polymer chains. The resultant transverse network of covalent cross-links strongly influences the mechanical and thermal properties of the polymer. In addition, the conjugated cross-links impart novel optical properties to the polymer such as thermochromism[3] and mechanochromism.[4] The notion that cross-linking of a host polymer is accomplished by a topochemical polymerization of the diacetylene units to polydiacetylene chains was originally put forth by Wegner[5] and is now accepted as the primary mechanism responsible for the structural changes introduced by reactions in the solid state.

Our group has been carrying out detailed investigations of the synthesis, characterization, optical, thermal, and mechanical properties of a series of diacetylene-containing segmented polyurethanes.[3a,4,6] This work has recently been extended to the diacetylene functionalization of polyamides[3b,7] in order to esablish the generality of this method for modifying polymer properties in a controlled manner. In general, for both polymer systems, diacetylene cross-polymerization has been found to significantly enhance the mechanical performance, improve thermal stability and solvent resistance, and introduce new optical properties such as thermochromism and mechanochromism.

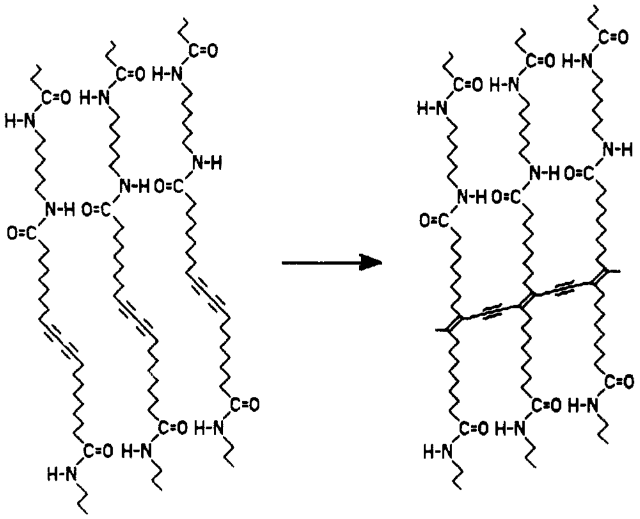

Figure 1. Schematic representation of the cross-polymerization of poly(hexamethylene-10,12-docosadiyne-1,22-diamide), or PADA 6,22.

Figure 1 shows a schematic of the cross-polymerization of the polymer examined in this paper: poly(hexamethylene-10,12-docosadiyne-1,22-diamide) (PADA 6,22). Previous investigations of fibers spun from this particular polyamide have shown that cross-linking dramatically increases tensile strength without rendering the fibers excessively brittle.[7] For example, a fiber formed by a dry-jet wet spinning process registered a 100% increase in ultimate tensile strength after exposure to 80 Mrad of electron beam radiation but the failure strain only reduced to 30%, thereby retaining a relatively high level of extension. In order to exhibit such levels of strain ability after radiation exposure, it was suggested that a large fraction of the material remained un-cross-linked. In fact, it is generally accepted that in semicrystalline diacetylene-containing polymers, the conversion to polydiacetylene chains takes place primarily within the most ordered or crystalline regions of the polymer due to the topochemical nature of the solid-state diacetylene polymerization. Recent work, however, has shown that diacetylene polymerization does not always occur exclusively within crystalline organizations.[8] For the segmented polyurethanes, the diacetylene groups are almost exclusively found in phase-separated hard domains due to the thermodynamic incompatibility of the diacetylene-containing hard segments and poly(alkyl oxide) soft segments.[3a] In contrast, the polyamides are synthesized from a diacetylene diacid and a diamine so that a diacetylene functionality is present in every repeat unit along the chain. Thus, the

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resultant semicrystalline material contains a similar weight fraction of reactive diacetylene groups in both the ordered crystalline regions and the disordered amorphous regions. The possibility therefore exists for some type of radiation-induced cross-linking in the amorphouise regions even if it does not involve the formation of a high molecular weight form of a polydiacetylene chain. Such cross-linking would greatly reduce the molecular mobility within these regions and most likely manifest itself on the macroscopic scale as embrittlement of the material.

The synthesis and optical, thermal, and mechanical properties of PADA 6,22 have been reported.[3b,7] Solid-state ^{13}C NMR has been used previously to confirm that the radiation-induced cross-linking occurs via the polymerization of diacetylene groups to polydiacetylene chains, as well as to provide a technique to estimate the extent of diacetylene conversion as a function of radiation dosage. NMR spectroscopy has also been employed to characterize the structural changes occurring during the high-temperature thermochromic transition of this material. This work will be the subject of a separate publication.[9] Previous workers have also used solid-state ^{13}C NMR to probe the structural changes induced during cross-polymerization of polyolefin-based macromonomers.[10] In this paper, wide-angle X-ray diffraction and NMR techniques are used to study the molecular organization and dynamics of a diacetylene-functionalized polyamide and the changes induced in these parameters by diacetylene cross-polymerization.

Experimental Section

The details of the synthesis and processing of PADA 6,22 into films and fibers have been provided.[3b,7] Solid-state ^{13}C nuclear magnetic resonance spectra were recorded on an IBM NR/200 AF (4.7-T) spectrometer operating at 50.3 MHz using a Doty Scientific probe for magic angle spinning (MAS). The chemical shift information listed below was collected with a cross-polarization pulse sequence using a 1-ms contact time: ^{13}C NMR (solid state) δ 19.6 ($\mathit{C}H_2C{\equiv}$), 25.9 ($\mathit{C}H_2CH_2C{=}O$), 30.1 (CH_2), 35.4 ($\mathit{C}H_2C{=}O$), 41.5 (CH_2NH), 64.9 (${\equiv}C{-}C{\equiv}$), 76.7 ($-C{\equiv}$), 173.0 ($C{=}O$).

Spin–lattice relaxation studies were conducted with a modified Torchia pulse sequence[11] utilizing a cross-polarization time of 500 μs and relaxation delay times ranging from 0.1 ms to 30 s. Peak intensities were plotted as a function of delay time and analyzed for the straight-line portion of the curve according to the equation $\ln M(t) = \ln C - t/T_1$, where $M(t)$ is the peak intensity as a function of delay time, T_1 is the spin–lattice relaxation time, and C is a constant related to the mass fraction of the component with relaxation time T_1. A least-squares fitting of the straight-line portion of the relaxation curves yielded the values of C from the y-intercept and T_1 from the inverse slope. In order to selectively observe the rigid component of the polymer, the same spin–lattice relaxation pulse sequence was employed with the relaxation delay time equal to 5 s.

Wide-angle X-ray diffraction patterns were recorded on a Rigaku system with a rotating anode generator. Solvent-cast films were measured in the reflection mode at step intervals of 0.5 deg for counting times of 2 s each. Fiber X-ray diffraction patterns were measured with a pinhole-collimated flat-film camera set up on an Enraf-Nonius Delft Diffractus 583. Fiber bundles were exposed to the beam for 24 h in a vacuum-evacuated chamber before and after a 40-Mrad dose of electrons. The sample-to-film distance was 170 mm for a maximum scattering angle of about 13° 2θ.

The polymers were cross-polymerized by exposure in air to high-energy electrons generated with a Van de Graff accelerator operated at 2.6 MeV. Precautions were taken in order to minimize sample heating during radiation exposure.

Results and Discussion

^{13}C Solid-State NMR Studies. Solid-state ^{13}C NMR was utilized to probe the molecular mobilities of PADA 6,22 through spin–lattice relaxation times (T_1), which are known to be sensitive to segmental motions of polymer chains. By comparison of the T_1's for the same material as a function of radiation dosage, overall mobility changes caused by diacetylene cross-polymerization were investigated. These changes were determined for both the amorphous and crystalline regions of the diacetylene-containing polyamide since the semicrystalline nature of the polymer provides a two-phase system in which chain segmental mobilities may be highly unequal.[12] For instance, when a direct-polarization (DP) pulse sequence with a short recycle delay is utilized, only the carbons of the amorphous regions with sufficiently short T_1's are observed. This is illustrated for PADA 6,22 in Figure 2 by a DP spectrum collected with a 1-s recycle delay. Also observed for other semicrystalline polymers, the DP spectrum is dominated by a broad envelope of methylene resonances with a peak centered at about 30 ppm (Figure 2, bottom). Although carbonyl and diacetylene carbons assuredly reside within the amorphous regions, their T_1's are inherently longer than those of the methylene carbons which prevents their observation in the DP spectrum, at least for this recycle time. The presence of the peak at 20 ppm, which is attributed to methylene carbons bonded to the diacetylene groups, provides evidence that diacetylene groups do exist within the more mobile amorphous regions of the polymer. As will be discussed later, the crystalline-phase spectrum typically exhibits multiple peaks in this region that are associated with the different well-defined molecular environments present in the crystalline domains. In the standard cross-polarization (CP) spectrum (Figure 2, top), contributions from the methylene groups in both the crystalline and noncrystalline phases are observed (all peak assignments are catalogued in detail in the Experimental Section).

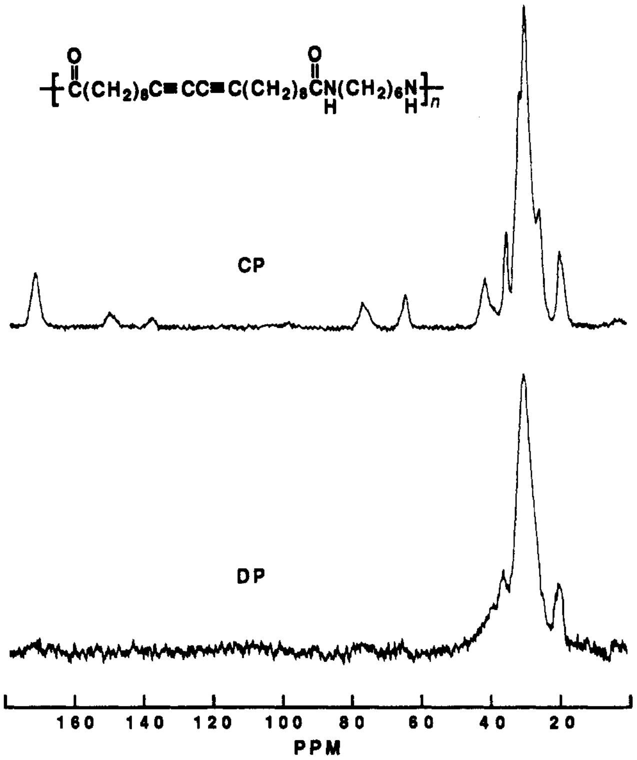

Figure 2. Comparison of the cross-polarization with the direct-polarization (single-pulse excitation with 1-s recycle delay) spectrum of PADA 6,22.

The T_1 spin–lattice relaxation curve for each methylene resonance of PADA 6,22 reflects the dynamic heterogeneity of macromolecular systems: The curves exhibit curvature initially but then behave linearly for longer delay times.

Table I. ^{13}C Spin–Lattice Relaxation Times of PADA 6,22

	0 Mrad		40 Mrad	
methylene carbon	rigid	mobile	rigid	mobile
$CH_2C\equiv$ (20 ppm)	73[a] (32%)[b]	1.2[c]	140 (20%)	0.8
$CH_2CH_2C{=}O$ (26 ppm)	99 (24%)	0.7	31 (22%)	0.6
CH_2 (30 ppm)	46 (44%)	1.2	31 (44%)	1.3
CH_2 (32 ppm)	41 (57%)	2.1	26 (51%)	2.2
$CH_2C{=}O$ (35 ppm)	35 (49%)	1.5	24 (51%)	1.9
CH_2NH (41 ppm)	34 (66%)	4.3	31 (60%)	3.5

[a] Rigid-component relaxation time in seconds. [b] Mass fraction of rigid component. [c] Mobile-component relaxation time (s) for data collected with delay times of 0–0.5 s.

Fitting the straight-line part of the data allows a relaxation time to be defined for the slowest-relaxing component of the sample, which for semicrystalline polymers is most likely the crystalline phase. Furthermore, by extrapolation of this straight line back to zero delay time, the mass fraction of this slowest-relaxing component may also be determined, assuming the peak intensity at zero delay time represents the total population of spins[13] (the optimum contact time was found to be 500 μs). Similar analysis of the short-delay-time portion of the relaxation curve for the interfacial and amorphous regions necessitates rather arbitrary selection of the dynamic boundary between these two phases (the lack of any long-range order within these regions results in a continuous distribution of relaxation times). Thus, for the data presented here, additional analyses simply include a mobile fraction T_1 determined for a fixed range of delay times (for the data presented here this range is 0–0.5 s). In any case, the spin–lattice relaxation times are not presented here as absolute quantities, but rather as useful parameters against which to gauge the effects of cross-polymerization on PADA 6,22. In order to characterize the motional changes induced in the chain segments upon cross-linking, ^{13}C spin–lattice relaxation times were measured for the methylene carbons of PADA 6,22 before and after 40 Mrad of electron beam radiation. These are presented in Table I and include rigid-component T_1's with respective mass fractions, as well as mobile-component T_1's determined for delay times of 0–0.5 s.

There are two primary conclusions that can be drawn from these data. First of all, the mass fractions of the rigid components either remain constant or become slightly smaller upon cross-linking to give the networklike structure. In fact, the mass fraction of the rigid component at 30 ppm, which is the chemical shift associated with the amorphous methylene carbons, remains constant at 44%. This fact coupled with the unchanged values for the mobile-components T_1's indicates that cross-linking is restricted to the crystalline regions. If cross-linking were occurring within the amorphous regions, then an increase would be observed for either the mobile-component T_1's or the rigid-component mass fractions as mobile carbons were transformed into rigid carbons. As it turns out, complete retention of mobility within the amorphous phase is realized after exposure of the polymer to 40 Mrad of electron beam radiation. This finding is significant in that it suggests that negligible random cross-linking of the amorphouse phase takes place, which is usually the primary outcome of the radiation treatment of nonfunctionalized semicrystalline polymers.

The second important change revealed in the data of Table I is a reduction of all of the rigid-component T_1's of the interior methylene carbons. This consistent decrease in relaxation times suggests that cross-polymerization results in a new crystalline structure with more mobile interior methylene segments. This, however, is in sharp contrast to the relaxation behavior of the methylene carbons adjacent to the diacetylene functionality. As opposed to all of the other methylene carbons of the polymer, the T_1 of these carbons increases significantly from 73 to 140 s upon irradiation. In addition, the rigid-component mass fraction of these carbons decreases from 32% to 20%. These latter changes reflect the more rigid environment in which the methylenes α to the unreacted diacetylene groups find themselves after some of the diacetylene groups have reacted. Clearly, the creation of polydiacetylene chains within the crystalline regions of the polymer reduces the mobility of the carbons directly attached to the newly created conjugated cross-links. For this radiation dosage, it was determined by NMR that roughly 50% of the total diacetylene groups in the sample have reacted.[3b] Since most of these react within the crystalline regions, the probability is quite high that an unreacted diacetylene group in a well-ordered crystalline lattice will be near a polydiacetylene cross-link. Apparently, the close proximity to these cross-links lowers the mobility of the α-methylene carbons. In addition, the reaction of rigid-component diacetylene groups produces a lower mass fraction of these carbons and also their α-methylene groups with respect to the total number in the sample. Thus, the smaller mass fraction of 20% signifies a decrease in the number of reactable diacetylenes within the crystalline regions.

The unusually high rigid-component T_1 (99 s) for the methylene carbons β to the carbonyl carbons (26 ppm) can be rationalized by considering the solid-state crystalline structure of a hydrogen-bonded polyamide.[14] With the methylenes packed into all-trans conformations, the β-methylene to the carbonyl is the most sterically restricted carbon in the structure due to the proximity of the methylene hydrogens to the double bond of the carbonyl. In contrast, the α-methylene to the carbonyl does not experience the same steric constraints since the hydrogens of this methylene group are facing 180° in the direction opposite the carbonyl oxygen. Upon cross-polymerization of the polymer, the relatively high T_1 of the β-methylenes is reduced to 31 s, which is in line with the T_1's for all of the other methylene groups. Clearly, some kind of structural modification occurs within the crystalline regions upon cross-polymerization which renders this methylene group as mobile as the other methylene groups (except, of course, the α-methylenes to the diacetylene). Although no conclusions can be drawn at this point with regard to this new structure, these data do suggest that the methylene groups may no longer exist in a tightly packed all-trans arrangement.

Cross-linking usually renders a polymeric system more rigid. However, the NMR relaxation data presented here reveal that cross-linking of the crystallites of PADA 6,22 increases the mobility of the methylene segments contained within these crystallites. The structural changes responsible for this observation were investigated by selectively observing the crystalline regions before and after cross-polymerization of the diacetylenes. From relaxation curves of the methylene groups, it was determined that the amorphous magnetization completely disappears after a delay time of 5 s. Thus, the NMR spectrum of the rigid component of PADA 6,22 was measured with a spin–lattice relaxation pulse sequence employing a 5-s relaxation delay time. The data are presented in Figure 3 for PADA 6,22 before and after exposure to 40 Mrad of electron beam radiation.

Immediately obvious are the changes due to the polymerization of the diacetylene groups to polydiacetylene

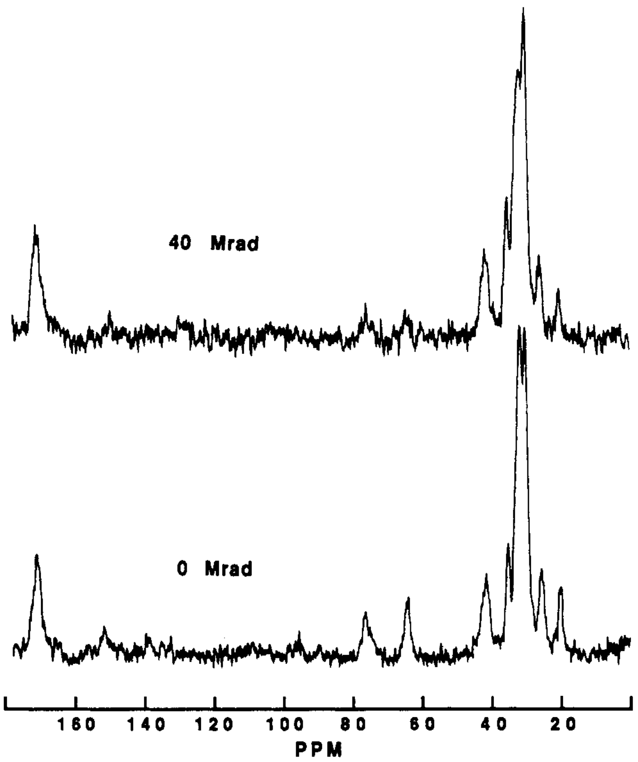

Figure 3. ^{13}C NMR spectra of the rigid component of PADA 6,22 before and after 40 Mrad of electron beam radiation.

chains. Described in detail elsewhere,[3b] these include an intensity reduction of the diacetylene peaks (77 and 65 ppm) and their α-methylene peak (20 ppm). More importantly, these spectra also reveal a structural transition within the methylene segments. Before irradiation, the resonances between 20 and 41 ppm represent methylene carbons within the crystalline regions, presumably ordered in all-trans conformations.[14] The peak at 30 ppm is due to the interior methylene groups of the hexamethylene diamine residue; this assignment is based on the fact that a similar peak does not exist in the rigid-phase spectrum of a structurally similar polymer which contains an aromatic diamine instead of the hexamethylene diamine. The 32 ppm peak, on the other hand, is due to the interior methylene groups of the diacetylene-containing diacid residue. Upon irradiation, the 32 ppm signal decreases in intensity and broadens with respect to the other peaks in the spectrum.

Together with information from molecular models, other solid-state NMR studies on polydiacetylenes with hydrogen-bonded side groups,[15] and the WAXD results presented in the following section, these data suggest a conversion of some of the interior methylenes surrounding the diacetylene groups from an all-trans conformational state to one containing gauche conformers. Further evidence for this conclusion was provided by heating the cross-polymerized material through its thermochromic transition and observing the rigid crystalline component with NMR.[9] At 130 °C, the 32 ppm methylene resonance regains its initial (0 Mrad) relative height. Upon cooling, the peak returns to its original cross-polymerized intensity. The reversibility of these changes indicates that the observed radiation-induced structural changes of the methylenes within the crystallites are not due to irreversible chemical reactions but are associated with conformation changes of the methylene groups.

The introduction of gauche conformers within the crystallites upon cross-polymerization accounts for the increased segmental mobility that was found in the ^{13}C spin–lattice relaxation measurements. Apparently, this increase in the local segmental mobility develops due to the more "amorphous-like" structure of the methylene segments contained within the cross-linked, hydrogen-bonded crystallites. It is reasonable to conclude that the newly formed polydiacetylene cross-links and the amide hydrogen bonds act as anchor points and thereby allow the development of more mobile methylene segments by preventing a major reorganization of the structure. If these constraint points were not tied to a macromolecular system, the entire cross-polymerized structure could reorganize to accommodate the diacetylene polymerization and, in the process, maintain a more rigid, trans-like structure. In fact, previous studies on the cross-polymerization of a disubstituted diacetylene monomer with hydrogen-bonded side groups have found that the entire side group rotates to retain the hydrogen bonds and its trans-bonded methylene groups.[16]

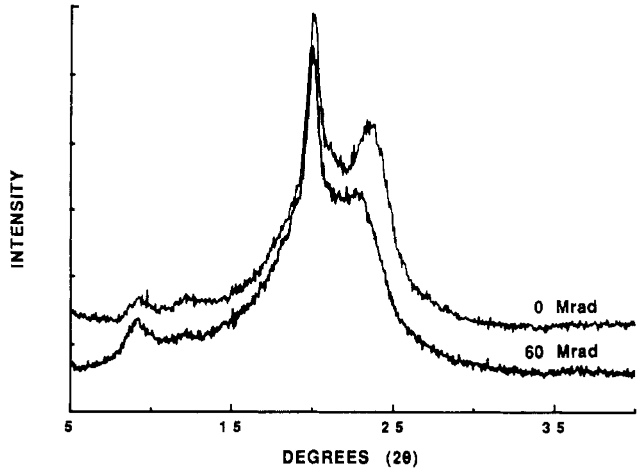

Figure 4. Wide-angle X-ray diffractograms of a solvent-cast film of PADA 6,22 before and after 60 Mrad of electron beam radiation.

Wide-Angle X-ray Diffraction. Since the NMR data indicated the generation of some radiation-induced structural changes within the crystalline regions, wide-angle X-ray diffraction was employed to further investigate these effects. The changes observed in the wide-angle X-ray diffraction patterns upon cross-polymerization are shown in Figure 4 for a solvent-cast film of PADA 6,22 before and after a 60-Mrad dose of electron beam radiation. Although the peak at $2\theta = 20.2°$ remains essentially constant, the peak at $2\theta = 23.2°$ has noticeably shifted in both position and intensity after the radiation treatment. Interpretation of these data first requires assignments of the diffraction peaks to respective molecular spacings.

Consultation of the literature reveals that all polyamides synthesized from a diacid and a diamine with an even number of carbons crystallize in a form that diffracts X-rays in a manner similar to that of PADA 6,22. In other words, most even–even polyamides such as Nylon 6,6 and Nylon 6,10 produce diffraction patterns with two primary peaks at roughly the same 2θ values as those shown in Figure 4.[17] The peak at $2\theta = 23.2°$ has been attributed to the spacing between the planes of polyamide chains which are hydrogen-bonded within the plane, so that its d spacing of 3.8 Å represents the distance between chains that are not hydrogen-bonded. The peak at $2\theta = 20.2°$ is due to diffraction from planes of polyamide chains which are not hydrogen-bonded within the plane, so that its d spacing of 4.4 Å represents the distance between hydrogen-bonded chains.[18]

Thus, the constancy of the $2\theta = 20.2°$ peak in Figure 4 indicates that order is retained between the chains that are hydrogen-bonded, at least in the vicinity of the amide groups, which are the primary scatterers along the chain backbone due to their higher electron densities. This is observed despite the fact that the hydrogen-bonded chains are the preferred reactants in the diacetylene polymerization of disubstituted diacetylenes with hydrogen-bonding side groups.[16,19] In fact, due to the topochemical nature of the diacetylene polymerization, a linear separation of less than 4 Å (based on an optimum stacking distance of 5 Å and an optimum stacking angle of 45°)[20] between the number 1 carbon of one diacetylene group and the number 4 carbon of the adjacent diacetylene group is required for the 1,4-addition to take place. This geometrical requirement is only satisfied in PADA 6,22 between the diacetylene groups of adjacent hydrogen-bonded chains. Since diacetylene polymerization occurs between the chains that are hydrogen-bonded, the distance between these chains should increase from 4.4 to 4.9 Å, the reported repeat-unit length for polydiacetylenes.[21]

On the contrary, an expansion is observed to occur between the sheets of hydrogen-bonded chains; an intensity decrease and shift to a larger *d* spacing for the $2\theta = 23.2°$ peak (Figure 4) indicates an overall loss of order, coupled with an increase in the average distance between these planes. Recalling the NMR data which suggested that cross-polymerization introduces gauche conformations into the methylene segments of the crystallites, the WAXD findings indicate that these gauche methylene conformations are primarily accommodated between the sheets of hydrogen-bonded chains. By definition, gauche-bonded segments describe larger dihedral angles than extended all-trans segments and therefore take up more space in a time-averaged model. Since an expansion between hydrogen-bonded chains is not observed in the diffraction patterns, it is suggested that the methylene groups nearer to the diacetylene units conform to locally accommodate the growing polydiacetylene cross-link. This accommodation might also involve the slight movement of the newly formed polydiacetylene chains out of the planes containing the host chains, thus contributing to the observed expansion and loss of order between these planes.

This is most easily observed with the aid of the CPK molecular models[22] shown in Figure 5 for a PADA 6,22 repeat unit both before and after cross-polymerization. These molecular models illustrate how the formation of gauche methylene groups is required to retain the hydrogen bonds and the resultant lattice expansion between the sheets that this conformational transition causes.

Because gauche conformations are assumed by the intracrystalline methylene groups originally extended in all-trans segments, a segment-length decrease along the chain axis direction would be expected with cross-polymerization. This possibility was examined by taking wide-angle X-ray photographs of PADA 6,22 drawn fibers both before and after 40 Mrad of electron beam radiation. The repeat-unit length of the nonirradiated polymer was nicely revealed as a prominent meridional reflection at $2\theta = 2.6°$ which corresponds to a *d* spacing of 34 Å. After 40 Mrad of electron beam radiation, this reflection does not appear at a larger 2θ angle, which would indicate a decrease along the polyamide chain axis, but rather it disappears completely. This may be explained by realizing that the radiation-induced change is not a simple crystallographic transition from one discrete set of unit cell parameters to another. In fact, since the methylene sequence is made up of eight carbons, there exist a large number of possible conformational transformations which could accommodate the PDA backbone while maintaining the hydrogen bonds. In other words, a shorter sequence, for example of four methylenes, might necessarily undergo a specific conformational transition which would be manifested as a more definite crystallographic transition. However, as evidenced by the intensity reduction of the original $2\theta = 23.2°$ peak, the methylene segments transform in a nonspecific manner to give a broader distribution of lattice spacings. This, in turn, indicates that the distance along the host polymer chain axis is reduced by varying amounts so that a single ultimate *d* spacing is not reached and coherent scattering to give a single diffraction peak is not possible. Thus, any substantial degree of diacetylene polymerization within the crystalline regions would result in a loss of coherence of the $2\theta = 2.6°$ spacing and the disappearance of this reflection from the diffraction pattern.

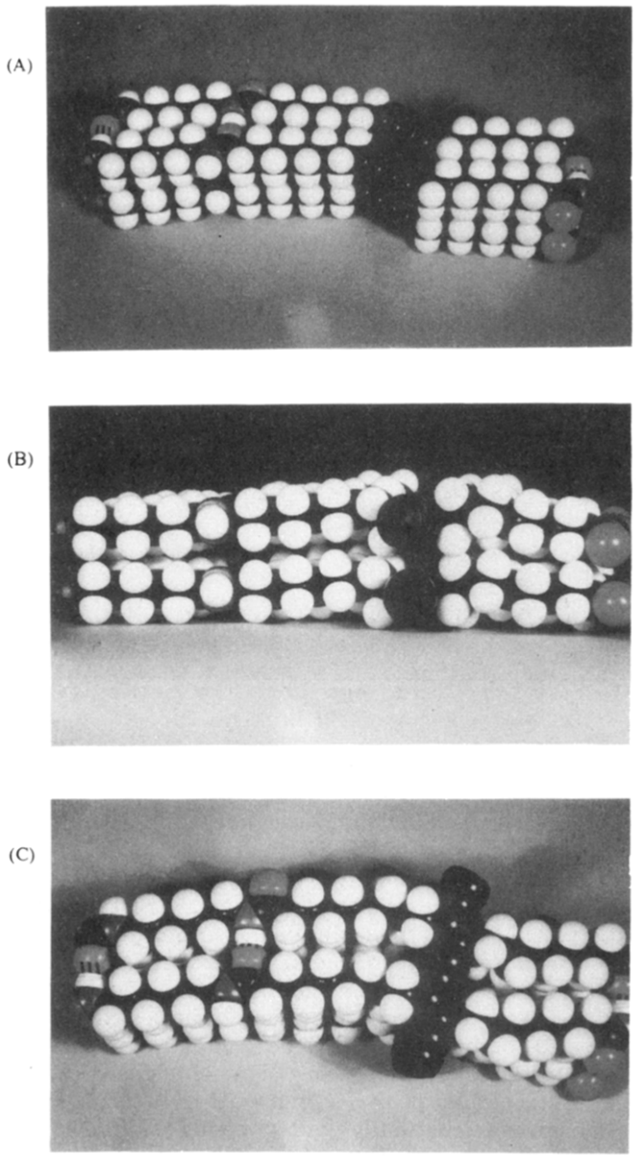

Figure 5. CPK space-filling molecular model of crystalline PADA 6,22: (A) before cross-polymerization, (B) after cross-polymerization illustrating expansion of spacing between sheets of hydrogen-bonded chains, (C) after cross-polymerization illustrating retention of spacing between hydrogen-bonded chains.

Conclusions

Results obtained by solid-state ^{13}C NMR and wide-angle X-ray diffraction studies have provided new insights into the nature of the molecular structure of PADA 6,22 and the changes induced in this structure upon radiation-induced cross-polymerization of the latent diacetylene functionalities contained in the backbone. The combined results of these techniques have shown that the methylene groups contained within the crystalline regions of the polymer undergo a trans to gauche conformatioinal transition that is accompanied by an expansion between the sheets of hydrogen-bonded chains. The spacing between the hydrogen-bonded chains remained constant, thereby indicating complete retention of the full hydrogen-bonding strength. In addition, NMR spin-lattice relaxation studies revealed complete retention of high mobility within the amorphous regions after cross-polymerization, coupled with nearly constant rigid-component mass fractions. This confirms that diacetylene polymerization is primarily restricted to the crystalline regions. It was also found that the average chain mobility within the crystallites increased upon cross-linking. The increased mobility within these regions was accounted for by the introduction of more gauche character into the all-trans methylene segments between the diacetylene groups and the hydrogen bonds of the host backbone.

The picture that emerges from this structural characterization of the cross-polymerization of PADA 6,22 makes it possible to connect many of the previously reported radiation-induced changes in macroscopic behavior with molecular-level descriptions. For example, it has been shown that irradiation greatly improves the moduli and ultimate tensile strengths of PADA 6,22 films and fibers without a significant reduction in strain ability and therefore toughness. These latest results suggest that this is due to the fact that diacetylene cross-polymerization is primarily restricted to the crystalline domains. Thus, the ultimate tensile strength is improved due to the production of the polydiacetylene cross-links within the crystallites, while the materials are not rendered uselessly brittle due to the diversion of the cross-links from the amorphous regions.

Acknowledgment. We thank the Office of Naval Research for partial support of this work. We are also grateful to Ken Wright of the MIT High Voltage Research Lab for the electron irradiations. Fiber spinning was performed by DuPont in cooperation with Len Buckley and Jim Katilaus of NADC.

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