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Study of the Solid-State Crosspolymerization of Poly(1,11-dodecadiyne) through Magic-Angle Carbon-13 NMR

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ABSTRACT: High-resolution carbon-13 NMR spectra of solid poly(1,11-dodecadiyne) before and after γ-irradiation are reported. The crosspolymerization reaction is shown to result in a conjugated backbone characterized by the acetylenic structure instead of by the butatriene possibility. Resolution of amorphous and crystalline contributions to the spectra is demonstrated. Evidence that crosspolymerization occurs predominantly in crystalline domains is also discussed.

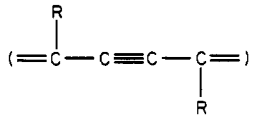
I. Introduction

The polymerization of diacetylene crystals has generated considerable interest as a solid-state reaction which occurs systematically throughout the crystal lattice.[1,2] Under appropriate conditions, the monomer can be converted to a macroscopic polymeric single crystal, the chains of which are fully conjugated. The polymerization can be initiated in several ways, including γ-irradiation,[1,3] UV irradiation,[4,5] heat,[6,7] and pressure. Recently, these reactions have been extended to include polymers as the starting material prior to irradiation.[8,9] The initial polymer (or "macromonomer") contains diacetylene groups in its repeat unit, which can react in a manner similar to that observed for the diacetylene monomers. Exposure to high-energy radiation initiates the reaction of diacetylene groups belonging to consecutive macromonomer chains and results in a systematic sheetlike structure which is covalently bonded in two dimensions. This procedure has been termed crosspolymerization in order to distinguish it from the random cross-linking which many polymers experience upon irradiation. The macromonomer which we have investigated in this work is poly(1,11-dodecadiyne):

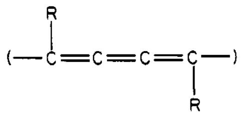
$$\lbrack (CH_2)_8-C\equiv C-C\equiv C \rbrack_x$$

A diagram of its crosspolymerization, as deduced from previously reported electron diffraction results,[9] is presented in Figure 1.

While diffraction work characterizes fully the molecular structure in the crystalline regions, there remain interesting questions to be answered. One of these concerns the electronic structure along the direction of crosspolymerization. Two forms have been observed in the polymerization of diacetylene monomers, the acetylenic (enyne) and butatriene structures:[10–14]



acetylenic



butatriene

Bond lengths from diffraction work can be used to discriminate between these two, but a more sensitive indication is desirable. This is true particularly for the crosspolymerized materials, where relatively few unique diffraction maxima are recorded. Another question deals with the semicrystalline nature of the macromonomer; the influence of the amorphous component on crosspolymerization is not well understood presently. Such consideration is not necessary in the polymerization of diacetylene monomers, which are completely crystalline under normal conditions.

These questions can be answered in part by the use of recently developed high-resolution techniques for ^{13}C NMR in rigid solids. The techniques consist of magic-angle spinning[15] and high-power decoupling[16] to coherently average certain line-broadening interactions. Cross polarization[17,18] from protons to carbons is also employed for sensitivity enhancement. Simultaneous use of these procedures can result in spectra of solid polymers in which chemically distinct carbon types have separately resolved resonances.[19,20] This capability is particularly attractive for the analysis of crosspolymerized poly(1,11-dodecadiyne), whose network structure makes it insoluble and infusible.

II. Experimental Section

The macromonomer was prepared by oxidative coupling of 1,11-dodecadiyne with a copper–pyridine catalyst. Details of the synthesis have been published previously.[8,21,22] Samples were stored at −10 °C and shielded from light prior to crosspolymerization. γ-Irradiation from a ^{60}Co source (23 Mrd) was used to crosspolymerize the macromonomer. It was also discovered that for some of the unirradiated samples crosspolymerization could be induced during packing of the material in the rotor by hand. The mechanical shear associated with twisting the plunger during packing was sufficient to initiate the reaction. When the macromonomer was packed with an effort to minimize such twisting, resonances indicative of crosspolymerization were not observed.

Carbon-13 cross-polarization (CP) magic-angle spinning (MAS) spectra were recorded at 38 MHz on a modified Nicolet NT-150 spectrometer. Radio-frequency field strengths of approximately

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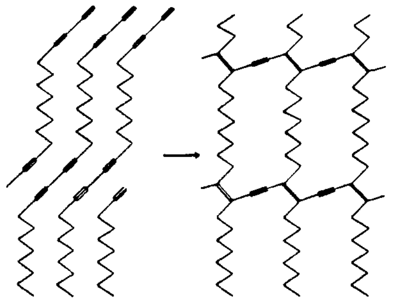

Figure 1. Crosspolymerization of poly(1,11-dodecadiyne), initiated by γ-irradiation.

50 kHz (as measured by ^{1}H $\pi/2$ pulse widths) were used in a single-coil, double-tuned probe. The ^{1}H radiofrequency was provided by a pair of coupled solid-state amplifiers (ENI 3200 L's), and the ^{13}C radiofrequency by a class C Drake L4B amplifier. Rotors were machined from poly(oxymethylene) and from poly(chlorotrifluoroethylene) and were spun at 3.5 and 2.2 kHz, respectively. Spectra of the macromonomer in deuterated chloroform solution were obtained on a Varian XL-100 spectrometer.

III. Results and Discussion

Carbon-13 spectra of poly(1,11-dodecadiyne) are shown in Figure 2 for samples both before and after γ-irradiation. The methylene carbons resonate at relatively high field, between 40 and 20 ppm. There are three separable contributions to this region: at 21.9 ppm the α-methylenes directly bonded to the acetylenic carbons (two per repeat unit), at 33.9 ppm the interior methylenes in crystalline regions (six per repeat unit), and a high-field shoulder at 30.9 ppm from the interior methylenes in amorphous regions. The assignment of crystalline and amorphous resonances will be discussed later. These shifts are in reasonable agreement with those recorded for the macromonomer in deuterated chloroform solution. In solution the α-methylene resonance appears at 19.2 ppm, and the interior methylene carbons are resolved into three peaks between 29.0 and 28.4 ppm. The interior carbon resonances are not resolved in the magic-angle spectra because of a number of line width contributions which are not completely averaged in solids (including isotropic chemical shift dispersions, distributions in anisotropic bulk magnetic susceptibility, deviations from the magic angle, etc.[23]). Differences in chemical shifts between the solid and solution spectra arise from solid-state shielding effects and from slight inaccuracies in referencing the magic-angle spectra. (The poly(oxymethylene) rotor resonance was set to be 89 ppm downfield from tetramethylsilane.)

The two acetylenic carbons of the macromonomer resonate farther downfield, at 79.2 and 66.5 ppm. The latter is assigned to the interior $\equiv$C–C$\equiv$ carbons of the diacetylene unit. The upfield shift relative to the exterior carbons arises from mutual anisotropic shielding of the sp bond. This assignment has been proposed previously on the basis of ^{13}C solution work: Babbitt and Patel[24] prepared soluble poly(diacetylenes) by attachment of special substituent groups on the backbone, and Bohlmann and Brehm[25] studied soluble acetylenic oligomers which were labeled at specific sites with ^{13}C.

The spectrum of γ-irradiated poly(1,11-dodecadiyne) is shown in Figure 2B. From the presence of the acetylenic carbon resonances at 79 and 67 ppm, it is clear that crosspolymerization is not complete. However, the appearance of two peaks at lower field, 131.6 and 108.3 ppm, indicates that formation of the network structure has begun. These peaks can be assigned respectively to the —C= and —C$\equiv$ carbons of the acetylenic structure along the direction of crosspolymerization. The absence of a resonance between 220 and 200 ppm suggests that the butatriene structure is not present to a significant degree.[26,27] These results agree with X-ray diffraction work[11,12] and with data of Babbitt and Patel,[24] who found that the acetylenic structure predominates in the backbone of certain soluble poly(diacetylenes). Theoretical treatment of the electronic structure of poly(diacetylene) backbones with restricted Hartree–Fock calculations also indicates that the acetylenic form is more stable.[10] Existence of the butatriene structure in similar materials has been reported in only a few instances.[13,14]

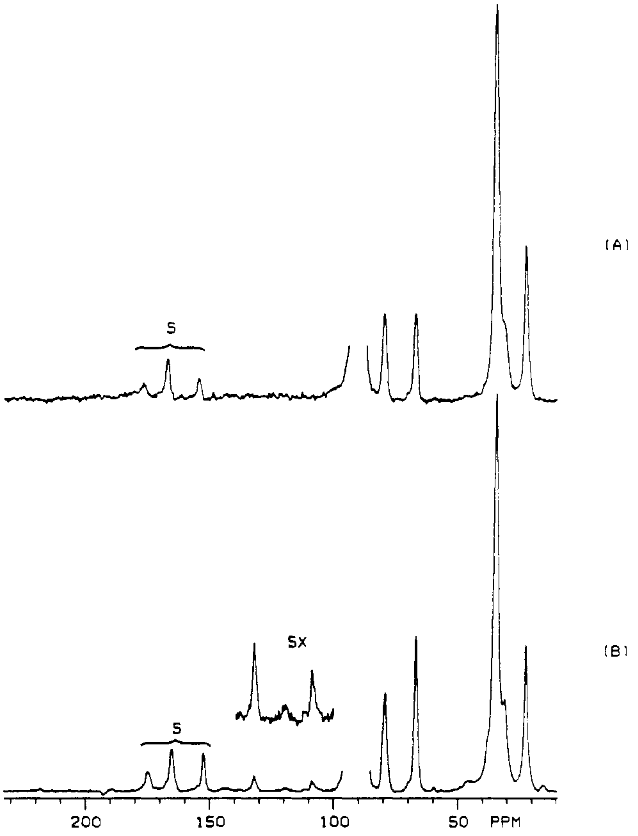

Figure 2. CP/MAS spectra showing the crosspolymerization of the macromonomer poly(1,11-dodecadiyne). (A) Unirradiated material, still in the macromonomer form. Spectrum recorded under normal cross-polarization conditions, with a 1-ms contact time and a delay between acquisitions of 2 s. 1300 transient were averaged. (B) Crosspolymerized macromonomer, irradiated in a cobalt-60 source (23 Mrd). Spectrum recorded with the "flip back" of proton magnetization following acquisition (ref 28). The contact time was 2.5 ms, with a delay between sequences of 8 s. 7500 transients were accumulated. "S" designates spinning sidebands. The truncated resonance at 89 ppm is due to the poly(oxymethylene) rotor.

The intensities of the macromonomer peaks at 79 and 67 ppm compared to those of the crosspolymerized material at 132 and 108 ppm suggest that relatively little network formation has taken place with a radiation dosage of 23 Mrd. This conclusion is inconsistent with two features of the diffraction results.[9] First, diffractometer traces indicate that a substantial fraction (roughly 50%) of the macromonomer exists in crystallites. Second, a relatively small residual of 0.13 for the structure of the crosspolymerized material suggests that essentially all chains in the crystalline regions of the macromonomer crosspolymerize upon irradiation. Therefore, the diffraction work points toward a large contribution of crosspolymerized material in the irradiated polymer. Our feeling is that the diffraction results are accurate and that the NMR intensities are strongly biased against the crosspolymerized material because of unfavorable relaxation times. The low conversion detected by NMR occurs despite our efforts to enhance signals from the rigid crosspolymerized material by modifying experimental parameters. The spectrum in Figure 2B was accumulated with an 8-s delay between successive pulse sequences, instead of the 2 s used in (A). Contributions from large rigid domains with long proton T_1's are enhanced by this change. A second modification was the lengthening of the cross-polarization contact time from 1 to 2.5 ms. Longer contact times should increase signals from the nonprotonated enyne carbons. Finally, we altered the cross-polarization pulse sequence to include "flip back" of the proton magnetization following acquisition.[28] This procedure enhances signals from carbons which are near protons with long T_1's and long $T_{1\rho}$'s (over what signals would be for these same carbons in a normal cross-polarization experiment). Since we have not measured the relaxation times for the crosspolymerized material, we are not certain of the effectiveness of each of the above modifications. (For example, if the proton $T_{1\rho}$'s are small, there will be no proton magnetization to flip back following acquisition.) However, the resonances at 132 and 108 ppm are considerably more intense in Figure 2B than they are in spectra recorded with conditions similar to those used to measure (A). We are presently working to obtain detailed knowledge of both proton and carbon relaxation times for this system. With such information quantitative estimates of the extent of crosspolymerization should be substantially more accurate than those which are now possible. Through this approach better agreement with the diffraction results is anticipated.

As mentioned earlier, the crosspolymerization of poly(1,11-dodecadiyne) has an added complication in that the macromonomer exists in both crystalline and amorphous phases. In the crystalline phase the chains are expected to be immobile and to have long ^{13}C T_1's relative to those in the amorphous phase. Proper selection of the NMR experiment can exploit these differences and can separate resonances from the crystalline and amorphous regions. Results for poly(1,11-dodecadiyne) partially crosspolymerized by mechanical shear are shown in Figure 3. The cross-polarization spectrum in (A) displays contributions from both crystalline and amorphous regions. The crystalline phase is slightly enhanced because of the static dipolar interactions required for polarization transfer. The spectrum in (B) was obtained with a single pulse excitation of the ^{13}C spins with a repetition time of 1 s. Only these carbons in mobile regions of the sample (those with T_1's less than 1 s) contribute to this spectrum; other carbon resonances are saturated. On comparison of (A) and (B), it is clear that the peaks at 120, 108, and 34 ppm are in rigid regions of the sample. In particular, the low-field methylene resonance at 34 ppm can be assigned to the interior methylene carbons in crystalline domains. The assignment of the 120 and 108 ppm resonances as indicative of crosspolymerization suggests that the network material exists in relatively rigid regions of the sample. These regions could be either crystallites or amorphous domains where chain mobility is sharply reduced by crosspolymerization. However, we feel it is more likely that the reaction is concentrated in crystalline regions, where the chains have more perfect registry. This interpretation is supported by electron diffraction results.[9]

As discussed above, the resonances at 120 and 108 ppm are assigned to the conjugated —C═ and —C≡ structures along the direction of crosspolymerization. The chemical shifts of these carbons for the sample of Figure 2 are 132 and 108 ppm. However, this shift difference is not apparently a result of systematic differences between crosspolymerization initiated by γ-irradiation and mechanical shear. The low-field resonance for both means of preparation was found to vary between 136 and 118 ppm among samples synthesized with the same procedure. The high-field resonance varies between 119 and 106 ppm but is always separated from the low-field peaks by at least 12 ppm. The fluctuation in chemical shift positions may be due to differing extents of conjugation along the crosspolymerization direction, but we have no direct evidence for this. The NMR evidence presented here supports only the appearance of a crosspolymerized structure which is predominantly acetylenic in character and which is represented by two resonances between 136 and 106 ppm.

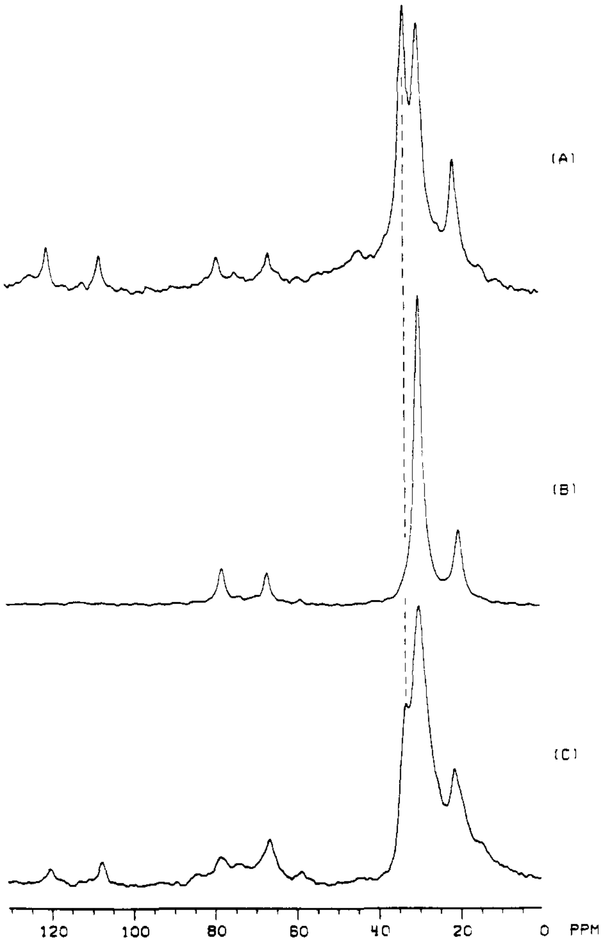

Figure 3. MAS spectra of the macromonomer crosspolymerized by mechanical shear. (A) Cross-polarization spectrum, with a 1-ms contact time and a 1-s delay between acquisitions. 5300 transients were accumulated. (B) Single-pulse excitation spectrum, with a 1-s delay between acquisitions. 1000 transients were averaged. (C) Single-pulse excitation spectrum with a 50-s delay between acquisitions. 1084 transients were accumulated.

There are two final comments concerning the separation of crystalline and amorphous resonances in these materials. First, the spectrum in Figure 3C shows the effect of increasing the delay time between consecutive acquisitions in the single-pulse excitation experiment. In (B) the delay is 1 s, whereas in (C) it is 50 s. A longer delay gives the carbon spins in rigid regions of the sample time to recover through normal spin–lattice relaxation processes. The resonances characteristic of the crosspolymerized backbone and of the crystalline methylene carbons are seen to recover toward the intensity level observed in the cross-polarization spectrum in (A). The second point is that it is possible to isolate crystalline and amorphous contributions to each resonance of the macromonomer, poly(1,11-dode-

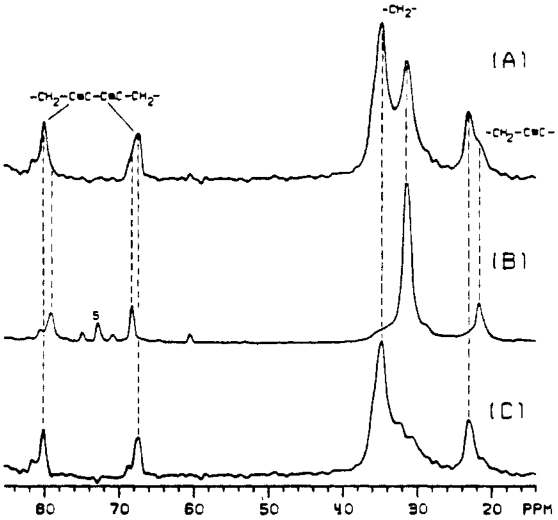

Figure 4. Identification of the crystalline and amorphous resonances in spectra of unirradiated poly(1,1-dodecadiyne). (A) CP/MAS spectrum, with contributions from both crystalline and amorphous regions. (B) Single-pulse excitation spectrum with a sequence repetition time of 2 s. High-power decoupling and magic-angle spinning were used. This spectrum represents the mobile amorphous fraction. "S" identifies the resonance of the glue used to secure the rotor cap. (C) Difference spectrum (A) − (B), emphasizing the spectrum of the crystalline component.

cadiyne). Results are shown in Figure 4. Spectrum A was obtained with cross polarization and has both crystalline and amorphous components. Spectrum B was obtained through single-pulse excitation with a delay of 1 s and therefore represents predominantly amorphous contributions. Spectrum C is a difference spectrum, intended to emphasize the spectroscopic contribution of the crystalline material. In our experience with solid polymers, such resolution between crystalline and amorphous components for each resonance is unusual. With a detailed knowledge of the relevant relaxation times, the resonances can be integrated to yield estimates of the relative crystalline and amorphous contributions to the sample.

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Registry No. Poly(1,11-dodecadiyne) (homopolymer), 77860-27-6.

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