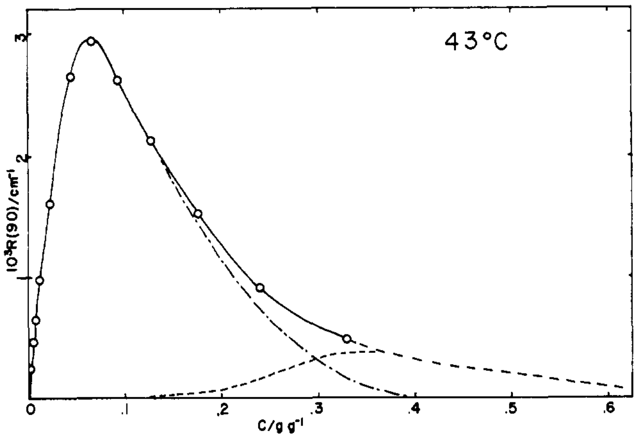

Figure 15. Plot of R_{vv} ($\theta = 90°$) as a function of concentration at 43 °C. Hollow circles denote experimentally measured excess Rayleigh ratio. Dash–dot curve denotes intensity contribution of the slow mode. Dash curve denotes intensity contribution of the fast gellike mode.

while the slower mode, which is related to the translational motion of the polymer coil, slows down and eventually disappears when the solution becomes so concentrated as to essentially form a gel (without permanent cross-links). The magnitude of the intensities contributing to the two modes varies as a function of concentration. Figure 15 shows plots of the excess Rayleigh ratio as a function of concentration. The absolute scattered intensity has been decomposed into two components at $C > 0.1$ g/g using results from the histogram analysis. The behavior of polystyrene in methyl acetate is similar to that of polystyrene in *trans*-Decalin near the upper Θ region.

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Registry No. Polystyrene, 9003-53-6.

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Structure Determination of the Macromonomer Poly(1,11-dodecadiyne) and Its Cross-Polymerized Product

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ABSTRACT: Electron diffraction patterns were obtained from the macromonomer and cross-polymerized crystals of poly(1,11-dodecadiyne). The macromonomer was cast in thin (<200 Å) films from chloroform solution. Cross-polymerization resulted from subsequent exposure of these samples to ^{60}Co γ radiation. Two orientations of the cross-polymerized crystals were obtained by varying the evaporation rate of solvent in the original macromonomer disposition. Thirty-six reflections for the cross-polymerized sample and eighteen reflections for the macromonomer were obtained. Refinement of the structures was accomplished with these data. The unit cell of both macromonomer and cross-polymerized material was monoclinic, space group $P2_1/n$.

Introduction

The cross-polymerization of the macromonomer poly(1,11-dodecadiyne) using UV, X-ray, or ^{60}Co γ radiation has recently been reported.[1] Upon cross-polymerization the sample changes from colorless to dark blue. The term macromonomer is used to describe the original polymer, which has a chemical repeat unit $(-(CH_2)_8-C{\equiv}C-C{\equiv}C-)_x$. The term cross-polymerization is utilized to distinguish systematic polymerization of the diacetylene units to a crystalline structure composed of sheets (as indicated in Figure 1) from the more familiar random cross-linking that many polymers undergo when exposed to radiation. The

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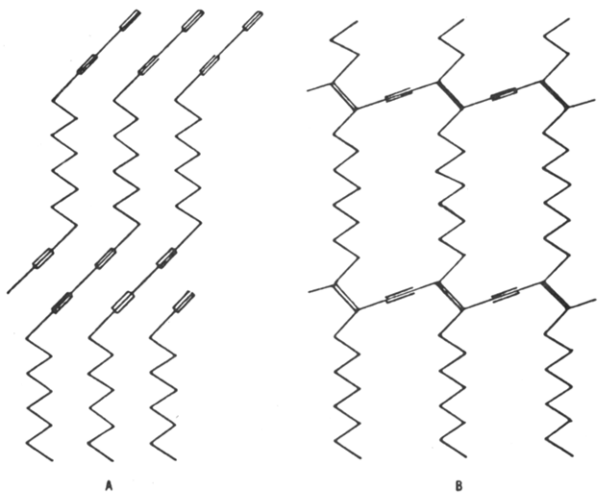

Figure 1. Model of cross-polymerization reaction.

preliminary crystal structure of the cross-polymerized material has been reported earlier[2] and is included here for purposes of comparison. The crystal structures (macromonomer and cross-polymerized) were refined by using electron diffraction data because of the limited information obtained from X-ray fiber patterns.[1] Moreover, electron diffraction analysis provides more accurate information about the location of the hydrogen atoms in comparison to what we get from X-ray analysis.[3]

Experimental Section

The macromonomer was prepared by oxidative coupling of $HC\equiv C-(CH_2)_8-C\equiv CH$ using copper–pyridine catalyst.[1,4,5] After purification[1] the polymer was dissolved in chloroform to make a dilute solution. A drop of this solution at 4 °C on a carbon-coated copper grid was evaporated to obtain single crystals. The diffraction pattern was obtained by a JEOL JEM 100B electron microscope at 100 kV under very low beam intensity using high-speed X-ray films.

The cross-polymerization was effected by γ irradiation (100 Mrd) of the macromonomer crystals. A second orientation of the crystals was obtained by casting a macromonomer film at room temperature.[2] The intensity data were collected with a high-precision photodensitometer. The diffraction maxima were quite sharp, so the peak heights were taken as the relative intensities. The structure was refined with the Lals Six[6] program, originally developed by Arnott and co-workers. Measurement of the thickness of the crystals was accomplished in the following way. The crystals on a carbon-coated copper grid were carbon-shadowed at an angle of 45°. Some part of the substrate remains unexposed to this shadowing due to the height of the crystal, which blocks the carbon particles. The unexposed strip manifests itself as a light strip at the edge of the crystal on an electron micrograph. Since the shadowing angle is 45°, the width of the strip is the thickness of the crystal.

Results and Discussion

The electron diffraction pattern of the macromonomer remains reasonably sharp for only 12 s. It disappears more quickly than that of the cross-polymerized material. Thus it is less stable under the electron beam. However, the diffraction pattern obtained by using high-speed X-ray films and appropriate developer gives patterns suitable for structure analysis. The X-ray fiber pattern indicates a twofold screw axis along *b* (chain axis).[1] The electron diffraction pattern shows that the a^*c^* lattice net contains the systematic absences $h + l =$ odd, which indicates an *n* glide perpendicular to the *b* axis. Therefore the assigned space group is $P2_1/n$. For the cross-polymerized material we found the same space group.[2] In fact, a quick comparison of the macromonomer diffraction pattern (Figure 2a)with the cross-polymerized diffraction pattern (Figure 2b) clearly indicates that the space group does not change with cross-polymerization. However, the cell volumn of the macromonomer is larger than that of the cross-polymerized material. This contraction of volume with cross-polymerization is observed experimentally. A comparison of the unit cell dimensions is given in Table I.

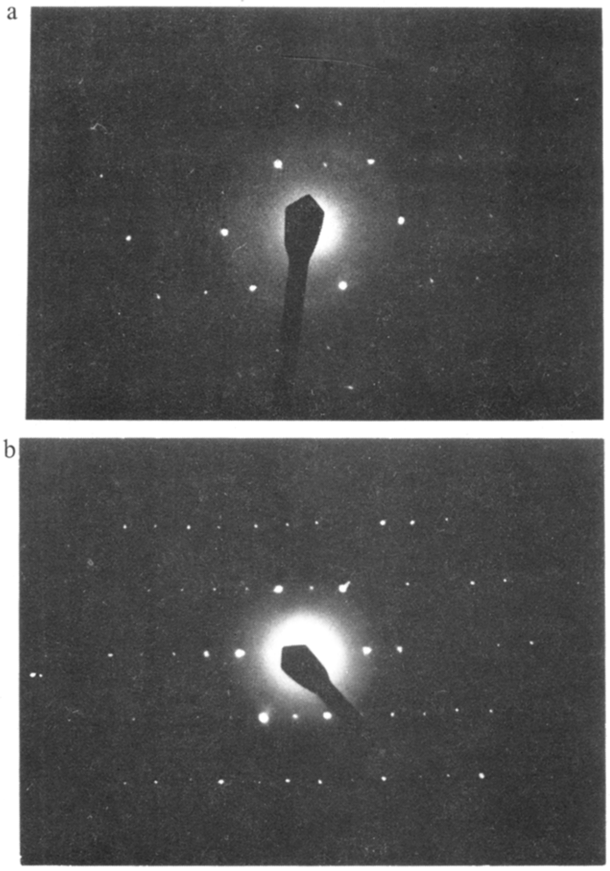

Figure 2. Selected-area diffraction patterns of (a) the macromonomer and (b) the cross-polymerized material.

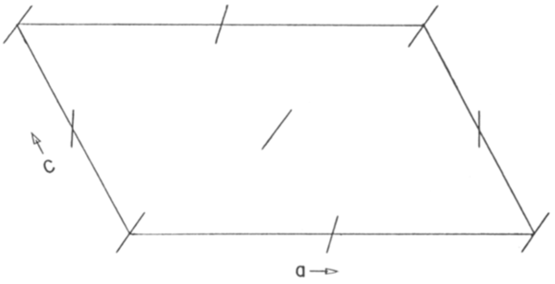

Figure 3. Starting model for the macromonomer structure refinement.

Table I
Comparison of Unit Cell Dimensions

cell parameter	macromonomer	cross-polymerized material
a, Å	13.25	9.17
b, Å	14.15 (chain axis)	12.25, (hydrocarbon chain axis)
c, Å	7.63	9.92, (diacetylene chain axis)
β, deg	118.50	123.50

Structure Refinement. Macromonomer. The starting model for refinement is shown in Figure 3. Much information about its structure is already known from the structure analysis of the cross-polymerized material. We

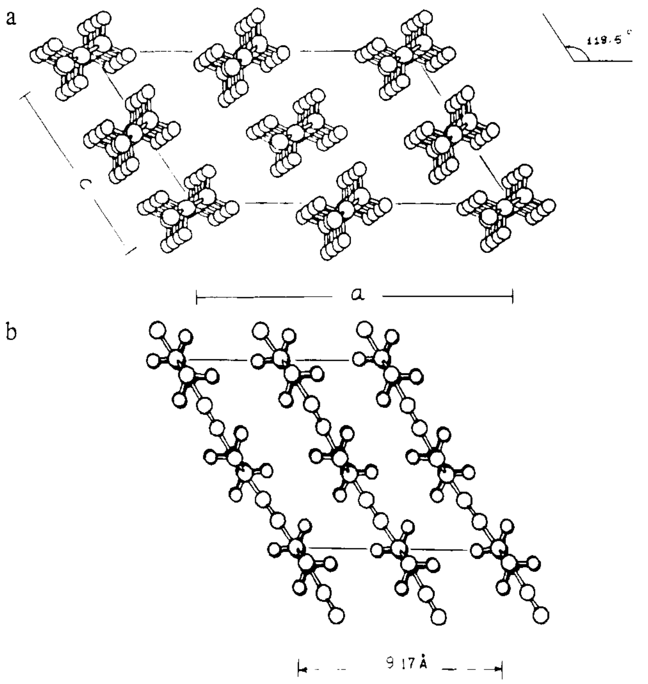

Figure 4. *ac* projections of (a) the macromonomer and (b) the cross-polymerized material.

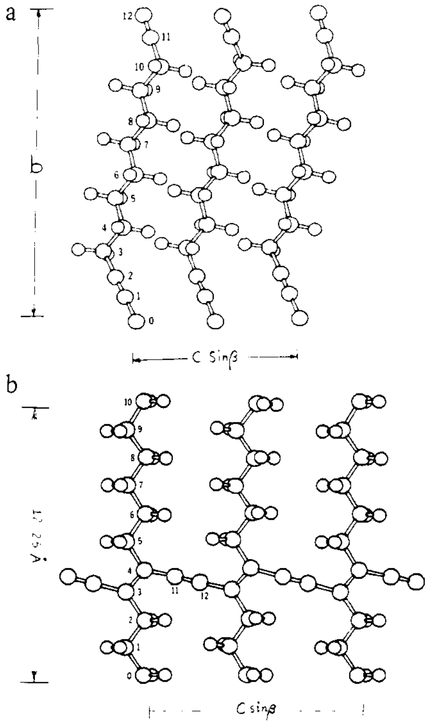

Figure 5. *bc* projections of (a) the macromonomer and (b) the cross-polymerized material.

Table II
Comparison of Calculated and Observed Intensities for the Macromonomer

hkl	*F*(calcd)	*F*(obsd)	*hkl*	*F*(calcd)	*F*(obsd)
200	3378	3769	202	1004	884
400	587	704	$30\bar{1}$	1311	1005
002	6397	6561	$\bar{1}03$	2013	2280
004	499	1163	$\bar{3}05$	1328	1377
$10\bar{1}$	208	495	103	1025	1062
$20\bar{2}$	4881	4198	$\bar{1}05$	821	698
$30\bar{3}$	472	866	$\bar{2}06$	591	605
$40\bar{4}$	449	390	$\bar{2}04$	2709	2565
101	1972	2084	301	915	1001

know that the chains in the unit cell will presumably be alternately up and down. A down chain is formed by rotating an up chain by 180° about the *a* axis. In this case also there are four chains per unit cell. The major difference is the absence of the diacetylene backbone in the macromonomer. For the cross-polymerized material the refined structure shows that the diacetylene rod lies in the plane of the planar zigzag. This configuration is also energetically favorable. Therefore having the diacetylene backbone essentially reduces the number of degrees of rotational freedom of the planar zigzag. In the case of the macromonomer no such restriction is involved. Thus the major structural aspect that is not known in this case is the orientation of the planar zigzag with respect to the *a* (or *c*) axis. Hence the whole refinement essentially involves variation of the angle between the zigzag plane and the *a* axis until a minimum residual is reached. Dynamical or rediffraction effects were neglected because the crystal thickness was less than 200 Å and there was a clear absence of $h + l$ = odd reflections.

Both carbon and hydrogen atoms were used for structure factor calculation. Initially we rotated the chains about the coordinate axes to orient them properly along the chain axis *b*. Then the angle (θ) the zigzag plane makes with the *a* axis was varied. The residual was defined as

$$R = \left\{ \frac{\sum_{m=1}^{N} w_m \Delta F_m^{\,2}}{\sum_{m=1}^{N} w_m F_m^{\,2}(\mathrm{obsd})} \right\}^{1/2}$$

$$\Delta F_m = |F_m(\mathrm{obsd}) - F_m(\mathrm{calcd})|$$

We kept $w_m = 1$ for all reflections.

A distinct minimum (0.13) of the residual was found for $\theta = 34°$, which effectively means that the zigzag plane is almost coincident with the *ac* diagonal. The *ac* and *bc* projections of the refined structure are given in Figure 4aand Figure 5a, respectively. A comparison of calculated and observed intensities is given in Table II.

Structure Refinement. Cross-Polymerized Material. Diffraction patterns for two different orientations were obtained for the cross-polymerized material. One corresponds to the a^*c^* lattice net and the other, the b^* $(h0\bar{h})$ net. The b^* $(h0\bar{h})$ net and the X-ray fiber pattern[1] showed a *b* axis repeat of 12.25 Å, which fits very well with the hydrocarbon chain repeat. The a^*c^* lattice net indicates an *ac* axis repeat distance of 9.92 Å, a doubling of the usual diacetylene chain repeat. As previously stated, the systematic absences are identical with those of the macromonomer diffraction pattern. The space group is $P2_1/n$, *b* axis unique.

The two chain axes (hydrocarbon and diacetylene) (along *b* and *c*, respectively) are perpendicular to each other. The refinement procedure and results have been described in detail in our earlier work.[2] The final residual was 0.13. The *ac* and *bc* projections of the refined structure are shown in Figure 4b and Figure 5b, respectively. A comparison of calculated and observed intensities is given in Table III. The doubling of the diacetylene repeat in the unit cell arises because the senses of the chains coupled by the diacetylene rod are not the same but alternate up and down. The bond angles and dihedral angles of the refined structures (macromonomer and cross-polymerized) are given in Tables IV and V.

Comparison of Structures. The unit cell parameters are given in Table I for both macromonomer and the cross-polymerized material. The *ac* projections are shown

Table III
Comparison of Calculated and Observed Intensities for the Cross-Polymerized Material

hkl	*F*(calcd)	*F*(obsd)	*hkl*	*F*(calcd)	*F*(obsd)
200	8099	7386	$14\bar{1}$	493	366
400	2369	2161	$16\bar{1}$	440	898
020	1532	1587	$31\bar{3}$	271	234
040	1202	1487	$11\bar{1}$	249	122
060	865	1143	$21\bar{2}$	814	244
080	682	887	$\bar{1}21$	293	548
002	5109	5188	$22\bar{2}$	539	601
004	817	1062	$\bar{2}22$	1063	1221
$10\bar{1}$	3031	3357	$32\bar{3}$	976	856
101	2575	2734	$42\bar{4}$	257	671
$\bar{1}03$	3458	3479	$40\bar{2}$	2431	2734
$\bar{1}05$	526	671	$40\bar{4}$	1091	1245
103	2357	2614	$30\bar{3}$	2864	3113
301	1052	1318	$50\bar{5}$	1554	1659
202	2345	2136	$50\bar{3}$	1293	1525
$20\bar{2}$	5329	5140	$\bar{3}05$	943	1318
$\bar{2}04$	949	1294	$30\bar{1}$	1430	1807
$12\bar{1}$	572	763	$60\bar{4}$	711	793

Table IV
Bond Angles and Dihedral Angles for the Macromonomer

atoms	bond angle, deg	dihedral angle, deg
$C^0C^1C^2$	180.00	
$C^1C^2C^3$	180.00	180.00
$C^2C^3C^4$	100.00	180.00
$C^3C^4C^5$	109.50	180.00
$C^4C^5C^6$	109.50	180.00
$C^5C^6C^7$	112.00	180.00
$C^6C^7C^8$	111.45	180.00
$C^7C^8C^9$	109.60	180.00
$C^9C^{10}C^{11}$	104.60	180.00
$C^{10}C^{11}C^{12}$	180.00	180.00
$C^2C^3H^{3A}$	107.5	60.00
$C^2C^3H^{3B}$	107.5	300.00
$C^3C^4H^{4A}$	107.5	60.00
$C^3C^4H^{4B}$	107.5	300.00
$C^4C^5H^{5A}$	107.5	60.00
$C^4C^5H^{5B}$	107.5	300.00
$C^5C^6H^{6A}$	107.5	60.00
$C^5C^6H^{6B}$	107.5	300.00
$C^6C^7H^{7A}$	107.5	60.00
$C^6C^7H^{7B}$	107.5	300.00
$C^7C^8H^{8A}$	107.5	60.00
$C^7C^8H^{8B}$	107.5	300.00
$C^8C^9H^{9A}$	107.5	60.00
$C^8C^9H^{9B}$	107.5	300.00
$C^9C^{10}H^{10A}$	107.5	60.00
$C^9C^{10}H^{10B}$	107.5	300.00

in Figure 4. Here we suggest a qualitative picture of the molecular mechanism of cross-polymerization. The theoretical repeat distance of the diacetylene backbone, we know, is approximately 4.9 Å. Now Figure 4 shows that the successive up and down chains along the *c* axis have a separation of about 4 Å, whereas in every other direction the separation is greater than or equal to approximately 7 Å. On the basis of the principle of least motion for a solid-state reaction, we can assert that the *c* axis will be the polymerization direction. Thus the molecules need only a slight rotation and translocation (direction invariant)[7] along the *c* axis to polymerize. Consequently, there is no change of the sense of the corresponding molecules. Therefore the space group remains unaltered. However, the parallel sheets, thus formed, slide along a van der Waals potential well to attain optimum close packing. This results in a contraction of unit cell volume.

Table V
Bond Angles and Dihedral Angles for the Cross-Polymerized Material

atoms	bond angle, deg	dihedral angle, deg
$C^0C^1C^2$	110.5	
$C^1C^2C^3$	109.60	180.00
$C^2C^3C^4$	105.00	180.00
$C^3C^4C^5$	106.50	180.00
$C^4C^5C^6$	112.50	180.00
$C^5C^6C^7$	112.50	180.00
$C^6C^7C^8$	112.50	180.00
$C^7C^8C^9$	108.50	180.00
$C^8C^9C^{10}$	112.00	180.00
$C^3C^4C^{11}$	124.03	0.00
$C^4C^{11}C^{12}$	180.00	0.00
$C^4C^5H^{5A}$	107.5	60.00
$C^4C^5H^{5B}$	107.5	300.00
$C^5C^6H^{6A}$	107.5	60.00
$C^5C^6H^{6B}$	107.5	300.00
$C^6C^7H^{7A}$	107.5	60.00
$C^6C^7H^{7B}$	107.5	300.00
$C^7C^8H^{8A}$	107.5	60.00
$C^7C^8H^{8B}$	107.5	300.00
$C^8C^9H^{9A}$	107.5	60.00
$C^8C^9H^{9B}$	107.5	300.00
$C^9C^{10}H^{10A}$	107.5	60.00
$C^9C^{10}H^{10B}$	107.5	300.00
$C^3C^2H^{2A}$	107.5	60.00
$C^3C^2H^{2B}$	107.5	300.00
$C^2C^1H^{1A}$	107.5	60.00
$C^2C^1H^{1B}$	107.5	300.00
$C^1C^0H^{0A}$	107.5	60.00
$C^1C^0H^{0B}$	107.5	300.00

We suspect that for a range of conversion from the macromonomer to the cross-polymerized phase there exists a solid solution since we never observed two phases present simultaneously. Magic-angle ^{13}C NMR studies (in the solid state), which will be reported later, support these conclusions.

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Registry No. poly(1,11-dodecadiyne), 77860-27-6; $(-(CH_2)_8-C{\equiv}C-C{\equiv}C)_x$, 83929-17-3.

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