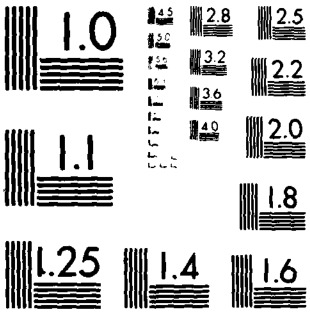
AD-A111 661   CASE WESTERN RESERVE UNIV CLEVELAND OH DEPT OF MACROM--ETC   F/G 11/9
STRUCTURE DETERMINATION OF THE MACROMONOMER POLY (1,11 - DODECA--ETC(U)
JUN 82   J B LANDO, M THAKUR   N00014-77-C-0213
UNCLASSIFIED   TR-5   NL

1 of 1
AD A111661

END
DATE
FILMED
10-82
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

10

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-77C-0213

TECHNICAL REPORT NO. 5

STRUCTURE DETERMINATION OF THE MACROMONOMER POLY (1, 11 - DODECADIYNE) AND ITS CROSSPOLYMERIZED PRODUCT

by

Jerome B. Lando and M. Thakur
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

Approved for Public Release: Distribution Unlimited

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER Technical Report No. 5	2. GOVT ACCESSION NO. AD-A111 661	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Structure Determination of the Macromonomer Poly (1, 11 - Dodecadiyne) and its Crosspoly - merized product		5. TYPE OF REPORT & PERIOD COVERED Technical Report March 1, 1981 - present
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Jerome B. Lando M. Thakur		8. CONTRACT OR GRANT NUMBER(s) N000 14-77C-0213
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE June 27, 1982
		13. NUMBER OF PAGES 14 plus figures
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) ONR Branch Office 536 South Clark Street Chicago, Illinois 60605		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION ST ENT (of abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY TES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Structure, Crosspolymerization, Poly(1,11-Dodecadiyne)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Electron diffraction patterns were obtained from the macromonomer and crosspolymerized crystals of Poly(1,11 Dodecadiyne). The macromonomer was cast in thin (< 200 A) films from chloroform solution. Crosspolymerization resulted from subsequent exposure of these samples to Co^{60} - γ radiation. Two orientations of the crosspolymerized crystals were obtained by varying the evaporation rate of solvent in the original macromonomer diposition. Thirty-six reflections for the crosspolymerized 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 crosspolymerized material was monoclinic, space group $P2_1/ln$.

1

INTRODUCTION

The crosspolymerization of the macromonomer poly(1,11 dodecadiyne), using uv, x-ray or Co^{60} γ- radiation has recently been reported (1). The term macromonomer is used to describe the original polymer which has a chemical repeat unit $\left((CH_2)_8 - C \equiv C - C \equiv C \right)_x$. The term crosspolymerization 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 crosslinking that many polymers undergo when exposed to radiation. The preliminary crystal structure of the crosspolymerized material has been reported earlier (2) and is included here for purposes of comparison. The crystal structures (macromonomer and crosspolymerized) were refined 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

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 JEOL JEM 100B electron microscope at 100 KV under very low beam intensity using high-speed x-ray films.

The crosspolymerization was affected by γ - irradiation (100 Mrad) 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 using a high precision photodensitometer. The diffraction maxima were quite sharp, so the peak-heights were taken as the relative intensities. The structure was refined using 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 seconds. It disappears more quickly than that of the crosspolymerized 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 two fold screw axis along b (chain axis) (1). The electron diffraction pattern shows that the a*c* lattice net contains the systematic absences $h + 1 = \text{odd}$, which indicates an n-glide perpendicular to the b-axis. Therefore the assigned space group is $P2_1/n$. For the crosspolymerized material we found the same space group (2). In fact a quick comparison of the macromonomer diffraction pattern (Figure 2a) with the crosspolymerized diffraction (Figure 2b) clearly indicates that the space group does not change with crosspolymerization. However the cell volume of the macromonomer is larger than that of the crosspolymerized material. This contraction of volume with crosspolymerization is observed experimentally. A comparison of the unit cell dimensions is given in Table 1.

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 crosspolymerized material. We 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 crosspolymerized 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 co-ordinate 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,

$$R = \left\{ \frac{\sum_{m=1}^{N} w_m \, \Delta F_m^2}{\sum_{m=1}^{N} w_m F_m^2(\text{obs})} \right\}^{1/2} , \quad \Delta F_m = \left| F_m(\text{obs}) - F_m(\text{calc}) \right|$$

we kept $w_m = 1$ for all reflections.

A distinct minimum (0.13) of the residual was found for θ = 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 4a and Figure 5a respectively. A comparison of calculated and observed intensities is given in Table 2.

Structure Refinement (Crosspolymerized Material)

Diffraction patterns for two different orientations were obtained for the crosspolymerized material. One corresponds to the a*c* lattice net and the other, b* $(ho\bar{h})$ net. The b* $(ho\bar{h})$ 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 ac axis repeat distance of 9.92Å, 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 Fibure 4b and Figure 5b respectively. A comparison of calculated and observed intensities is given in Table 3. 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 alternately up and down. The bond angles and dyhedral angles of the refined structures (Macromonomer and Crosspolymerized) are given in Table 4 and 5.

Comparison of Structures

The unit cell parameters are given in Table 1 for both macromonomers and the crosspolymerized material. The ac projections are shown in Figure 4a & 4b. Here we suggest a qualitative picture of the molecular mechanism of crosspolymerization. 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 solid state reaction, we can assert that the c-axis will be the polymerization direction. Thus the molecules need only a slight rotation and translation (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 Waal's potential well to attain optimum close packing. This results in a contraction of unit cell volume.

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

REFERENCES

1. Day, D.R. and Lando, J.B., submitted to J. of Polym. Sci., Polym Letts., 19, 227 (1981)
2. Thakur, M.K. and Lando, J.B., Structure Property Relationship of Polymer Solids, P. Anne Hiltner, editor, Plenum Press Publishers Ltd., in press.
3. Vainstein, B.K., Diffraction of X-rays by Chain Molecules, (1966) 53.
4. Campbell, I. and Eglinton, G., Organic Syntheses 45, 39.
5. Campbell, I. and Galbraith, A., J. Amer. Chem. Soc. 82, 889 (1959)
6. Arnott, S., P.J. Campbell Smith, Acta Cryst. A34, 3 (1978).
7. Baughman, R.H., J. Chem. Phys. 12 1511 (1974).

ACKNOWLEDGEMENT:

The support of this work by the Office of Naval Research under Contract N0014-77C-0213 is gratefully acknowledged.

Table 1

Cell Parameters	Macromonomer	Crosspolymerized
a	13.25 Å	9.17 Å
b	14.15 Å (chain axis)	12.25 Å (Hydrocarbon chain axis)
c	7.63 Å	9.92 Å (Diacetylene chain axis)
β	118.50 A°	123.50 A°

Table 2
(Macromonomer)

h	k	l	F - calc	F - obs
2	0	0	3378	3769
4	0	0	587	704
0	0	2	6397	6561
0	0	4	499	1163
1	0	-1	208	495
2	0	-2	4881	4198
3	0	-3	472	866
4	0	-4	449	390
1	0	1	1972	2084
2	0	2	1004	884
3	0	-1	1311	1005
-1	0	3	2013	2280
-3	0	5	1328	1377
1	0	3	1025	1062
-1	0	5	821	698
-2	0	6	591	605
-2	0	4	2709	2565
3	0	1	915	1001

TABLE 3
(Crosspolymerized)

h	k	1	F - CALC	F - OBS
2	0	0	8099	7386
4	0	0	2369	2161
0	2	0	1532	1587
0	4	0	1202	1487
0	6	0	865	1143
0	8	0	682	887
0	0	2	5109	5188
0	0	4	817	1062
1	0	-1	3031	3357
1	0	1	2575	2734
-1	0	3	3458	3479
-1	0	5	526	671
1	0	3	2357	2614
3	0	1	1052	1318
2	0	2	2345	2136
2	0	-2	5329	5140
-2	0	4	949	1294
1	2	-1	572	763
1	4	-1	493	366
1	6	-1	440	898
3	1	-3	271	234
1	1	-1	249	122
2	1	-2	814	244
-1	2	1	293	548
2	2	-2	539	601
-2	2	2	1063	1221
3	2	-3	976	856
4	2	-4	257	671
4	0	-2	2431	2734
4	0	-4	1091	1245
3	0	-3	2864	3113
5	0	-5	1554	1659
5	0	-3	1293	1525

Table 3 continued

(Crosspolymerized)

h	k	l	F - CALC	F - OBS
-3	0	5	943	1318
3	0	-1	1430	1807
6	0	-4	711	793

Table 4
(Macromonomer)

Atoms Constructing the angle	Bond Angle	Dihedral Angle
$C^0\ C^1\ C^2$	180.00	
$C^1\ C^2\ C^3$	180.00	180.00
$C^2\ C^3\ C^4$	100.00	180.00
$C^3\ C^4\ C^5$	109.50	180.00
$C^4\ C^5\ C^6$	109.50	180.00
$C^5\ C^6\ C^7$	112.00	180.00
$C^6\ C^7\ C^8$	111.45	180.00
$C^7\ C^8\ C^9$	109.60	180.00
$C^8\ C^9\ C^{10}$	109.60	180.00
$C^9\ C^{10}\ C^{11}$	104.60	180.00
$C^{10}C^{11}C^{12}$	180.00	180.00
$C^2\ C^3\ H^{3A}$	107.5	60.00
$C^2\ C^3\ H^{3B}$	107.5	300.00
$C^3\ C^4\ H^{4A}$	107.5	60.00
$C^3\ C^4\ H^{4B}$	107.5	300.00
$C^4\ C^5\ H^{5A}$	107.5	60.00
$C^4\ C^5\ H^{5B}$	107.5	300.00
$C^5\ C^6\ H^{6A}$	107.5	60.00
$C^5\ C^6\ H^{6B}$	107.5	300.00
$C^6\ C^7\ H^{7A}$	107.5	60.00
$C^6\ C^7\ H^{7B}$	107.5	300.00
$C^7\ C^8\ H^{8A}$	107.5	60.00
$C^7\ C^8\ H^{8B}$	107.5	300.00

Table 4 continued (Macromonomer)

Atoms Constructing the angle	Bond Angle	Dihedral Angle
$C^8\ C^9\ H^{9A}$	107.5	60.00
$C^8\ C^9\ H^{9B}$	107.5	300.00
$C^9\ C^{10}H^{10A}$	107.5	60.00
$C^9\ C^{10}H^{10B}$	107.5	300.00

Table 5
(Crosspolymerized)

Atoms Constructing the angle	Bond Angle	Dihedral Angle
C^0 C^1 C^2	110.5	
C^1 C^2 C^3	109.60	180.00
C^2 C^3 C^4	105.00	180.00
C^3 C^4 C^5	106.50	180.00
C^4 C^5 C^6	112.50	180.00
C^5 C^6 C^7	112.50	180.00
C^6 C^7 C^8	112.50	180.00
C^7 C^8 C^9	108.50	180.00
C^8 C^9 C^{10}	112.00	180.00
C^3 C^4 C^{11}	124.03	0.00
C^4 $C^{11}C^{12}$	180.00	0.00
C^4 C^5 H^{5A}	107.5	60.00
C^4 C^5 H^{5B}	107.5	300.00
C^5 C^6 H^{6A}	107.5	60.00
C^5 C^6 H^{6B}	107.5	300.00
C^6 C^7 H^{7A}	107.5	60.00
C^6 C^7 H^{7B}	107.5	300.00
C^7 C^8 H^{8A}	107.5	60.00
C^7 C^8 H^{8B}	107.5	300.00
C^8 C^9 H^{9A}	107.5	60.00
C^8 C^9 H^{9B}	107.5	300.00
C^9 $C^{10}H^{10A}$	107.5	60.00

Table 5 continued (Crosspolymerized)

Atoms Constructing the angle	Bond Angle	Dihedral Angle
$C^9\ C^{10}\ H^{10B}$	107.5	300.00
$C^3\ C^2\ H^{2A}$	107.5	60.00
$C^3\ C^2\ H^{2B}$	107.5	300.00
$C^2\ C^1\ H^{1A}$	107.5	60.00
$C^2\ C^1\ H^{1B}$	107.5	300.00
$C^1\ C^0\ H^{0A}$	107.5	60.00
$C^1\ C^0\ H^{0B}$	107.5	300.00

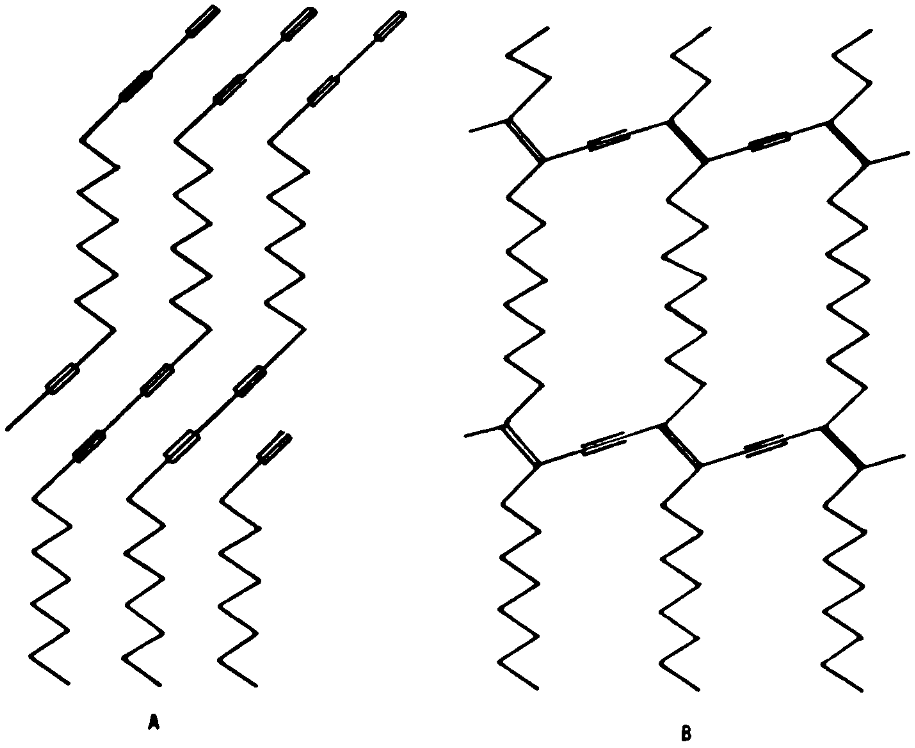


Figure (1)

Model of Crosspolymerization

Electron Diffraction Pattern (Macromonomer)

Figure 2a

Electron Diffraction Pattern (Crosspolymerized)

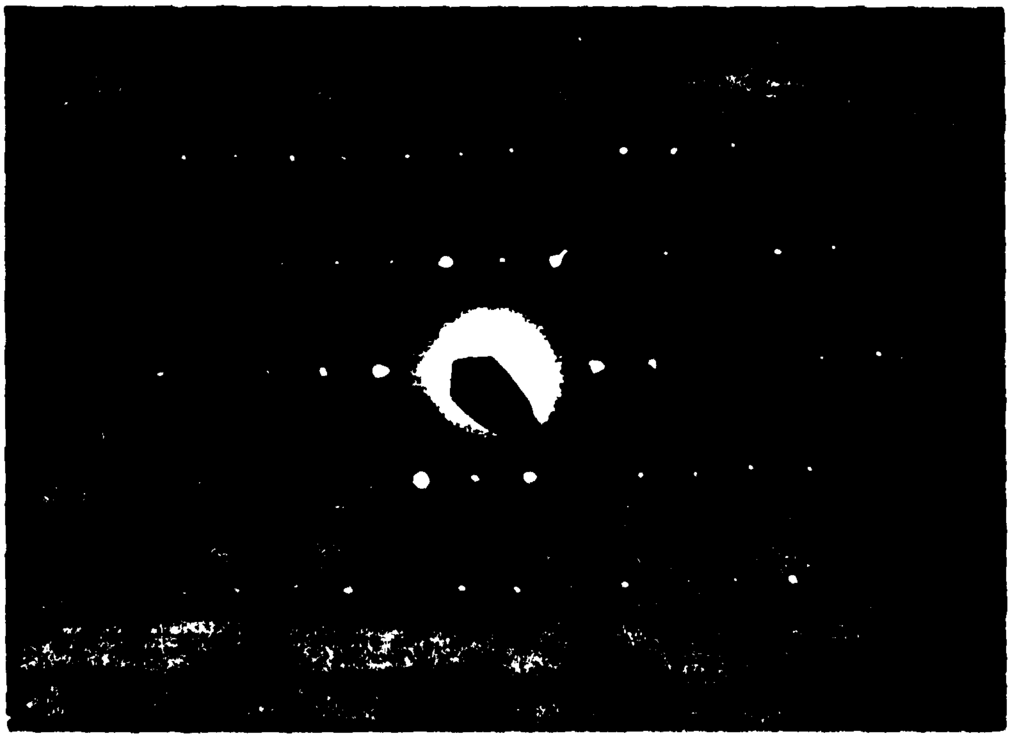


Figure 2b

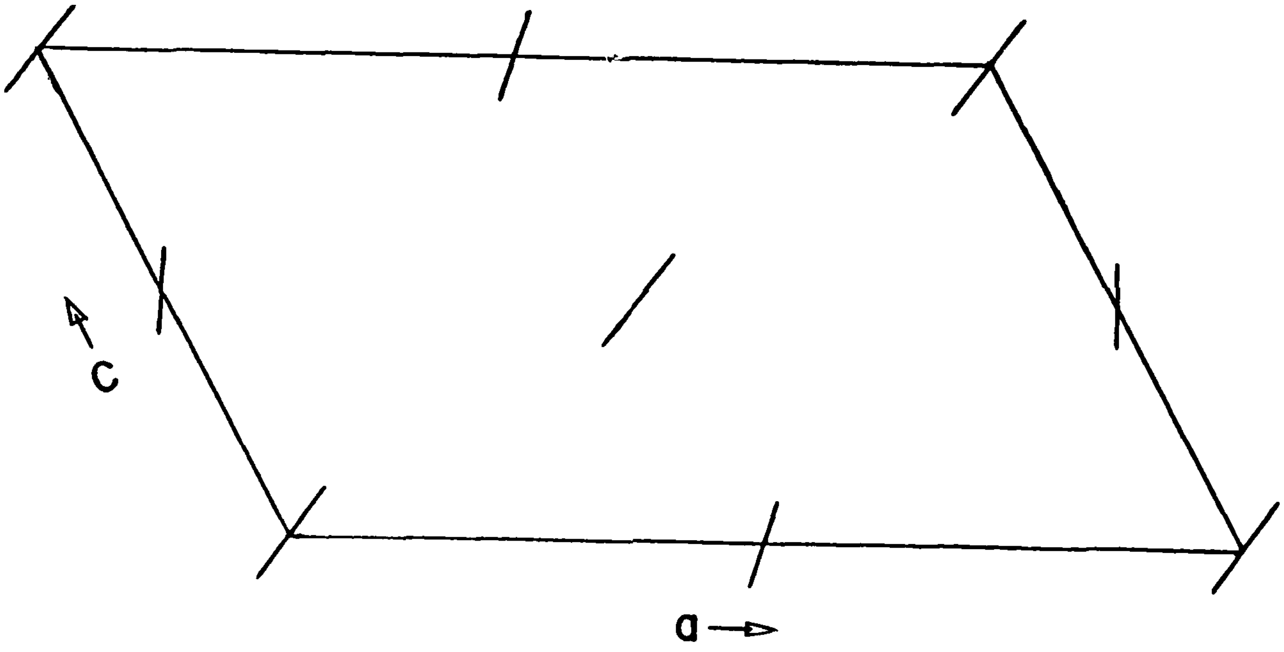


Figure 3. Model For Refinement of the Macromonomer Structure

ac Projection (Macromonomer)

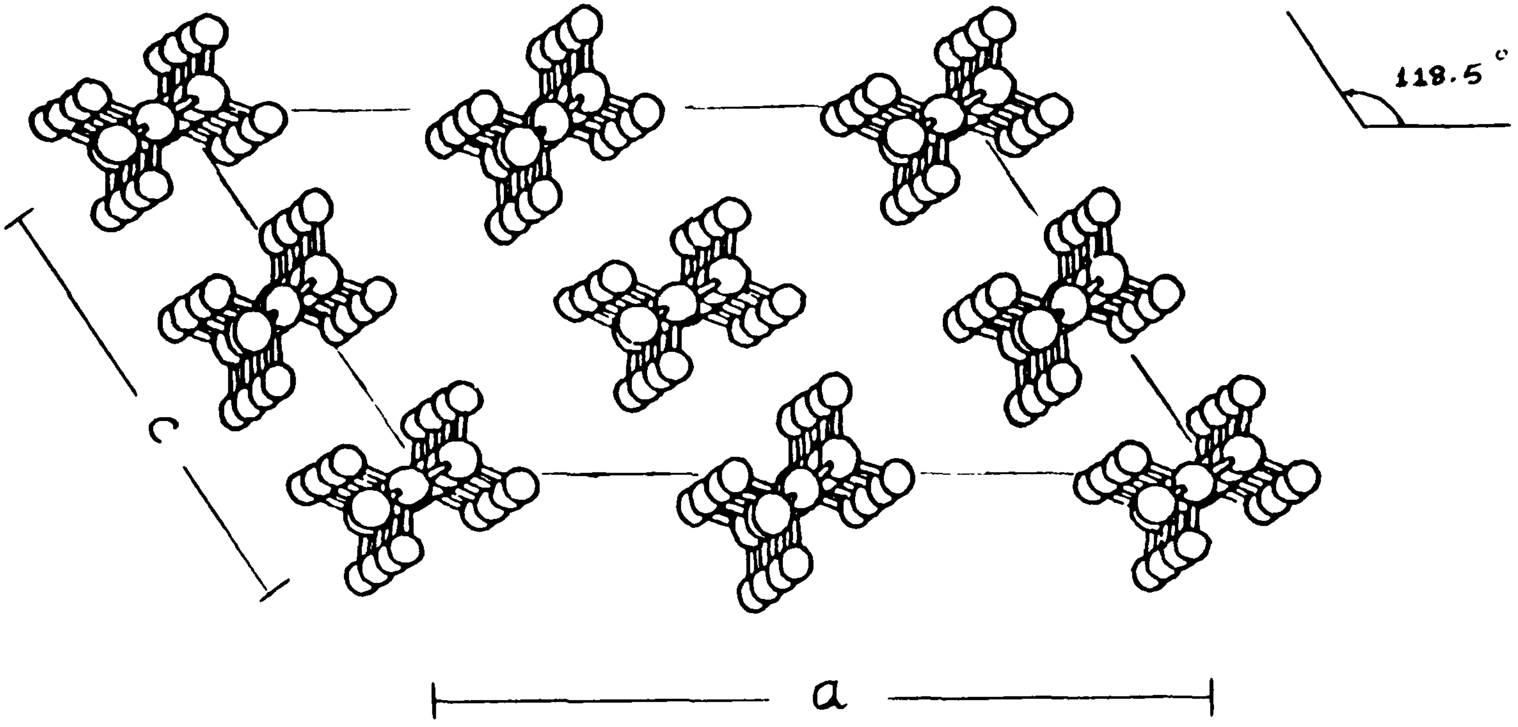


Figure 4a

ac Projection (Crosspolymerized)

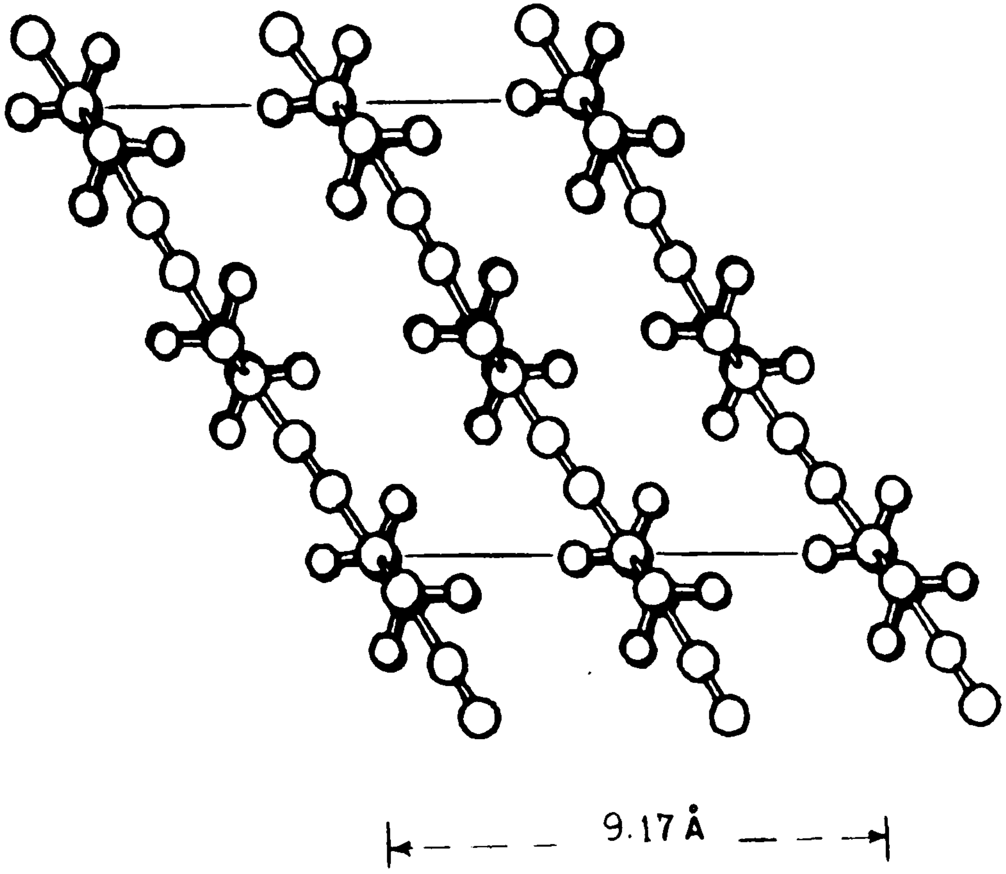


Figure 4b

bc Projection (Macromonomer)

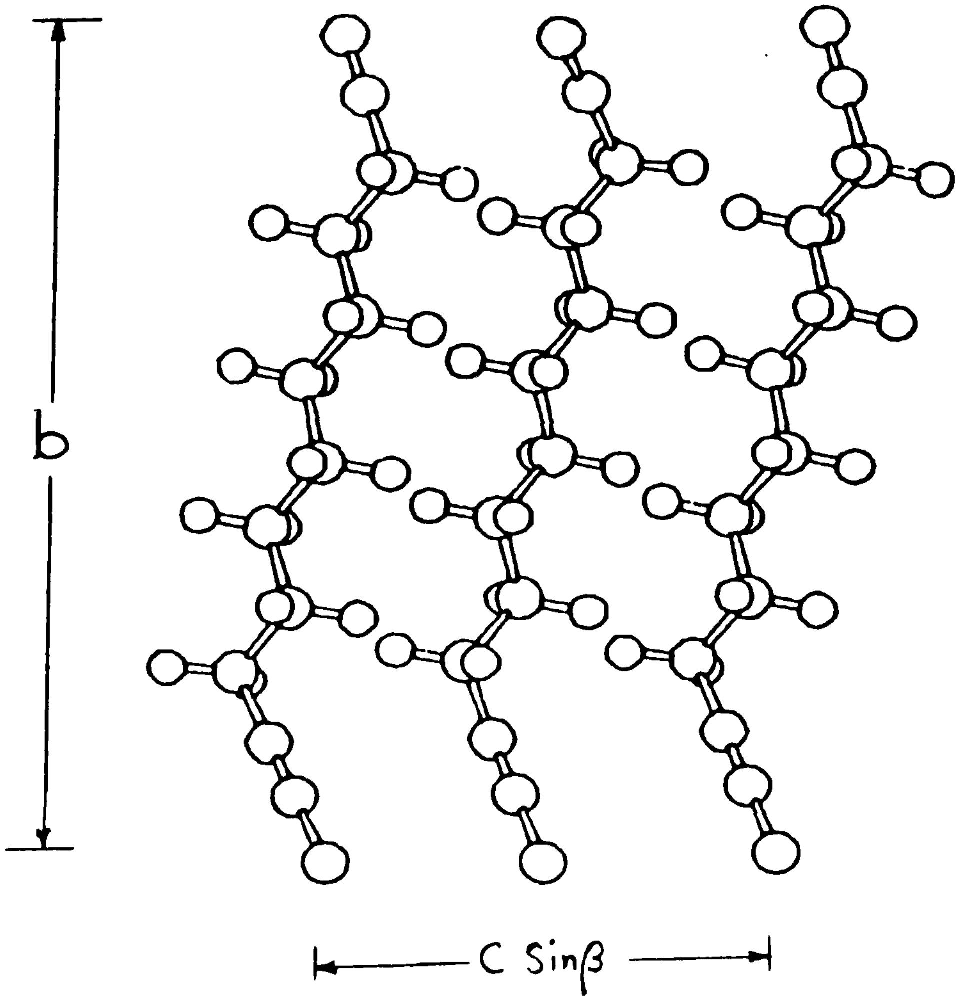


Figure 5a

bc Projection (Crosspolymerized)

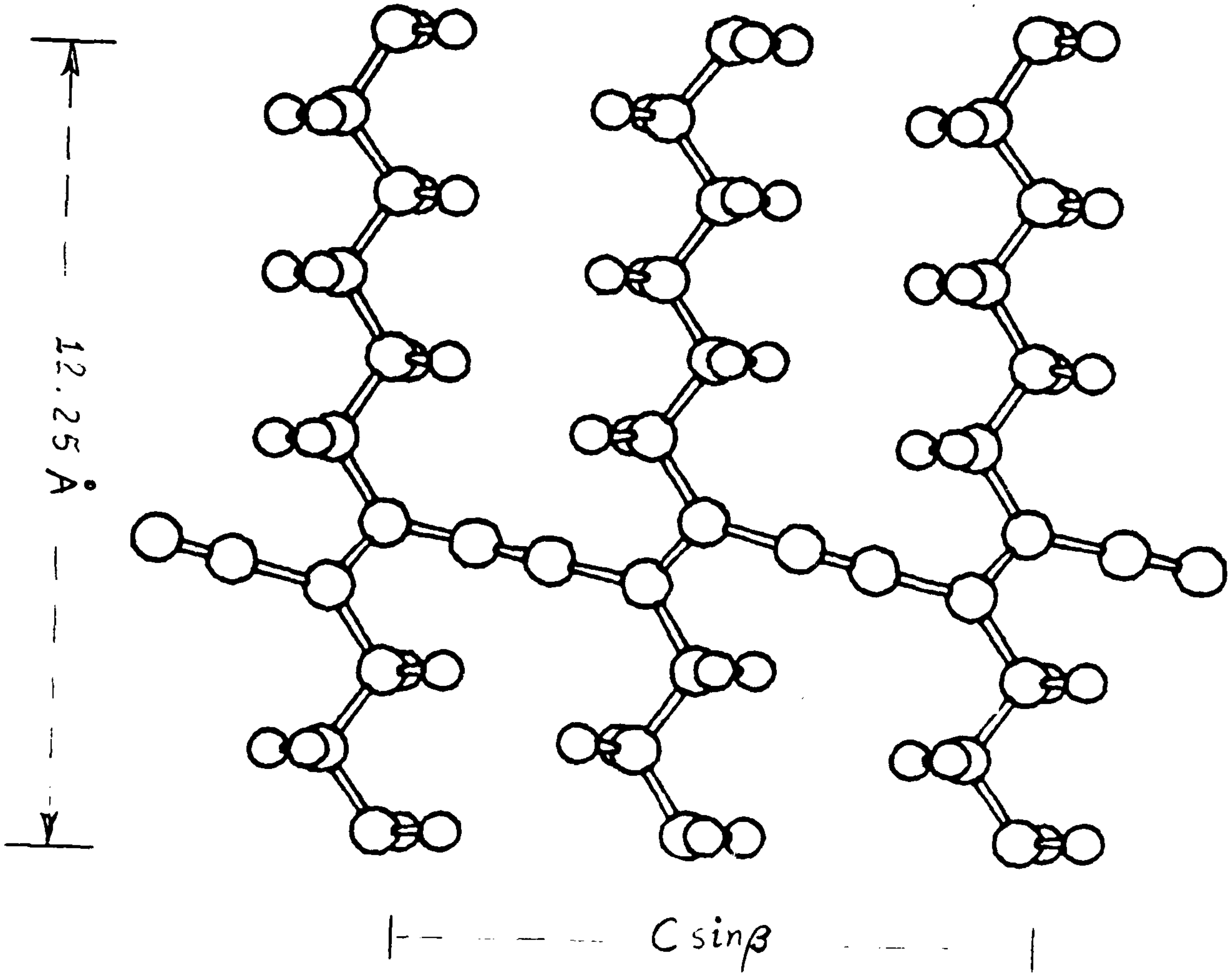


Figure 5b

DATE
FILMED

3-8