

4

DTIC FILE COPY

AD-A197 607

OFFICE OF NAVAL RESEARCH  
CONTRACT NO. N00014-86-K-0772  
TECHNICAL REPORT NO. 8

X-Ray Diffraction by Thermotropic Main-chain Polymers  
Having Side Groups: Part C. Semiflexible Polyesters

by

Hui H. Chin, Leonid V. Azaroff, Agya R. Saini, and  
Robert W. Lenz\*

Liquid Crystalline Polymer Research Center  
University of Connecticut  
Storrs, CT 06268

\*Polymer Science Department  
University of Massachusetts  
Amherst, MA 01003

Prepared for Publication  
in  
Journal of Polymer Science

July 12, 1988

DTIC  
SELECTED  
JUL 26 1988  
D  
CE

REPRODUCTION IN WHOLE OR IN PART IS PERMITTED FOR ANY  
PURPOSE OF THE UNITED STATES GOVERNMENT.

THIS DOCUMENT HAS BEEN APPROVED FOR PUBLIC RELEASE  
AND SALE; ITS DISTRIBUTION IS UNLIMITED.

REPORT DOCUMENTATION PAGE

|   |  |   |  |
|---|--|---|--|
| 1a REPORT SECURITY CLASSIFICATION<br>Unclassified   |  | 1b RESTRICTIVE MARKINGS<br>None   |  |
| 2a SECURITY CLASSIFICATION AUTHORITY  |  | 3 DISTRIBUTION AVAILABILITY OF REPORT<br>Approved for Public Release,<br>Distribution Unlimited |  |
| 2b DECLASSIFICATION/DOWNGRADING SCHEDULE  |  |   |  |
| 4 PERFORMING ORGANIZATION REPORT NUMBER(S)<br>Technical Report No. 9  |  | 5 MONITORING ORGANIZATION REPORT NUMBER(S)  |  |
| 6a NAME OF PERFORMING ORGANIZATION<br>University of Connecticut   | 6b OFFICE SYMBOL<br>(if applicable)        | 7a NAME OF MONITORING ORGANIZATION<br>Office of Naval Research                                  |  |
| 6c ADDRESS (City, State, and ZIP Code)<br>Storrs, CT 06268  |  | 7b ADDRESS (City, State, and ZIP Code)<br>800 North Quincy Avenue<br>Arlington, VA 22217        |  |
| 8a NAME OF FUNDING/SPONSORING ORGANIZATION  | 8b OFFICE SYMBOL<br>(if applicable)<br>ONR | 9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>N00014-86-K-0772                              |  |
| 8c ADDRESS (City, State, and ZIP Code)<br>800 North Quincy Avenue<br>Arlington, VA 22217  |  | 10 SOURCE OF FUNDING NUMBERS  |  |
|   |  | PROGRAM ELEMENT NO  | PROJECT NO   |
|   |  | TASK NO   | WORK UNIT ACCESSION NO   |
| 11 TITLE (Include Security Classification)<br>X-Ray Diffraction by Thermotropic Main-chain Polymers Having Side Groups: Part C. Semiflexible Polyesters (Unclassified)  |  |   |  |
| 12 PERSONAL AUTHOR(S)<br>Hui H. Chin, Leonid V. Azaroff, Anja R. Saini, and Robert K. Lenz  |  |   |  |
| 13a TYPE OF REPORT<br>Technical, Interim  | 13b TIME COVERED<br>FROM TO 07/13/86       | 14 DATE OF REPORT (Year, Month, Day)<br>1986-07-13  | 15 PAGE COUNT<br>23  |
| 16 SUPPLEMENTARY NOTES<br>Submitted to J. Polym. Sci.: Part B: Polym. Phys. (LCPRC Publication No. )  |  |   |  |
| 17 COSATI CODES   |  | 18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)                |  |
| FIELD   | GROUP                                      | SUB GROUP   | X-ray diffraction, Thermotropic aromatic polyesters, Liquid Crystalline Polymers |
|   |  |   |  |
| 19 ABSTRACT (Continue on reverse if necessary and identify by block number)<br>Semiflexible thermotropic aromatic polyesters with lateral groups were aligned magnetically and mechanically in monodomains after separation into high-molecular-weight (polymer) and low-molecular-weight (oligomer) fractions. Based on the total x-ray intensity distributions recorded for a series of seven different substituents in the arylsulfonyl substituted group, a novel smectic structure was determined for H, F, Cl, OCH <sub>3</sub> , and CH <sub>3</sub> in the para-position while a normal nematic alignment prevailed when it contained Br or NO <sub>2</sub> . |  |   |  |
| 20 DISTRIBUTION AVAILABILITY OF ABSTRACT<br><input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS   |  | 21 ABSTRACT SECURITY CLASSIFICATION<br>Unclassified   |  |
| 22a NAME OF RESPONSIBLE INDIVIDUAL<br>Dr. Kenneth J. Wynne  |  | 22b TELEPHONE (Include Area Code)<br>(202) 696-4410   | 22c OFFICE SYMBOL<br>ONR   |

X-Ray Diffraction by Thermotropic Main-chain Polymers  
Having Side Groups: Part C. Semiflexible Polyesters

HUI H. CHIN, LEONID V. AZÁROFF, AGYA R. SAINI, Institute of  
Materials Science, University of Connecticut, Storrs, CT 06268,  
and ROBERT W. LENZ, Polymer Science Department,  
University of Massachusetts, Amherst, MA 01003, USA.

|                    |                                     |
|--------------------|-------------------------------------|
| Accession For      |                                     |
| NTIS GRA&I         | <input checked="" type="checkbox"/> |
| DTIC TAB           | <input type="checkbox"/>            |
| Unannounced        | <input type="checkbox"/>            |
| Justification      |                                     |
| By _____           |                                     |
| Distribution/      |                                     |
| Availability Codes |                                     |
| Dist               | Special                             |
| A-1                |                                     |



SYNOPSIS

Semiflexible thermotropic aromatic polyesters with lateral groups were aligned magnetically and mechanically in monodomains after separation into high-molecular-weight (polymer) and low-molecular-weight (oligomer) fractions. Based on the total x-ray intensity distributions recorded for a series of seven different substituents in the arylsulfonyl substituted group, a novel smectic structure was determined for H, F, Cl, OCH<sub>3</sub>, and CH<sub>3</sub> in the *para*-position while a normal nematic alignment prevailed when it contained Br or NO<sub>2</sub>.

## INTRODUCTION

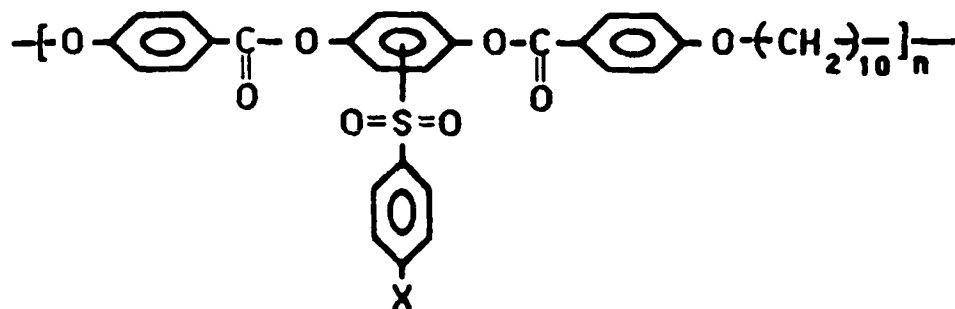
It is possible to regain some of the tensile properties that are sacrificed when flexible spacers are inserted periodically in a rigid polymer chain by aligning the chains parallel to each other. One way to do this is to utilize the dipoles present on the anisometric monomers along the chain by placing the liquid-crystalline polymer (LCP) in a magnetic field.<sup>1,2</sup> Because of their relatively high viscosity, alignment of LCP chains requires fairly strong magnetic fields. An alternative means of aligning the chains is provided by mechanical shear, either by drawing fibers<sup>3</sup> or producing sheets,<sup>4</sup> thus regaining some of the anisotropic mechanical properties of the LCPs themselves.

The present study was undertaken to determine the molecular 'structure' of semiflexible polyesters having comparable molecular structures to the more rigid LCPs discussed in Part B of this series<sup>5</sup> by employing the relative intensities of all recordable x-ray reflections, as well as their disposition in reciprocal space. As discussed elsewhere,<sup>6</sup> this had not been done extensively prior to 1987 but at least one successful analysis has been reported since then.<sup>7</sup> A novel aspect of the present analysis is the use of interactive graphics to construct model structures in three dimensions. This, in turn, enables the iterative structure analysis to proceed rapidly and easily.

As already described in a preliminary report, most of the thermotropic polyesters examined were amorphous initially and consisted primarily of long-chain molecules having a molecular weight average ranging from over 8,000 up to 11,500 in addition to a fraction of oligomers present, as revealed by the GPC curves recorded.<sup>8</sup> Since carrying out the structure analysis requires well aligned LCP samples, an effort was made to establish what role, if any, may be played by the oligomers present. The results of this study are also reported below.

## EXPERIMENTAL

The present study was carried out on thermotropic polyesters based on a triad ester mesogenic unit containing an arylsulfonyl substituted hydroquinone group and a decamethylene spacer group of the following structure:



where X=H, Cl, F, Br, CH<sub>3</sub>, OCH<sub>3</sub>, and NO<sub>2</sub>. The thermal transition points, as determined by DSC, have been reported previously.<sup>8</sup>

The as-polymerized polyesters were separated into high-molecular weight (polymer) and low-molecular weight (oligomer) fractions by repeated fractional precipitation using chloroform as the solvent and methanol as the nonsolvent. Subsequent GPC measurements were carried out using three Waters Associates Ultrastyrigel columns with actual pore sizes of 50, 100, and 1,000 nm, as described elsewhere.<sup>9</sup> The two segregated fractions were then examined under nitrogen on an indium-calibrated DuPont DSC-910 to check their respective thermal transition points. The resulting data is presented in Table I.

## X-Ray Analysis

Both the predominantly polymer and oligomer fractions were packed in Lindenmann glass capillaries (0.8 mm diam.) and placed inside a special furnace (about 10°C above their respective T<sub>m</sub> in Table I) in a uniaxial magnetic field of 15 tesla. After 5-6 hours at that temperature, the samples were quenched by dousing with liquid nitrogen or by cooling in air. (No significant differences were noted.) Additional fiber samples were

prepared by extrusion from the nematic melt (air quenched). The x-ray diffraction intensities were recorded photographically using a Buerger precession camera which is equally suited for normal-beam photography (Laue arrangement) or for exploring the reciprocal lattice without any distortion. Cu K $\alpha$  radiation from an 18 KW rotating-anode generator was monochromatized by a bent graphite crystal. A Quantiment 900 was used to measure the recorded intensity profiles and Evans and Sutherland PS300 interactive graphics to model 3-D molecular structures.

## RESULTS AND DISCUSSION

### Molecular Weight Differences

The GPC curves obtained for all the substituents except NO<sub>2</sub>, which was not readily soluble, are epitomized by those shown in Fig. 1 for the polymer and oligomer-rich fractions. Clearly, the separation is far from complete although, as can be seen in Table I, their respective molecular-weight averages differ by a factor of three or more. As expected from previous observations,<sup>8,9</sup> both  $T_m$  and  $T_i$  increase with increasing molecular weight on proceeding from the as-polymerized sample. It is surprising, however, that the reverse is not always true, the melting temperatures for oligomers containing H, OCH<sub>3</sub>, and F are actually higher than those for the as-received polymers. Whether this is related to the fact that H, F, and OCH<sub>3</sub>-containing oligomers tend to crystallize below  $T_m$ , whereas the others do not, has not been established as yet.

### X-Ray Diffraction Results

For all practical purposes, no significant differences were observed between the x-ray diffraction photographs of magnetically and mechanically aligned samples. More unexpectedly, no differences were observed between

magnetically aligned polymer and oligomer-rich samples despite their viscosity differences. This may be attributable, however, to the high field strength (15 tesla) of the superconducting magnet employed. It is quite likely that a study of the threshold field strength required to align the LCPs present would show a molecular size effect since considerably lower field strengths (by more than one order of magnitude) are adequate for aligning small-molecule liquid crystals.<sup>10</sup>

The present series of thermotropic polyesters yielded essentially two kinds of x-ray diffraction intensity distributions. Figure 2 typifies the one for H, F, Cl, CH<sub>3</sub>, and OCH<sub>3</sub> substituents in the lateral group while Fig. 3 shows the distribution when the substituent is either Br or NO<sub>2</sub>. Aside from certain variations in the relative lengths of the reciprocal-lattice vectors (Table II) note the relative sharpness of the meridional reflections in Fig. 2 and their virtual absence in Fig. 3. In fact, Table II shows that the reciprocal-lattice vectors to the meridional maxima and the broad equatorial reflections have identical lengths, within experimental error of measurement. The off-meridian reflections typical of short-range chain-to-chain ordering in semiflexible LCPs, however, are again the same for all samples diffracting like Fig. 2 but lie at different distances from the origin of reciprocal space in Fig. 3 and their respective vectors form a different angle with the meridian (chain direction). This, as well as the significantly weaker intensities of 00 $\ell$  reflections in Fig. 3, will play an important role in the structure analyses described next.

For ease of reference, the off-axis reflections in Figs. 2 and 3 are labelled 'h0 $\ell$ ' in Table III. Single quotation marks are used in this case and for the broad equatorial 'hk0' reflection to stress the absence of a lattice (unit cell) to which the Miller indices can be referred. The choice of these designations is convenient nevertheless because it properly

locates the region of reciprocal space where such reflections occur in the case of true crystals. Note that, in the present LCP case, the intensity distribution in reciprocal space is cylindrically symmetric about the chain direction (meridian) so that Figs. 2 and 3 are ' $h0\ell$ '-type cross sections of the actual distributions. This means that the x-ray samples must consist of cylindrically arrayed parallel monodomains. The absence of any evidence of amorphous diffraction halos further indicates that virtually all the chains are extended in such parallel monodomains as also evidenced by the lack of any arcing of the equatorial reflection. Its breadth, however, suggests that the diffraction angles corresponding to the intensity values at half-maximum intensity be used to calculate the range of interchain separation as suggested in Part A.<sup>11</sup> This range turns out to be 0.30 to 0.45 nm. for the photograph in Fig. 2.

#### Structure Analyses

The availability of interactive graphics instruments that enable the rapid construction of three-dimensional models, that can be viewed by stereoscopic optics while their conformation and spatial disposition is undergoing change, greatly facilitates an iterative approach to analyzing the positions and relative intensities of diffraction maxima. Moreover, individual monomers or components can be color coded to further ease their visualization while 'fitting' them into an appropriate model. Figure 4 represents three basic ways available for depicting a molecule. Figure 4a shows a filled out molecular chain with each atom represented by a sphere of the appropriate Van der Waals radius. Alternatively, Fig. 4b portrays the skeletal outline of the atomic centers while Fig. 4c is the same as Fig. 4b except that the volume of rotation of the aromatic rigid core is represented by an eight-sided prism (because our instrument cannot depict cylinders). For present purposes, the latter representation proved most

convenient (especially when viewed in color) because it makes it easier to observe the packing of the chain molecules in three dimensions.

Reference to Table II shows that the intensity distributions for polyester chains containing H, F, Cl, CH<sub>3</sub>, and OCH<sub>3</sub> in the lateral groups are virtually identical. The prominent off-axis reflections (Fig. 2) strongly suggest that these lateral groups should lie along pyramidal 'h0l' planes in the monodomains so that the relative longitudinal displacement of chains like those in Fig. 4c were adjusted in the graphical model so that the lateral groups were lying along such 'h0l' planes as indicated in Fig. 5a. The other constraint placed on the chains was that they had to be parallel and that they could not encroach on each other's space but, otherwise, they were free to rotate about the chain axes and to move longitudinally or laterally. A best 'fit' under these constraints is shown in a side view in Fig. 5a and in an end view (along the chains) in Fig. 5b. It is not surprising that the end view shows that there is no regularity in the side-to-side array of the chains, in conformity with what is observed in Fig. 3. The interchain separations in Fig. 5b range from 0.30 to 0.45 nm. and are consistent with the measured density.

An examination of the model in Fig. 5a shows that the monomer units are arrayed in virtual layers perpendicular to the chain axes. In fact, the spacing of the most clearly discernible layering corresponds to one-third of the repeat unit along the chain. This explains, of course, why 003 is the most intense meridional reflection in Fig. 2. What was not realized until the final molecular model (Fig. 5) was developed was that the side-to-side alignment that such an array produces is more typical of smectic ordering rather than the nematic ordering previously assumed.<sup>12</sup> Note that this is unlike the smectic ordering in small-molecule (monomer) liquid crystals in which neighboring molecules tend to have parallel orientations within a common layer.

When the interplanar separation and inclination of the pyramidal planes is altered to fit the ' $h0\ell$ ' values for Br or  $\text{NO}_2$ , placing no other restrictions on the chain positions (as before) other than that their end view should be like that in Fig. 5b, then a best 'fit' occurs for the model shown in side view in Fig. 6. Since the side-to-side packing separations could not change by much, the major accommodations had to take place by longitudinal displacements of the chains. Not surprisingly, such a nematic packing disrupts the coherency of  $(00\ell)$  'layers' and modifies the shape and relative intensities of  $00\ell$  reflections. Their absence (or very low intensity) in Fig. 3 supports the model (Fig. 6) in which, incidentally, the chains are not rigid so that the monomer units comprising them may be slightly splayed and not strictly periodically spaced along the chain axis (as well as randomly rotated about this axis). In fact, the model in Fig. 6 is an idealization of what the actual molecular array is like but it does represent in two dimensions the most likely organizational ordering (structure) in these thermotropic polyesters having either Br or  $\text{NO}_2$  substituents in the lateral groups.

#### CONCLUSIONS

By utilizing all the intensity information in reciprocal space, i.e., the relative intensity magnitudes as well as their spatial disposition, it is possible to devise molecular models for semiflexible thermotropic polyesters aligned in monodomain-like arrays. Abetted by the availability of interactive graphics to facilitate model construction, modification, and examination in three dimensions, a new kind of smectic alignment has been discovered to occur in polyesters having certain substituents in their lateral groups while a more usual nematic packing occurs for other substituents. The reason for these different forms of aggregation is not understood at present.

We want to express our appreciation to Dr. A. Furukawa for synthesizing the polymers and to the Francis Eitter National Magnet Laboratory of M.I.T. for providing access to their superconducting magnet for this study which was supported by the Defense Advanced Research Projects Agency through ONR Grant N00014-86-C772 establishing the LCF Research Center at The University of Connecticut.

## References

1. C. Noel, L. Monuerie, M. F. Achard, F. Hardouin, G. Sigaud, and H. Gasparoux, *Polymer*, **22**, 578 (1981).
2. F. Hardouin, M. F. Achard, and H. Gasparoux, L. Liebert, and L. Strzetecki, *J. Polym. Sci.: Part B: Polym. Phys.* **20**, 975 (1982).
3. R. Capasso, A. Roviello, A. Sirign, and P. Iarelli, *J. Polym. Sci.: Part B: Polym. Phys.* **25**, 2431 (1987).
4. M. Kyotani and H. Kanetsuna, *J. Macromol. Sci.-Phys.* **B26**, 325 (1987).
5. H. H. Chin, L. V. Azaroff, and R. W. Lenz, *J. Polym. Sci.: Part B: Polym. Phys.* , (1988).
6. L. V. Azaroff, *Mol. Cryst. Liq. Cryst.* **145**, 31 (1987).
7. R. M. Richardson, A. J. Leadbetter, M. A. Mazid, and P. A. Tucker, *Mol. Cryst. Liq. Cryst.* **149**, 329 (1987).
8. H. H. Chin, L. V. Azaroff, A. Furukawa, and F. W. Lenz. *Mol. Cryst. Liq. Cryst.* **155**, 337 (1988).
9. G. A. Meyer, J. F. Johnson, H. H. Chin, and L. V. Azaroff, *J. Liq. Chromatogr.* , (1988).
10. L. V. Azaroff, *Mol. Cryst. Liq. Cryst.* **60**, 73 (1980).
11. L. V. Azaroff, *J. Polym. Sci.: Part B: Polym. Phys.* , (1988).
12. A. Furukawa and R. W. Lenz, *Macromol. Chem. Macromol. Symp.* **2**, 3 (1986).

TABLE I

## Molecular Weight and Thermal Data

| Substituent      | Sample         | Molecular Weight |          | Transition Temp's.  |                     |
|------------------|----------------|------------------|----------|---------------------|---------------------|
|                  |                | Wt. Ave          | No. Ave. | T <sub>m</sub> (°C) | T <sub>g</sub> (°C) |
| H                | As-polymerized | 9,200            | 6,700    | 100                 | 170                 |
|                  | Polymer        | 13,400           | 10,700   | 145                 | 178                 |
|                  | Oligomers      | 5,000            | 3,300    | 138                 | 169                 |
| CH <sub>3</sub>  | As-polymerized | 9,000            | 5,400    | 95                  | 145                 |
|                  | Polymer        | 11,200           | 7,400    | 98                  | 151                 |
|                  | Oligomers      | 2,500            | 1,000    | 92                  | 125                 |
| OCH <sub>3</sub> | As-polymerized | 7,100            | 4,500    | 86                  | 126                 |
|                  | Polymer        | 11,200           | 7,400    | 98                  | 144                 |
|                  | Oligomers      | 3,000            | 1,300    | 99                  | 126                 |
| F                | As-polymerized | 9,200            | 5,200    | 95                  | 161                 |
|                  | Polymer        | 11,000           | 8,900    | 124                 | 170                 |
|                  | Oligomers      | 4,600            | 2,800    | 105                 | 142                 |
| Cl               | As-polymerized | 8,500            | 2,600    | 101                 | 154                 |
|                  | Polymer        | 11,300           | 7,800    | 102                 | 160                 |
|                  | Oligomers      | 3,300            | 400      | 98                  | 145                 |
| Br               | As-polymerized | 8,500            | 4,200    | 93                  | 147                 |
| NO <sub>2</sub>  | As-polymerized | ---              | ---      | 91                  | 153                 |

TABLE II  
Reciprocal Lattice Vectors

| Substituent $hkl$ | 003   | 005   | 006   | 007   | ' $h0l$ ' | ' $hko$ ' |
|-------------------|-------|-------|-------|-------|-----------|-----------|
| H                 | 0.160 | 0.267 | 0.319 | 0.370 | 0.096     | 0.36      |
| F                 | 0.160 | 0.267 | 0.321 | 0.372 | 0.096     | 0.36      |
| Cl                | 0.160 | 0.270 | 0.320 | 0.370 | 0.093     | 0.36      |
| CH <sub>3</sub>   | 0.160 | 0.267 | 0.320 | 0.370 | 0.096     | 0.36      |
| OCH <sub>3</sub>  | 0.160 | 0.267 | 0.320 | 0.372 | 0.096     | 0.36      |
| Br                | 0.162 | 0.267 | 0.320 | 0.372 | 0.089     | 0.36      |
| NO <sub>2</sub>   | 0.160 | 0.271 | 0.318 | 0.374 | 0.085     | 0.36      |

### Figure Captions

- Fig. 1. Gel Permeation chromatograms for  $\text{CH}_3$  substituent.
- High-molecular-weight fraction (polymer).
  - Low-molecular-weight fraction (oligomers).
- Fig. 2. Zero-level precession photography of H-substituted polyester ( $\bar{\mu}=15^\circ$ ,  $F=100$  mm).
- Fig. 3. Zero-level precession photograph of Br-substituted polyester ( $\bar{\mu}=16^\circ$ ,  $F=60$  mm). (A square absorbing film attenuates the central region of this photograph).
- Fig. 4.
- Atomic shells filled out.
  - Skeletal outline of molecules.
  - Polygonal prisms joined to skeletal flexible chain units and lateral groups.
- Fig. 5. Packing model for H, F, Cl,  $\text{CH}_3$ , and  $\text{OCH}_3$  substituents.
- Side view with  $(h0l)$  planes indicated.
  - End view showing the projections of the aliphatic chains within the octagons.
- Fig. 6. Side view of packing model for Br and  $\text{NO}_2$  substituents.

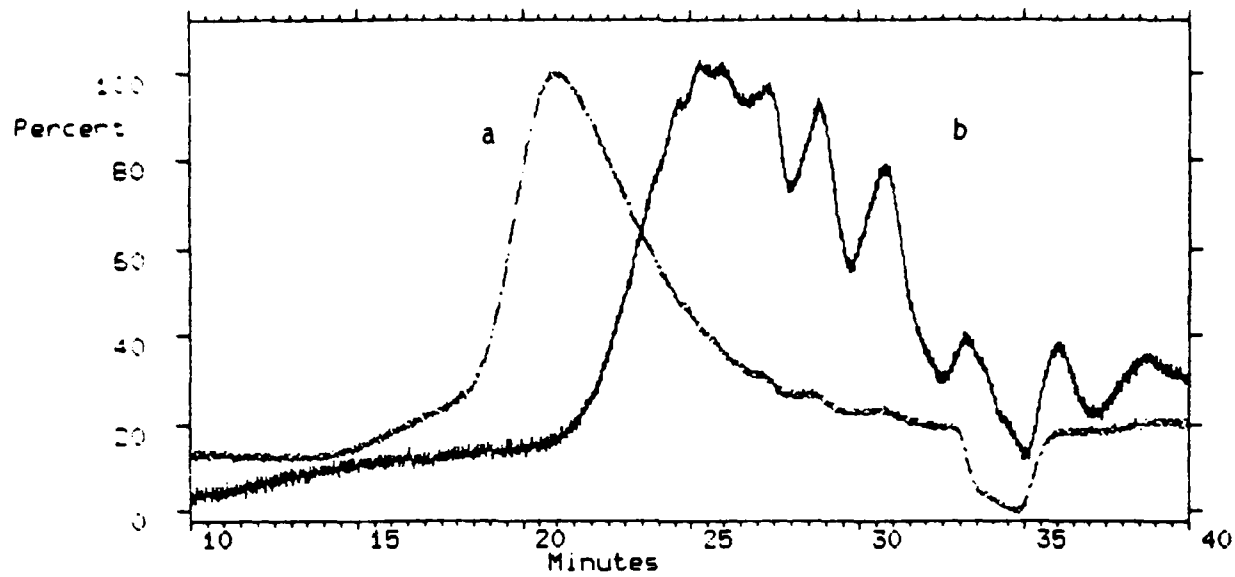
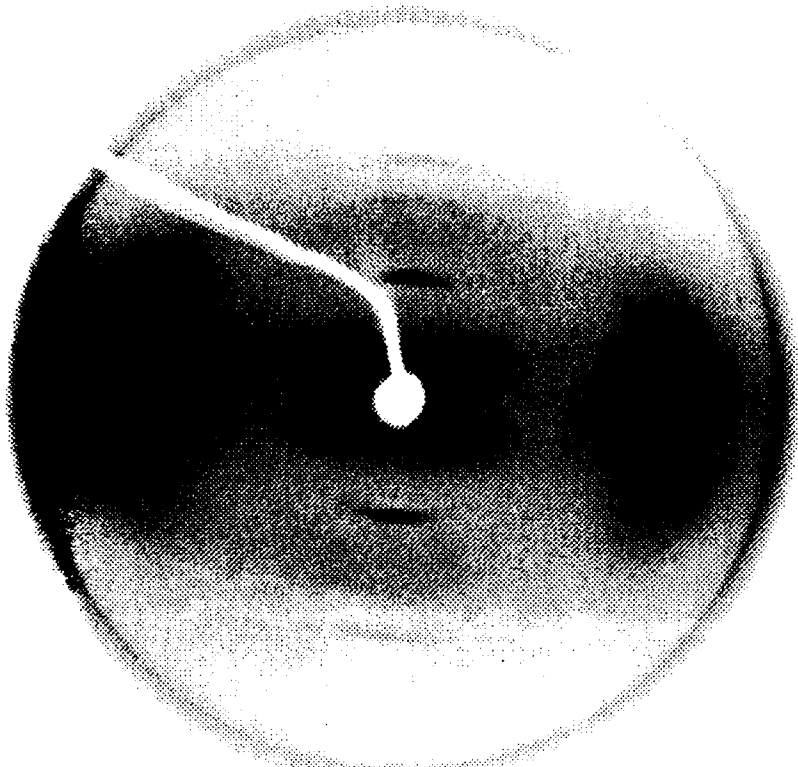


Fig. 1

H-110

No 1029

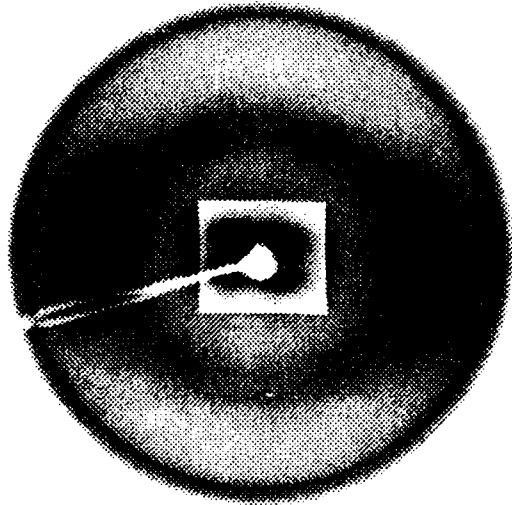


————— Base line

Fig. 2

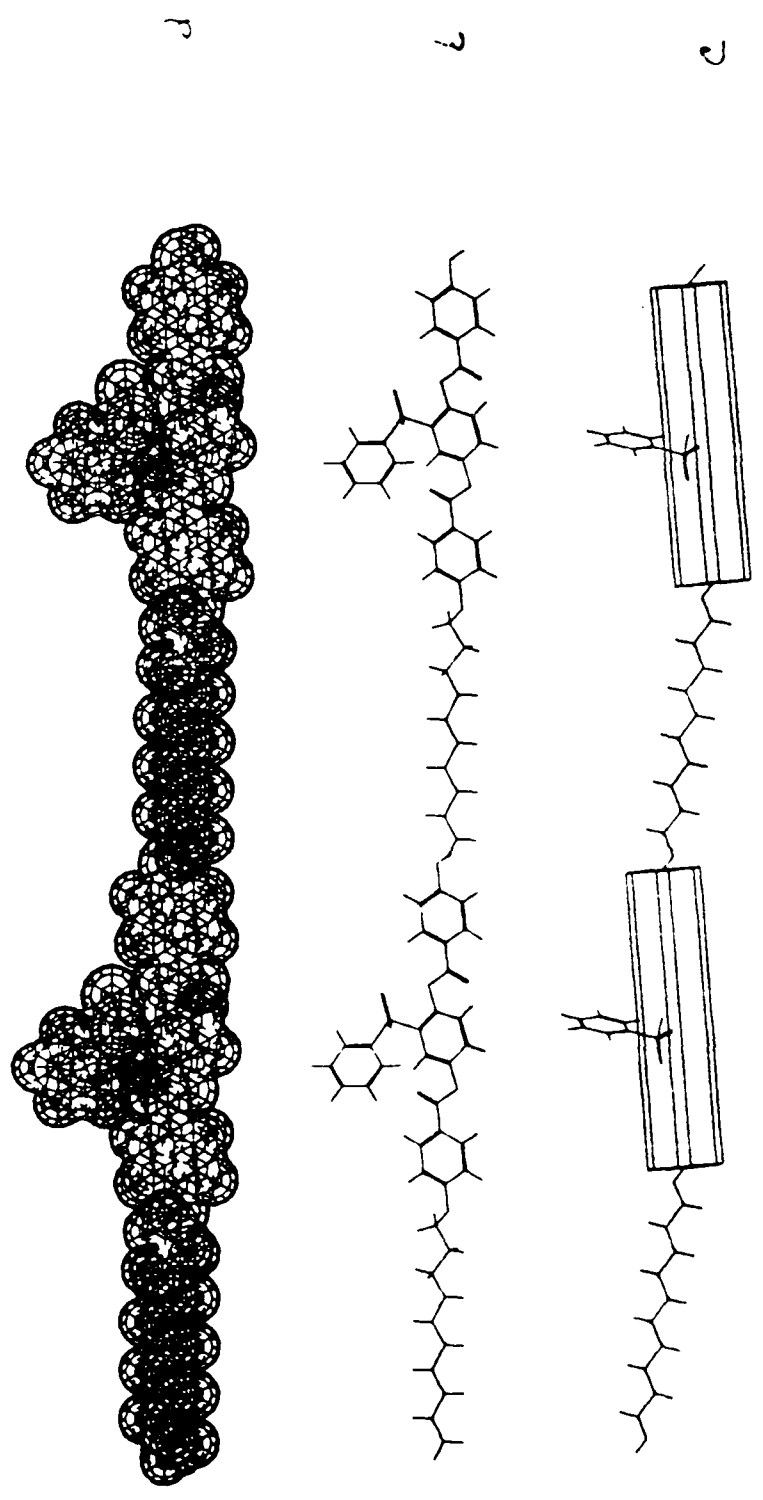
CHIN et al.

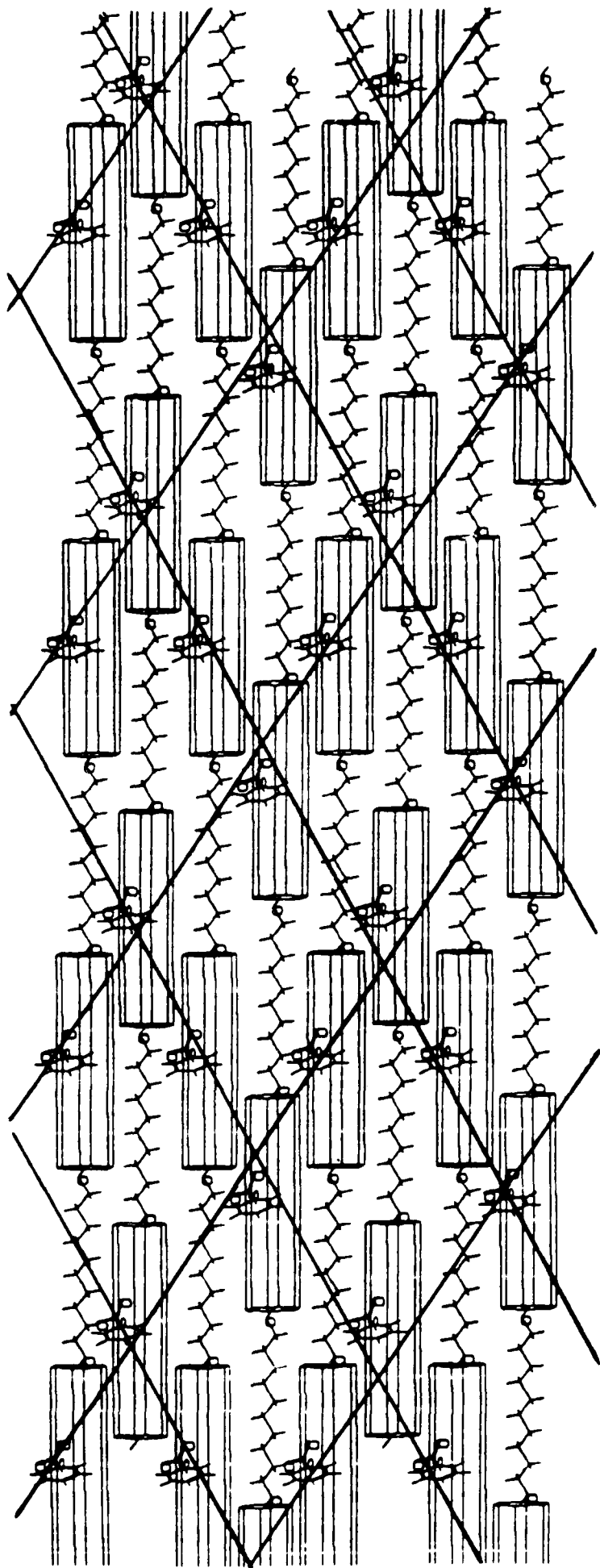
Bv-410



No 1095

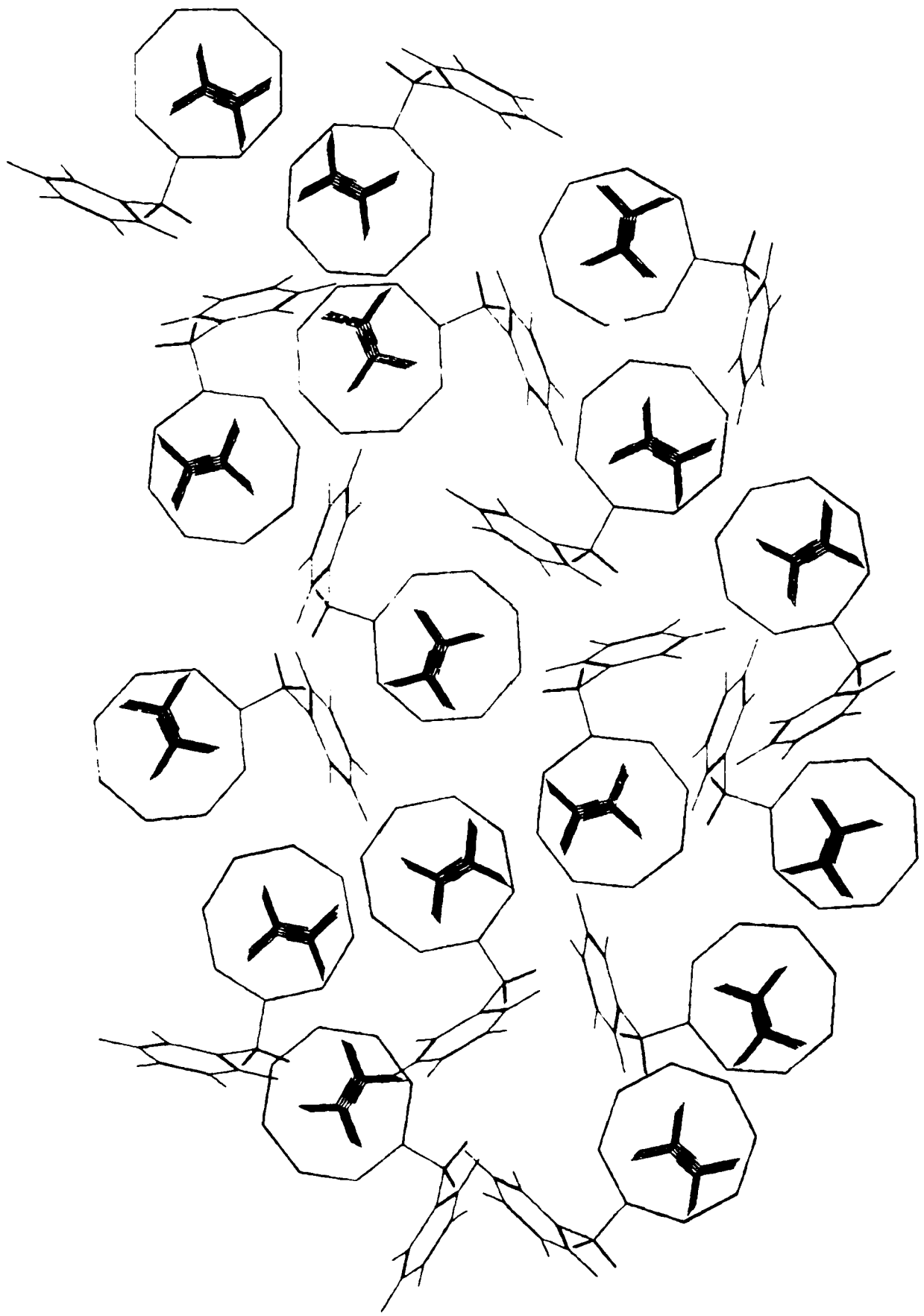
-----  
Fig 3  
-----  
-----





a

Fig. 5 ~~7~~ (part a)



b

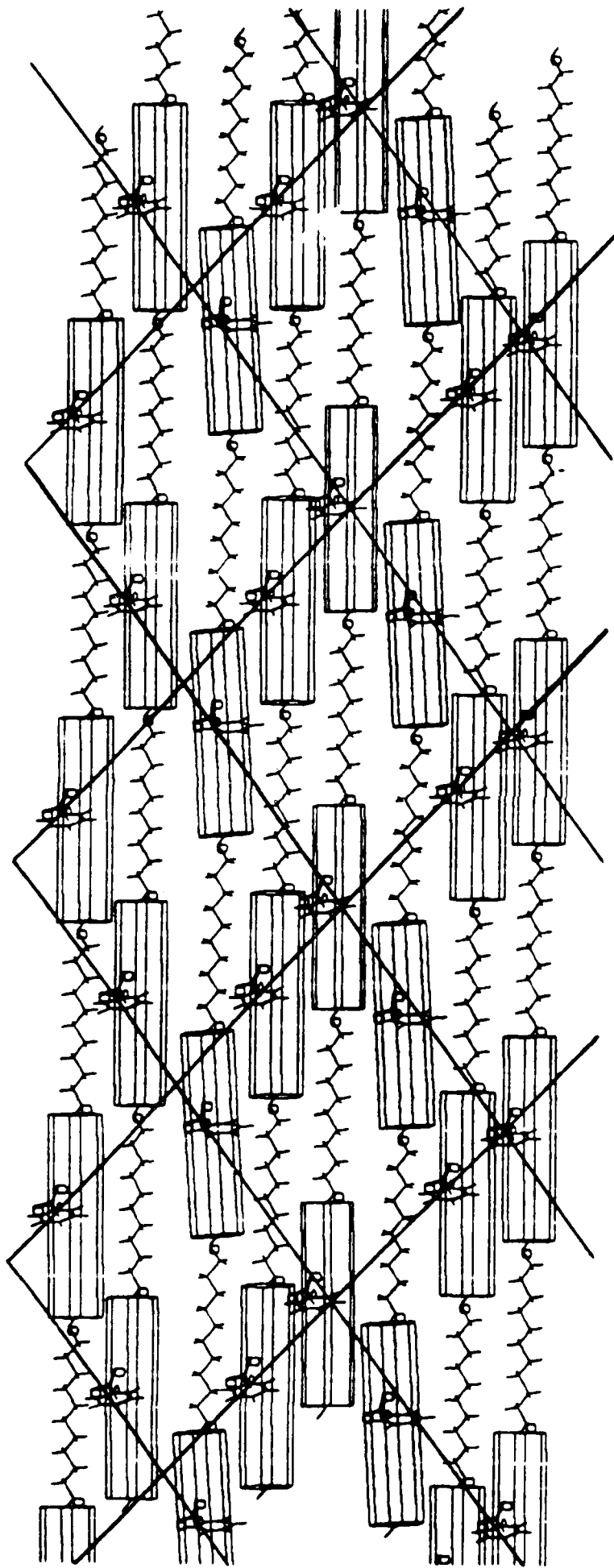


Fig. 6 (~~Fig. 6~~)

TECHNICAL REPORT DISTRIBUTION LIST, GEN

|   | <u>No.<br/>Copies</u> |  | <u>No.<br/>Copies</u> |
|---|-----------------------|--|-----------------------|
| Office of Naval Research<br>Attn: Code 1113<br>800 N. Quincy Street<br>Arlington, Virginia 22217-5000                             | 2                     | Dr. David Young<br>Code 334<br>NORDA<br>NSTL, Mississippi 39529  | 1                     |
| Dr. Bernard Douda<br>Naval Weapons Support Center<br>Code 50C<br>Crane, Indiana 47522-5050  | 1                     | Naval Weapons Center<br>Attn: Dr. Ron Atkins<br>Chemistry Division<br>China Lake, California 93555             | 1                     |
| Naval Civil Engineering Laboratory<br>Attn: Dr. R. W. Drisko, Code L52<br>Port Hueneme, California 93401                          | 1                     | Scientific Advisor<br>Commandant of the Marine Corps<br>Code RD-1<br>Washington, D.C. 20380                    | 1                     |
| Defense Technical Information Center<br>Building 5, Cameron Station<br>Alexandria, Virginia 22314                                 | 12<br>high<br>quality | U.S. Army Research Office<br>Attn: CRD-AA-IP<br>P.O. Box 12211<br>Research Triangle Park, NC 27709             | 1                     |
| DTNSRDC<br>Attn: Dr. H. Singerman<br>Applied Chemistry Division<br>Annapolis, Maryland 21401                                      | 1                     | Mr. John Boyle<br>Materials Branch<br>Naval Ship Engineering Center<br>Philadelphia, Pennsylvania 19112        | 1                     |
| Dr. William Tolles<br>Superintendent<br>Chemistry Division, Code 6100<br>Naval Research Laboratory<br>Washington, D.C. 20375-5000 | 1                     | Naval Ocean Systems Center<br>Attn: Dr. S. Yamamoto<br>Marine Sciences Division<br>San Diego, California 91232 | 1                     |

ENID

DATE

9-88

DT/C