$$\bar{m} = \frac{1}{\theta} \int_0^\infty m \exp(-t/\theta) \, dt \qquad (26)$$

Since it is not possible to express $m$ analytically in terms of time, this equation is integrated numerically up to the point where $f_1$ is reduced to a value of $10^{-10}$. Beyond this point an integration using equations for homopolymerization is employed as done previously in ref 4a.

The average monomer composition in the product stream, $\bar{f}_1$, is calculated by summing the residual monomer from each hypothetical BR

$$\bar{f}_1 = \frac{\bar{M}_1}{\bar{M}}$$

$$= \frac{1}{\theta} \frac{\int_0^\infty f_1(1 - m) \exp(-t/\theta) \, dt}{(1 - \bar{m})} \qquad (27)$$

The average copolymer composition is then calculated from this result as

$$\bar{F}_1 = \frac{f_1^0 - \bar{f}_1(1 - \bar{m})}{\bar{m}} \qquad (28)$$

The CCD represents the fraction of copolymer molecules having compositions ranging from that formed instantaneously at zero conversion, $F_1^0$, to that value of $F_1$ obtained at some advanced conversion. This is equivalent to saying that the CCD represents the fraction of the copolymer product formed between time zero and time $t_{F_1}$ at which the instantaneous composition being formed is $F_1$. Since, in the SCSTR, the fraction of molecules retained for $t_{F_1}$ or greater is

$$\frac{1}{\theta} \int_{t_{F_1}}^\infty \exp(-t/\theta) \, dt = \exp(-t_{F_1}/\theta) \qquad (29)$$

then, on a basis of 1 mol of reaction mixture, the number of moles of copolymer formed in this time period with composition between $F_1$ and $F_1^0$ is

$$m_{F_1} \exp(-t_{F_1}/\theta)$$

Similarly

$$\frac{1}{\theta} \int_0^{t_{F_1}} m \exp(-t/\theta) \, dt$$

moles of copolymer are contributed from molecules spending less than $t_{F_1}$ units of time in the reactor. Normalizing by dividing by the total moles formed, the CCD becomes

$$\frac{1}{\bar{m}} \left( \frac{1}{\theta} \int_0^{t_{F_1}} m \exp(-t/\theta) dt + m_{F_1} \exp(-t_{F_1}/\theta) \right) \qquad (30)$$

The differential distribution can be obtained by differentiating the CCD giving

$$\frac{1}{\bar{m}} \frac{dm}{dF_1} \exp(-t_{F_1}/\theta) \qquad (31)$$

The quantity $dm/dF_1$ can be obtained from the differential copolymer composition equation for BR, eq 13.

# Structural Studies of the Optically Active and Racemic Poly(propylene sulfides)

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ABSTRACT: The crystal structure of optically active poly(propylene sulfide) and racemic poly(propylene sulfide) were studied by X-ray diffraction. All reflections of X-ray fiber photographs of the optically active polymer were indexed by the orthorhombic unit cell; the cell dimensions are $a = 9.95$ Å, $b = 4.89$ Å, and $c$ (fiber axis) $= 8.20$ Å, and the space group is $P2_12_12_1$-$D_2^4$. Two molecular chains characterized by a twofold screw axis pass through the unit cell. The crystal structure of the optically active polymer is very similar to that of racemic poly(propylene oxide). The fact that the fiber photograph of the racemic polymer gives the same X-ray pattern as the optically active polymer suggests that the both polymers have the same crystal structure. Namely, it may be concluded that the racemic polymer sample consists of the two kinds of optically active crystallites, $R$ (rectus) and $S$ (sinister).

S everal authors have investigated the crystal structure of racemic poly(propylene oxide) by X-ray diffraction since the report of Natta, Corradini, and Dall'-Asta[2a] in 1956. Stanley and Litt[2b] have considered that the oxygen atoms and methylene groups are almost inter-

changeable and it is possible that optically active and *dl* unit cells are present at the same time. But in the recent report by Cesari, Perego, and Marconi,[3] no attention is paid to this question. In order to justify the conclusion of Stanley and Litt, two problems should be cleared up: one is the crystal structure of optically active poly(propylene oxide) and the other is the differ-

(1) (a) Osaka University; (b) Laboratoire de Chimie Macromoléculaire.
(2) (a) G. Natta, P. Corradini, and G. Dall'Asta, *Atti Acad. Naz. Lincei, Rend., Cl. Sci. Fis., Mat. Nat.*, **20**, 408 (1956); (b) E. Stanley and M. Litt, *J. Polym. Sci.*, **43**, 453 (1960).

(3) M. Cesari, G. Perego, and W. Marconi, *Makromol. Chem.*, **94**, 194 (1966).

ence between the X-ray photograph of the racemic polymer and that of the optically active polymer. However, the crystal structure of optically active poly-(propylene oxide) has not been reported up to the time of writing. In addition, in the case of poly(propylene oxide), it is difficult to distinguish by X-ray method the possible difference between the structure of the optically active polymer and that of the racemic polymer, since the scattering power of the oxygen atom is very similar to that of the methylene group. But in the case of poly(propylene sulfide), we may expect easily to be able to detect the difference, if any, in the crystal structures of the two polymers, since the scattering power of the sulfur atom is measurably different from that of methylene group.

The present paper reports the results of structural investigations carried out on an optically active poly-(propylene sulfide) and the racemic poly(propylene sulfide) by X-ray diffraction.

## Experimental Section

**Preparation of Samples.** In this study, two kinds of samples, the optically active polymer and the racemic polymer of poly(propylene sulfide), were used. These polymers were prepared by methods given in the literature.[4,5] The optically active polymer was prepared from (−)-propylene sulfide using cadmium tartrate:[4] optical rotation of the monomer, $[\alpha]^{25}_D$ −25.6° (neat); optical rotation of the polymer, $[\alpha]^{25}_D$ −95.6° (CHCl$_3$) and −82.6° (benzene). The racemic polymer was prepared from racemic propylene sulfide using 1:1 diethylzinc–water as catalyst.[5] The intrinsic viscosity of this polymer was $[\eta]_{100\ ml/g}$ = 3.2 (after extraction with hot methyl ethyl ketone). The melting point measured by using the polarizing microscope was about 50° for the optically active polymer and about 45° for the racemic polymer. Well-oriented fibers of the optically active polymer was prepared by elongating a piece of the raw sample at room temperature. The samples thus obtained (diameter about 0.2 mm) were used in the X-ray analysis of the optically active poly(propylene sulfide).

**X-Ray Measurement.** Nickel-filtered Cu Kα X-ray radiation (wavelength λ 1.5418 Å) was used. The photographs were taken with a cylindrical camera (diameter 100.0 mm) and a Weissenberg camera (diameter 57.3 mm). The measurement of the Bragg angles was calibrated by reference to those of aluminum powder. The reflection intensities were recorded with the multiple film method and measured by visual comparison with a standard intensity scale. To the intensities thus obtained corrections were applied in the usual fashion. Thirty-eight independent reflections on the equatorial, first, second, and third layers were available.

The fiber photographs of the optically active poly(propylene sulfide) and the racemic poly(propylene sulfide) are given in Figure 1.

**X-Ray Analysis. Unit Cell and Space Group.** All the reflections of the photographs (Figure 1) are indexed by an orthorhombic unit cell. The fiber period (the c parameter) was determined with fairly high accuracy by using the 006 reflection in a Weissenberg photograph, which was taken by setting the uniaxially oriented specimen with the fiber axis perpendicular to the camera axis. The cell dimensions are as follows: $a$ = 9.95 Å, $b$ = 4.89 Å, and $c$ = 8.20 Å (fiber period).

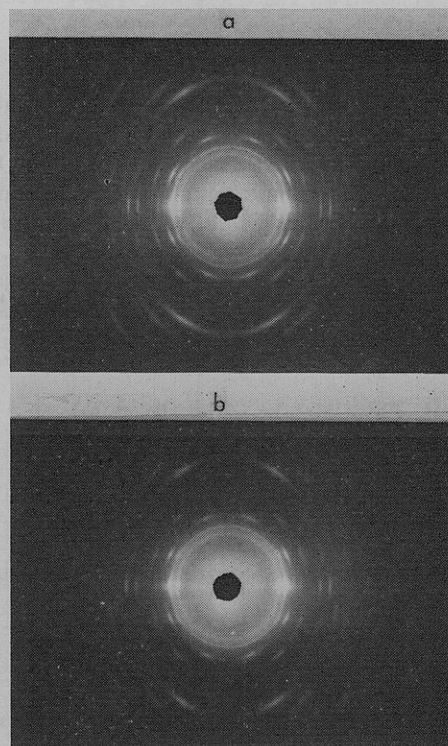Assuming four monomeric units in the unit cell, the calcu-



Figure 1. X-Ray fiber photographs: a, optically active poly(propylene sulfide); b, racemic poly(propylene sulfide).

lated density is 1.24 g/cm$^3$. This value is acceptable in comparison with the observed density measured by the flotation method (CaCl$_2$ aqueous solution), 1.16 g/cm$^3$. The systematic absences are $h00$ when $h$ is odd, $0k0$ when $k$ is odd, and $00l$ when $l$ is odd. Therefore the most acceptable space group is P2$_1$2$_1$2$_1$-D$_2$$^4$.

**Chain Configuration and Conformation.** We considered at first that the main chain conformation is essentially extended planar zigzag, since the observed fiber period 8.20 Å corresponds approximately to the calculated value 8.45 Å, which was calculated assuming the planar zigzag form (bond lengths C–C = 1.54 Å, C–S = 1.815 Å; bond angles C–C–S = C–S–C = 109.5°). The molecular chain contains two monomeric units in the identity period, and the two molecular chains pass through the unit cell. Since the space group P2$_1$2$_1$2$_1$-D$_2$$^4$ has four equivalent general positions, the chain axis must coincide with a twofold screw axis of the space group. Thus, the molecular conformation of poly(propylene sulfide) is characterized by a twofold screw axis. Consequently it is clear that crystalline poly(propylene sulfide) has an isotactic configuration. Poly(propylene sulfide) has a true asymmetric carbon atom in each monomeric unit, –CH(CH$_3$)CH$_2$S–, so there are two kinds of optical isomers of isotactic poly(propylene sulfide).[6] These planar zigzag models are illustrated and the corresponding Fischer projections are also given in Figure 2. According to the nomenclature proposed by Cahn, Ingold, and Prelog,[7] the absolute configurations of these two optical isomers can be indicated by the italic letters $R$ (rectus) and $S$ (sinister). In this case, the absolute configuration of the monomers was determined as $S$ for the levorotatory enantiomer and $R$ for the dextrorotatory enantiomer.[8] The absolute configuration of the corresponding polymers should be the same, as we know that there is no inversion of con-

(4) N. Spassky and P. Sigwalt, *Bull. Soc. Chim. Fr.*, **12**, 4617 (1967).

(5) J. P. Machon and P. Sigwalt, *C. R. Acad. Sci., Paris*, **260**, 549 (1965).

(6) M. L. Huggins, G. Natta, V. Desreux, and H. Mark *J. Polym. Sci.*, **56**, 153 (1962).

(7) R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1960).

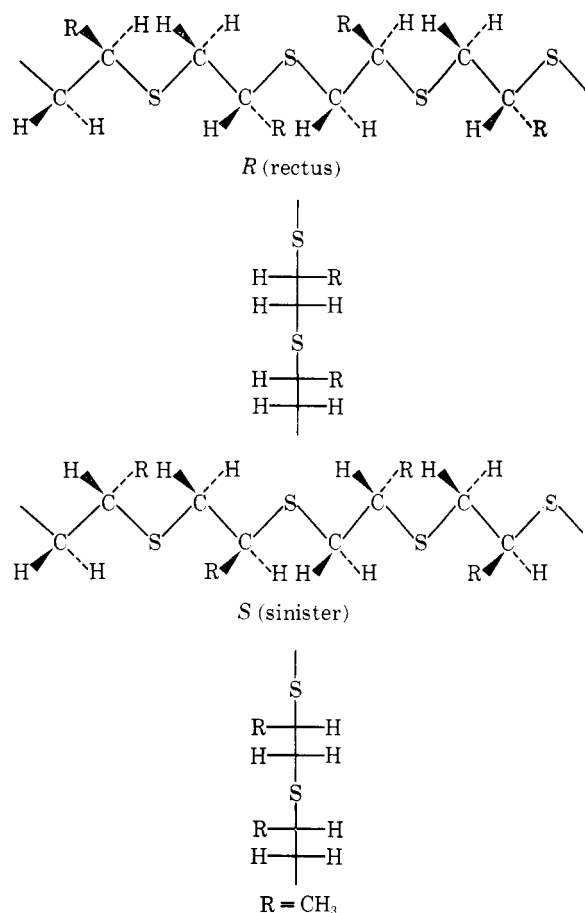(8) N. Spassky and P. Sigwalt, *Tetrahedron Lett.*, 3541 (1968)

Figure 2. Absolute configurations of the isotactic poly-(propylene sulfide).

figuration during polymerization by an anionic mechanism. Thus, the optically active polymer in this study is of *S* configuration.

The fact that the observed fiber period is smaller than the calculated one by 0.25 Å suggests that the molecular chain is not a fully extended planar zigzag.

**Structure Factor Calculation.** Starting from a model of a fully extended planar zigzag chain, the atomic parameters
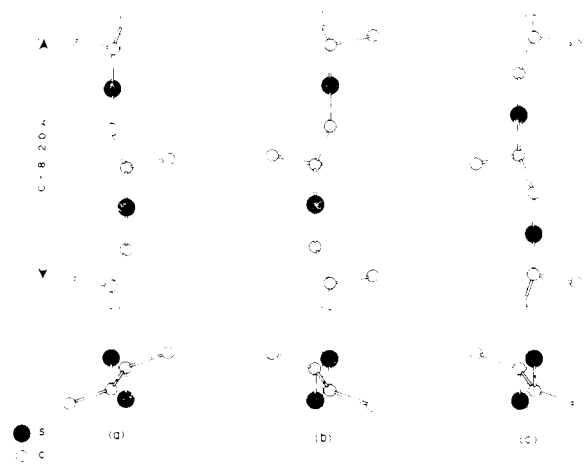


Figure 3. Molecular chains of the isotactic poly(propylene sulfide): (a) "up" molecular chain of *R* polymer; (b) "up" molecular chain of *S* polymer; (c) "down" molecular chain of *R* polymer.

TABLE I

ATOMIC COORDINATES AND THERMAL PARAMETERS OF POLY(PROPYLENE SULFIDE)

|  | $x/a$ | $y/b$ | $z/c$ | $B$, Å$^2$ |
|---|---|---|---|---|
| C$_1$ | 0.284 | −0.063 | 0.010 | 5 |
| C$_2$ | 0.436 | −0.088 | 0.041 | 12 |
| C$_3$ | 0.216 | 0.063 | 0.161 | 5 |
| S | 0.245 | −0.155 | 0.336 | 5 |

were refined by trial and error, giving a discrepancy factor ($R$ factor $= \Sigma^{'}|F_o| - |F_c||/\Sigma^{'}F_o|$) of 13% for all the observed reflections. In this structure factor calculation the contribution of the hydrogen atoms was not taken into account since this contribution was negligibly small for almost all reflections. The final atomic coordinates and the isotropic thermal parameters are listed in Table I. The thermal parameter $B$ of the carbon atom of the methyl group has a large value. It may be concluded that the carbon atom of the side chain vibrates more vigorously than the other skeletal atoms. The agreement between the observed and calculated structure factors is shown in Table II.

**Results and Discussion**

**Molecular and Crystal Structure of the Optically Active Polymer.** The molecular structure of poly-(propylene sulfide) is not a fully extended planar zig-zag form. Figure 3 shows clearly the deviation from planarity. The C–S bonds do not take the exact *trans* form, but deviate by ±20° symmetrically.

This molecular structure is very similar to that of racemic poly(propylene oxide) as reported by Cesari, *et al.*[3] The values of the internal rotation angles for
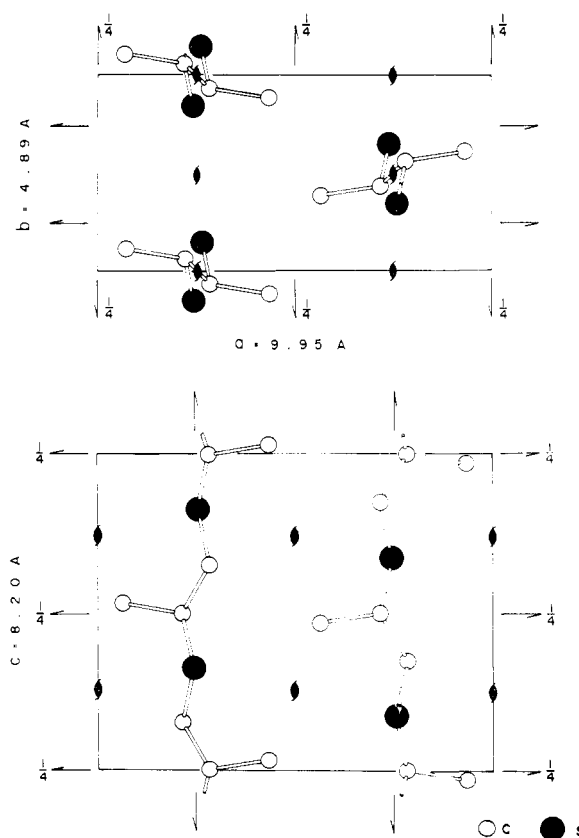


Figure 4. Crystal structure of poly(propylene sulfide).

## TABLE II
### COMPARISON BETWEEN OBSERVED AND CALCULATED STRUCTURE FACTORS

| h k l | $\sqrt{I_o}{}^a$ | $\sqrt{I_c}{}^b$ | h k l | $\sqrt{I_o}{}^a$ | $\sqrt{I_c}{}^b$ |
|---|---|---|---|---|---|
| 2 0 0 | 51.4 | 52.9 | 2 0 2 }  0 1 2 } | 21.0 | 13.6 |
| 1 1 0 | 57.9 | 67.0 | | | |
| 2 1 0 | 17.2 | 8.3 | 1 1 2 | | 4.9 |
| 3 1 0 | 27.7 | 31.7 | 2 1 2 | 9.5 | 10.9 |
| 4 0 0 | 33.8 | 34.4 | 3 0 2 | 15.6 | 17.5 |
| 0 2 0 | | 5.6 | 3 1 2 | 11.7 | 9.9 |
| 1 2 0 | 14.9 | 9.2 | 4 0 2 | | 7.3 |
| 4 1 0 | | 1.0 | 0 2 2 | | 7.8 |
| 2 2 0 | | 0.4 | 1 2 2 | 16.9 | 16.9 |
| 3 2 0 | | 3.2 | 4 1 2 }  2 2 2 } | 10.2 | 11.4 |
| 5 1 0 | 20.0 | 24.1 | | | |
| 4 2 0 | | 2.2 | 5 0 2 }  3 2 2 } | 16.2 | 15.6 |
| 6 0 0 | 17.3 | 19.5 | | | |
| 1 3 0 | 21.2 | 16.3 | 5 1 2 | | 4.8 |
| 6 1 0 | | 2.0 | 4 2 2 | | 6.5 |
| 2 3 0 | | 5.9 | 6 0 2 | | 4.7 |
| 5 2 0 | | 3.0 | 0 3 2 }  1 3 2 } | 15.3 | 16.6 |
| 3 3 0 | 13.7 | 14.8 | | | |
| 6 2 0 }  7 1 0 }  4 3 0 } | 13.2 | 10.1 | 6 1 2 | | 7.6 |
| | | | 2 3 2 }  5 2 2 } | 16.4 | 19.4 |
| 2 0 1 }  0 1 1 } | 18.1 | 13.4 | 3 3 2 }  7 0 2 } | 12.3 | 13.1 |
| 1 1 1 | 27.0 | 31.6 | 6 2 2 }  7 1 2 }  4 3 2 } | 14.4 | 16.6 |
| 2 1 1 | 22.7 | 19.9 | | | |
| 3 0 1 | | 8.0 | | | |
| 3 1 1 | 19.7 | 20.6 | 1 0 3 | | 4.6 |
| 4 0 1 | | 1.3 | 2 0 3 }  0 1 3 } | 28.9 | 28.4 |
| 0 2 1 | 16.7 | 14.9 | | | |
| 1 2 1 | 11.0 | 8.9 | 1 1 3 | | 8.5 |
| 4 1 1 }  2 2 1 } | 21.8 | 22.4 | 2 1 3 | 29.3 | 29.4 |
| | | | 3 0 3 | | 0.9 |
| 5 0 1 }  3 2 1 } | 16.0 | 15.1 | 3 1 3 | | 6.5 |
| | | | 4 0 3 | | 3.5 |
| 5 1 1 | 11.6 | 16.6 | 0 2 3 | | 3.1 |
| 4 2 1 | 14.3 | 15.5 | 1 2 3 | 35.7 | 33.5 |
| 6 0 1 | | 4.8 | 4 1 3 }  2 2 3 } | 19.4 | 22.9 |
| 0 3 1 | | 2.2 | | | |
| 1 3 1 | | 0.3 | 5 0 3 }  3 2 3 } | 25.0 | 24.2 |
| 6 1 1 | >0 | 8.8 | | | |
| 2 3 1 | | 1.8 | 5 1 3 | | 6.5 |
| 5 2 1 | | 6.6 | 4 2 3 | | 5.5 |
| 3 3 1 | | 0.3 | 6 0 3 | | 4.6 |
| 7 0 1 | | 4.5 | 0 3 3 | | 9.5 |
| 6 2 1 | >0 | 12.4 | 1 3 3 | | 1.5 |
| 1 0 2 | 16.0 | 14.3 | 6 1 3 | >0 | 14.7 |

[a] The observed structure factors $\sqrt{I_o}$'s were put on the same scale as the $\sqrt{I_c}$ ($= \sqrt{mF_c{}^2}$)'s by setting $\Sigma k\sqrt{I_o} = \Sigma\sqrt{mF_c{}^2}$, where $k$ is the scale factor and $m$ is the multiplicity.    [b] $\sqrt{I_c}$'s of the reflections which overlap on X-ray fiber photographs are $\sqrt{\Sigma mF_c{}^2}$.

poly(propylene sulfide) are given in Table III, compared with the corresponding values for racemic poly(propylene oxide).

The molecular arrangement of poly(propylene sulfide) in the lattice is shown in Figure 4. Cell dimensions of poly(propylene sulfide) and poly(propylene oxide) are given in Table IV. The $a$ and $b$ parameters are very nearly the same for the both polymers; only the $c$ parameters show a large difference. This difference may be primarily due to the difference in the bond lengths (C–O = 1.43 Å; C–S = 1.815 Å). Thus the crystal structure (the cell dimensions, the molecular structure,

and the molecular arrangement) of poly(propylene sulfide) is similar to that of poly(propylene oxide). From this point of view, it may be concluded that poly(propylene sulfide) is the isomorphous crystal of poly(propylene oxide).

The crystal structure and the molecular structure of polythiomethylene,[9] [–CH₂S–]n, which is the first member ($m = 1$) of the polythioethers [–(CH₂)mS–]n ($m = 1, 2, 3, \ldots$), are similar to those of polyoxymeth-

(9) G. A. Carazzolo and G. Valle, *Makromol. Chem.*, **90**, 66 (1966).

TABLE III

INTERNAL ROTATION ANGLES OF POLY(PROPYLENE
SULFIDE) COMPARED WITH THE CORRESPONDING
VALUES OF POLY(PROPYLENE OXIDE)[a]

$$—CH_2—\overset{\tau_1}{CH}—X—\overset{\tau_2}{CH_2}—\overset{\tau_3}{CH}—X—$$
$$\underset{CH_3}{|} \qquad \underset{CH_3}{|}$$
$$X = S \text{ or } O$$
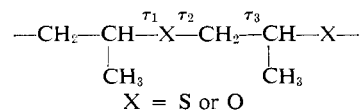
|  | Internal rotation angles, deg | |
|  | Poly-(propylene sulfide) | Poly-(propylene oxide) |
| --- | --- | --- |
| $\tau_1$ (main chain) | 160 | 165 |
| $\tau_1$ (side chain) | 290 | 285 |
| $\tau_2$ | 200 | 195 |
| $\tau_3$ | 180 | 180 |

[a] See ref 3.

TABLE IV

CELL DIMENSIONS OF POLY(PROPYLENE SULFIDE) COMPARED
WITH THOSE OF POLY(PROPYLENE OXIDE)[a]

| Polymers | $a$, Å | $b$, Å | $c$, Å |
| --- | --- | --- | --- |
| Poly(propylene sulfide) | 9.95 | 4.89 | 8.20 |
| Poly(propylene oxide) | 10.46 | 4.66 | 7.03 |

[a] See ref 3.

ylene,[10] while poly(ethylene sulfide),[11] [–CH₂CH₂S–]ₙ, which is the second member ($m = 2$) of the polythioether series, has crystal and molecular structures which differ observably from those of poly(ethylene oxide).[12] It may be noted here that the crystal and molecular structures of poly(propylene sulfide) are similar to those of poly(propylene oxide).

Figure 5 is the electron density projection on (001) plane synthesized with eleven independent *hk*0 reflections.

**Structure of the Racemic Polymer.** As shown in Figure 1, the fiber photographs of the optically active polymer and the racemic polymer are essentially identical.
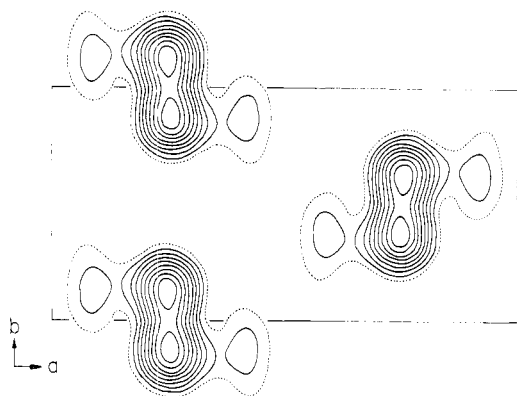


Figure 5. Electron density map projected on (001) plane. Contours are at intervals of 2 e⁻/Å², beginning with the 2 e⁻/Å² contour, which is shown by the broken line.

(10) T. Uchida and H. Tadokoro, *J. Polym. Sci., Part A-2*, **5**, 63 (1967).

(11) Y. Takahashi, H. Tadokoro, and Y. Chatani, *J. Macromol. Sci.*, **B2**, 361 (1968).

(12) H. Tadokoro, Y. Chatani, T. Yoshihara, S. Tahara, and S. Murahashi, *Makromol. Chem.*, **73**, 109 (1964).

Now, as for the structure of the crystalline racemic polymer, four possible models are considered as shown in Figure 6; in (a) an *R*-monomeric unit and an *S*-monomeric unit exist alternately in a molecular chain; in (b) an *R*-polymer chain and an *S*-polymer chain pass through a unit cell; in (c) *R*-polymer chains and *S*-polymer chains exist in a crystallite in a 1:1 statistical ratio; and in (d) each crystallite is composed only of *R*-polymer chains or only of *S*-polymer chains.

Case a is excluded from the X-ray evidence as well as the similarity of the infrared spectra of the isotactic poly(propylene sulfide) and the racemic poly(propylene sulfide) obtained by the KBr-disk method (Figure 7). Case b is excluded in view of the space group (P2₁2₁2₁-D₂⁴) and case c is excluded by the structure factor calculations. These calculations are carried out with the assumption that the "up" molecular chain and the "down" enantiomorphous molecular chain exist with the probability of 1:1 statistical ratio. The methyl groups of both chains take the same position, since methyl groups have a large effect on the packing of the
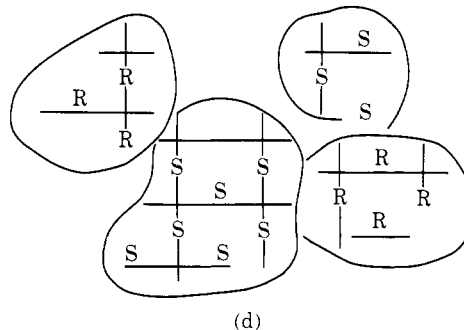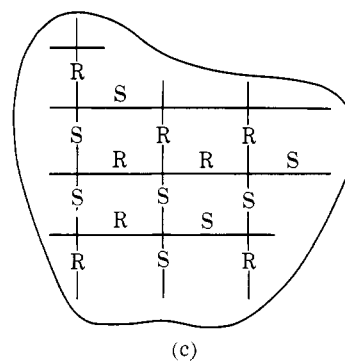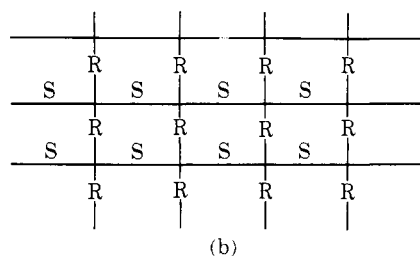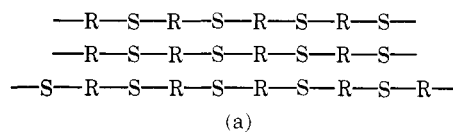


Figure 6. Four possible structural models of the racemic polymer: (a) intramolecular racemization (syndiotactic polymer); (b) racemization in a unit cell; (c) racemization in a crystallite; (d) racemization between crystallites.
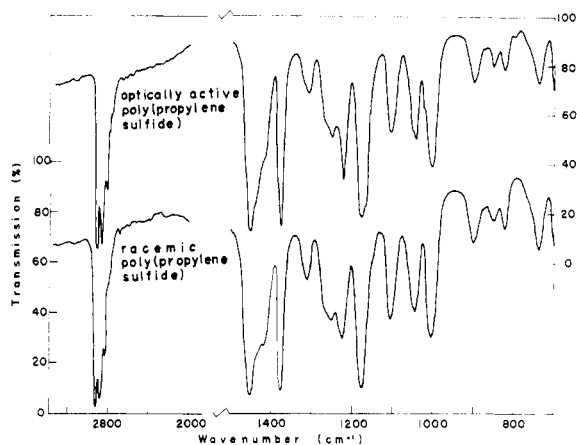
Figure 7. Infrared spectra of the optically active poly-(propylene sulfide) and the racemic poly(propylene sulfide).

molecular chains. This relation between the "up" S-polymer chain and the "down" R-polymer chain is illustrated in Figure 3b and c. Consequently the lattice projection along the c axis of the assumed statistical model is identical with that of the optically active polymer. Accordingly the structure factors of the hk0 reflections are the same as those of the optically active polymer, but the structure factors of the hkl ($l \neq 0$) reflections are observably different from the optically active case and in very poor agreement with the observed data.

From these results, it seems most reasonable to conclude that crystalline racemic poly(propylene sulfide) consists of crystallites composed of R-polymer chains only and of S-polymer chains only.

It would be interesting to establish whether optically active crystallites exist also in the case of racemic poly(propylene oxide).

# Nuclear Magnetic Resonance Studies on the Microstructure of Ethylene Copolymers. III. Solvent Effects on Proton Resonance Spectra of Ethylene–Vinyl Acetate Copolymers[1,2]

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ABSTRACT: Effects of solvent on the proton nmr spectra of ethylene–vinyl acetate (E–VA) copolymers have been investigated. In solutions of benzene and alkylbenzenes the solvent molecules selectively associate with the acetate methyl groups of E–VA dyads. The heats and entropies of complex formation were obtained by analyzing the temperature dependence of the observed spectra. It was found that presence of polar substituent in the aromatic solvent molecules (e.g., halobenzenes and pyridine) precludes the formation of polymer–solvent complex. Moreover, these complexes seem to have a steric dependence since bulky alkylbenzenes impede their formation. For E–VA copolymers containing more than 62.5 mol % of ethylene, the methylene protons of the alkanelike sequences give rise to two resonance peaks in aromatic solution spectra. These peaks can be assigned to the methylene groups of the two types of intramolecular structure, "polymeric" and "monomeric," similar to those observed in the spectra of oligomeric polyethylene. The "polymeric" structure probably arises from intramolecular chain folding.

The utility of solvent effects in high-resolution nmr spectroscopy of polymers has been well recognized. In a systematic study of the solvent effects, Ramey and Messick[3] have demonstrated that proton resonances of the pendant groups in a variety of homopolymers can be resolved into the peaks corresponding to the various stereochemical sequence placements. For some oligomers of polyethylene, it was also possible to identify the two types of intramolecular structure, i.e., "polymeric" and "monomeric" species, from the 1-chloronaphthalene solution spectra.[4] In our earlier work, we utilized the ester proton resonance spectra in appropriate solvents for characterizations of monomer sequence distributions in ethylene–vinyl formate (E–VF) and ethylene–vinyl acetate (E–VA) copolymerizations.[1,2]

Recently, the nmr technique has been applied to investigate the polymer–solvent interactions in solution. By examining the benzene solution spectra of poly(methyl methacrylate) (PMMA) at various temperatures, Nagai and Nishioka were able to deduce the π-complex formation between benzene molecules and the monomer units of the polymer.[5] In addition, the extent of the complexes formed was found to depend on the stereochemical configurations of the monomer units in PMMA.[6]

In this study, proton nmr spectra of E–VA copolymers dissolved in a number of solvents were obtained. From the benzene and alkylbenzene solution spectra, we have deduced the existence of π-complex formation between the copolymer segments and the solvent molecules. Indications of the intramolecular structures in the ethylene sequences of E–VA polymers, similar to

(1) Part I: T. K. Wu, *J. Phys. Chem.*, **73**, 1801 (1969).
(2) Part II: T. K. Wu, to be published.
(3) K. C. Ramey and J. Messick, *J. Polym. Sci., Part A-2*, **4**, 155 (1966).
(4) K.-J. Liu, *ibid., Part A-2*, **5**, 1209 (1967).

(5) M. Nagai and A. Nishioka, *ibid., Part A-1*, **6**, 1655 (1968).
(6) K.-J. Liu, *ibid., Part A-1*, **5**, 1199 (1967).