Structural Study of the Polymerization of 2,3-Dichlorobutadiene in the Thiourea Canal Complex. Structural Change during Canal Polymerization and the Crystal Structure of the Resultant Polymer

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ABSTRACT: The crystal structure of poly(2,3-dichlorobutadiene) obtained by radiation polymerization of the 2,3-dichlorobutadiene–thiourea canal complex was analyzed. The monoclinic cell having the cell dimensions of a = 5.34 Å, b = 9.95 Å, c(fiber axis) = 4.80 Å, β = 93.5°, and the space group $P2_1/a\text{–}C_{2h}{}^5$ contains two monomeric units. The polymer chain has a high content of *trans*-1,4-enchainment, and presents a conformation of $(trans\text{-}S'\text{–}T\text{–}\bar{S}')_n$, where T is *trans*, and S and $\bar{S}$ are clockwise and counterclockwise skew forms, respectively. Poly(2,3-dichlorobutadiene) obtained by radical polymerization has the same crystal structure, but contains a small amount of 1,2-addition. The structural change during the canal complex polymerization was also investigated. The symmetry of the monomer–thiourea and the polymer–thiourea complex crystals deviate from the rhombohedral (D_{3d}) which is usually found for many thiourea complexes. They are monoclinic (C_{2h}) but pseudohexagonal in such a way that the crystal structures are very similar to but slightly deformed from the usual honeycomblike structure of thiourea complexs. Under γ- or X-irradiation the monomers combine with each other in the thiourea canals without destroying the canal structure. The length of canal occupied by one monomer is 6.25 Å (two monomers in the period of the canal) in the monomer–thiourea complex, but is shortened to 4.80 Å in the polymer–thiourea complex. The polymer chain in the canal has the same conformation as that in the polymer crystal.

It is well known that the radiation polymerization of various monomers in urea or thiourea canal complexes gives stereospecific polymers. For example, poly(vinyl chloride) thus obtained was found to be more syndiotactic than usual,[1,2] and poly(2,3-dichlorobutadiene) and poly(2,3-dimethylbutadiene) were reported to be highly 1,4-*trans* tactic.[3,4] However, attention has been paid mainly to the stereospecificities of the resultant polymers, and little is as yet known about the detailed molecular and crystal structures of these polymers. Moreover, crystal structure analyses of such monomer complexes and polymer complexes might offer much useful informations to elucidate such stereospecific polymerizations.

From such a point of view, we are undertaking structural studies on canal complex polymerization. In the present paper, for the sake of convenience, the crystal structure analysis of poly(2,3-dichlorobutadiene) will be presented first, and then the investigation of the structural change during the canal complex polymerization will be reported.

Experimental Section

Samples. Monomer–Thiourea Complex. 2,3-Dichlorobutadiene, which was kindly supplied by Dr. Ryutani of Denki Kagaku Kogyo K.K., was separated from inhibitor by distillation. A mixture of 2 ml of a nearly saturated methanol solution of thiourea and 0.1 ml of 2,3-dichlorobutadiene was kept at −30° for 1 week. The monomer–thiourea complex was obtained as needlelike single crystals of about 5 mm length and of 0.3 mm diameter.

Polymer–Thiourea Complex. The monomer–thiourea complex crystals sealed in glass capillaries with the mother liquid were irradiated by γ-rays from a cobalt 60 source at −78° (total dose 2.4 × 10^6 rads). These crystals kept their original shapes after polymerization.

Uniaxially Oriented Polymer Samples. The needlelike single crystals of the polymer–thiourea complex were washed with boiling methanol to remove thiourea, and by this means the polymer having an uniaxial orientation was obtained (denoted as sample A hereafter). Poly(2,3-dichlorobutadiene) was also obtained by radical polymerization. Uniaxially oriented samples of this polymer were obtained by elongation four times in water at 90–100° (sample B).

X-Ray Diffraction. Monomer–Thiourea Complex. Throughout the present study nickel-filtered Cu Kα radiation (wavelength 1.542 Å) was used. A single crystal was sealed in a thin-walled Lindemann glass capillary without the mother liquid. Figure 1a shows a rotation photograph of the monomer–thiourea complex taken at −50°. In the canal complex the monomer is polymerized by X-rays as well as γ-rays. Therefore we have not yet succeeded in obtaining a precise intensity measurement for the monomer complex.

Polymer–Thiourea Complex. Figure 1b shows a rotation photograph of the polymer–thiourea complex obtained by γ-irradiation of the monomer–thiourea complex. As just mentioned, polymerization occurs by X-rays too. The samples polymerized by X-rays and γ-rays gave the same X-ray patterns.

Oriented Polymer. Both the polymer samples (A and B) gave essentially the same fiber patterns (Figure 1c). Sample A had slightly lower crystallinity than sample B, but showed a better orientation than sample B. We therefore used these two samples in a complementary fashion; the fiber photograph of sample B was used principally for the determination of the cell dimensions, and sample A for the intensity measurement. Measurement of the Bragg angles was calibrated by reference to those of aluminum powder. The reflection intensities of the fiber photographs were recorded with the multiple-film technique using a cylindrical camera.

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(1) I. Sakurada and K. Nanbu, *Kogyo Kagaku Zasshi*, **80**, 307 (1959).

(2) D. M. White, *J. Amer. Chem. Soc.*, **82**, 5678 (1960).

(3) H. Clasen, *Z. Elektrochem.*, **60**, 982 (1956).

(4) J. F. Brown, Jr., and D. M. White, *J. Amer. Chem. Soc.*, **82**, 5671 (1960).

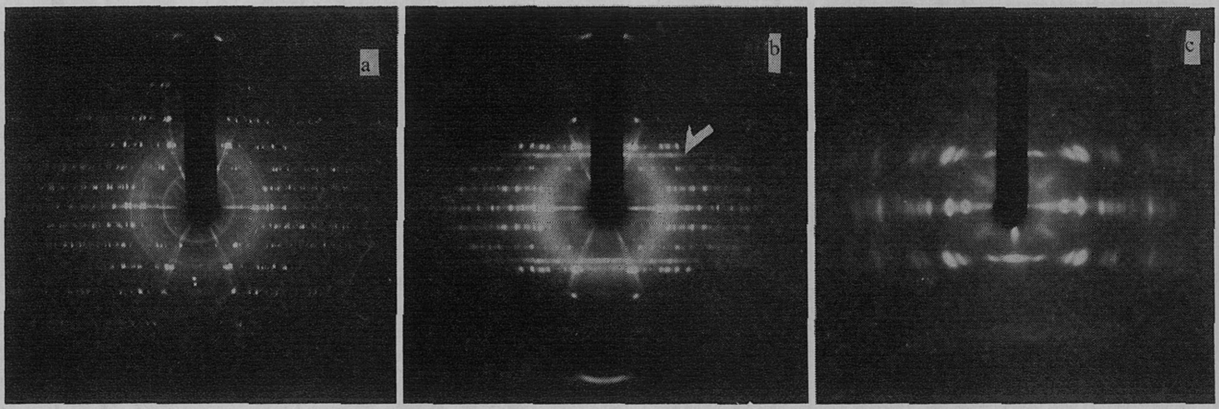

Figure 1. (a) X-Ray rotation photograph of 2,3-dichlorobutadiene–thiourea complex. The rotation axis is the long axis of the needlelike crystal; (b) X-ray rotation photograph of poly(2,3-dichlorobutadiene)–thiourea complex; (c) X-ray fiber phtotograph of poly(2,3-dichlorobutadiene).

In order to record the 00*l* reflections which are located near the meridian, a Weissenberg photograph was taken with the direction perpendicular to the fiber axis as the rotation axis; the 001, 002, 003, and 004 reflections were thus observed. In all, 35 independent reflections were available. Their intensities were estimated visually and corrected for Lorentz and polarization factors.

Structure Determination of Polymer Crystal

Unit Cell and Space Group. All of the reflections in the fiber photograph could be satisfactorily indexed on a monoclinic unit cell having the cell dimensions of a = 5.34 Å, b = 9.95 Å, c(fiber axis) = 4.80 Å, and β = 93.5° (see Table II). The assumption of two monomeric units per unit cell leads to a calculated density of 1.61 g/cm^3, which seems reasonable when compared with the measured density (by the flotation method) of 1.53 g/cm^3. From the systematic absences of the reflections; $h0l$ when h is odd and $0k0$ when k is odd, the space group was determined to be $P2_1/a$–C_{2h}^5.

Chain Conformation and Chain Arrangement. The observed fiber period of poly(2,3-dichlorobutadiene) was found to be 4.80 Å. The infrared spectrum indicated the absence of 1,2- or 1,4-*cis* addition, whereas sample B showed a small content of 1,2-addition. Therefore, it is clear that the polymer obtained by canal complex polymerization is highly 1,4-*trans* tactic, as reported by Brown and White.[4]

The observed fiber period of 4.80 Å is satisfied by the chain conformation

$$\begin{array}{c} -\mathrm{C}-\mathrm{C}-\mathrm{C}{=}\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{C}{=}\mathrm{C}- \\ T\quad S\ \ \textit{trans}\ \ \bar{S}\quad T\quad S\ \ \textit{trans} \end{array}$$

In this representation, T means *trans*, and S and $\bar{S}$ are clockwise and counterclockwise skew forms, respectively. This conformation possesses only two kinds of center of symmetry; one is at the center of the C=C double bond and the other at the center of the C(H$_2$)—C(H$_2$) single bond.

On the other hand, it takes four asymmetric units to give the symmetry of $P2_1/a$, but there can be only two chains in the unit cell. Therefore, each molecular unit should possess one of twofold symmetry: a twofold screw axis, a glide plane, or a center of symmetry. It is apparent that the 1,4-*trans* polymer chain cannot have either a glide plane or a twofold screw axis as its own symmetry element. Only the above model fullfills the space group $P2_1/a$ if the two kinds of center of symmetry of the chain are fixed at centers of symmetry of the unit cell; each molecular unit consists of two asymmetric halves related by the center of symmetry. Accepting this condition, refinement of the structure was accomplished by trial and error procedures in structure factor calculation and a diagonal least-squares method in which the values of $\Sigma(\sqrt{I_o} - \sqrt{I_c})^2$ were minimized. $\sqrt{I}$'s of the reflections which overlap on the fiber photograph are $\sqrt{\Sigma mF^2}$. The utility of a least-squares refinement in polymer structure analysis is not always satisfactory owing to the limited number of observable reflections. But this refinement reduced the reliability factor $R(=\Sigma|\sqrt{I_o} - \sqrt{I_c}|/\Sigma\sqrt{I_o})$ to 0.15 without any conflict in the resultant structure. In structure factor calculation, an isotropic thermal factor was used and the contribution of the hydrogen atoms was ignored. The final atomic coordinates and the coefficient of thermal factors are given in Table I. A tabulation of the calculated and observed structure factors is shown in Table II.

TABLE I
ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	x/a	y/b	z/c	B, Å^2
Cl	0.799	0.637	0.570	11.4
C(H)	0.570	0.513	0.615	9.3
C(H$_2$)	0.560	0.450	0.907	11.4

Result of Structure Analysis of Polymer

Molecular Structure. The molecular chain has *trans*-1,4-enchainment, which has already been reported by Brown and White[4] from the fiber period and the infrared spectrum. The bond lengths, bond angles, and internal rotation angles derived from the final atomic coordinates are shown in Figure 2. No abnormal bond lengths and bond angles are found. All the atoms attached to the double bonded pair of carbon atoms are in a plane. The internal rotation angle about the single bond C—C adjacent to the double bond C=C is 105° (nearly skew form) and that of the single bond C(H$_2$)—C(H$_2$) is exactly 180° (*trans* form), because of the existence of the center of symmetry in the midpoint of the bond. This conformation (*trans*-S'–T–$\bar{S}'$) is

TABLE II
COMPARISON BETWEEN OBSERVED AND CALCULATED SPACINGS AND STRUCTURE FACTORS

hkl	d_o, Å	d_c, Å	$\sqrt{I_o}^a$	$\sqrt{I_c}$
020	5.00	4.98	39.7	35.5
110	4.73	4.70	42.1	43.2
120	3.65	3.64	82.3	81.6
130	2.82	2.82	49.1	50.8
200		2.67		18.2
210	2.57	2.57	27.0	30.4
040	2.47	2.49	28.6	23.8
220	2.34	2.35	29.1	27.6
140	2.26	2.25	26.5	17.6
230	2.08	2.08	23.6	18.0
150	1.87	1.86	11.5	13.6
240	1.82	1.82	44.6	34.6
310	1.75	1.75	20.5	21.6
320 060	1.67	1.67 1.66	21.6	22.3
250 160	1.59	1.59 1.58	29.1	23.4
011	4.29	4.32	24.1	20.6
−111 021	3.45	3.45 3.45	14.0	15.7
111	3.23	3.27	36.6	35.8
−121	2.95	2.96	62.7	59.5
121	2.84	2.84	47.2	37.6
031		2.73		6.9
−131		2.46		3.8
131 −201	2.39	2.39 2.39	24.6	30.0
−211		2.32		1.6
201	2.26	2.27	19.0	20.7
211 041	2.21	2.21 2.21	29.2	33.4
−221		2.15		13.7
221		2.07		4.9
−141		2.06		3.2
141		2.02		5.4
−231		1.94		3.8
231 051	1.84	1.87 1.84	11.0	14.3
−151		1.75		4.9
151 −241	1.72	1.72 1.72	34.1	26.7
−112 022	2.19	2.18 2.16	15.5	19.7
112	2.10	2.09	10.8	16.5
−122	2.05	2.04	10.1	19.1
122 032	1.97	1.96 1.94	18.2	24.1
−132 −202	1.84	1.85 1.84	13.5	16.7
−212 132	1.80	1.81 1.80	15.5	18.8
202 042 −222 212	1.72	1.73 1.73 1.72 1.70	11.5	20.7
001	4.79	4.80	41.2	47.5
002	2.41	2.40	23.2	22.9
003	1.59	1.60	7.1	1.4
004	1.20	1.20	9.2	3.1

[a] $\sqrt{I} = \sqrt{mF^2}$; F is a structure factor, and m is the multiplicity factor for the fiber photograph. $\sqrt{I}$'s of the reflections which overlap on the fiber photograph are $\sqrt{\Sigma mF^2}$.

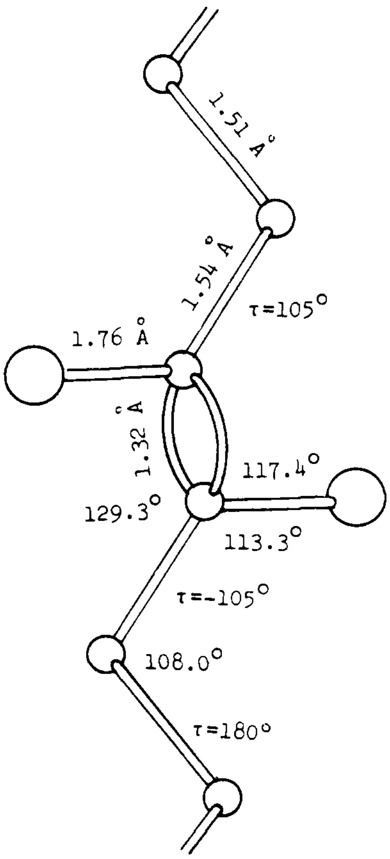

Figure 2. Bond lengths, bond angles, and internal rotation angles of poly(2,3-dichlorobutadiene).

TABLE III
INTERCHAIN ATOMIC DISTANCES

$Cl_2 \cdots Cl_2''$	3.49 Å
$Cl_1 \cdots Cl_2'$	3.56 Å
$Cl_1 \cdots C_2'$	3.83 Å
$Cl_2'' \cdots C_3$	3.91 Å
$Cl_2'' \cdots C_4$	3.96 Å
$Cl_1 \cdots C_3'$	4.29 Å
$Cl_1 \cdots C_1'$	4.32 Å

essentially the same as those of the other *trans*-1,4-diene polymers; polybutadiene,[5,6] β-gutta-percha,[7] polychloroprene,[7] and polypentadiene.[8]

Crystal Structure. In Figure 3 the packing of the molecular chains in the unit cell is shown. The centers of symmetry of the molecular chains coincide with those of the unit cell. The arrangement of the molecular chains side by side is very similar to that found in even-*trans*-polyalkenamers[9] crystallized in the monoclinic form rather than in *trans*-1,4-polybutadiene.[5]

Some short interchain atomic distances are listed in Table III. The molecular chains contact through the Cl · · · Cl or Cl · · · C pairs and there is no direct C · · · C contact. These values are those usually found in the structures of organic compounds.

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[5] S. Iwayanagi, I. Sakurai, T. Sakurai, and T. Seto, *J. Macromol. Sci. Phys*, *B2*, 163 (1968).

[6] G. Natta and P. Corradini, *Angew. Chem.*, **68**, 615 (1956).

[7] C. W. Bunn, *Proc. Roy. Soc., Ser. A*, **180**, 40 (1942).

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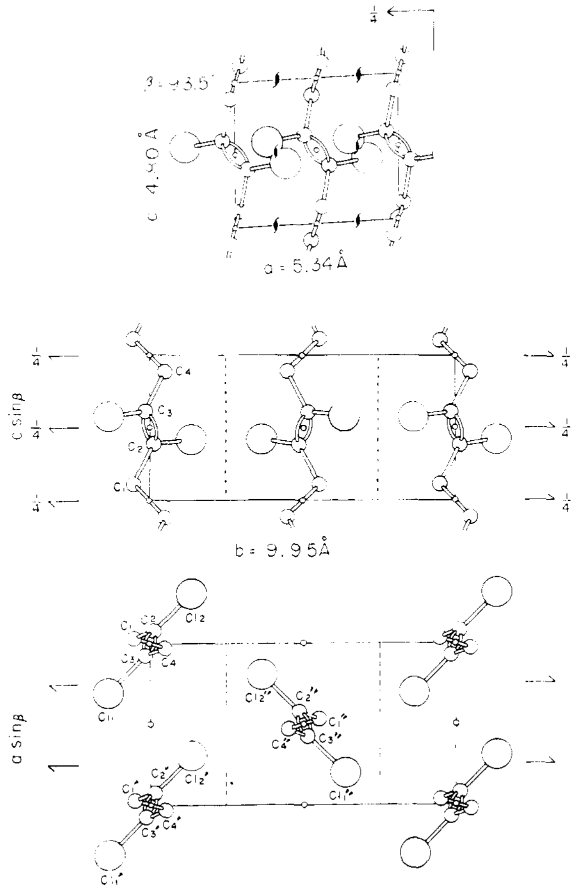

Figure 3. Crystal structure of poly(2,3-dichlorobutadiene).

Another crystalline modification was found when the sample B was stretched at higher temperature than 100°. In this modification the fiber period is the same as that in the structure described here. Therefore it is clear that the two modifications have their origin in difference of the chain arrangement and not of chain conformation. We will report this modification in another paper.

Structure Change by Polymerization

Brown and White[4] have already proposed a model of the thiourea canal complex polymerization. According to them, the guest molecules included in the canals of the thiourea molecules are polymerized along the canal. The case of 2,3-dichlorobutadiene must be the same as this case. Actually, as shown in Figure 1, the irradiation polymerization of the monomer–thiourea complex seems to take place without destroying the canal structure.

It may be desirable, however, to elucidate the detailed structural change in the course of polymerization. Since, unfortunately, the monomer–thiourea complex is unstable at room temperature, and the polymerization occurs under X-rays even at a quite low temperature, say −60°, the crystal structure of the monomer–thiourea complex is still uncertain. However, the Weissenberg photographs of the monomer–thiourea complex and also the polymer–thiourea complex showed that their crystal systems clearly deviate from the D_{3d} symmetry of the well-known rhombohedral structure in the cycloparaffin–thiourea complex analyzed by Lenné.[10] The unit cell of the polymer–thiourea complex could be determined; a = 9.87 Å, b = 15.83 Å, c = 12.53 Å, β = 114.1°, and space group C_{2h}^5–$P2_1/a$. Though the unit cell of the monomer–thiourea complex is not determined, the c period and the ab-projected cell dimensions are the same as those of the polymer–thiourea complex. Therefore the crystal systems of both the complexes are different from D_{3d}.

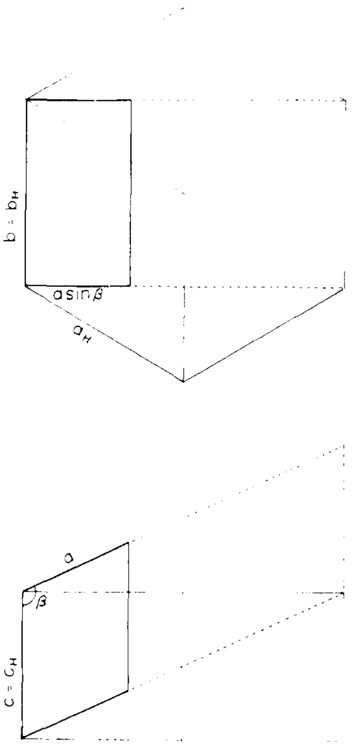

Figure 4. Transformation of the hexagonal cell to the monoclinic cell.

However, from the plane distances and diffraction intensities, both the canal complexes with the monomer and the polymer might have structures similar to that of the honeycomblike thiourea complex with cycloparaffins. That is, the present monoclinic cell and the rhombohedral cell in hexagonal setting can be transformed into each other by the relation

$$\vec{a} = 2/3\vec{a}_{\mathrm{H}} + 1/3\vec{b}_{\mathrm{H}} + 1/3\vec{c}_{\mathrm{H}}$$
$$\vec{b} = \vec{b}_{\mathrm{H}}$$
$$\vec{c} = \vec{c}_{\mathrm{H}}$$

The rhombohedral cell (a_{H} = 15.8 Å, c_{H} = 12.5 Å in hexagonal setting[10]) can be transformed into a monoclinic cell having the cell dimensions of a = 10.0 Å, b = 15.8 Å, c = 12.5 Å, and β = 114.5°. The relation between both the cells is shown in Figure 4. The same situation was found in the case of squalene–thiourea complex,[11] in which the monoclinic cell dimensions are a = 10.14 Å, b = 15.72 Å, c = 12.72 Å, and β = 115°.

In Figure 5 is shown the (hk0) two-dimensional Patterson map of the polymer–thiourea complex. From this map, it is clear that the canal structure of the

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(10) H. U. Lenné, *Acta Crystallogr.*, 7, 1 (1954).

(11) N. Nicolaides and F. Laves, *Z. Kristallogr.*, **121**, 283 (1965).

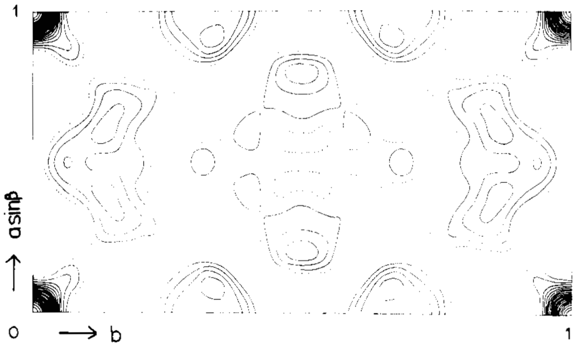

Figure 5. (*hk*0) Patterson map of the polymer–thiourea complex.

thiourea molecules is essentially the honeycomblike structure. The Patterson map, however, suggests that the canal structure is deformed slightly from the exact hexagonal form, and that in the canal the polymer chain does not orient randomly but specifically about the *c* axis (the chain direction). We suppose that this is the reason why the crystal system of the complex is not rhombohedral but monoclinic. The present unit cell thus contains twelve thiourea molecules. The detailed crystal structure analysis is now going on and will be reported soon later.

Upon consideration of many thiourea canal complexes[10,12] and the present polymer–thiourea complex, we assert that if the ratio of the *c* length and the length of the canal occupied by the guest molecule (or monomeric unit in the case of chain polymer) is irrational, there must appear layer lines not corresponding to the *c* length of the canal. Particularly in the present case, the guest molecule contains chlorine atoms having an appreciable X-ray scattering power. However, the monomer–thiourea complex does not show such a layer line. Therefore in the present monomer–thiourea complex, the ratio must be rational. On the other hand, from an elementary analysis of the complex, the mole ratio of the thiourea and the monomer was found to be 3.12, deviating slightly from a rational value of 3.0. The discrepancy might be caused by the fact that the complex is unstable at room temperature. In any case, from the X-ray diffraction and the elementary analysis, one can conclude that the mole ratio is 3.0. This means two monomers occupy the *c* period of 12.5 Å along the canal, *i.e.*, 6.25 Å per monomer. In the case of 2,3-dimethylbutadiene,[4] the length of canal occupied by one monomer was estimated to be 5.72 Å from the elementary analysis data alone. But according to our preliminary X-ray study, the case of 2,3-dimethylbutadiene is entirely similar to case of 2,3-dichlorobutadiene; the crystal system is monoclinic and the canal length occupied by one monomer is 6.25 Å.

As the polymerization proceeds, the X-ray photograph of the monomer–thiourea complex gives rise to the two continuous scatterings which lie parallel to the layer lines but do not correspond to the *c* length of the canal. They are shown by arrows in Figure 1b. The intensities of these streaks are proportional to the polymer yield. Therefore, these streaks can be attributed to the resultant polymer chains which behave as a system of linear gratings regularly arranged in the *xy* plane but with random *z* coordinates. Several crystals of different preparations have X-ray photographs having, in addition to the continuous lines, discrete reflections. These reflections must be attributed to some sort of interrelation between the polymer chains in adjacent canals.

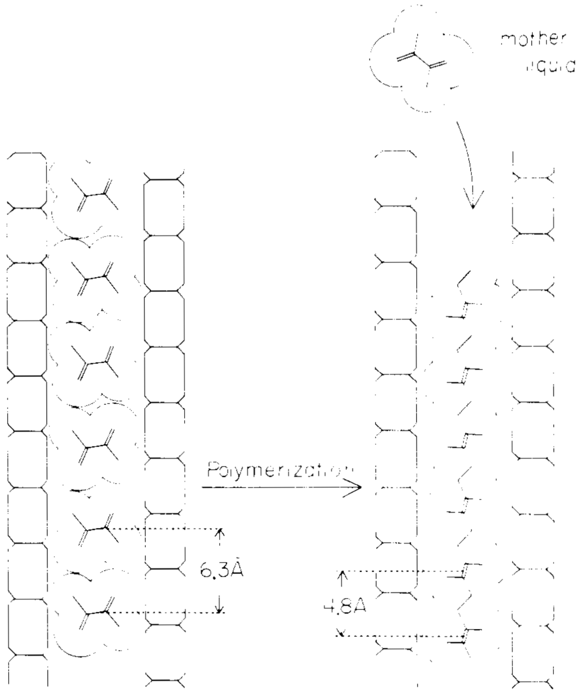

Figure 6. Schematical representation of the thiourea cana-
complex polymerization of 2,3-dichlorobutadiene. Oriental
tions of monomers are not defined and tentatively shown.

The identity period derived from these layer lines, 4.80 Å, implies the period of the resultant polymer chain in the direction of the canal axis, and this identity period coincides with the fiber period of the polymer crystal obtained from the canal complex after removal of thiourea. Therefore, it could be said that the polymer chain in the thiourea canal has the same conformation as the structure described in the present paper. The cross section of the polymer chain having such a conformation is about 7.6 Å × 5.0 Å, including the van der Waals' radii. The usual thiourea canal of the rhombohedral system is known to be able to include guest molecules having diameters of up to 7.0 Å. Therefore, the deformation of the honeycomblike canal of the present case might be again supported from this geometrical viewpoint.

From these facts above mentioned, it must be concluded that polymerization in the canal is accomplished by a shortening of 1.45 Å (from 6.25 Å to 4.80 Å) per monomer. From the X-ray diffraction of the polymer–thiourea complex, the mole ratio of thiourea and the monomeric unit of polymer was calculated to be 2.32, if one infinite polymer chain without end groups occupies each canal. From the elementary analysis, the corresponding value was 2.65 (*cf.* in the case of the monomer–thiourea complex, the corresponding value is 3.0). In any event, such a shortening must introduce some vacancies in the canals. Nevertheless, the polymer–thiourea complex is quite stable at room temperature. This may be due to the fact that the guest

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(12) H. U. Lenné, *Z. Kristallogr.*, **118**, 439 (1963).

molecule in the present case is the long chain molecule and that the vacancy effect is compensated by a maintenance force of surrounding regular canals, or any monomer in the mother liquid immersed in the canals filling the vacancies and participating in the polymerization. It may be supposed that this is one of the reasons why the mole ratios in the monomer–thiourea complex and the polymer–thiourea complex are not in accord. A schematic representation of the polymerization is shown in Figure 6.

It is an interesting subject for future study to correlate the structures of the thiourea complexes with the monomer and the polymer. Structural studies along this line may be able to elucidate characteristics of many stereospecific polymerizations in urea or thiourea canal complexes.

Model Butadiene Polymerizations. I. An Investigation of 2:1 and 1:1 Ratios of *sec*-Butyllithium to Butadiene

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ABSTRACT: The reaction of *sec*-butyllithium with 1,3-butadiene in 1:1 or 2:1 molar ratios produced principally monolithio- and dilithiooctenes along with small amounts of 3,8-dimethyldecane, 3,4,7-trimethylnonane, and butadiene oligomers. Hydrolysis of the product mixture produced the corresponding olefins and alkanes from the lithio compounds. The relative amounts of 1- and 2-olefins produced from the lithiooctene were dependent on hydrolysis conditions. Further reaction of the octenyllithium adduct with *sec*-butyllithium also gave product distributions dependent upon hydrolysis conditions and led to the conclusion that the lithiooctene adduct was an allylic complex (B in Scheme I). The nuclear magnetic resonance spectrum of the monolithiooctenes in cyclohexane and perdeuteriobenzene supported the proposal of an allylic-type complex. The lithio product mixture was also hydrolyzed with D_2O and the deuterium-labeled positions and compounds were identified by glc–mass, infrared, and nuclear magnetic resonance. Dideuteriooctenes were observed which indicated that metallation of the octenyllithium complex occurred.

The steric course of the polymerization of 1,3-butadiene by alkyllithium has been thoroughly studied. The amount of pendant vinyl unsaturation is affected by polar additives, temperature, and concentration of the alkyllithium initiator, but unaffected by the organic moiety of the alkyllithium.[1] The course of the butadiene addition reactions as affected by experimental conditions has been previously determined by characterization of the resulting butadiene polymers or oligomers and necessarily has been related to the polymer or oligomer macrostructure.[2] In the current studies, the emphasis of reaction conditions *vs.* structure is placed upon the resulting microstructure through specific identification of reaction products and sequence distributions in oligomers. The products from a 1:1 and 2:1 molar ratio of *sec*-butyllithium and 1,3-butadiene have been characterized in this manner. The sequence distributions of oligomers formed from 1:2 and 1:3 product ratio are reported in parts II and III of this series.[3,4] By an extensive examination of the initiation, early propagation, and termination reactions of 1,3-butadiene and *sec*-butyllithium, we have obtained information concerning the mechanism of polymerization *vs.* incipient structure.

Experimental Section

The 1:1 and 2:1 reaction of *sec*-butyllithium and 1,3-butadiene were conducted in both polar and nonpolar media and for periods of time that depended upon depletion of the alkyllithium. The lithioolefins that formed precipitated slowly at 25° and quite rapidly at elevated temperatures. *sec*-Butyllithium was used instead of *n*-butyllithium because of a larger rate of initiation with butadiene which would minimize polymer or oligomer formation.[5] After hydrolysis of the product mixtures with water or deuterium oxide, the products were separated by preparative gas chromatography and identified by infrared, nuclear magnetic resonance, and mass spectrometry. A Perkin-Elmer Model 900 with flame ionization detector and a Silicone GE-Versilube F-50 liquid phase 150 ft × 0.01 in. i.d. column was used for the glpc measurements. Nuclear magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer (at 60 MHz). A Perkin-Elmer Model 21 spectrometer was used for the infrared investigations. Mass spectra were obtained on a combination Perkin-Elmer F-11 glpc–cec Model 21-130 mass spectrometer.

Butadiene was Phillips Special Purity dried by vapor phase passage through a 3-ft activated alumina column at 50°. Tetrahydrofuran was Eastman White Label dried at room temperature over 4A molecular sieves and stored under nitrogen. The *sec*-butyllithium was purchased as 1.4 *N* cyclohexane solutions from Foote Mineral. Solvent standards were obtained by hydrolysis of the alkyllithium solutions followed by the same separation and drying procedure used for the various reaction mixtures.

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