$$\frac{\langle r^2\rangle_0^{1/2}}{M^{1/2}} \times 10^3 \simeq 700$$

For $M = 11{,}000$, $r_0 \sim 74$ Å. If we assume that the molecules extend over a region of about twice r_0, then the upper limit of the domain diameter is about 300 Å. The diameter of the domain calculated from the chord length through the styrene phase is well within this limit.

Electron micrographs have also shown that in some instances S–B–S block copolymers have a regular hexagonal arrangement. Extrapolating from the electron microscopic work on the very thin film, it is very tempting to assume that this regular array of domains is also the structure of the bulk copolymer. Lewis, *et al.*,[5] and McIntyre, *et al.*,[4] have indeed proposed a macrolattice structure of polystyrene domains from SAXS studies on the S–B–S block copolymer. In their analyses of the scattering data, they have both assumed that intensity maxima correspond to the maxima of the interparticle interference function. As pointed out, this is true only for perfect crystals and does not apply to a fluid or amorphous polymer, since "the position of intensity maxima depends in a very complex way on the structure of the arrangement of the particles and on the particular structure of each particle."[21] So before we can use the analyses of Lewis, *et al.*, and McIntyre, *et al.*, we have to establish by independent means that a three-dimensional superlattice is the structure of S–B–S block copolymer.

It has, however, been shown that this block copolymer does have a structural regularity of styrene domains when processed in a certain way. With an extruded rod of S–B–S block copolymer, Keller, *et al.*,[22] have observed a single-crystal pattern of hexagonal structure when the X-ray beam is parallel to the extrusion direction. They concluded that these patterns were caused by the hexagonal packing of very long cylinders lying parallel to the extrusion direction. But the existence of such remarkable ordering phenomena in the bulk state of an S–B–S block copolymer in which no orientation was induced has yet to be proved.

Acknowledgments. The author wishes to thank Professor H. Brumberger for his critical comments and Professor O. Kratky who kindly provided a polyethylene standard sample. He is also grateful to the management of Esso Research and Engineering Company for permission to publish this work.

(21) Reference 10, p 114.

(22) A. Keller, E. Pedemonte, and F. M. Willmonth, *Kolloid-Z. Z. Polym.*, **238**, 387 (1970).

Structural Evidence of Radiation-Induced Thiourea Canal Polymerization of 2,3-Disubstituted 1,3-Butadienes

Yozo Chatani* and Sadao Nakatani

Department of Polymer Science, Faculty of Science, Osaka University,
Toyonaka, Osaka, 560, Japan. *Received April 3, 1972*

ABSTRACT: The highly 1,4-trans tactic polymerization of 2,3-dichloro-1,3-butadiene and 2,3-dimethyl-1,3-butadiene in thiourea canals by γ irradiation is supported by structural evidence based upon crystal structure analyses of the monomer–thiourea complexes, the polymer–thiourea complexes, and the resultant polymers for both the dienes. The canal polymerizations of both the dienes are analogous to each other from a structural viewpoint. The monomer–thiourea complexes are stoichiometric compounds; the mole ratio of thiourea and the monomers is 3:1. In other words, two monomers occupy the canal period of 12.5 Å. The monomers are included in the thiourea canals, which are evidently deformed from the well-known honeycomb-like hexagonal prisms. The crystals have monoclinic symmetry $P2_1/a$. The deformation of the thiourea canals is attributed to the molecular shape, size, and packing mode of the guest molecules. The packing modes of the monomers and the deformed canals are favorable for 1,4-trans tactic polymerization, and polymerization in the canals can be performed with only a slight change of the canal shape and size. The resultant polymer–thiourea complexes are nonstoichiometric compounds, but the space group is again $P2_1/a$ as in the monomer complexes. The 1,4-trans tactic polymer chains in the canals take a nearly T-S-trans-$\bar{\text{S}}$ conformation (T, trans; S and $\bar{\text{S}}$, clockwise and counterclockwise skew forms, respectively), the identity period of which is 4.80 Å.

Radiation-induced polymerization of various monomer–urea or monomer–thiourea complexes is very attractive as a unique polymerization method.[1–4] Presumably, monomers polymerize in urea or thiourea canals subject to a spatial control which may be different from steric controls by catalysts. But it is still not beyond the stage of speculation as to what the structures of the complexes are and why a special control for polymerization is possible. It should be noted that urea was reported to form molecular complexes, such as urea–oxalic acid,[5] urea–dioxane,[6] and urea–poly(ethylene oxide),[7] with entirely different structures from the well-known hexagonal canal structures of *n*-hydrocarbon–urea complexes.[8] Unfortunately, most monomer–urea or monomer–thiourea complexes which are important in polymer chemistry are unstable or do not exist at room temperature, and this seems to have prevented detailed study of this

---

(1) H. Clasen, *Z. Elektochem.*, **60**, 982 (1956).

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

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

(4) D. M. White, *ibid.*, **82**, 5678 (1960).

(5) J. H. Sturdivant, A. Schuch, and L. L. Merrit, Jr., American Crystallographic Association Meeting, Pennsylvania State University, 1950.

(6) O. Redlich, C. M. Gable, A. K. Dunlop, and R. W. Millar, *J. Amer. Chem. Soc.*, **72**, 4153 (1950).

(7) H. Tadokoro, Y. Yoshihara, Y. Chatani, and S. Murahashi, *J. Polym. Sci., Part B*, **2**, 363 (1964).

(8) A. E. Smith, *Acta Crystallogr.*, **5**, 224 (1952).

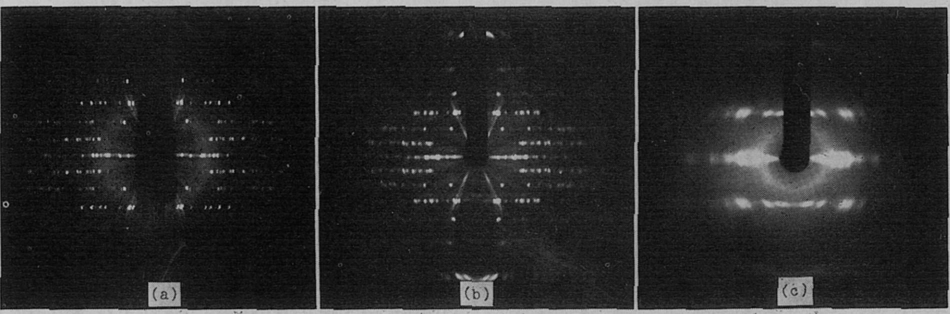


Figure 1. (a) X-Ray rotation photograph of 2,3-dimethylbutadiene–thiourea complex. The rotation axis is the long axis of the needlelike crystal. (b) X-Ray rotation photograph of poly(2,3-dimethylbutadiene)–thiourea complex. (c) X-Ray fiber photograph of poly(2,3-dimethylbutadiene after removing thiourea from the single crystal of the poly(2,3-dimethylbutadiene)–thiourea complex. The halo in Figure 1a is originated from the glass capillary and not from the sample.

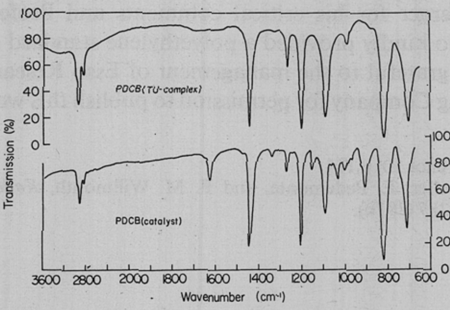


Figure 2. Infrared spectra of poly(2,3-dichlorobutadiene) obtained by canal polymerization (top) and by a radical polymerization with azobisisobuthyronitrile catalyst (bottom).

problem. We have been aiming to elucidate the specificity of polymerization of some urea– or thiourea–monomer complexes from a structural viewpoint, and it has become clear that the structures of the complexes and hence the details of the mode of polymerization are by no means uniform but are peculiar to each monomer.

In a previous paper[9] we reported preliminarily that single crystals of 2,3-dichloro-1,3-butadiene–thiourea complex are transformed into single crystals of poly(2,3-dichlorobutadiene)–thiourea complex by γ irradiation, and that the polymer chains aggregated to form uniaxially oriented crystalline fibers upon removing the thiourea with boiling methanol. Furthermore, the X-ray crystal structure analysis showed that the resultant polymer had a highly 1,4-trans tactic configuration. The present paper is concerned with the detailed structural evidence for the specificity of thiourea canal polymerization of two 2,3-disubstituted 1,3-butadienes, *i.e.*, 2,3-dichloro-1,3-butadiene and 2,3-dimethyl-1,3-butadiene, based upon the structures of the complexes.

Experimental Section

Sample. For precise analysis of the crystal structures and the structural study of the polymerization, single crystals are necessary. In a previous paper[9] the methods of preparation of (1) single crystals of the monomer–thiourea complex, (2) single crystals of the polymer–thiourea complex, and (3) uniaxially oriented polymer samples from the single crystals of the polymer–thiourea complex were reported for 2,3-dichlorobutadiene. The same procedures were applied in the case of 2,3-dimethylbutadiene. Both the monomer–thiourea complexes were grown as needle crystals from each methanol solution at −30°. Radiation polymerization of the single crystals of the monomer–thiourea complexes was carried out at −78° using γ rays from a cobalt-60 source of the radiation laboratory of this university. Irradiation dose rate and total doses were 1×10^5–2.5×10^5 rads/hr and 2.5×10^6–5.0×10^6 rads, respectively.

X-Ray Diffraction. Throughout the present study, Cu Kα radiation was used. Single crystals used for X-ray diffraction were 0.2–0.3 mm in diameter and 5–10 mm in length. Diffraction intensities of the monomer–thiourea and polymer–thiourea complexes were taken by using Weissenberg photographs and were visually estimated by comparison with a standard intensity scale for layer lines of l = 0–3. The monomer–thiourea complexes are not stable at room temperature and so X-ray diffraction photographs were taken at −100° for 2,3-dichlorobutadiene and −120° for 2,3-dimethylbutadiene. Single crystals were exchanged for new ones for each layer line. Under such conditions polymerization by X-rays was substantially suppressed during exposure of the X-ray photograph for intensity measurements. It should be mentioned that the monomer–thiourea complexes and hence the polymer–thiourea complexes, especially in the case of 2,3-dichlorobutadiene, appeared sometimes as twin crystals. Therefore, samples free of twinning were chosen.

The fiber photographs of the resultant polymers obtained by removal of thiourea were taken by a cylindrical camera. Figure 1a–c shows the rotation photographs of the monomer–thiourea complex, the polymer–thiourea complex, and the fiber photograph, respectively, of the polymer of 2,3-dimethylbutadiene. The corresponding photographs for 2,3-dichlorobutadiene were reported previously.[9]

Small-angle X-ray diffraction photographs of the single crystal of the poly(2,3-dichlorobutadiene)–thiourea complex in rotation about the needle axis and the resultant uniaxially oriented polymer sample were taken with a camera distance of 22.5 cm.

Infrared Spectra of Polymers. Because of the lack of a suitable solvent for casting (only soluble in hot tetralin), films of polymer samples for infrared measurement were prepared by hot rolling the needlelike polymer samples at 80°. The films of polymers thus obtained had dimensions of about 2 × 8 mm and 20–30-μ thickness, so the infrared spectra were measured with a Hitachi EPI 2 microscopic spectrometer.

Structural Specificity of Polymerization and Structures of Polymers

With respect to the process of polymerization and polymer crystallization, the following characteristic features were found. (1) Polymerization occurs in single crystals of the monomer–thiourea complex whether the crystals exist with or without the mother liquid, provided that polymerization of free monomer in the mother liquid is prevented. (2) Polymerization in the complex crystals takes place even if an inhibitor (*N*-nitrosomethylaniline and *p*-*tert*-butylcatechol) is present in the mother liquid. (3) Polymerization takes place without destroying the original single-crystal habit. This

---

[9] Y. Chatani, S. Nakatani, and H. Tadokoro, *Macromolecules*, 3, 481 (1970).

TABLE I
CRYSTALLOGRAPHIC DATA[a]

	DCB–TU complex	PDCB–TU complex	DMB–TU complex	PDMB–TU complex	Cyclohexane–TU complex	
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Trigonal	
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$R\bar{3}c$	
Cell dimensions, Å	$a = 9.8$	$a = 9.91$	$a = 9.61$	$a = 10.40$	$a_h = b_h = 15.8$	$(a = 10.0)$[b]
	$b = 15.9$	$b = 15.85$	$b = 15.54$	$b = 15.47$	$c_h = 12.5$	$(b = 15.8)$
	$c = 12.5$	$c = 12.5$	$c = 12.6$	$c = 12.5$		$(c = 12.5)$
	$\beta = 114°$	$\beta = 114.1°$	$\beta = 114.0°$	$\beta = 114.4°$		$(\beta = 114.5°)$
	(at −100°)		(at −120°)			
No. of molecules per unit cell						
Host	12	12	12	12	18	(12)
Guest	4	5.2[c]	4	5.2[c]	6	(4)
Calculated density, g/cm³	1.31	1.44[c]	1.20	1.22[c]	1.36	

[a] DCB, 2,3-dichlorobutadiene; PDCB, poly(2,3-dichlorobutadiene); DMB, 2,3-dimethylbutadiene; PDMB, poly(2,3-dimethylbutadiene); TU, thiourea. [b] Unit cell dimensions expressed by the monoclinic system. [c] Ideal values satisfied when the canals are filled with polymer chains of infinite length; see text.

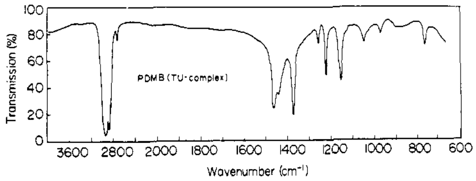


Figure 3. Infrared spectrum of poly(2,3-dimethylbutadiene) obtained by canal polymerization.

feature was examined by X-ray diffraction. (4) When single crystals of the polymer–thiourea complexes were washed with boiling methanol to remove thiourea, the polymer chains aggregated to form uniaxially oriented crystalline fibers.

Brown and White[3] have already suggested that poly(2,3-dichlorobutadiene) and poly(2,3-dimethylbutadiene) obtained by canal polymerization are highly 1,4-trans tactic, as deduced from infrared spectra and fiber identity periods in X-ray photographs. Figure 2 shows infrared spectra of two samples of poly(2,3-dichlorobutadiene). The polymer obtained by radical polymerization shows 910- and 1650-cm⁻¹ bands which are characteristic of 1,2 addition, while no such bands appear for the polymer prepared by canal polymerization. Figure 3 shows the infrared spectrum of poly(2,3-dimethylbutadiene) prepared by canal polymerization. Comparison with the spectra of polymers obtained by an anionic[10] or a Ziegler-type catalyst[11] shows that the 1620- and 890-cm⁻¹ bands for 1,2 addition and the 1200-cm⁻¹ band for 1,4-cis addition have disappeared in the spectrum of the polymer prepared by canal polymerization. The X-ray crystal structure analysis of poly(2,3-dichlorobutadiene)[9] revealed that the molecular structure was 1,4-trans tactic and that the conformation was a sequence of nearly T-S-trans-$\bar{S}$, as shown in Figure 4, where T means *trans* and S and $\bar{S}$ are the clockwise and counterclockwise skew forms, respectively. Poly(2,3-dichlorobutadiene) and poly(2,3-dimethylbutadiene) obtained by canal polymerization and crystallization as mentioned above are different in crystal structure; the former is monoclinic ($a = 5.34$, $b = 9.95$, c (fiber axis) $= 4.80$ Å, $\beta = 93.5°$, $P2_1/a$, two chains per unit cell), and the latter orthorhombic ($a = 9.13$, $b = 13.00$, c (fiber axis) $= 4.70$ Å, $Pna2_1$, four chains per unit cell).[12] Nevertheless, the molecular conformations are essentially the same except for a minor difference in fiber period. Recently, however, poly(2,3-dichlorobutadiene) subjected to hot rolling above 100° was found to form another crystal modification which is isomorphous to that of poly(2,3-dimethylbutadiene), *i.e.*, $a = 8.81$, $b = 12.34$, c (fiber axis) $= 4.80$ A, $Pna2_1$, four chains per unit cell.[12]

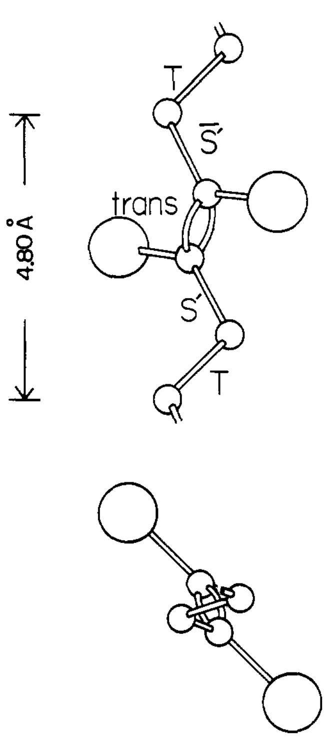


Figure 4. Molecular conformation of poly(2,3-disubstituted butadienes): T, trans; S′ and $\bar{S}'$; nearly clockwise and counterclockwise skew forms, respectively.

Structures of Complexes

Unit Cell and Space Group. Unit cell dimensions, space group, and mole ratio of host (thiourea) and guest (monomer or monomeric unit) in the monomer–thiourea and polymer–thiourea complexes for both the dienes are tabulated in Table

---

(10) H. Yuki, Y. Okamoto, and H. Takano, *Polym. J.*, **2**, 663 (1971).
(11) T. F. Yen, *J. Polym. Sci.*, **38**, 272 (1959).
(12) Y. Chatani, manuscript in preparation.

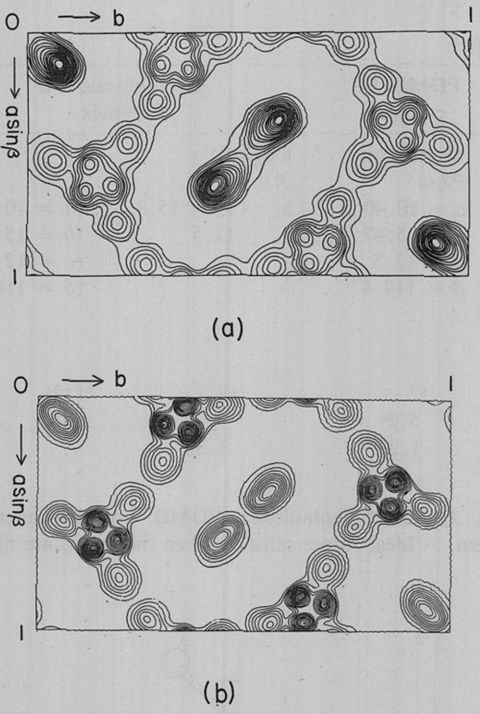


Figure 5. Fourier projection along the canal axis: (a) 2,3-dichlorobutadiene–thiourea complex, (b) 2,3-dimethylbutadiene–thiourea complex. Contours are drawn at 4, 6, 8, ... e Å^{-2}.

I. The cyclohexane–thiourea complex,[13] which is the well-known honeycomb-like canal structure of a trigonal system, is also shown as a reference. Both the monomer– and polymer–thiourea complexes belong to the monoclinic system. But as already mentioned in a previous paper,[9] these monoclinic cells and the trigonal cell in a hexagonal setting can be transformed approximately into each other by the relations

$$a \approx 2/3a_{\mathrm{h}} + 1/3b_{\mathrm{h}} - 1/3c_{\mathrm{h}}$$

$$b \approx b_{\mathrm{h}}$$

$$c \approx -c_{\mathrm{h}}$$

The values in parentheses for the cyclohexane–thiourea complex in Table I are cell dimensions represented tentatively by the monoclinic system. The cell dimensions of these complexes are, however, slightly different from each other, reflecting the shapes and sizes of guest molecules. From systematic absences of reflections, the space groups of all the complexes are uniquely determined to be $P2_1/a\text{-}C_{2h}{}^5$. The mole ratios of host and guest molecules were decided by X-ray crystal structure analyses, as shown later in this paper. It is noteworthy that the mole ratio estimated by weighing or elementary analysis of polycrysalline samples is not always reproducible, and it is concluded that this leads to erroneous conclusions because of incompleteness of complex formation, escape of guest molecules, and specific surface effects of fine crystallites.

Crystal Structures of Monomer–Thiourea Complexes. We suggested from (*hk*0) Patterson synthesis of the poly(2,3-dichlorobutadiene)–thiourea complex that the gross canal structure of the thiourea molecules is essentially the honeycomb-like structure, which is deformed from a regular hexagonal prism, and that the polymer chains in the canals orient in a definite fashion about the canal axis (*c* axis).[9] Such information was confirmed and refined by Fourier syntheses and subsequent least-squares method for these complexes. The results are presented here.

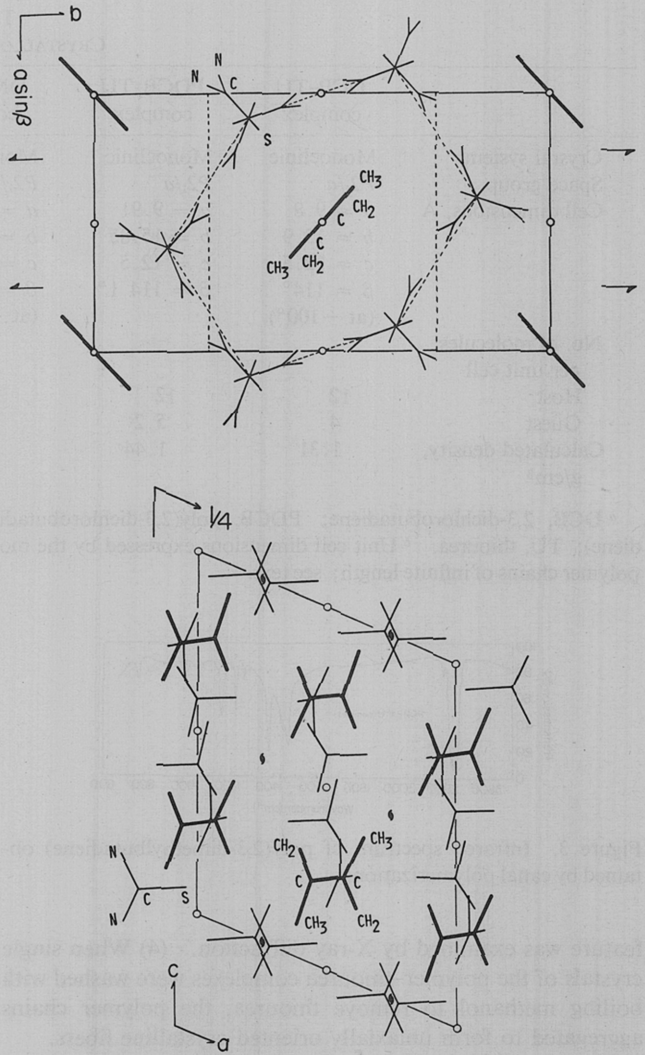


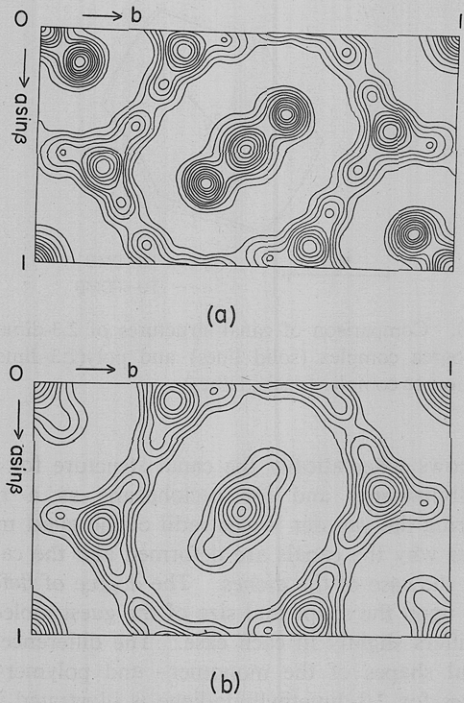
Figure 6. End and side views of the crystal structure of 2,3-dimethylbutadiene–thiourea complex. Thick lines indicate monomers.

Figure 5 shows the Fourier projections along the canal axis of the 2,3-dichlorobutadiene– and 2,3-dimethylbutadiene–thiourea complexes. Figure 6 shows the crystal structure of the 2,3-dimethylbutadiene–thiourea complex. In both the cases the canal structures of the thiourea molecules and arrangements of monomers are quite analogous. The canal sections are deformed from a regular hexagon. Moreover, the monomers orient in a definite fashion in the canals; a possibility of time- or space-averaged rotational disorder about the canal axis is entirely ruled out. The lengths of three diagonal lines in the canal cross section (between one corner and the opposite corner, which are defined by the intersecting points of three C–S bonds in the end view) are 11.6, 10.7, and 8.7 Å for the case of 2,3-dimethylbutadiene, while the lengths of the canal edges in the end view are almost equal at 5.20–5.30 Å. In more detail, however, four out of six of the canal walls of the thiourea complex are considerably bent, *i.e.*, in the end view the C–S bonds do not lie on straight edges of the canal walls. This can be seen in Figure 6 (top) and more clearly in Figure 9.

The intervals of the thiourea molecules along the canal axis are almost equal and equal to 1/6*c*, as is also true for the

---

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



(a)

(b)

Figure 7. Fourier projection along the canal axis: (a) poly(2,3-dichlorobutadiene)–thiourea complex, (b) poly(2,3-dimethylbutadiene)–thiourea complex. Contours are drawn at 4, 6, 8 . . . e Å^{-2}

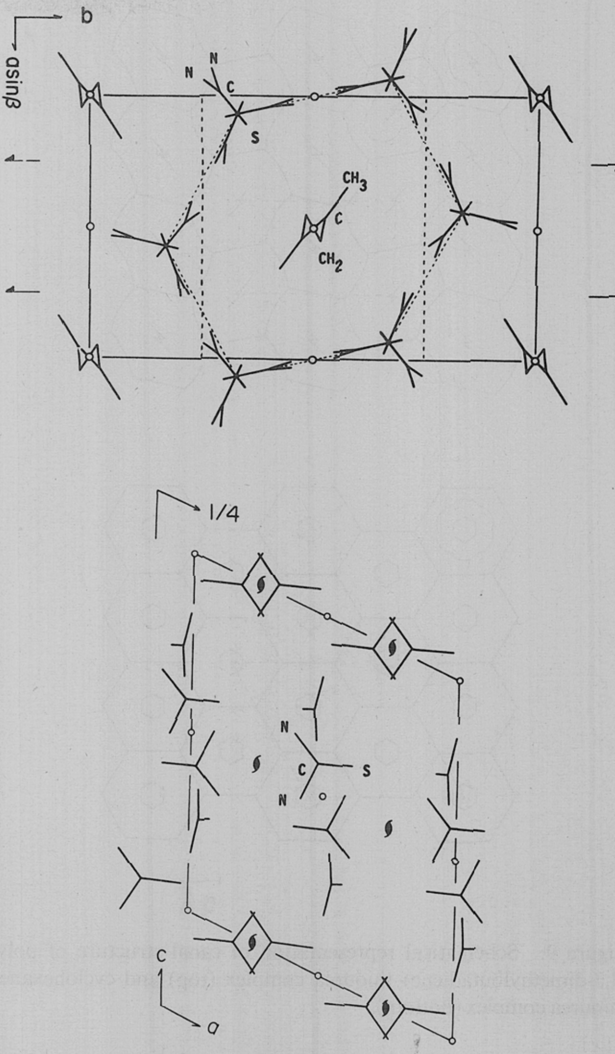


Figure 8. End and side views of the crystal structure of poly(2,3-dimethylbutadiene)–thiourea complex. Polymer chains in the side view are omitted as shown in the text.

cyclohexane–thiourea complex. As a result, the intermolecular $N\cdots S$ distances range from 3.25 to 3.51 Å and average to 3.37 Å for the 2,3-dimethylbutadiene–thiourea complex (*cf.* 3.32 and 3.48 Å in the cyclohexane–thiourea complex, and 3.42 and 3.51 Å in the thiourea crystal[14]).

There are two monomers related by a center of symmetry in the canal period of 12.5 Å; *i.e.*, one monomer occupies a length of 6.25 Å. Accordingly, both the monomer–thiourea complexes are stoichiometric compounds; there are 12 thiourea molecules and 4 monomers in the unit cell (the mole ratio of thiourea and monomer is 3:1). The monomer molecules are planar and the two methylene groups are in the trans configuration about the center C–C single bond. In the canals the planar monomers do not stack flat as in a stack of coins, but are almost vertical; the molecular plane tilts at an angle of 5° to the canal axis for 2,3-dichlorobutadiene, and at an angle of less than 1° for 2,3-dimethylbutadiene. The monomers contact one another at the normal van der Waals distances; the closest intermolecular $C(H_2)\cdots C(H_3)$ distance is 3.68 Å.

Crystal Structures of Polymer–Thiourea Complexes. Fourier projection along the canal axis for poly(2,3-dichlorobutadiene)- and poly(2,3-dimethylbutadiene)–thiourea complexes are shown in Figure 7. The crystal structure of the poly(2,3-dimethylbutadiene)–thiourea complex is shown in Figure 8.[15] The canal structure, *i.e.*, the deformation of the canal section from a regular hexagon, the orientation of the guest molecules, and the bend of the canal walls, is quite similar to what is observed for the monomer–thiourea complexes. But the most distinctive feature of the diffraction patterns of the polymer–thiourea complexes is that the polymers give independent layer lines from those of the thiourea lattice. From the extra layer lines the identity periods of the polymer chains were estimated to be 4.80 Å for 2,3-dichlorobutadiene and 4.75 Å for 2,3-dimethylbutadiene. This indicates that the conformations of the polymer chains in the canals are the most stable form, $\text{T-S}'\text{-trans-}\bar{\text{S}}'$, as shown in Figure 4. Accordingly, the polymer–thiourea complexes are nonstoichiometric compounds: 2.6 monomeric units in the canal period of 12.5 Å. This implies that there are 12 thiourea molecules and 5.2 monomer units in the unit cell (the mole ratio of thiourea to monomeric unit is 2.33:1 as shown in Table I). It is noteworthy, however, that this mole ratio derived from the X-ray data is the ideal value satisfied only when the canals are filled with polymer chains of infinite length. The mole ratio in the original monomer–thiourea complexes is 3:1 as already mentioned. Therefore, it may be presumed that the actual polymer–thiourea complexes cannot have such an ideal mole ratio of 2.33:1. We shall discuss this point later.

Another problem with the polymer–thiourea complexes is how the polymer chains are arranged in the canals. Since the polymer chains exist in each canal with a definite orientation about the canal axis, as shown in Figures 7 and 8, the cell

(14) N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, 2551 (1958).

(15) As shown later in the text, the polymer–thiourea complexes are nonstoichiometric compounds. But the equatorial reflections (*hk*0) appear as coherent scatterings of the thiourea lattice and the polymer. The (*hk*0) Fourier synthesis, therefore, gives the projected structure of both the host and guest molecules. On the other hand, the layer lines, except the extra layer lines due to the polymer chains, are essentially regarded as diffractions by the thiourea lattice alone. Therefore the atomic coordinates of thiourea molecules were refined by the least-squares method using the layer-line reflections.

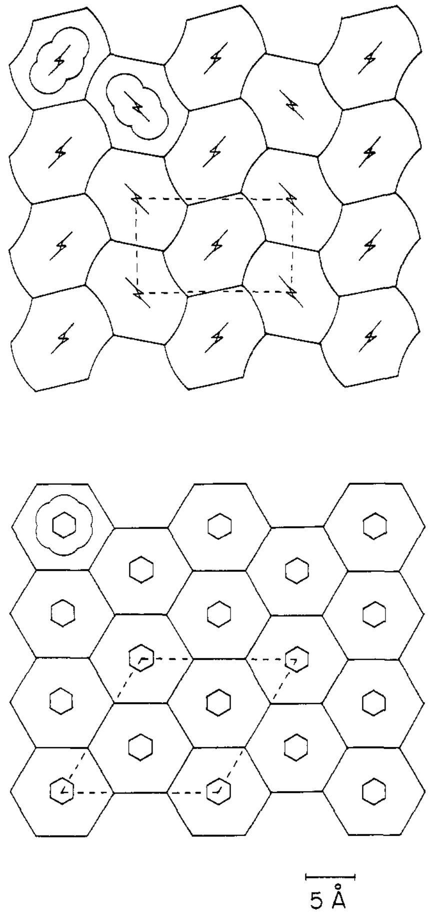


Figure 9. Schematical representation of canal structure of poly(2,3-dimethylbutadiene)–thiourea complex (top) and cyclohexane–thiourea complex (bottom).

dimensions in the cross section of the canal are the same as those of the thiourea lattice. But the identity period of the polymer chains is irrational with respect to that of the thiourea lattice. Therefore, the three-dimensional arrangement of the polymer chains can be treated as an independent lattice from that of the thiourea. From the reflections of the extra layer lines, the polymer lattice was determined. The cell dimensions were $a = 9.95$, $b = 15.47$, c (fiber axis) $= 4.75$ Å, $\beta = 107.3°$, space group $P2_1/a$, and two chains per unit cell for poly(2,3-dimethylbutadiene). Such a polymer lattice indicates that the polymer chains in each canal are correlated with respect to their mutual levels. But there is no definite relationship between the mutual levels of the thiourea lattice and the polymer lattice, and so the polymer chains are not included in the side view of Figure 8. In the case of the poly(2,3-dichlorobutadiene)–thiourea complex, the layer lines of the polymer are continuous streaks.[9] This indicates that the polymer chains have random z coordinates in the canals; there is no correlation between polymer chains in each canal with respect to their mutual levels. But several crystals of different preparations gave X-ray photographs having, in addition to the streaks, broad but discrete reflections, and from these reflections the cell dimensions of the polymer lattice were determined to be $a = 9.16$, $b = 15.85$, c (fiber axis) $= 4.80$ Å, $\beta = 99°$, space group $P2_1/a$, and two chains per unit cell.

The canal shapes and the deformation of canals in both the monomer- and polymer–thiourea complexes could be attributed to the shapes and sizes of the guest molecules. Figure 9 shows schematically the canal structure for poly(2,3-dimethylbutadiene) and for cyclohexane as a reference. Considering the van der Waals radii of the guest molecules, it is clear why the canals are deformed and the canal walls bent for the case of the dienes. The degree of deformation depends upon the shape and size of the guest molecule, and hence differs slightly in each case. The difference between the canal shapes of the monomer- and polymer–thiourea complexes for 2,3-dimethylbutadiene is illustrated in Figure 10.

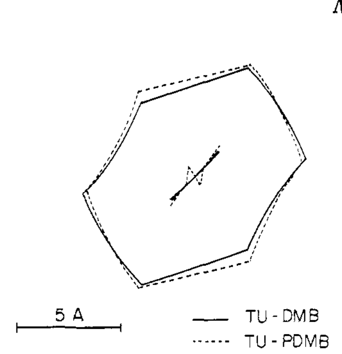


Figure 10. Comparison of canal structures of 2,3-dimethylbutadiene–thiourea complex (solid lines) and poly(2,3-dimethylbutadiene)–thiourea complex (dashed lines).

Discussion

Figure 11 shows schematically the process of canal polymerization and polymer crystallization for 2,3-disubstituted butadienes. Since the crystal structures of the monomer- and polymer–thiourea complexes for 2,3-dichlorobutadiene and 2,3-dimethylbutadiene are isomorphous, this picture is applicable to both the dienes except for minor differences in relative longitudinal arrangement of polymer chains in the canals and in the chain arrangement in the polymer crystals.

Canal Polymerization. The crystal structure analyses reveal that the monomers polymerize in the thiourea canals and the polymer–thiourea complex is formed without destroying the original single-crystal habit. We can imagine easily with the help of a molecular model that 1,4-enchainment of adjacent monomers followed by internal rotations of the two $C(H_2)$–C single bonds adjoining double bonds in the opposite sense produces the T-S-trans-$\bar{S}$ conformation of a 1,4-trans polymer. If this is true, the polymerization does not require overall molecular rotation of the monomer in the canal nor a large canal deformation from the original form. Figure 12 shows this situation. This enchainment is, however, accomplished by a shortening of 1.45 Å (from 6.25 to 4.80 Å) in the monomer interval. Therefore, successive long-range translational displacements (diffusion) of monomers in the canals are necessary in order for polymerization to occur. It is likely that monomer diffusion is an important factor in the temperature dependence of the polymerization rate and the molecular weight distribution of the resultant polymer. It is also fully expected that such a diffusion of monomers produces some vacancies in the canals. As already mentioned, the mole ratio of host to guest molecules is 3:1 for the monomer–thiourea complexes, but 2.33:1 for the ideal polymer–thiourea complex. When polymerization of the single crystal is done without the mother liquid, the mole ratio of host and guest molecules does not alter before and after polymerization. Carefully prepared single crystals of polymer–thiourea complex were not accompanied by thiourea crystals produced by degradation of the canal complex. Therefore it is probable that, since the polymer–thiourea complexes are very stable,

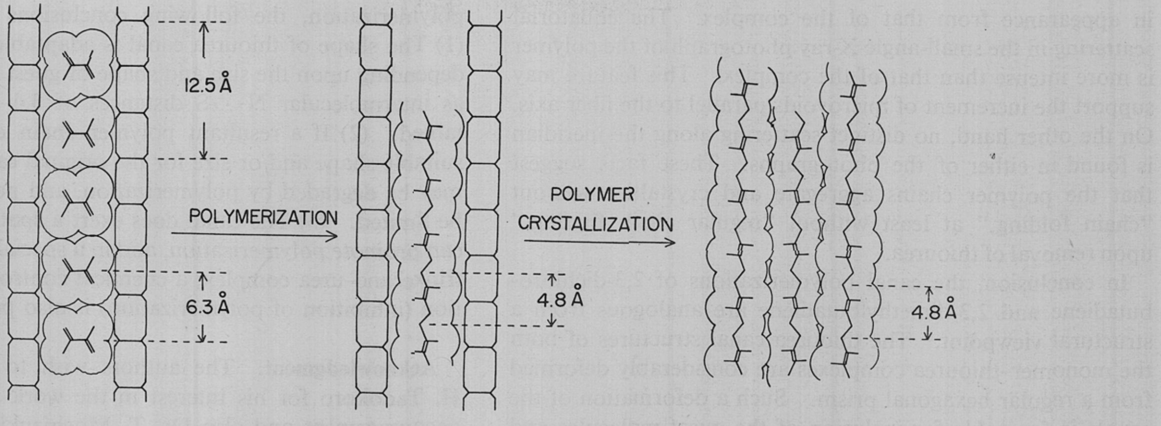


Figure 11. Schematical representation of the thiourea canal polymerization and the polymer crystallization for 2,3-disubstituted butadienes.

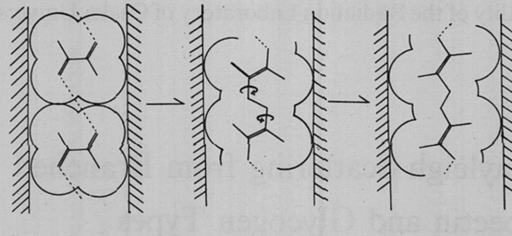


Figure 12. Schematic representation of 1,4-trans enchainment in the thiourea canal.

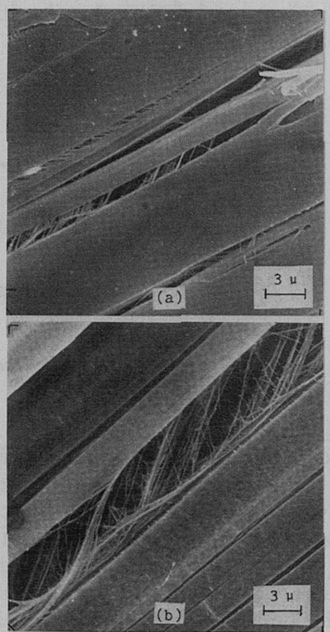


Figure 13. Scanning electron photomicrographs: (a) poly(2,3-dichlorobutadiene)–thiourea complex, (b) poly(2,3-dichlorobutadiene) (by courtesy of Dr. T. Mochizuki of Kuraray Co., Ltd.).

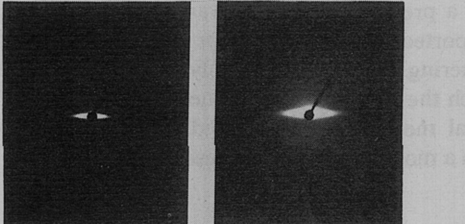


Figure 14. Small-angle X-ray diffraction photograph of poly(2,3-dichlorobutadiene)–thiourea complex (left) and poly(2,3-dichlorobutadiene) after removing thiourea (right).

the vacancy effect, which leads to a degradation of the thiourea canals, must be compensated by a maintenance force of surrounding regular canal parts. It is also clear, however, from the X-ray diffraction patterns, as shown in Figure 1b, that the polymer–thiourea complexes are smaller than the monomer–thiourea complexes in crystallite size and also have a somewhat paracrystalline nature. These situations may be attributed to the slight change of the canal shape and size from the monomer complex to the polymer complex and the vacancy effect upon polymerization.

Brown and White[3] examined some copolymerizations in the thiourea canals. According to them, 2,3-dichlorobutadiene and 2,3-dimethylbutadiene gave a copolymer with a high yield, but a mixture of vinylidene chloride with 2,3-dichlorobutadiene gave a small quantity of a nearly pure homopolymer of the diene, and that with 2,3-dimethylbutadiene gave no polymer at all. Since both the dienes form isomorphous complexes, as elucidated in the present paper, the high-yield copolymerization of both the dienes can be understood. On the other hand, the failure of vinylidene chloride to copolymerize with either of the dienes may be due to failure to achieve a comonomer–thiourea complex. Recently the authors found that vinylidene chloride formed a complex with thiourea with trigonal symmetry $R\bar{3}c$, as for the cyclohexane–thiourea complex. Furthermore, in this case the canal structure was appreciably changed to a paracrystalline state by polymerization. It was further observed that 1,3,5-trioxecane (trioxane) did not polymerize in the trioxecane–urea complex. Presumably, urea walls behave as an inhibitor for the cationic polymerization of trioxecane.

Polymer Crystallization. Figures 13 and 14 are scanning electron photomicrographs and small-angle X-ray diffraction photographs, respectively, of a single crystal of the poly(2,3-dichlorobutadiene)–thiourea complex and the uniaxially oriented polymer after removal of thiourea. There is no drastic difference between the samples in appearance in the electron photomicrographs. They are composed of an array of very fine needles. But, considering only the unit cell volume of the polymer complex and of the polymer, the sample of the complex must have a volume about 40% of the original one by removal of thiourea. Therefore it is no wonder that the single-crystal habit of the polymer complex is lost and only the orientation of the chain axis is retained in the polymer sample. Referring to the volume decrement, there must be an increase in microvoids between crystallites along the fiber axis in the polymer sample, since the size is not much altered in appearance from that of the complex. The equatorial scattering in the small-angle X-ray photograph of the polymer is more intense than that of the complex. This feature may support the increment of microvoids parallel to the fiber axis. On the other hand, no distinct scattering along the meridian is found in either of the photographs. These facts suggest that the polymer chains aggregate and crystallize without "chain folding," at least without "regular chain folding," upon removal of thiourea.

In conclusion, the canal polymerizations of 2,3-dichlorobutadiene and 2,3-dimethylbutadiene are analogous from a structural viewpoint. The thiourea canal structures of both the monomer–thiourea complexes are considerably deformed from a regular hexagonal prism. Such a deformation of the canals is favorable for inclusion of the guest molecules and also for 1,4-trans tactic polymerization. Though there is too little information about the structures of canal complexes to permit generalizations concerning the specificity of canal polymerization, the following conclusions are permissible. (1) The shape of thiourea canal is adaptable to some extent, depending upon the size and shape of guest molecule so long as intermolecular N···S distances of 3.4–3.5 Å are maintained. (2) If a resultant polymer chain cannot assume a suitable shape and/or size for the original canal, the complex may be degraded by polymerization, and polymer yield may be limited. (3) The canal does exert a spatial control which can promote polymerization, and in a special case, such as the trioxecane-urea complex, a chemical control for polymerization (inhibition of polymerization) is also possible.

Acknowledgment. The authors wish to thank Professor H. Tadokoro for his interest in the work and his constant encouragement and also Dr. T. Mochizuki of Kuraray Co. Ltd. for preparation of the scanning electron microscopic photographs. The authors also wish to acknowledge the hospitality of the Radiation Laboratory of Osaka University.

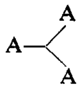
Angular Distribution of Rayleigh Scattering from Branched Polycondensates. Amylopectin and Glycogen Types

Walther Burchard

Institute of Macromolecular Chemistry, University of Freiburg, 78 Freiburg i. Br., West Germany. *Received May 5, 1972*

ABSTRACT: The polycondensation of trifunctional monomers with groups A, B, and C of different reactivities is considered under the restriction that group A can react only with either group B or C. This condensation leads to polymers of the branched structure of amylopectin and glycogen with no possibility of gel formation. Simple formulas for the weight and number averages of the degree of polymerization and for the z averages of the mean-square radius of gyration and of the particle scattering factor are derived with the aid of the cascade theory developed by Good and by Gordon. For large DP_w, the mean-square radius of gyration $\langle S^2 \rangle_z$ is found to increase proportionally with the square root of the weight-average degree of polymerization but linearly with the number average. This behavior is interpreted in terms of the heterogeneity which at large DP_w is $DP_w/DP_n \cong DP_w^{1/2} \cong DP_n$. The Zimm plots of the particle scattering factor exhibit significant upturns. This behavior deviates from the linear Zimm plots of the particle scattering factors of randomly branched polycondensates, and it is explained by the considerably narrower molecular weight distributions compared with the random cases.

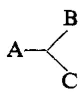
In a previous paper Kajiwara, Burchard, and Gordon[1] reported a new method for the calculation of the particle scattering factor of randomly branched polycondensates in which the simple case of homopolymers built up from f-functional monomers was treated. For example, when $f = 3$ such a monomer can be represented by



I

where each of the A groups has equal probability of reaction with any other unreacted A group of another molecule.

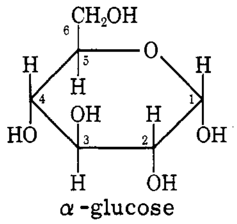
A consequent extension of such a reaction is the consideration of monomers of the type



II

where A, B, and C have different reactivities. In this paper branched polymers which are formed by the condensation of this type of monomer will be treated, but with the restriction that group A can react only with either group B or C, and that all other conceivable possibilities are excluded.

This type of condensation has some biological significance, because the branching of saccharides resulting in glycogen, amylopectin, and dextran is of this kind. In these polysaccharides the three groups A, B, and C are respectively in the C1, C4, and C6 positions on the glucose ring, A is an aldehydic OH group, and B and C are alcoholic groups.



α-glucose

Two sorts of α-glycosidic bonds (*i.e.*, C1–C4 and C1–C6) can

---

[1] K. Kajiwara, W. Burchard, and M. Gordon, *Brit. Polym. J.*, 2, 110 (1970).