Structural Investigation of Radiation-Induced Urea Canal Polymerization of 1,3-Butadiene

Yozo Chatani* and Shinichiro Kuwata

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received March 18, 1974*

ABSTRACT: The formation of a highly trans-1,4-tactic polymer by the radiation-induced canal polymerization of 1,3-butadiene in the urea adduct was examined by structural viewpoints based mainly upon crystal structure analyses of the monomer–urea adduct and the polymer–urea adduct of 1,3-butadiene. Crystals of the monomer–urea adduct are orthorhombic $P2_12_12_1$ with cell dimensions of $a = 8.20$, $b = 14.20$, and $c = 11.00$ Å at −120°. The unit cell contains two urea canals along the *c* axis, and the canals are slightly deformed from regular hexagonal prisms owing to the inclusion mode of the monomer molecules. The monomer molecules are aligned in the canals at an interval of 7.27 Å along the canal axis so as to be favorable to trans-1,4 polymerization. Crystals of the polymer–urea adduct are hexagonal $P6_122$ with $a = b = 8.22$, and $c = 11.01$ Å and one urea canal per unit cell, and the urea canals have pure hexagonal prismlike cavities. The polymer chains are included in the canals with an identity period of 4.84 Å. Since the difference between the canal shapes of both adducts is small, single crystals of the monomer–urea adduct can transform into single crystals of the polymer–urea adduct by irradiation. However, since the canal polymerization requires considerable shortening of the monomer interval (from 7.27 to 4.84 Å per monomer molecule), the polymerization must produce some amount of vacancies in the canals, and thus some extent of urea (about 30%) which cannot accommodate the polymer chains crystallizes into usual tetragonal crystals. The characteristics of the canal-polymerized polymer were examined by infrared absorption, X-ray diffraction, DSC measurement, and electron microscopy.

In previous papers,[1,2] the highly trans-1,4 tactic polymerization of 2,3-dimethylbutadiene and 2,3-dichlorobutadiene by γ-ray irradiation in the thiourea canals (adducts) was supported by structural evidences based upon crystal-structure analyses of the monomer–thiourea adducts, polymer–thiourea adducts, and resulting polymers of both dienes. The formation of a urea adduct with 1,3-butadiene was reported by Clasen,[3] and the radiation-induced urea canal polymerization of 1,3-butadiene was found by White[4] to produce an extremely regular trans-1,4 polymer. However, as was pointed out previously,[2] structures of adducts of urea or thiourea with polymerizable monomers and hence the details of the mode of canal polymerization are by no means the same but are peculiar to each monomer. The present paper is concerned from structural viewpoints with the characteristics of the urea canal polymerization and the resulting polymer of 1,3-butadiene.

Experimental Section

Samples. Samples used in the present study were prepared in the following way.

needlelike crystal of monomer–urea adduct
↓ canal polymerization (γ-ray irradiation at −78°)
needlelike crystal of polymer–urea adduct
↓ polymer crystallization (removal of urea with water)
uniaxially oriented fibrous polymer

Monomer–Urea Adduct. A 40% saturated urea–2-propanol solution at 30° (25 ml) with a trace (5 μl) of methanol was cooled to −78° in an ampoule. Precooled butadiene (3 ml) was added to the solution and sealed *in vacuo* at −78°. Precipitated urea crystals in the ampoule were dissolved by elevating the temperature and the ampoule was cooled slowly (1°/15 min) to −40° and was stored. Needlelike crystals about 0.3 mm in diameter and 20 mm in length which are suitable for X-ray study were thus obtained. After removal of the mother liquid, the ampoule was sealed again. Polycrystalline monomer–urea adduct was also prepared by the method of White.[4] Since the adduct dissociated immediately above about −20°, it was handled in a Dry Ice box.

Polymer–Urea Adduct. The monomer–urea adduct was irradiated at −78° by γ-rays from a cobalt-60 source of the Radiation Laboratory of Osaka University. The irradiation dose rate and total dosage were 2×10^5 or 5×10^5 rad/hr and 1.2×10^6 or 1.5×10^7 rad, respectively. Single crystals of the monomer–urea adduct were transformed into the polymer–urea adduct preserving the original crystal shape. The polymer–urea adduct decomposed at 142°.

Polymer Samples. The polymer–urea adduct was washed with water at 25 or 100° in order to remove urea. From single crystals of the polymer–urea adduct, uniaxially oriented fibrous polymer samples were directly obtained. They were dried *in vacuo.* No other treatments, such as recrystallization, fractionation, and annealing, were made for the polymer samples. When the irradiated adduct was warmed slowly to room temperature, more tight fibrous samples were obtained; probably the postpolymerization progressed during the warming. As reference polymer samples, 90 and 98% *trans*-1,4-polybutadiene prepared by the use of $VCl_3 \cdot Al(Et)_3$ catalyst were used.

X-Ray Diffraction. Throughout the present study, nickel-filtered Cu *Kα* radiation was used. Rotation photographs and equiinclination Weissenberg photographs about the needle axis (*c* axis) were taken for the monomer–urea adduct and polymer–urea adduct. Especially, the photographs of the monomer–urea adduct were taken at −120°. At that temperature the canal polymerization by X-rays was substantially suppressed during exposure of one photograph. Reflection intensities estimated by comparison with a standard intensity scale were corrected for Lorentz-polarization factors. A fiber photograph of the canal-polymerized polymer was taken with a cylindrical camera. Figures 1a–c show the rotation photographs of the monomer–urea and polymer–urea adducts and the fiber photograph, respectively.

Small-angle X-ray diffraction photographs of the polymer–urea adduct, the canal-polymerized polymer, and the 90% trans-1,4 polymer were taken using a Rigaku-Denki small-angle X-ray diffractometer with a pin-hole optics.

DSC Measurement. DSC measurements were made for the polymer–urea adduct and the canal-polymerized polymers on a Rigaku-Denki YDS differential scanning calorimeter. The scans were taken at a speed of 15°/min and the scanning range of 25–160°. The instrument was calibrated with the calorimetric standard benzoic acid.

Infrared Spectrum. Infrared spectra of the polycrystalline polymer–urea adduct and the polymers were obtained using the KBr disk technique. Uniaxially oriented polymer films of 15–20 μm thicknesses were prepared from the canal-polymerized fibrous polymer samples by rolling along the fiber direction, and their infrared dichroisms were measured with a Hitachi EPI2 microscopic spectrometer.

Results and Discussion

Monomer–Urea Adduct. The X-ray diffraction patterns of the monomer–urea adduct suggested to us that the

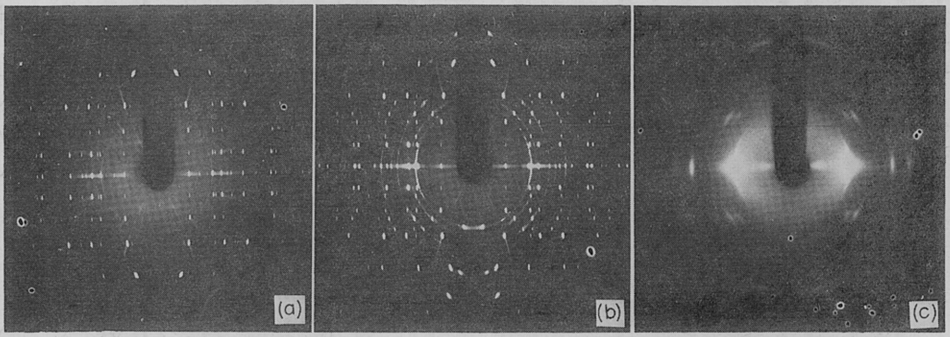

Figure 1. (a) X-Ray rotation photograph of the monomer–urea adduct taken at −120°. The rotation axis is the canal axis. (b) X-Ray rotation photograph of the polymer–urea adduct taken at room temperature. (c) X-Ray fiber photograph of the polymer obtained from the polymer–urea adduct.

gross structure of the adduct was similar to that of the well-known *n*-paraffin–urea adducts of hexagonal system $P6_122$ with cell dimensions of $a = b = 8.223$ and $c = 11.005$ Å, in which six urea (host) molecules per unit cell form the honeycomb-like canal having a cavity of about 5-Å diameter along the *c* axis.[5] However, the crystal symmetry (orthorhombic $P2_12_12_1$) of the monomer–urea adduct was certainly different from the usual hexagonal $P6_122$. (It should be noted that from the X-ray measurement the monomer–urea adduct crystals found often appeared as microscopic twinned crystals, which were composed of three orthorhombic crystals rotating every 120° about the canal axis, with a hexagonal symmetry.) The crystallographic data are shown in Table I. Since the *b* dimension, 14.20 Å, is just $3^{1/2}$ times the *a* dimension, 8.20 Å, this orthorhombic cell must contain two urea canals, *i.e.*, 12 urea molecules. The appearance of the orthorhombic symmetry instead of the hexagonal symmetry should be ascribable to a slight deformation of the urea canals from regular hexagonal canals due to a definite angular disposition of butadiene (guest) molecules about the canal axis as in the case of 2,3-dimethylbutadiene–thiourea adduct.[2] The deformed thiourea canals with the monoclinic symmetry $P2_1/a$ in the 2,3-dimethylbutadiene–thiourea adduct were revealed to retain substantially the canal structure of thiourea molecules in the well-known rhombohedral adduct ($R\bar{3}c$).[6] Similarly, the deformed urea canals with the orthorhombic symmetry $P2_12_12_1$ can retain essentially the urea-canal structure of the hexagonal adduct as shown later. In the first step of structure analysis, the mole ratio of the host to the guest had to be decided. The X-ray rotation photograph (Figure 1a) showed an extra layer line whose periodicity does not correspond to the periodicity along the *c* axis of the crystal, and this layer line should be attributed to scatterings by the guest molecules. The identity period, c_m, of the extra layer line, 7.27 Å, indicates the interval of monomer molecules in the canal. The ratio of the *c* dimension (period of the urea canal, 11.00 Å) to c_m is expressed approximately by $2c = 3c_m$, *i.e.*, approximately three monomer molecules exist in a length of twice the urea-canal period. Therefore, the orthorhombic cell contains 12 urea molecules and 3.02 monomer molecules; the mole ratio is thus approximately 4:1 but exactly 3.97:1 (Clasen[3] reported the mole ratio of 4.2:1 by measurement of the dissociation pressure of the adduct). The monomer packing in the urea canal having the interval of 7.27 Å could be realized as shown in the side view in Figure 3 or Figure 10, when the molecular dimensions of butadiene determined by Almenninger, *et al.*,[7] and the normal van der Waals radii were used. In the case of 2,3-dimethylbutadiene–thiourea adduct, the mole ratio of host to guest is rationally 3:1, and the guest molecules take definite dispositions to the host molecules.[2] On the other hand, in the butadiene–urea adduct, the mole ratio is irrational and hence the array of guest molecules in each canal seems to take an uncertain level to the framework of the host. If that is so, guest molecules give independent streak-like layer lines, l_m, in the rotation photograph, except the equatorial layer line, in which host and guest molecules are coherent in X-ray scatterings. In order to confirm this packing of guest molecules, a calculation of cylindrically averaged diffraction intensities about the canal axis, which should be compared with the rotation photograph, was done using eq 1 for the array of butadiene molecules located as in Figure 3 or Figure 10.

Table I
Crystallographic Data for the Monomer–Urea and Polymer–Urea Adducts of 1,3-Butadiene

	Monomer–urea adduct	Polymer–urea adduct
Crystal system	Orthorhombic	Hexagonal
Space group	$P2_12_12_1$	$P6_122$
Cell dimensions, Å	$a = 8.20 \pm 0.02$ $b = \sqrt{3}a = 14.20 \pm 0.03$ $c = 11.00 \pm 0.03$ (at −120°)	$a = b = 8.22 \pm 0.01$ $c = 11.01 \pm 0.02$
Number of host–guest molecules per cell (mole ratio)	12–3.02 (3.97)	6–2.28[a] (2.63)[a]

[a] Ideal adduct, in which canals are filled with endless polymer chains.

$$I(R,l_m/c_m) = \sum_j \sum_{j'} f_j f_{j'} J_0(2\pi R r_{jj'}) \exp[2\pi i l_m(z_j - z_{j'})/c_m] = \sum_j f_j^2 + 2\sum_{j>j'}\sum f_j f_{j'} J_0(2\pi R r_{jj'}) \cos(2\pi l_m z_{jj'}/c_m) \quad (1)$$

$R = [(2 \sin \theta/\lambda)^2 - (l_m/c_m)^2]^{1/2}$; θ, Bragg angle; λ, wavelength; l_m, order of layer line of the monomer; c_m, monomer interval along the canal axis; f_j, atomic scattering factor of *j*th atom; J_0, Bessel function of zeroth order; $r_{jj'}$ and $z_{jj'}$, radial and axial components of interatomic distance between *j* and *j*'th atoms in the monomer molecule. Figure 2 (top) shows the calculated intensities. The result gave the strong extra layer line of 7.27 Å (first layer line) and the scarcely detectable second layer line as observed experimentally.

The structure of urea canal was determined by the least-squares refinement with data of $F(hk1) - F(hk5)$. Subse-

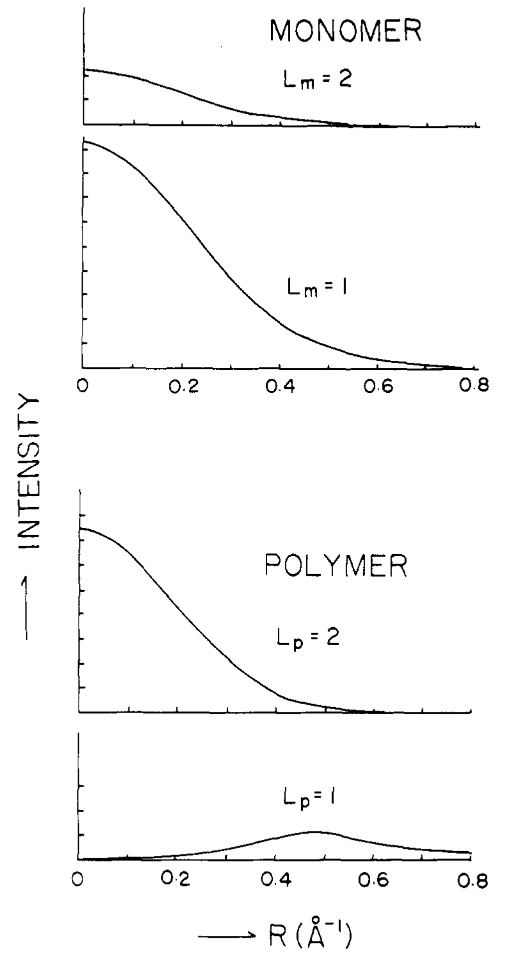

Figure 2. Calculated cylindrically averaged X-ray diffraction intensities of extra layer lines for the monomer–urea adduct (top) and the polymer–urea adduct (bottom).

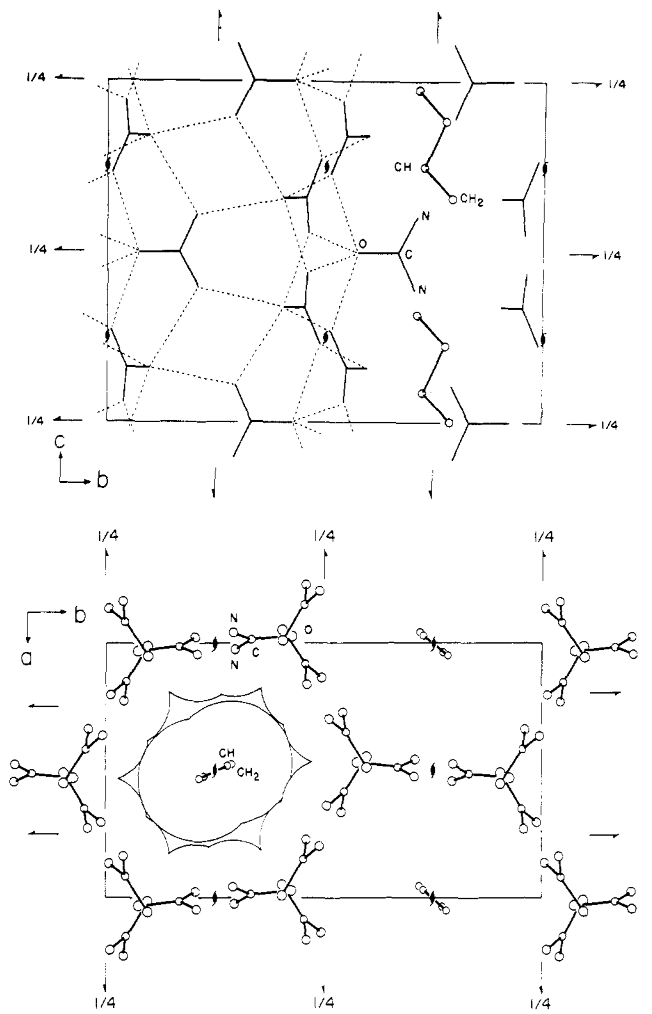

Figure 3. Crystal structure of the monomer–urea adduct. In the left part of the side view (top), the N–H···O hydrogen bonding scheme is indicated by broken lines, and in the right part the included monomer molecules are shown. The relative heights of monomer molecules to urea molecules are arbitrary as shown in the text.

quently, the angular position of guest molecule about the canal axis was determined by the least-squares refinement with $F(hk0)$, where xy coordinates and thermal parameters of urea molecules were fixed as obtained from the consideration of $F(hk1) - F(hk5)$. The final atomic coordinates and thermal parameters are shown in Table II. Table III lists the observed and calculated structure factors (see paragraph at end of paper regarding supplementary material). The discrepancy factor R $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.094 for all observed reflections. The crystal structure is shown in Figure 3. The averaged bond lengths and bond angles for three nonequivalent urea molecules are as follows: C–O, 1.30 Å; C–N, 1.35 Å; O–C–N, 123°; N–C–N, 118.5°. Though the canals are slightly deformed from regular hexagonal prisms, the scheme of N–H···O hydrogen bondings between urea molecules is the same as that in the hexagonal adduct, *i.e.*, the framework of canal is composed of three interpenetrating helices of urea molecules with the same sense (either right-handed or left-handed helices). There are 12 independent N–H···O hydrogen bond distances; they are ranged from 2.82 to 3.08 Å and are averaged to be 2.99 Å.

The guest molecules are included with a definite angular disposition about the canal axis and have cross-sectional dimensions of 3.8 × 5.4 Å^2 about the canal axis. Therefore, the deformation of the urea canals seems to be quite reasonable. However, as shown in the end view in Figure 3, the cavity of the canal has a slight allowance for oscillation of guest molecules about the canal axis. Also, since the canal axis is in accordance with a twofold screw axis in the $P2_12_12_1$ crystal, the guest molecules might be arranged statistically turning 180° about the canal axis in canal by canal.

Polymer–Urea Adduct. The procedure of structure analysis of the polymer–urea adduct was similar to that of the monomer–urea adduct. The polymer–urea adduct belongs to the hexagonal system $P6_122$. The cell dimensions are shown in Table I. Table IV lists the atomic coordinates and thermal parameters. Table V is the list of observed and calculated structure factors (see paragraph at end of paper regarding supplementary material). The final R factor was 0.11. The crystal structure is shown in Figure 4. The structure of urea canal is substantially the same as that of the n-paraffin–urea adduct:[5] C–O, 1.27 Å; C–N, 1.35 Å; O–C–N, 119.7°; N–C–N, 120.6°, and two kinds of N–H···O hydrogen bond distances are 2.98 and 3.00 Å. The canal is a regular hexagonal prism. The orthorhombic symmetry in the monomer–urea adduct disappears by transformation from the monomer–urea adduct into the polymer–urea adduct. However, since the deformation due to the transformation is small, crystals of the polymer–urea adduct can retain the single-crystal habit.

One problem about the polymer chains in the canals should be noted. The molecular chains of *trans*-1,4-polybutadiene in the low-temperature crystalline form take the T-S-trans-$\bar{S}$ (T, trans; S, skew) conformation with an identity period of 4.83 Å.[8] In the rotation photograph of the

Table II
Atomic Coordinates and Thermal Parameters for the Monomer–Urea Adduct

Atom	x	y	z	B, Å^2
O(1)	0.0090	0.0937	0.1559	4.15
C(1)	0.1431	0.0462	0.1616	3.02
N(11)	0.1994	0.0110	0.2672	2.93
N(12)	0.2276	0.0438	0.0585	4.08
O(2)	0.0554	0.0967	0.8402	4.27
C(2)	−0.0754	0.0438	0.8421	4.08
N(21)	−0.1617	0.0360	0.9462	4.21
N(22)	−0.1307	0.0036	0.7355	4.19
O(3)	0.0295	0.0725	0.5005	5.48
C(3)	0.0118	0.1642	0.4997	3.36
N(31)	0.0391	0.2108	0.6039	5.26
N(32)	−0.0282	0.2054	0.3941	4.54
H(11)	0.286	−0.038	0.283	4.85
H(12)	0.146	0.013	0.348	4.65
H(13)	0.332	0.016	0.044	3.13
H(14)	0.187	0.067	0.981	3.55
H(21)	−0.267	0.008	0.954	4.32
H(22)	−0.125	0.067	0.020	3.86
H(23)	−0.222	−0.045	0.722	4.18
H(24)	−0.078	0.001	0.654	4.54
H(31)	0.044	0.281	0.616	4.23
H(32)	0.070	0.182	0.691	3.53
H(33)	−0.053	0.275	0.373	4.34
H(34)	−0.048	0.177	0.310	3.71
C(G1)	0.524	0.207	0.000[a]	8.60
C(G2)	0.510	0.219	0.219[a]	8.65
H(G1)[b]	0.501	0.243	−0.094[a]	8.60
H(G2)[b]	0.569	0.139	0.009[a]	8.60
H(G3)[b]	0.557	0.153	0.231[a]	8.60

[a] Arbitrary values relative to the host molecules as shown in the text. [b] Parameters of hydrogen atoms in the guest molecule were assumed. Equivalent positions are (x,y,z), $(\frac{1}{2}+x,\bar{y},\frac{1}{2}-z)$, $(\bar{x},\frac{1}{2}-y,\frac{1}{2}+z)$, and $(\frac{1}{2}-x,\frac{1}{2}+y,\bar{z})$.

Table IV
Atomic Coordinates and Thermal Parameters for the Polymer–Urea Adduct

Atom	x	y	z	B, Å^2
O	0.3194	0.6806	0.4167	6.35
C	0.4086	0.5914	0.4167	6.18
N	0.4377	0.5261	0.5227	6.75
H(1)	0.394	0.544	0.598	6.9
H(2)	0.506	0.458	0.519	6.9
C(H)[a]	0.000	0.045	0.051	7.3
C(H$_2$)[a]	0.085	0.044	0.176	7.3
H(CH)[a]	−0.085	0.109	0.052	7.3
H(CH$_2$)[a]	0.146	−0.043	0.173	7.3
H(CH$_2$)[a]	0.206	0.181	0.179	7.3

[a] Since the polymer chain is randomly disposed about the canal axis, parameters in the table are tentatively given for the T-S-trans-S̄ polymer as described in the text. Coordinates of the remaining atoms in the monomeric unit are obtained by a inversion symmetry operation at (0,0,0).

polymer–urea adduct (Figure 1b), we observed a very weak layer line with a period of 2.42 Å corresponding to the second layer line for the above molecular chain. In the pure hexagonal canal, the polymer chains must orient statistically about the canal axis, since the polymer chain axis is in accordance with a sixfold screw axis in the $P6_122$ crystal. Two assumptions of free rotating polymer chains (time averaged or space averaged) about the chain axis and of randomly disposed chains in six equivalent sites were examined for the T-S-trans-S̄ polymer chain. For the free-rotating model, the structure factor of the equator is expressed as eq 2.

$$F(hk0) = F_{\mathrm{urea}}(hk0) + F_{\mathrm{polymer}}(hk0) \qquad (2)$$

$$F_{\mathrm{polymer}}(hk0) = w\sum_j f_j \mathrm{J}_0(2\pi R r_j)$$

r_j, radial coordinate of jth atom from the chain axis; w, weight deduced from the mole ratio of host to guest (monomeric unit); w = 2.28 (11.01 Å/4.84 Å) when the summation is made for all atoms in one monomeric unit. Both models gave essentially the same reasonable $F(hk\,0)$ values. The cylindrically averaged intensities of extra layer lines, l_p, were also calculated in a good approximation by using the free-rotating model.

$$I(R,l_p/c_p) = \left|\sum_j f_j \mathrm{J}_0(2\pi R r_j)\exp(2\pi \mathrm{i} l_p z_j/c_p)\right|^2 \qquad (3)$$

z_j, axial coordinate of jth atom; c_p, identity period of polymer chain, 4.84 Å. The result shown in Figure 2 (bottom) indicates that the second layer line is observable while the first layer line is not detectable as observed experimentally.

The infrared spectrum of the polymer–urea adduct is quite similar to those of the n-paraffin–urea adducts.[9,10] The absorption bands of the polymer (guest component) in the adduct are very weak; only the 966 cm^{-1} [τ(C=C) − γ(CH)], 2850 cm^{-1} [ν_s(CH$_2$)], and 2925 cm^{-1} [ν_a(CH$_2$)] bands were observed. These bands are in accordance with those of the polymer samples. Therefore, no further information about the polymer conformation in the canal could be obtained.

The polymer–urea adduct was found to decompose at 142° from the DSC measurement as shown in Figure 5a. Another endothermic peak at 129° in Figure 5a is ascribable to the fusion of usual urea crystals (tetragonal $P\bar{4}2_1m$, $a = b$ = 5.661, and c = 4.712 Å).[11] In practice, coexistence of urea crystals in the polymer–urea adduct sample was clearly demonstrated by the X-ray diffraction (Figure 1b). The separated urea crystals orient in two preferable ways; though there is a small amount of polycrystalline urea too, the [001] and [110] axes of urea orient along the canal axis. As is well-known, *trans*-1,4-polybutadiene has a first-order transition from the low-temperature form to the high-temperature form at about 55–76°, depending upon the conditions of preparation of the sample.[12] There is no peak in this region for the polymer–urea adduct. That is, all polymer chains are included in the urea canals, while free urea crystals exist. It is a characteristic in the canal polymerization of butadiene that the monomer–urea adduct is transformed into the polymer–urea adduct with accompanying urea crystals as a by-product. The problem concerning this will be discussed in the following sections.

Polymer. The canal-polymerized polybutadiene is estimated to be almost 100% trans-1,4 polymer from its infrared spectrum: both the 910-cm^{-1} band arising from 1,2 addition and the 740-cm^{-1} band from cis-1,4 addition cannot be seen, while a weak but clear band at 910 cm^{-1} is found for the 98% trans-1,4 polymer. The infrared spectrum of the oriented canal-polymerized polymer gave the same dichroism as a stretched 98% trans-1,4 polymer. The X-ray fiber pattern (Figure 1c) is also essentially the same as the usual one. However, as shown in Figure 6 which presents X-ray diffraction curves for three different polymer samples taken at 25°, the features of the canal-polymerized polymers are scarcely detectable amorphous scatterings and rather broad crystalline diffractions. These features imply that the canal-polymerized polymers have high crys-

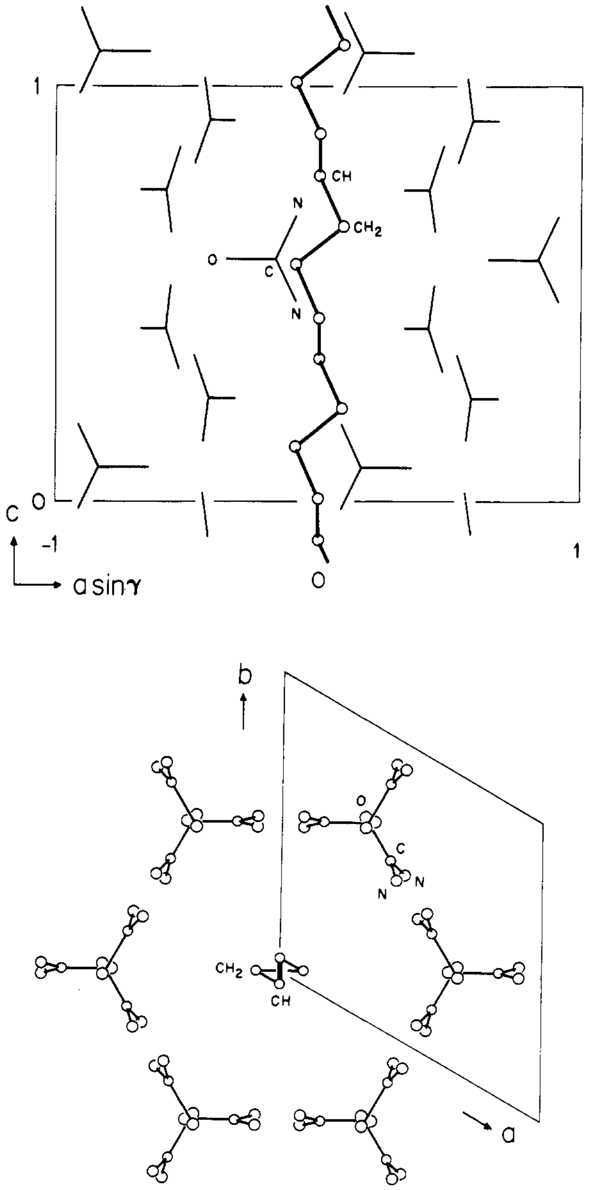

Figure 4. Crystal structure of the polymer–urea adduct. The N–H · · · O hydrogen bonding scheme is essentially the same as that of the monomer–urea adduct.

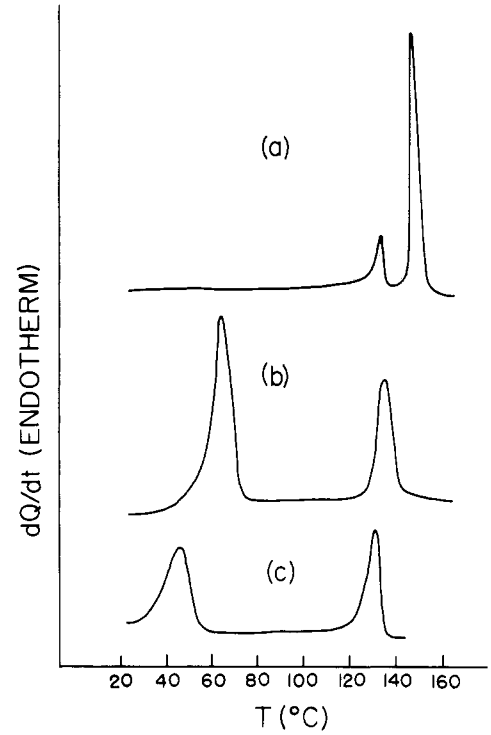

Figure 5. DSC thermograms: (a) the polymer–urea adduct; (b) the canal-polymerized polymer (removal of urea at 100°); (c) the canal-polymerized polymer (removal of urea at 25°).

tallinities, but the crystallites are rather small and/or somewhat paracrystalline.

Table VI shows calorimetric data for the canal-polymerized polymers with the data of Bermudez and Fatou for a predominantly trans-1,4 polymer.[13] In the table the crystallinities of the low-temperature crystalline form (form I) $X_{\rm I}$ and of the high-temperature form (form II) $X_{\rm II}$ were estimated by using the relationship of the observed heat of transition $\Delta H_{\rm I}$ *vs.* $X_{\rm I}$ and of the observed heat of fusion $\Delta H_{\rm II}$ *vs.* $X_{\rm II}$, proposed by Bermudez and Fatou (Figure 6 in ref 13). The crystallinities of the canal-polymerized polymers are comparable with those of single crystals grown from *n*-heptane solutions.[14] The $X_{\rm I}$ of the sample obtained by removal of urea at 25° is exceptionally small, but the increment of $X_{\rm II}$ of this sample may be due to promotion of crystallization during the DSC measurement.

The small-angle X-ray diffraction of an oriented 90% trans-1,4 polymer gave a discrete reflection with a long spacing of 200 Å calculated according to Bragg's law, along the fiber axis, while the canal-polymerized polymer as well as the polymer-urea adduct did not show such a spot (Figure 7). Ng, Stellman, and Woodward[14] reported that solution-grown single crystals have lamellar thicknesses of about 94–110 Å. It is conceivable that the canal-polymerized polymers do not contain any periodic heterogeneous structure in a dimension of 100–200 Å along the fiber axis. From the mechanism of the canal polymerization and of the polymer crystallization, it is likely that the extended polymer chains in the canals aggregate preferably with each other and crystallize in a mode of intermolecular crystallization rather than of intramolecular crystallization.

Figure 8 shows a transmission electron micrograph of the canal-polymerized polymer. The photograph shows a gross lamellar structure of about 2000-Å thickness. The interpretation of this structure is still uncertain, but in the case of the canal polymerization of 2,3-dichlorobutadiene, the obtained polymer was composed of fine needlelike fibrils and had no such lamellar structure.[2] The canal polymerization of 2,3-dichlorobutadiene was performed without breaking-up of the thiourea canals even if large vacancies were produced in the canals due to the polymerization. Therefore, the gross lamellar structure in the canal-polymerized polybutadiene might be interpreted as follows. That is, in the case of urea-canal polymerization of butadiene, owing to the significant shortening of monomer interval upon polymerization and a less stability of urea-canal framework without guest molecules, the urea canals are broken up at regions where some vacancies of neighboring canals are concentrated, say with an interval of observed 2000 Å.

Canal Polymerization. From the present structural studies, the urea-canal polymerization and the polymer crystallization of butadiene can be schematically represented as shown in Figure 9. Ohmori, *et al.*,[15] reported an esr study of preirradiated polycrystalline butadiene–urea adduct. They proposed that the mechanism of canal polymerization is of a radical type, starting from the allyl type radical $CH_3CH{=}\dot{C}H_2$ produced by proton transfer from a urea molecule to a butadiene anion radical, which may be produced by capture of an ejected electron. Though the details of the structure of such an imperfection site cannot be ac-

Table VI
Calorimetric Data and Estimated Crystallinity

	Transition			Fusion		
Polymer	T_t, deg	ΔH_I, cal/g	X_I, %	T_m, deg	ΔH_{II}, cal/g	X_{II}, %
Canal polymerized polymer (removal of urea at 25°)	35.5	14.8	66	123	13.5	86
Canal polymerized polymer (removal of urea at 100°)	55.0	24.3	92	128	12.0	84
Bermudez and Fatou's data[a]	50 ~52	11.5 ~13.7	57 ~64	100 ~103	4.8 ~7.1	40 ~54

[a] Lower and upper values in their studies are shown.

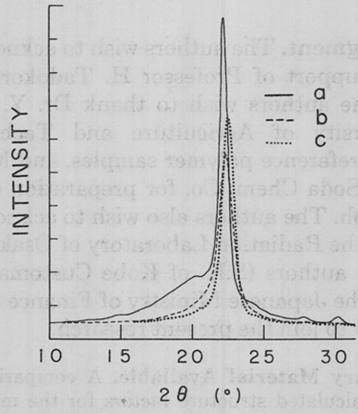

Figure 6. X-Ray diffraction curves of three polymer samples: (a) the 98% trans-1,4 polymer; (b) the canal-polymerized polymer (removal of urea at 25°), (c) the canal-polymerized polymer (removal of urea at 100°).

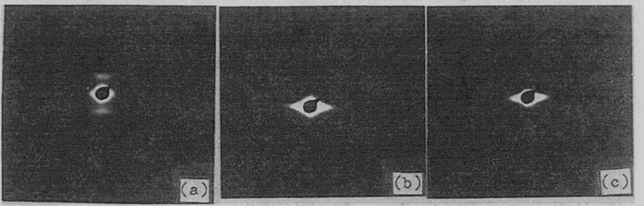

Figure 7. Small-angle X-ray diffraction photographs: (a) the 98% trans-1,4 polymer; (b) the polymer–urea adduct; (c) the canal-polymerized polymer (removal of urea at 100°). The polymer chain axis is vertical in each photograph.

quired, the polymerization must start by an addition reaction of the nearest neighboring monomer molecule to the radical in a canal. The alignment of monomer molecules in the canal seems to be favorable to trans-1,4 addition. However, the polymerization requires considerable shortening of monomer interval: from 7.27 to 4.84 Å per monomer molecule. From the geometrical viewpoint alone, it appears that the monomer molecules can travel in the canal without any large hindrance. As an approximation, the van der Waals potential energy for one monomer molecule as a function of translational coordinate (z) along the canal axis and rotation angle (ϕ) about the canal axis was estimated

$$V(z,\phi) = \sum_i \sum_j (B_{ij}/r_{ij}^{12} - A_{ij}/r_{ij}^{6}) \qquad (4)$$

using eq 4. The summation was made for atom pairs between one monomer molecule and surrounding urea molecules with interatomic distances r_{ij} less than 7 Å. The constants A_{ij} and B_{ij} were taken from Gō and Scheraga.[16] Figure 10 shows the potential energy map, where the origin (0,0) is chosen as the molecular plane of the guest molecule

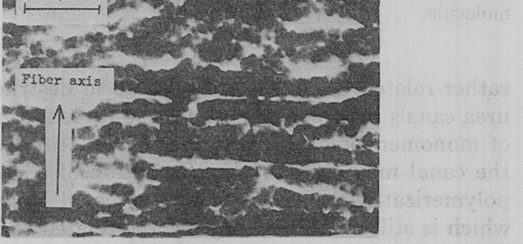

Figure 8. Transmission electron micrograph of the canal-polymerized polymer (removal of urea at 100°).

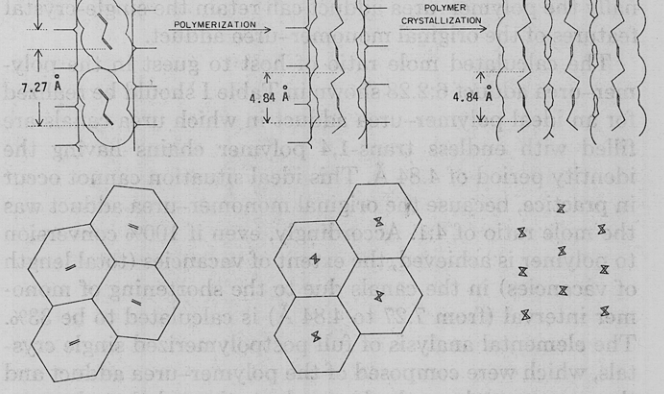

Figure 9. Schematic representation of the urea-canal polymerization and the polymer crystallization for 1,3-butadiene.

and is parallel to the ac plane (at this stage, the C(G1) atom denoted in Table II is at $x = 0.561$, $y = 0.250$, and $z = 0.0$ in the fractional coordinates), and ϕ is taken counterclockwise. Since the canal axis is in accordance with a twofold screw axis

$$V(z,\phi) = V(z + c/2, \phi + 180°) \qquad (5)$$

The potential energy minima are at $\phi = 120$ and 300°, which are consistent with the result of crystal structure analysis, and the potential barrier against the translation of a guest molecule along the canal axis at the two angular positions is only 0.5 kcal/mol. Yoshii, *et al.*,[17] studied the temperature dependence of the canal polymerization of butadiene. According to their study, the postpolymerization of preirradiated butadiene–urea adduct at −196° is suppressed at −90° in practice but proceeds significantly at −78° and is promoted gradually with elevating temperature. Since the potential barrier for the translation of monomer molecule along the canal axis is not so high, the temperature dependence of the canal polymerization may be

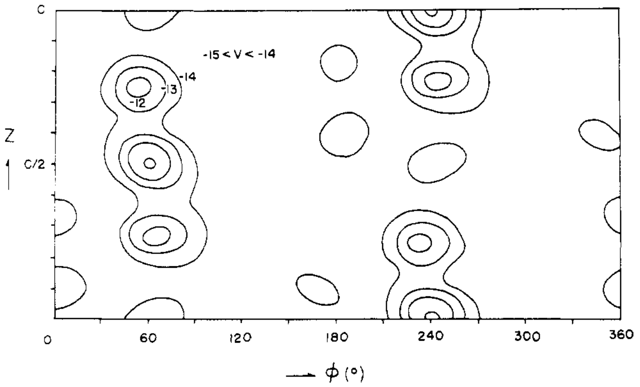

Figure 10. Potential energy contours (kcal/mol) as a function of angular position ϕ and translational position z of the monomer molecule.

rather related occurrence of some local destruction of the urea canals by which a free space suitable for enchainment of monomer molecules is formed. The local destruction of the canal may occur by the formation of a vacancy upon polymerization. The heat of the canal polymerization, which is still unknown, may also be related to such a local structure change. However, the details of such a local change are still an open question. In any event, from the facts of the appreciable shortening of monomer interval upon polymerization and of the growth of urea crystals, it is likely that some reconstruction of crystal lattices takes place in the vicinity of growing polymer chain end, but finally the polymer-urea adduct can retain the single-crystal features of the original monomer-urea adduct.

The calculated mole ratio of host to guest in the polymer-urea adduct 6:2.28 shown in Table I should be realized for an ideal polymer-urea adduct in which urea canals are filled with endless trans-1,4 polymer chains having the identity period of 4.84 Å. This ideal situation cannot occur in practice, because the original monomer-urea adduct was the mole ratio of 4:1. Accordingly, even if 100% conversion to polymer is achieved, the extent of vacancies (total length of vacancies) in the canals due to the shortening of monomer interval (from 7.27 to 4.84 Å) is calculated to be 33%. The elemental analysis of full postpolymerized single crystals, which were composed of the polymer-urea adduct and the urea crystals as the by-product, showed that the conversion to polymer was almost 100%, because the mole ratio of urea to monomeric unit did not alter from that in the original monomer-urea adduct. On the other hand, from the calorimetric data (measurement of the heat of fusion of urea crystals in Figure 5a) of this sample, we estimated the weight fractions of urea existing as the polymer-urea adduct and as the urea crystals, assuming that the polymer-urea adduct did not decompose prior to the fusion of urea crystals (*cf.* in the case of polyethylene-urea adduct,[18] which was not accompanied by urea crystals, no endothermic peak for the fusion of urea crystals was observed prior to the decomposition of the adduct at 148°). From these data and the mole ratio in the ideal polymer-urea adduct, we estimated the weight fractions of urea existing in the following three states: urea which constructs the ideal polymer-urea adduct, 68%; urea which constructs canals with vacancies, 4%; tetragonal urea crystal, 28%. Therefore, it seems likely that there are no long vacancies in the polymer-urea adduct, and hence some extent of urea (about 30%) which cannot accommodate polymer chains crystallizes into tetragonal crystals. This fact does not conflict with the fact that the calculation of structure factors $F(hk0)$ for the polymer-urea adduct (see eq 2) gave the reasonable result by assuming that the mole ratio was similar to that of the ideal polymer-urea adduct. Therefore, if the monomer-urea adduct is subjected to irradiation for a long time coming into contact with excess monomer, it might be expected that separated urea crystals upon polymerization can form the monomer-urea adduct again with free monomer molecules, and the adduct undergoes polymerization.

Acknowledgment. The authors wish to acknowledge the interest and support of Professor H. Tadokoro of Osaka University. The authors wish to thank Dr. Y. Tanaka of Tokyo University of Agriculture and Technology for supplying the reference polymer samples, and Mr. K. Ogawara of Toyo Soda Chem. Co. for preparation of the electron micrograph. The authors also wish to acknowledge the hospitality of the Radiation Laboratory of Osaka University. One of the authors (S.K. of Kobe Customs) expresses his thanks to the Japanese Ministry of Finance for offering an opportunity to join the present research.

Supplementary Material Available. A comparison between observed and calculated structure factors for the monomer-urea adduct (Table III) and the polymer-urea adduct (Table V) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number *Macro*-75-12.

References and Notes

(1) Y. Chatani, S. Nakatani, and H. Tadokoro, *Macromolecules*, **3**, 481 (1970).
(2) Y. Chatani and S. Nakatani, *Macromolecules*, **5**, 597 (1972).
(3) H. Clasen, *Z. Elektrochem.*, **60**, 982 (1956).
(4) D. M. White, *J. Amer. Chem. Soc.*, **82**, 5678 (1960).
(5) A. E. Smith, *Acta Crystallogr.*, **5**, 224 (1952).
(6) H. U. Lenné, *Acta Crystallogr.*, **7**, 1 (1954).
(7) A. Almenninger, O. Bastiansen, and M. Trutterberg, *Acta Chem. Scand.*, **12**, 1221 (1958).
(8) S. Iwayanagi, I. Sakurai, T. Sakurai, and T. Seto, *J. Macromol. Sci., Phys.*, **2**, 163 (1968).
(9) P. H. H. Fischer and C. A. McDowell, *Can. J. Chem.*, **38**, 187 (1960).
(10) R. A. Durie and R. J. Harrisson, *Spectrochim. Acta*, **18**, 1505 (1962).
(11) P. Vaughan and J. Donohue, *Acta Crystallogr.*, **5**, 530 (1952).
(12) M. Takayanagi, K. Imada, A. Nagai, T. Tatsumi, and T. Matsuo, *J. Polym. Sci., Part C*, **No. 16**, 867 (1967).
(13) S. F. Bermudez and J. Ma. G. Fatou, *Eur. Polym. J.*, **8**, 575 (1972).
(14) S.-B. Ng, J. M. Stellman, and A. E. Woodward, *J. Macromol. Sci., Phys.*, **7**, 539 (1973).
(15) T. Ohmori, T. Ichikawa, and M. Iwasaki, *Bull. Chem. Soc. Jap.*, **46**, 1383 (1973).
(16) N. Gō and H. A. Scheraga, *Macromolecules*, **6**, 525 (1973).
(17) F. Yoshii, N. Hayakawa, T. Abe, N. Tamura, K. Kobayashi, and N. Sakamoto, 22nd Symposium of the Society of Polymer Science, Japan, Abstract II-13, 1973.
(18) K. Monobe and F. Yokoyama, U.S.-Japan Joint Seminar on Polymer Solid State, Cleveland, Ohio, 1972.