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Studies on Polymers from Cyclic Dienes. VI. Radiation Polymerization of the Thiourea Complex of Cyclopentadiene[*1]

Chuji Aso, Toyoki KUNITAKE and Yoshikazu ISHIMOTO

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka

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Cyclopentadiene was found to polymerize as its thiourea complex when irradiated with γ-rays from ^{60}Co. The conditions of preparing the complex were an important factor in increasing the conversion, the use of 50 vol% aqueous acetone giving the best results. The polymer yield increased with dose and with temperature. The apparent activation energy of the polymerization was 2.7 kcal/mol. The polycyclopentadiene thus obtained was concluded from its NMR and IR spectral data to have mainly the 1, 4-structure.

As we have already reported, the structure of polycyclopentadiene (1, 4- or 1, 2-structure) can be estimated from its NMR spectrum.[1)]

1, 4-Structure 1, 2-Structure

Polycyclopentadienes obtained with various catalysts possessed comparable amounts of both 1, 4- and 1, 2-structures. In cationic polymerization with Friedel-Crafts catalysts, the content of the 1, 2-structure varied from 40% to 60%, and several Ziegler-type catalysts gave polymers containing about 40% of the 1, 2-structure.[2)]

Brown and White obtained polymers by irradiating the thiourea complexes of various dienes.[3)] The irradiation of the cyclopentadiene complex

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1) C. Aso, T. Kunitake, K. Ito and Y. Ishimoto, *J. Polymer Sci.*, **B4**, 701 (1966).

2) C. Aso, T. Kunitake and Y. Ishimoto, *ibid.*, in press.

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

by the same authors, however, gave endo-dicyclopentadiene as the main product, along with a trace amount of a liquid polymer. The canal copolymerization of this monomer with 2, 3-dimethylbutadiene, 2, 3-dichlorobutadiene, and 1, 3-cyclohexadiene was reported to be possible.

Considering the formation of stereoregular poly(1, 3-cyclohexadiene) by Brown and White and the rapid dimerization of cyclopentadiene, it was felt necessary to reinvestigate the canal polymerization of cyclopentadiene, in which we expected to obtain a polymer with the regular structure.

Experimental

Materials. Cyclopentadiene was obtained by degradative distillation of dicyclopentadiene, dried with molecular sieve 3A and redistilled before use under nitrogen. Because of its facile dimerization, cyclopentadiene was kept at low temperatures. Commercial first-grade thiourea was used without further purification. Solvents were purified by the usual methods.

Polymerization Procedures. The thiourea complex was prepared by a modified Brown and White procedure. Given amounts of thiourea and solvents were placed in a 100 m*l* Erlenmeyer flask and shaken at room temperature. Most of the thiourea remained undissolved. After cooling to −20°C in a freezer, monomer was pipetted in. A large amount of a white precipitate (canal complex) was formed. The contents were shaken well and kept in the same freezer. After the solution had been aged for 40 hr, the precipitate was filtered and air-dried on a filter for 10 min in order to remove the solvent. The precipitate was then placed in ampoules, which were sealed under nitrogen with cooling. Then the ampoules were irradiated with γ-rays from ^{60}Co at given temperatures. After given reaction periods, the ampoules were opened and the contents poured into 500 m*l* of methanol containing a small quantity of antioxidants under nitrogen, stirred magnetically for more than one hour, centrifuged and dried *in vacuo*. The polymer yield was calculated on the basis of the quantity of the monomer used.

Measurements. Viscosities were measured in benzene at 30°C using a modified Ubbelohde viscometer. Infrared spectra were obtained with a Nippon Bunko DS 301 spectrometer. Nuclear magnetic resonance spectra of the polymer were taken with a Varian A60 spectrometer using carbon tetrachloride solution of approximately one mer unit/*l* concentration at about 37°C.

Results and Discussion

Polymerization. Some of the polymerization results are given in Table 1. Contrary to the finding of Brown and White[3] polycyclopentadiene was readily obtained through the thiourea-canal polymerization. The solvent system used for the preparation of the complex had a strong influence on the polymer yield. The best results were obtained when the thiourea complex was prepared in 50 vol% aqueous acetone. When water, methanol, pyridine or acetone were used as solvents for the adduct formation, polymer yields were zero or trace (Expt. 6-9, 6-10, 6-11, 3-2, and 8-5). Seemingly the solvent must have suitable solubility for both monomer and thiourea. When a mixture of thiourea and cyclopentadiene was aged either with or without acetone, and irradiated without removing the liquid (Expt. 3-1, 3-4, and 6-7), polymers were obtained at −80°C. However, the structure of the polymers thus obtained was quite different from that of the canal polymerization (the 1, 2-structure content: 38% (Method 1), 25%(Method 2); $D/(A+B+C)=0.42$), indicating polymerization of the uncomplexed monomer (see below). The amount of solvent (Expt. 3-6, and 6-6) and the order of mixing (Expt. 2-1, 2-2, and 3-4) affect formation of the thiourea complex appreciably. Brown and White did not find much variation in polymerizability with the solvent used for preparing the thiourea complex of 2, 3-dimethylbutadiene. The strong solvent effect on the thiourea-cyclopentadiene system would imply that the formation of a canal complex suitable for polymerization is much more difficult with cyclopentadiene than with 2, 3-dimethylbutadiene. The addition of dicyclopentadiene (Expt. 12-1, 12-2, and 12-3) decreases the polymer yield and seems to lower its molecular weight, as recovery of the polymer on reprecipitation from toluene and methanol decreases with the amount of dicyclopentadiene added.

Figure 1 (Tables 1 and 2) gives the relationship between polymer yield and dose at 0°C and −80°C. Although the data are somewhat scattered, the yield increases linearly with dose. The rate of polymerization is 15.5%/MR at 0°C and 2%/MR at −80°C. The apparent activation energy obtained from these values is 2.7 kcal/mol. This low value seems to be common in canal polymerization. For instance, the activation energy for the urea-canal polymerization of acrylonitrile

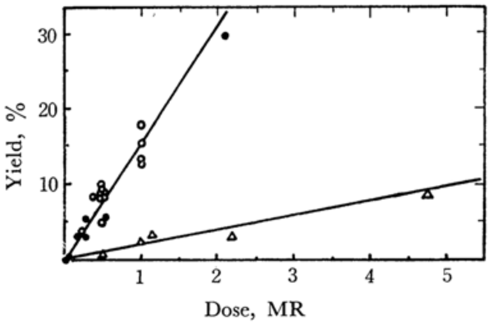

Fig. 1. Relationship between polymer yield and dose.

△: −80°C, ●, ○=0°C.

The amount of the monomer used is somewhat different between black and white circles.

TABLE 1. RADIATION POLYMERIZATION OF CYCLOPENTADIENE-THIOUREA ADDUCT

No.	Solvent	ml	Thiourea g	Monomer ml	Aging °C	Aging hr	Irradiation °C	Irradiation MR	Yield %	Remark
1-2	H_2O-acetone (1:1)	40	16	3.6	−20	53	−80	4.60	8.5	[η]=0.13
2-1	H_2O-acetone (1:1)	10	8	3	−20	64	−80	1.14	3.2	
2-2	H_2O-acetone (1:1)	10	8	3	−20	64	−80	2.17	3.2	
3-4	H_2O-acetone (1:1)	10	8	3	−20	40	−80	4.36	0	a
3-6	H_2O-acetone (1:1)	400	40	10	−20	26	−80	3.29	1.7	
6-6	H_2O-acetone (1:1)	200	20	7	−20	50	−80	3.28	0.3	
3-2	H_2O	10	8	3	0	40	−80	4.36	0	
3-3	acetone	10	8	3	−20	40	−80	4.36	trace	
3-5	acetone	10	8	3	−20	40	−80	4.36	7.9	b
3-1	acetone	10	8	3	−20	40	−80	4.36	2.7	b
6-7	none		8	3	−20	50	−80	3.28	1.9	[η]=0.32
6-9	methanol	20	8	3	−20	50	−80	3.28	trace	
6-10	pyridine	20	8	3	−20	50	−80	3.28	trace	
6-11	acetone	20	8	3	−20	50	−80	3.28	trace	
7-1	H_2O-acetone (1:1)	20	16	6	0	40	0	0.96	0.6	
7-2							−80	0.96	0.6	
7-3	H_2O-acetone (1:1)	20	16	6	−20	40	0	0.96	8.1	[η]=0.32
7-4							−80	0.96	0.9	mp 79—94°C
8-2	H_2O-acetone (1:1)	10	8	3	−20	39	0	2.02	17.6	c
8-3	H_2O-acetone (1:1)	10	8	2	−20	39	0	2.02	15.0	
8-5	H_2O	10	8	3	0	39	0	2.02	0	
9-1	H_2O-acetone (1:1)	10	8	3	−20	65	0	2.08	29.6	$\eta_{sp/c}=0.36$ (0.5 g/dl)
9-4	H_2O-acetone (1:1)	10	8	5	−20	65	0	2.08	12.0	c
12-1	H_2O-acetone (1:1)	10	8	3	−20	36	0	2.18	17.4	DCPD 1 vol % added
12-2	H_2O-acetone (1:1)	10	8	2.9	−20	36	0	2.18	18.9	DCPD 5 vol % added
12-3	H_2O-acetone (1:1)	10	8	2.7	−20	36	0	2.18	9.8	DCPD 10 vol% added

a : Monomer and thiourea were added in this order to the solvent kept at 0°C.
b : Polymerized without removing solvent.
c : The added monomer was aged without shaking.

is 0.62 kcal/mol between −50 and −196°C.⁴⁾ Since initiation is a high energy process and since the termination process would not contribute to the apparent activation energy in the present system, the low activation energy obtained would be ascribed only to the propagation process in the canal.

Polymer Structure. Figures 2a and 2b show NMR spectra of some of the polymers obtained in the thiourea-canal polymerization. When these spectra are compared with that of a cationically-obtained polymer (Fig. 2c)²⁾ it is apparent that peak B is almost lacking in the former. In the previous paper,¹⁾ it was concluded from comparison with the spectrum of 3, 5-dimethylcyclopentene that peak A was assigned to the β-methylene proton in the 1, 4-structure, while the α-methine proton in the 1, 4-structure seems to be included in peak C. Therefore, the absence of peak B strongly indicates that the polymer is composed mainly of the 1, 4-structure.

The content of the 1, 2-structure in polycyclopentadiene was shown to be estimated according to the following equation¹⁾:

Method 1

$$[1,2\text{-structure}]\% = \frac{(B+C)-A}{A+(B+C)} \times 100$$

Method 2

$$[1,2\text{-structure}]\% = \left(1-\frac{A}{D}\right) \times 100$$

Table 3 gives the calculated contents of the 1, 2-structure in the polymer obtained by the canal polymerization. These contents are always much lower than those obtained for cationic polymers. The D/(A+B+C) values are in most cases lower than 0.5, indicating migration of the double

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4) M. Kawasaki, T. Maekawa, K. Hayashi and S. Okamura, *J. Macromol. Chem.*, **1**, 489 (1966).

TABLE 2. RADIATION POLYMERIZATION OF CYCLOPENTADIENE-THIOUREA ADDUCT

No.	Solvent	m*l*	Thiourea g	Monomer m*l*	Aging		Irradiation		Yield %	Remark
					°C	hr	°C	MR		
10-1	H_2O-acetone (1:1)	10	8	3	−20	42	0	0.0073	trace	
10-2	H_2O-acetone (1:1)	10	8	3	−20	42	0	0.0439	0.5	
10-3	H_2O-acetone (1:1)	10	8	3	−20	42	0	0.132	3.1	
10-5	H_2O-acetone (1:1)	10	8	3	−20	42	0	0.439	5.8	$\eta_{sp/c}=0.34$ (0.5 g/d*l*)
13-1	H_2O-acetone (1:1)	40	32	12	−20	36	0	0.219	3.0	
13-2	H_2O-acetone (1:1)	20	16	4	−20	60	−80	0.494	0.5	
13-2′							−80	1.01	2.4	
13-3	H_2O-acetone (1:1)	10	8	3	−20	60	0	0.219	5.5	
15-1	H_2O-acetone (1:1)	60	48	24	−20	40	0	0.400	9.4	a
15-3							0	0.400	8.3	b
16-2	H_2O-acetone (1:1)	20	16	8	−20	40	0	0.287	8.4	
16-3	H_2O-acetone (1:1)	20	16	8	−20	40	0	0.983	13.6	
17	H_2O-acetone (1:1)	20	16	8	−20	40	0	1.01	18.1	
18-1	H_2O-acetone (1:1)	20	16	8	−20	41	0	0.394	9	
18-2	H_2O-acetone (1:1)	20	16	8	−20	41	0	0.394	10	
18-3	H_2O-acetone (1:1)	20	16	8	−20	41	0	0.394	5	
19-1	H_2O-acetone (1:1)	80	64	32	−20	41	0	1.01	12.8	
19-2							0	1.01	15.6	
193							0	0.406	8.1	
194							0	0.406	9.1	

a : The reaction mixture was poured into methanol 2 min after irradiation is over.
b : Similarly 17 hr later.

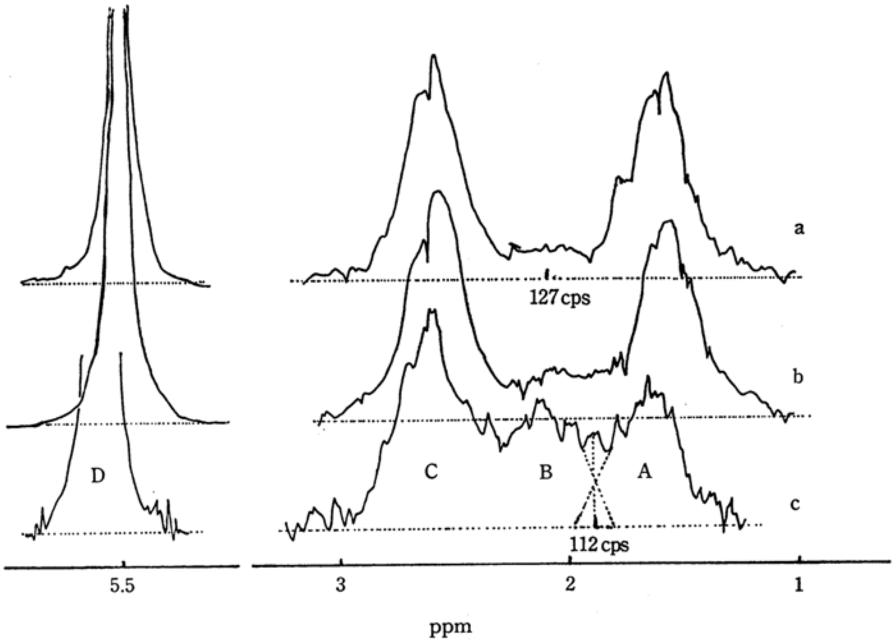

Fig. 2. NMR spectra of polycyclopentadiene.

a : Canal polymer No. 19-1 in Table 3: spectra obtained at 55°C.
b : Canal polymer No. 19-1 in Table 3: spectra obtained at 37°C.
c : Polymer obtained in toluene with $SnCl_4$ catalyst.

Table 3. Structure of the canal polymer determined by the NMR method

No.	Dose MR	1, 2-Structure %		$\frac{D}{A+B+C}$	$\frac{A}{C}$
		Method 1	Method 2		
1-2	4.60	9	−15	0.40	0.98
7-3	0.96	9	−32	0.35	0.91
9-1	2.08	11	−7	0.41	1.02
10-2	2.18	18	−11	0.39	—
10-3	0.132	0	−16	0.41	0.99
10-5	0.439	4	−2	0.47	1.10
13-1	0.219	15	3	0.44	—
19-1	1.01	18(10)	4(2)	0.43(0.46)	0.91(0.96)
19-2	1.01	(11)	(−11)	(0.40)	(0.98)
19-3	0.406	(13)	(9)	(0.48)	(0.99)
19-4	0.406	12(12)	14(−11)	0.51(0.41)	1.00(1.00)

Data in parentheses are obtained from NMR spectra at 55°C.
Measurement was at about 37°C if not mentioned otherwise.

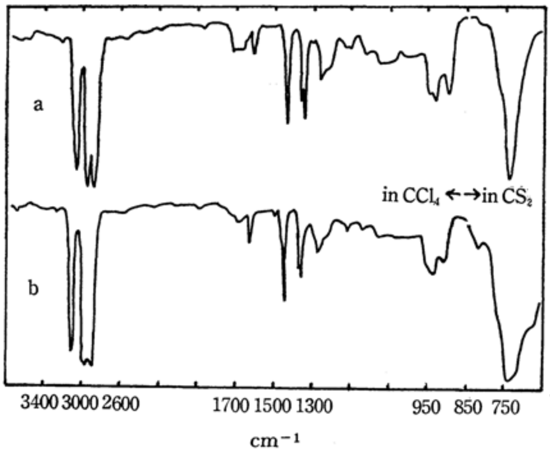

Fig. 3. IR spectra of polycyclopentadiene.
a : Canal polymer
b : Polymer obtained at −50°C in toluene with $AlCl_3$ catalyst

bond; therefore, the 1, 2-structure contents calculated by Method 2 are lower than those calculated by Method 1. The 1, 2-structure contents calculated by Method 1 (which are considered to be more reliable than those calculated by Method 2; see Ref. 2) vary from 0 to 18%. This variation and lower amounts of the olefin proton are not understandable for the polymerization proceeding in the canal where steric restriction must be quite severe. The canal polymerization of 2, 3-dimethylbutadiene (with thiourea)³⁾ and of butadiene (with urea)⁵⁾ gave crystalline 1, 4-*trans* polymers, and these results were rationalized by considering the arrangement of the monomer in the canal. Formation of crystalline poly(1, 3-cyclohexadiene) was interpreted in the same way.³⁾ A consideration of the steric arrangement of the cyclopentadiene-thiourea complex using a molecular model similarly suggests the 1, 4-*trans* propagation of cyclopentadiene, and the 1, 2-type propagation seems improbable within the normal canal structure.

Thus, the presence of the 1, 2-structure may be attributed to the artifact due to the present NMR assignment. For polycyclopentadiene obtained with Friedel-Crafts catalysts and with Ziegler catalysts, peak A and peak (B+C) were separated at 112 cps (60 Mc) assuming that the area belonging to peak A above 112 cps and the area belonging to peak B below 112 cps cancel each other (see Fig. 2c). In cases where peak B can be assumed to be absent as in the present case, however, the supposed separation of peak A and peak (B+C) at 112 cps may be erroneous, since the area between peak A and peak C might as well be ascribed to the overlapping of these two peaks. Thus if peak A and peak C are separated at 127 cps (the middle point between peak A and peak C) assuming that peak B is absent, then the area ratios (A/C) are obtained as given in the last column of Table 3. The ratios are, in most cases, close to unity, showing that the amounts of the β-methylene and the α-methine proton are almost the same. The structure of the polymer thus seems to be quite regular, being composed mostly of the 1, 4-type structure. On the other hand, the smaller-than-theoretical amount of the olefin proton cannot be explained.

Table 4. Effect of irradiation on structure of polycyclopentadiene polymer sample obtained at 0°C in toluene with $SnCl_4$ catalyst
Irradiation: 0°C, 0.192 MR (4.35×10^4 R/hr)

	1, 2-Structure %		$\frac{D}{A+B+C}$
	Method 1	Method 2	
Before irradiation	49.9	52.3	0.53
After irradiation	48.3	51.5	0.54

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5) D. M. White, *J. Am. Chem. Soc.*, **82**, 5678 (1960).

TABLE 5. RADIATION POLYMERIZATION OF CRYSTALLINE CYCLOPENTADIENE
^{60}Co: 4.50×10^4 R/hr, Irradiation temperature: −196°C (liquid nitrogen)

No.	Dose MR	Yield %	$[\eta]^{30°}_{C_6H_6}$	1, 2-Structure %		$\frac{D}{A+B+C}$
				Method 1	Method 2	
4-1	0.73	0.41	0.79	55	55	0.48
4-2	1.03	0.44				
4-3	1.80	0.64				
4-4	2.91	0.97	0.71	51	57	0.57
5-10[a]	5.46	0.80	0.83			
5-11[b]	5.46	0.74				
5-12	5.46	1.07	0.93	49	47	0.48

a: 1.4 mol% of triethylamine added to monomer.
b: 0.2 mol% of 2, 6-di-*t*-butyl-*p*-cresol added to monomer.

Since it has been reported that diene polymers are isomerized by ionizing radiation, a polymer sample obtained cationically was irradiated at 0°C. Table 4 compares the polymer structure before and after irradiation. There is no difference in the polymer structure, indicating an absence of the double bond migration upon this extent of irradiation. In addition, the variation in the D/(A+B+C) values cannot be correlated with dose, as can be seen from Table 3. Therefore, the decrease in the olefin proton, if any, must occur during propagation.

The infrared spectrum of polycyclopentadiene obtained by the thiourea canal polymerization is shown in Fig. 3. The IR spectrum of a cationically-obtained polymer is also shown for comparison. Some differences can be noted between these two spectra.

The peak at 750 cm^{-1} (δ_{CH}, out of plane) is much sharper than that of the cationic polymer, suggesting that one type of the double bond is predominant. The $\nu_{C=C}$ peaks at 1620 cm^{-1} are similar in both spectra. A somewhat broad peak at around 1700 cm^{-1} is observed only in the canal polymer. A similar peak is found in the spectrum of 3, 5-dimethylcyclopentene[2)]—a model compound for the 1, 4-structural unit. Aliphatic ν_{CH} peaks at 2860 and 2980 cm^{-1} are separated better than those in the cationic polymer. A characteristic peak for trisubstituted double bonds at 830 cm^{-1} is observed with polymethylcyclopentadiene.[6)] This peak is also found for highly isomerized polycyclopentadiene (*e. g.*, with $AlBr_3$ catalyst), indicating formation of a trisubstituted double bond by isomerization. No such peak is found for the canal polymer, again showing that isomerization, if any, is not extensive. In general, the peaks are sharper with the canal polymer and support the idea that the polymer structure is simpler than that of the cationic polymer, consisting predominantly of the 1, 4-structure.

Radiation Polymerization in the Solid State. The solid-state polymerization of cyclopentadiene by γ-rays has already been reported by Okamura *et al.*,[7)] although they did not discuss the polymer structure. In the present polymerization system it is possible for the monomer outside the canal to polymerize. In order to check this possibility, cyclopentadiene was polymerized at −196°C in the solid state and its structure was investigated by the NMR method. Table 5 shows the results. The polymer contains about equal amounts of the 1, 2- and 1, 4-structures. These contents are much more similar to those of the cationic polymer than to those of the canal polymer. Therefore, polymerization inside and outside the canal give polymers of different structure. Judging from the polymer structure, the solid-phase polymerization may include a cationic propagating species.

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6) C. Aso and O. Ohara, *Macromol. Chem.*, in press.

7) H. Hamada, K. Hayashi and S. Okamura, Reprint for the 14th Annual Meeting of the Chemical Society of Japan (April, 1961), p. 238.