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Cationic Polymerization of Cyclic Dienes. IX.* The Structure of Poly(1,3-cyclohexadiene) and Poly(cis, cis-1,3-cyclooctadiene)

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SUMMARY

The structure and properties of poly(1, 3-cyclohexadiene) and poly(cis, cis-1, 3-cyclooctadiene) obtained in the cationic polymerization were investigated.

The structure of polycyclohexadiene was almost independent of the polymerization conditions (catalyst, $\text{SnCl}_4\text{-CCl}_3\text{COOH}$ or $\text{BF}_3 \cdot \text{OEt}_2$; solvent, CH_2Cl_2 or benzene), and the polymer consisted of either 1, 4 or 1, 2 structural unit. The NMR spectra of the polymer showed the loss of double bond, which was explained in terms of chain branching. The polymer softened at 114-130°C, and was quickly oxidized by air.

The structure of polycyclooctadiene was almost unaffected by the catalyst (TiCl_4 , SnCl_4 , or BF_3) but was dependent on the solvent (toluene or CH_2Cl_2). In methylene chloride, the branch-free polycyclooctadiene was produced and the polymer consisted almost exclusively of 1, 4 structural units. Infrared spectra of the polymer showed a number of characteristic absorptions which were sensitive to the polymerization conditions. Some of them were affected by heating and swelling and were assumed to be conformation-sensitive bands. The rest was insensitive to these treatments and was assumed to be a configuration-sensitive band. The polymer was amorphous and softened at 172-184°C. It was oxidized by air very slowly as compared with polycyclopentadiene and polycyclohexadiene.

*For the previous paper of this series, see Ref. [1].

INTRODUCTION

The polymerization of conjugated dienes yields two sorts of structural isomers, namely, 1, 2 polymer and 1, 4 polymer. Their relative importance is a function of polymerization conditions. This problem has been dealt with on polycyclopentadiene (PCPD)[2] and polymethylcyclopentadiene (PMCPD)[3] in our earlier papers.

The polymerization of conjugated dienes usually accompanies chain branching. Branched PCPD [2] and PMCPD [3] have been obtained in the cationic polymerization. The synthesis of branching-free polymers of cyclic dienes is desirable.

PCPD and PMCPD were found to be oxidized quickly. The ring size of the monomer may have a bearing on this. The synthesis of polymers that are resistant to oxidation will be useful.

In this connection, poly(1, 3-cyclohexadiene) (PCHD) and poly(cis, cis-1, 3-cyclooctadiene) (PCOD) were synthesized in the cationic polymerization, and the structure and properties of these polymers were investigated.

EXPERIMENTAL

Materials

The syntheses and purification of CHD and COD have been described in previous papers [1, 4], and the purifications of the solvents and catalysts have also been described.

Boron trifluoride (BF_3) was generated by heating sodium fluoroborax [$\text{Na}_2\text{O}(\text{BF}_3)_4$] with concentrated sulfuric acid.

Procedures

The polymerizations were carried out as described in earlier papers. CHD was polymerized by SnCl_4 -TCA and $\text{BF}_3 \cdot \text{OEt}_2$ in toluene and methylene chloride at 0°C . COD was polymerized by TiCl_4 , TiCl_4 -TCA, SnCl_4 -TCA, and BF_3 in toluene and methylene chloride at -78°C . The determination of conversion and molecular weight has been described in previous papers [1, 4].

The structure of polymer was analysed by IR and NMR spectra and X-ray diagram. IR spectrum of polymer was measured as KBr disk. NMR spectrum of polymer was measured as carbon tetrachloride solution at 60 Mc using tetramethyl silane as an internal standard.

RESULTS AND DISCUSSION

Poly(1, 3-Cyclohexadiene)

Properties of Polymer. The methanol-insoluble PCHD's were white powder and their intrinsic viscosities ranged from 0.04 to 0.12. They softened at 114 - 130°C .

The polymer was soluble in aromatic hydrocarbons and some other organic solvents. The polymer was oxidized by air more slowly than PCPD or PMCPD, and turned pale yellow and insoluble in organic solvents.

Infrared Study. The infrared spectrum of a PCHD is shown in Fig. 1. Very few differences were found among infrared spectra of PCHD prepared under various conditions.

NMR Study. As was described in the Introduction, 1, 2 and 1, 4 polymers will be produced in the cationic polymerizations of CHD. The area ratio of various proton peaks in the NMR spectra of PCHD is variable, depending on the polymer structure, as explained in Table 1.

An NMR spectrum of PCHD is shown in Fig. 2. A sharp peak at $\tau = 4.38$ was ascribed to olefinic protons (H_O). Two peaks at $\tau = 8.00$ and 8.40 were ascribed to H_α and H_β , respectively. This assignment was made in accordance with Aso's assignment [5]. The results of NMR spectroscopy on the polymers obtained under various conditions are summed up in Table 2.

With respect to $H_O/(H_\alpha + H_\beta)$, the observed values ranged from 1/3.6 to 1/4.5 and are somewhat smaller than the theoretical value of 1/3. This means that about 20% of cyclohexene double bonds in the polymer had been lost. The presence of chain branching in the polymer would be the most probable reason for the loss of double bond. The decrease of $H_O/(H_\alpha + H_\beta)$ ratio with increasing conversion (Table 2) supports this conclusion.

The idea that the attack of a propagating ion on a cyclohexene unit in the polymer, results in chain branching, may be ruled out because cyclic olefins were not chain transfer agents for the polymerization of CPD in our preliminary experiments [6]. Alterna-

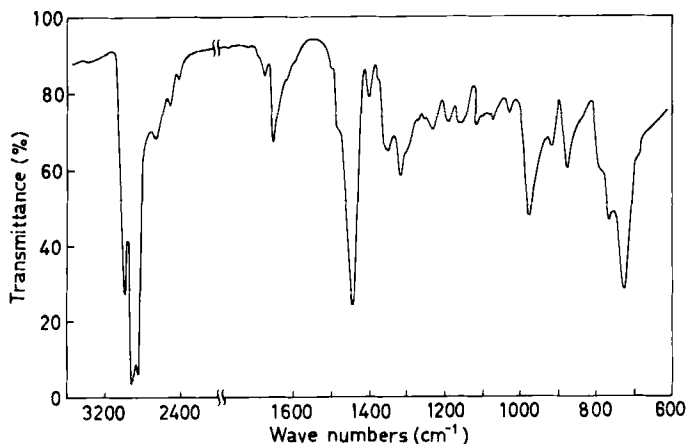


Fig. 1. Infrared spectrum of polycyclohexadiene. KBr disk. Polymer obtained by SnCl_4 -TCA in methylene chloride at 0°C .

Table 1. Expected NMR Data

	1, 2-Polycyclohexadiene	1, 4-Polycyclohexadiene
Structure		
$H_\gamma/(H_\alpha + H_\beta)$	1/3	1/3
H_α/H_β	1/1	1/2

Table 2. NMR Data of Polycyclohexadiene Prepared under Various Conditions

a. Effect of conversion on $H_\gamma/(H_\alpha + H_\beta)$. Solvent, CH_2Cl_2 ; $[M]_0 = 1.05$ mole/liter.				
Catalyst	$SnCl_4$ -TCA		$BF_3 \cdot OEt_2$	
Concentration, mmole/liter	—		4.76	
Conversion, %	38	87	48 ^a	76 ^a
$H_\gamma/(H_\alpha + H_\beta)$	1/3.9	1/4.5	1/3.6	1/4.2
b. Effect of catalyst concentration on $H_\gamma/(H_\alpha + H_\beta)$. Solvent, CH_2Cl_2 ; $[M]_0 = 1.05$ mole/liter.				
Catalyst	$SnCl_4$ -TCA		$BF_3 \cdot OEt_2$	
Concentration, mmole/liter	4.15	2.86	4.76	1.98
Conversion, %	29 ^a	24 ^a	48 ^a	48 ^a
$H_\gamma/(H_\alpha + H_\beta)$	1/4.4	1/4.2	1/3.6	1/3.7

^aDetermined by gas chromatography.

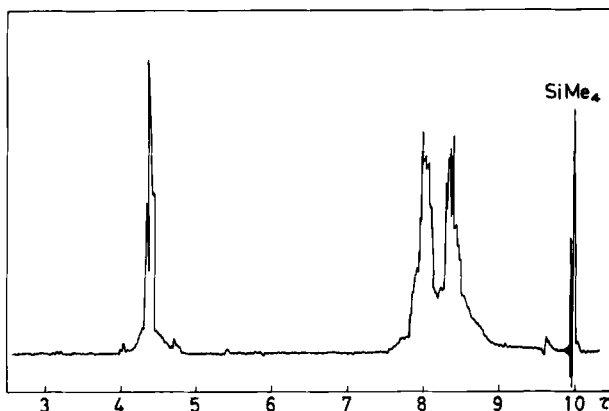
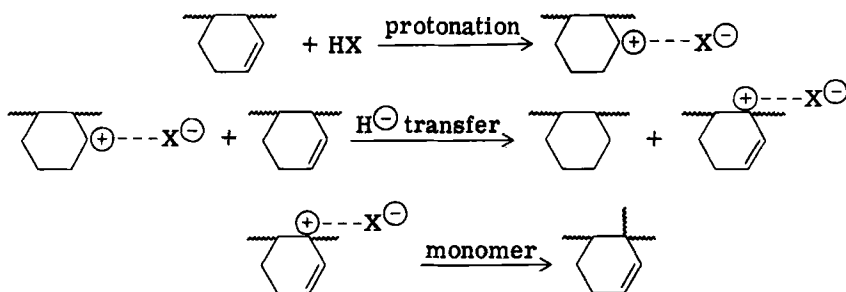


Fig. 2. Nuclear magnetic resonance spectrum of polycyclohexadiene. Polymer obtained by SnCl_4 -TCA in methylene chloride at 0°C .

tively, the interaction between a catalyst and a double bond of cyclohexene unit in PCHD is proposed as a source of chain branching, in accordance with Deno and Pittman [7].



As catalyst molecules may be distributed partly to the monomer (polymerization) and partly to the double bond (chain branching), always at a given ratio, the catalyst concentration would not affect the degree of chain branching, as was actually observed (Table 2).

The estimation of the peak areas at $\tau = 8.00$ and 8.40 was difficult. In addition, the loss of double bond in the polymer makes a quantitative discussion on H_α/H_β difficult. On a qualitative level, H_α/H_β decreased in the order CH_2Cl_2 - SnCl_4 -TCA system $>$ CH_2Cl_2 - $\text{BF}_3 \cdot \text{OEt}_2$ system $>$ benzene- SnCl_4 -TCA system. However, the variation of H_α/H_β according to the polymerization condition was not so significant.

In Table 2, SnCl_4 -TCA caused more chain branching than $\text{BF}_3 \cdot \text{OEt}_2$ under comparable conditions.

Poly(cis, cis-1, 3-cycloöctadiene)

Properties of the Polymer. The methanol-insoluble PCOD's were white powders and had a high softening temperature. For example, the polymer obtained in the $\text{TiCl}_4\text{-H}_2\text{O-CH}_2\text{Cl}_2$ system had an intrinsic viscosity of 0.101 and a softening temperature of 172-184°C. Polycyclohexadiene of comparable molecular weight had a softening temperature of 114-130°C. Polycycloöctadiene is soluble in aromatic hydrocarbons, decalin, chlorinated hydrocarbons, tetrahydrofuran, etc. However, polymers produced in methylene chloride using high catalyst concentrations were insoluble in common organic solvents, which suggests cross-linking.

Polycycloöctadiene was more resistant to auto-oxidation than polycyclopentadiene [2]. Only a weak absorption due to carbonyl group (1720 cm^{-1}) appeared in the IR spectrum of polycycloöctadiene standing in air at room temperature for 40-45 days. Even after 200 days at room temperature, the carbonyl absorption was not strengthened and the polymer remained white. The viscosity of the polymer was not changed after standing for a long time at room temperature. However, at elevated temperatures the polymer was oxidized. It turned yellow, and carbonyl absorption appeared strongly after about 10 min at 130°C and after about 6 min at 150°C.

Infrared Study. Polycycloöctadienes obtained using $\text{TiCl}_4\text{-TCA}$ as a catalyst showed different IR spectra depending on the solvent used. The IR spectrum of polycycloöctadiene obtained in toluene is shown in Fig. 3, for example. Characteristic absorptions appeared at $1530, 1510, 1350, 725,$ and 690 cm^{-1} , but none of them was detect-

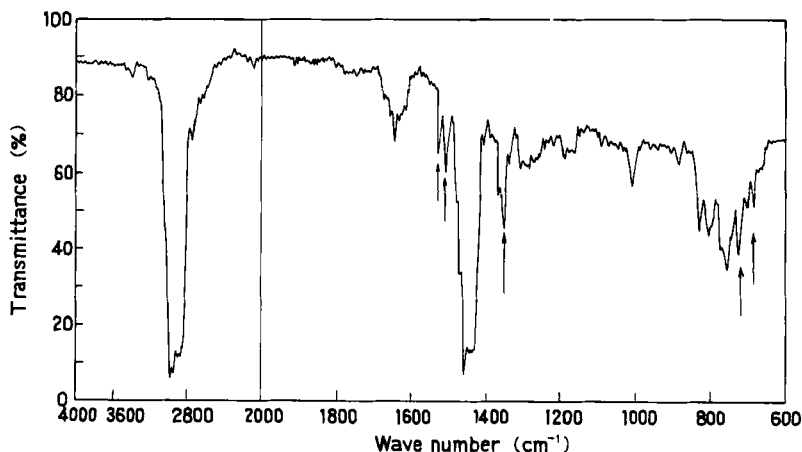


Fig. 3. Infrared spectrum of polycycloöctadiene. KBr disk. Polymer obtained by $\text{TiCl}_4\text{-TCA}$ in toluene at -78°C ; $[\text{C}]_0$, 34.8 mmole/liter; $[\text{M}]_0$, 0.73 mole/liter; conversion, 30.2%.

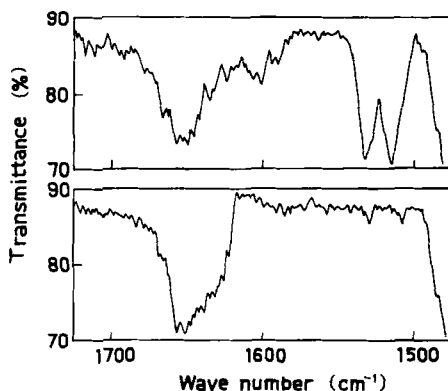


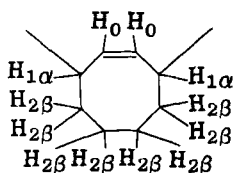
Fig. 4. Difference of infrared spectra of polycyclooctadienes obtained under various conditions. (A): TiCl_4 -TCA, toluene, -78°C ; $[\text{C}]_0$, 34.8 mmole/liter; $[\text{M}]_0$, 0.73 mole/liter; conversion, 34.2%. (B): TiCl_4 -TCA, methylene chloride, -78°C ; $[\text{C}]_0$, 10.0 mmole/liter; $[\text{M}]_0$, 0.73 mole/liter; conversion, 34.3%.

able in the IR spectrum of the polymer obtained in methylene chloride. The variation of absorptions at 1510 - 1530 cm^{-1} is shown in Fig. 4.

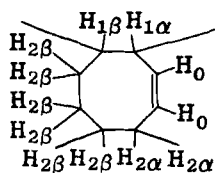
The absorptions at 1510 and 1350 cm^{-1} were affected not only by the polymerization solvent but also by the catalyst concentration, the monomer concentration, and the conversion. The absorptions at 1530 , 725 , and 690 cm^{-1} were affected either by heating the polymer in vacuum at 180°C and cooling it at the rate of 10°C/hr , or by boiling the polymer in a nonsolvent such as *n*-hexane. The change of the absorption at 1530 cm^{-1} is shown in Fig. 5.

As shown in Fig. 5, the absorption at 1530 cm^{-1} vanishes when thermally treated or swollen in *n*-hexane. The same phenomenon was observed with the absorptions at 725 and 690 cm^{-1} . It is hard to imagine that the polymer configuration is altered during those treatments. The absorptions at 1530 , 725 , and 690 cm^{-1} are believed to be sensitive to the polymer conformation.

NMR Study. When a linear polymer is formed by the polymerization of COD, there are two modes of propagation, as shown below:



1, 4 structural unit



1, 2 structural unit

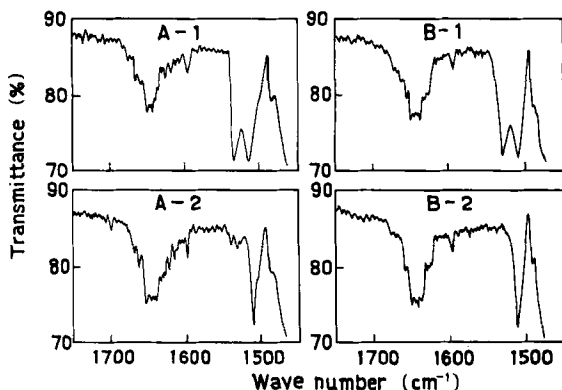


Fig. 5. Change of infrared spectra of polycyclooctadienes obtained by TiCl_4 -TCA in toluene at -78°C . Polymerization conditions: $[\text{C}]_0$, 34.8 mmole/liter; $[\text{M}]_0$, 0.73 mole/liter; conversion, 34.2%. A-1, untreated; A-2, thermally treated; B-1, untreated; B-2, swollen in *n*-hexane.

NMR spectra of polycyclooctadienes obtained in toluene and methylene chloride are shown in Fig. 6, together with those of *cis*-cyclooctene and COD, which were used as the standard to make assignment of the polymer spectra. The NMR peak at 4.80τ was ascribed to H_0 , that at 7.70 - 7.80τ to $\text{H}_{1\alpha} + \text{H}_{1\beta} + \text{H}_{2\alpha}$, and that at 8.45τ to $\text{H}_{2\beta}$. Using this assignment, the area ratios of several NMR peaks were calculated with various polycyclooctadienes obtained under different conditions. The analysis is given in Table 3.

The polymer consisting of 1, 4 structural units exclusively should have the ratio $\text{H}_0 : \text{H}_{1\alpha} + \text{H}_{1\beta} + \text{H}_{2\alpha} : \text{H}_{2\beta} = 1 : 1 : 4$. The 1, 2 polymer should have the ratio 1 : 2 : 3. The insight of the data shown in Table 1 tells us that the polymers produced in methylene chloride consist almost exclusively of 1, 4 structural units. On the other hand, with reference to polymers produced in toluene, the peak area due to H_0 was small and that due to $\text{H}_{1\alpha} + \text{H}_{1\beta} + \text{H}_{2\alpha}$ was large as compared with the peak area due to $\text{H}_{2\beta}$. This indicates that the polymers produced in toluene are branched, and that the branch-free portion of the polymer consists of 1, 4 structural unit. The peak due to $\text{H}_{1\alpha} + \text{H}_{1\beta} + \text{H}_{2\alpha}$ of the polymer produced in toluene shifted to a higher magnetic field, by 0.10 ppm, than that of the polymer produced in methylene chloride. This would have been caused by the decrease of double bonding in the polymer because of branching. This prevents us from determining whether the branching takes place from 1, 4 or 1, 2 structural unit.

As discussed above, the nature of the catalyst used did not affect the structure of the polymer very much. However, the influence of the solvent used was very important. Such a profound effect of sol-

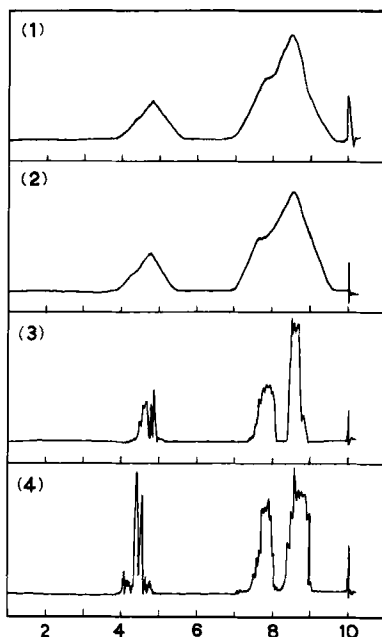


Fig. 6. Nuclear magnetic resonance spectra of polycyclooctadiene and related compounds. (1) Polycyclooctadiene. TiCl_4 -TCA, toluene, -78°C ; $[\text{C}]_0$, 34.8 mmole/liter; $[\text{M}]_0$, 0.73 mole/liter; conversion, 30.5%. (2) Polycyclooctadiene. TiCl_4 - H_2O , methylene chloride, -78°C ; $[\text{C}]_0$, 10.0 mmole/liter; $[\text{M}]_0$, 0.73 mole/liter; conversion, 11.7%. (3) Cis-cyclooctene. (4) Cis, cis-1,3 cyclooctadiene.

vent on the polymer structure has not been observed in the cationic polymerizations of CPD and CHD.

Trans-cyclooctene has been known to form silver ion complex strongly, and it is easily separated from the mixture of cis- and trans-cyclooctenes by argentation [8]. The experimental findings shown in Table 3, namely, that the polymers produced in methylene chloride have 1,4 structural units and are nearly branch-free, may be accounted for by the consideration that the 3,8-disubstituted cyclooctene unit in the polymer assumes a cis configuration so that the access of cationic species to the double bond for branching is hindered.

X-Ray Study. Polymers obtained by TiCl_4 -TCA in toluene or in methylene chloride were treated by heating or swelling in n-hexane. The untreated and treated polymers were subject to X-ray investigation.

Table 3. Analysis of NMR Spectra of Polycyclooctadiene Obtained in Various Conditions

Solvent	Catalyst	[C] ₀ , mmole/liter	[M] ₀ , mole/liter	Con- version, %	H ₀	H _{1α} + H _{1β} + H _{2α}	H _{2β}
CH ₂ Cl ₂	TiCl ₄ -H ₂ O ^a	70.0	0.73	49.0	1.00	1.05	4.01
C ₆ H ₅ CH ₃	TiCl ₄ -TCA	34.8	0.73	30.5	0.65	1.30	4.01
C ₆ H ₅ CH ₃	TiCl ₄ -TCA	35.0	0.73	22.0	0.60	1.40	4.01
C ₆ H ₅ CH ₃	TiCl ₄ -TCA	45.0	0.73	28.0	0.55	1.43	4.01
CH ₂ Cl ₂	SnCl ₄ -TCA	50.0	0.73	7.6	0.96	1.40	4.01
CH ₂ Cl ₂	BF ₃ -H ₂ O ^a	n. d.	0.73	27.5	0.96	1.10	4.01
C ₆ H ₅ CH ₃	BF ₃ -H ₂ O ^a	n. d.	0.73	10.7	0.69	1.62	4.01

^aCocatalyst was not added deliberately. Water inevitably present in the solution may have acted as cocatalyst.

Although polymers obtained in methylene chloride were in a regular 1, 4 structure, they were amorphous. Although the IR spectra of polymers obtained in toluene were changeable by crystallization treatment such as heating and swelling, they remained amorphous.

To conclude, it was first established that in methylene chloride a branch-free PCOD was obtained. In that solvent COD is polymerized almost exclusively via 1, 4 propagation. PCOD was also unique among polymers of cyclic dienes in that it was resistant to auto-oxidation.

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REFERENCES

- [1] Y. Imanishi, K. Matsuzaki, S. Kohjiya, and S. Okamura, *J. Macromol. Sci.*, **A3**, 237 (1969).
- [2] Z. Momiyama, Y. Imanishi, and T. Higashimura, *Kobunshi Kagaku*, **23**, 56 (1966).
- [3] S. Kohjiya, Y. Imanishi, and S. Okamura, *J. Polymer Sci.*, **A-1(6)**, 809 (1968).
- [4] Y. Imanishi, T. Yamane, S. Kohjiya, and S. Okamura, *J. Macromol. Sci.*, **A3**, 223 (1969).
- [5] C. Aso, T. Kunitake, and Y. Ishimoto, *J. Polymer Sci.*, **A-1(6)**, 1163 (1968).
- [6] Y. Imanishi, unpublished work.
- [7] N. C. Deno and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **86**, 1744 (1964).
- [8] (a) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953). (b) M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

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