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The Attempted Cationic Polymerization of 1, 1-Dimethylcyclopropane and Phenylcyclopropane

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1, 1-Dimethylcyclopropane and phenylcyclopropane gave the oligomer by aluminum bromide-catalyzed polymerization in *n*-hexane or in methylene chloride at 0°C. The polymerization reactivity of 1,1-dimethylcyclopropane was lower than that of styrene, and the content of cyclopropane units in their copolymers was decreased by a lowering of the temperature. The polymerization of 1,1-dimethylcyclopropane in the presence of polystyrene gave a graft polymer by chain transfer reaction. The polymerization of the cyclopropanes by a coordinated catalyst, $C_2H_5AlCl_2/TiCl_3$, in *n*-heptane at room temperature gave polymers with molecular weights of above 1200. The results are discussed in comparison with those of the polymerization of the corresponding vinyl monomers.

Cyclopropyl compounds polymerize in the presence of Lewis acids to give an oligomer.[1-3] The polymerizations of 1, 1-dimethylcyclopropane and phenylcyclopropane catalyzed by Lewis acids and a coordinated catalyst will be attempted in this work as an experiment preliminary to the copolymerization of the vinyl monomer with a cyclopropyl compound. 1, 1-Dimethylcyclopropane will be referred to isobutene in terms of their structures, especially, as growing terminal cations, while phenylcyclopropane will be referred to styrene. The results will be discussed in comparison with those of the polymerization of the corresponding vinyl monomers.

Experimental

Materials.—1, 1-Dimethylcyclopropane was prepared from 1, 3-dibromo-2, 2-dimethylpropane according to the method given by Shortridge et al.[4] B. p. 20.8°C; lit.[4] b. p. 20.63°C.

Phenylcyclopropane was obtained following the method of Dale et al.[5] B. p. 68.5—69.0°C/12 mmHg, n_D^{20} 1.5320; lit.[5] b. p. 69°C/12 mmHg, n_D^{20} 1.5320.

The monomers and solvents were carefully purified by the usual methods. Boron trifluoride - diethyl etherate, and stannic and titanic chlorides were distilled prior to use. The other catalysts, obtained commercially, were used without further purification.

Procedure.—*Polymerization by Lewis Acid.*—Into a glass stoppered test tube the monomer and solvent were taken and chilled to a given temperature. Then the catalyst solution was added. After a given time, ammoniac or acidic methanol was added to the reaction system in order to stop the polymerization. The resulting product was precipitated by the addition of a large amount of methanol, or, in some cases, it was fractionally distilled from the reaction system.

Polymerization by Coordinated Catalyst.—The polymerization was carried out in *n*-heptane in a sealed tube at room temperature, using a catalyst which had been aged for an hour. After a given time, the contents of the tube were poured into a large amount of isopropanol containing hydrochloric acid in order to precipitate the resulting polymer and remove the residual catalyst. The polymer was washed several times with pure methanol, and then dried under reduced pressure.

Results

The Polymerization of 1, 1-Dimethylcyclopropane.—In order to examine the catalytic activity, 1, 1-dimethylcyclopropane was polymerized in methylene chloride at 0°C by using various Lewis acids, such as aluminum bromide, aluminum chloride, stannic chloride, titanic chloride and boron trifluoride - diethyl etherate. Aluminum bromide-catalyzed polymerization afforded an oligomer with the molecular weight of 390, whereas no product was obtained by using the other Lewis acids.

The effects of the solvents are shown in Table I. In alkane (*n*-hexnane) the reaction proceeded very fast and gave an oligomer. The fast reaction in toluene, however, gave a liquid product. The infrared spectra of the products obtained in *n*-hexane and in toluene are shown in Fig. 1. The spectrum of the product obtained in *n*-hexane agreed with that of poly-1, 1-dimethylcyclopropane,[3] whereas the spectrum of the product obtained in toluene contained aromatic absorption bands. The absorptions at 1890, 1780 and 810 cm^{-1} indicated that the para-substitution of toluene by attacking the alkyl cation. Thus aromatic compounds

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[1] H. Pines, W. D. Huntsman and V. N. Ipatieff, *J. Am. Chem. Soc.*, **75**, 2315 (1953).

[2] C. F. H. Tipper and D. A. Walker, *J. Chem. Soc.*, **1959**, 1352.

[3] A. D. Ketley, *J. Polymer Sci.*, **B1**, 313 (1963).

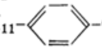
[4] R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *J. Am. Chem. Soc.*, **70**, 946 (1948).

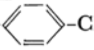
[5] W. J. Dale and P. E. Swartzentruber, *J. Org. Chem.*, **24**, 955 (1959).

Table I. Aluminum bromide-catalyzed polymerization of 1, 1-dimethylcyclopropane*1

Solvent	Reaction time min.	Conversion %	Mol. wt.	Appearance
n-Hexane	0.5	>90	370	Viscous liquid
Methylene chloride	16	1.2	—	Viscous liquid
Toluene	1	>40*2	170*3	Liquid

*1 $[\mathrm{Monomer}]_0=3.0$ mol./l.
$[\mathrm{AlBr_3}]_0=0.007$ mol./l., 0°C

*2 Separated from the reaction mixture by distillation. It boiled at 145—149°C under slightly reduced pressure. The yield was calculated as C_5H_{11}--CH_3.

*3 Calcd. value for C_5H_{11}--CH_3 is 162.

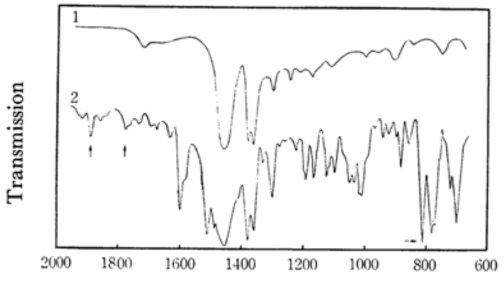


Fig. 1. Infrared spectra of the reaction products from 1, 1-dimethylcyclopropane in *n*-hexane (1) and toluene (2).

seem to be unsuitable as solvents for the cyclopropane polymerization.

The Copolymerization of 1, 1-Dimethylcyclopropane with Styrene.—The copolymerization of 1, 1-dimethylcyclopropane with styrene was attempted in the presence of aluminum bromide. The results are given in Table II.

The rate of the polymerization of 1, 1-dimethylcyclopropane was markedly lower than that of styrene, and the copolymer containing the higher concentration of styrene units resulted from the equimolar mixture of the monomers. The cyclopropane unit content of this copolymer decreased with a lowering of the temperature.

The infrared spectrum of the copolymer agreed with that of polystyrene, and no evidence for the presence of the para-substituted styrene units was obtained.

The Graft Polymerization of 1, 1-Dimethylcyclopropane onto Polystyrene.—1, 1-Dimethylcyclopropane was polymerized in the presence of polystyrene to produce a graft polymer by the attack of the growing cyclopropane cation on the benzene nucleus of polystyrene. Table III shows the results of the graft polymerization. *n*-Hexane-insoluble polystyrene, obtained by radical polymerization, was used as the backbone. The entire polymer recovered after the polymerization of cyclopropane was soluble in *n*-hexane. This indicates that the high-molecular-weight polystyrene initially used was modified. The rubbery polymer recovered was fractionated by the *n*-hexane - isopropanol system (Table III). The infrared spectra

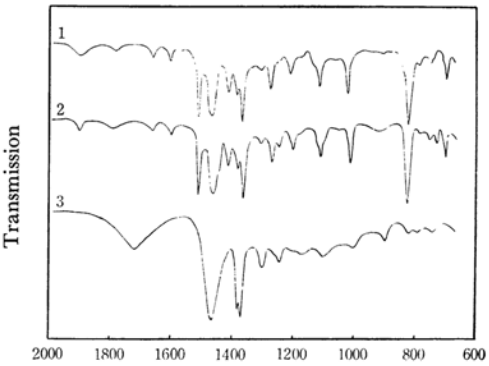


Fig. 2. Infrared spectra of the graft polymer 1: first fraction, 2: second fraction, 3: third fraction.

Table II. Copolymerization of styrene with 1, 1-dimethylcyclopropane*

Monomer composition		Solvent	Reaction temp. °C	Reaction time min.	Conversion %	Carbon content in polymer %	Polymer composition		Mol. wt.
1, 1-Dimethylcyclopropane	Styrene						Cyclopropane	Styrene	
0	100	CH₂Cl₂	0	0.25	97.1	91.68	23	87	1320
50	50		0	1.0	28.0				
100	0		0	16	1.2				
0	100	CH₂Cl₂	−15	0.25	95.9	91.87	8	92	—
50	50		−15	1.0	21.6				
100	0		−15	20	0.4				
0	100	CH₂Cl₂	−30	0.25	93.0	91.94	7	93	2400
50	50		−30	0.5	14.8				
100	0		−30	25	0.2				
50	50	*n*-C₆H₁₄	0	20	11.9	90.46	35	65	1890
50	50		−15	20	10.4	91.72	12	88	—

* $[M_1+M_2]_0=3.0$ mol./l., $[\mathrm{AlBr_3}]_0=0.007$ mol./l.

TABLE III. POLYMERIZATION OF 1,1-DIMETHYLCYCLOPROPANE IN THE PRESENCE OF POLYSTYRENE

Polymerization condition and result:
Polystyrene: 0.1170 g., 1,1-Dimethyl cyclopropane: 5.0 ml., CH_2Cl_2: 8.0 ml., $AlBr_3$: 0.49 g., Reaction time: 75 hr., Reaction temp.: 0°C.
Whole polymer recovered: 0.4200 g., Content of polystyrene in the polymer: 27.9%.

Fractionation of the polymer recovered:
Sample initially used: 0.3963 g.
First fraction (Precipitate in *n*-hexane 20 ml. - isopropanol 30 ml.): 0.1510 g. (38.1%). Rubbery substance.
Second fraction (Precipitate in *n*-hexane 20 ml. - isopropanol 40 ml.): 0.0544 g. (13.7%). Rubbery substance.
Third fraction (Methanol insoluble): 0.1819 g. (45.9%). Viscous liquid.

of the first and the second fractions contained a strong absorption at 820 cm^{-1} (Fig. 2). This indicates the presence of the para-substituted styrene units, an evidence of grafting. The third fraction was found from its infrared spectrum to be the homopolycyclopropane (Fig. 2).

The Polymerization of Phenylcyclopropane.—The polymerization of phenylcyclopropane (3.0 mol./l.) was attempted in the presence of aluminum bromide (0.07 mol./l.) in *n*-hexane at 0°C. After 15 sec., the exothermic reaction gave a viscous liquid at about a 90% conversion. About 60% of the product was distilled off below 200°C/1.5 mmHg. The molecular weight of the distillate at 200°C/1.5 mmHg was 320. The infrared spectrum of this fraction is shown in Fig. 3. The absorptions at 2000—1700 cm^{-1} indicated the presence of 1,2-disubstituted benzene units. The presence of 1,4-disubstituted benzene units was also confirmed by the absorption at 810 cm^{-1}.

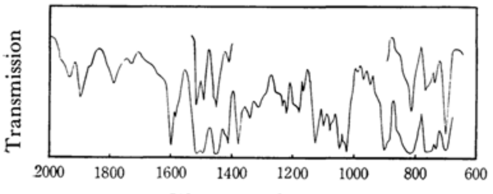
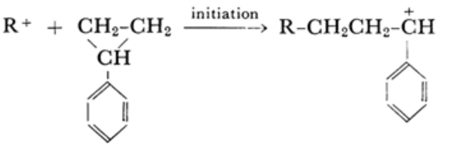
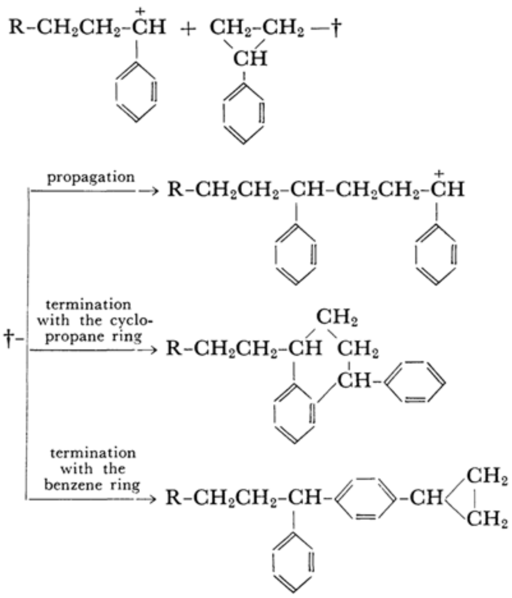


Fig. 3. Infrared spectrum of the reaction product from phenylcyclopropane.

Thus the reaction scheme may be expressed as follows:



(1)



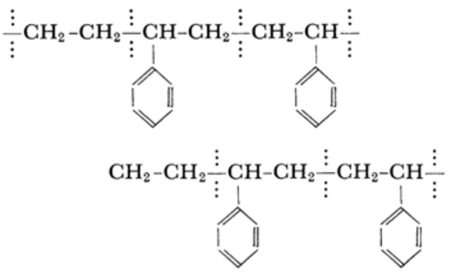
(2)

(3)

(4)

The Coordinated Polymerization of Cyclopropanes.—The polymerization of 1,1-dimethylcyclopropane with $C_2H_5AlCl_2/TiCl_3$ catalyst (Al/Ti=2) in *n*-heptane at room temperature for 18 days gave a waxy polymer with the molecular weight of 1240 in a 66% conversion. Phenylcyclopropane also gave a resinous polymer, this one with the molecular weight of 1480 in a 45% conversion. The other catalyst systems, $(C_2H_5)_2AlCl/TiCl_3$ and $(C_2H_5)_3Al/TiCl_3$, did not show any catalytic activity for the cyclopropane polymerization.

The degradation temperature of the polyphenylcyclopropane was found by the differential thermal analysis to be 430°C. If the polyphenylcyclopropane has the following structure (I), the thermal degradation of this polymer may give styrene and ethylene in the ratio of 2/1;



(I)

Styrene and ethylene in the degradation products at 450°C of this polymer were detected on a gas chromatogram, though the quantitative analysis was unsuccessful because of the complexity of the by-products.

The infrared spectrum of this polymer, shown in Fig. 4, contained the absorption band at 820 cm^{-1}, showing the presence of 1,4-disubstituted benzene units arising from chain transfer reaction, besides the structure I.

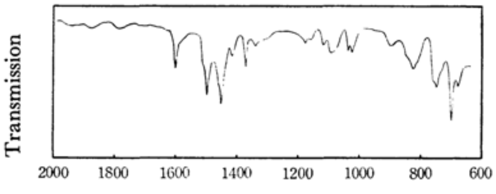


Fig. 4. Infrared spectrum of polyphenylcyclopropane.

Discussion

Dainton, Devlin and Small,[6] using the semiempirical method, evaluated the heat of polymerization as 13.7 kcal./mol. for isobutene and 20.4 kcal./mol. for 1, 1-dimethylcyclopropane. These values suggest that the reactivity of 1, 1-dimethylcyclopropane is higher than that of isobutene. However, the results of the Lewis acid-catalyzed polymerizations of the cyclopropanes mentioned above indicate that the polymerization reactivity of the cyclopropanes is lower than that of the corresponding vinyl monomers.

1, 1-Dimethylcyclopropane was less reactive than styrene in the homopolymerization and in the copolymerization (see Table II), though, in general, isobutene was more reactive than styrene.[7] The content of cyclopropane units in the 1, 1-dimethylcyclopropane-styrene copolymer was influenced by the reaction temperature, for it decreased with a lowering of the temperature. This may be explained by the difference in the activation energies of the propagation reaction, as in the other copolymerization.[8,9]

The graft polymer was obtained in the polystyrene-1, 1-dimethylcyclopropane system, though the polystyrene-isobutene system did not give the graft polymer.[10] If the reactivities of the growing terminal cations of 1, 1-dimethylcyclopropane and isobutene are similar because of the similarity in the structure of their cations, this also indicates the lower reactivity of the cyclopropane monomer as compared with that of the vinyl monomer.

Phenylcyclopropane did not afford a high polymer under the conditions under which styrene gives a high polymer. This can be explained by the fact that the termination proceeds much further than the propagation in this polymerization because of the lower reactivity of the cyclopropane.

The cationic polymerization of vinylcyclopropane gave results which indicate that the cyclopropyl group has a lower reactivity than the vinyl group.[11]

A more quantitative study will be published later.

The authors wish to thank the Osaka Research Laboratory of the Japan Gas Chemical Co. for supplying the raw material and for the differential thermal analysis and the gas chromatographic measurements.

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[7] J. P. Kennedy, "Copolymerization," Ed. by G. E. Ham, Interscience Publishers, New York (1964), p. 306.

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