SHORT COMMUNICATION

The Polymerization of 1, 1-Dichloro-2-vinylcyclopropane

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The ring-opening polymerization of cyclopropane derivatives has attracted keen interest recently. However, only a few reports that the oligomers of cyclopropane[1] and alkyl- or aryl-cyclopropanes[2] have been obtained have appeared. We have studied the polymerization of 1, 1-dichloro-2-vinylcyclopropane (I).

The compound I was prepared by the method of Woodworth and Skell.[3] We carried out bulk or solution polymerization in a nitrogen atmosphere with a sealed tube. I failed to polymerize when such usual ionic catalysts as $BF_3\cdot(C_2H_5)_2O$, $AlCl_3$, $TiCl_4$, $Et_3Al\text{-}TiCl_4$ and Na (in liq. NH_3) were used, although in some

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[1] L. Harris, A. A. Ashdown and R. T. Armstrong, *J. Am. Chem. Soc.*, **58**, 852 (1936); H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **17**, 351 (1947); R. J. Scott and H. E. Gunning, *J. Phys. Chem.*, **56**, 156 (1952).

[2] H. Pines, W. D. Huntsman and V. N. Ipatieff, *J. Am. Chem. Soc.*, **75**, 2315 (1953); A. D. Ketrey, *Polymer Letter*, **1**, 313 (1963); A. Yamada, M. Yanagita and S. Suzuki, *Rikagaku Kenkyusho Hokoku*, **37**, 429 (1961).

[3] R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **79**, 2542 (1957).

* Measured by the cryoscopic method in benzene.

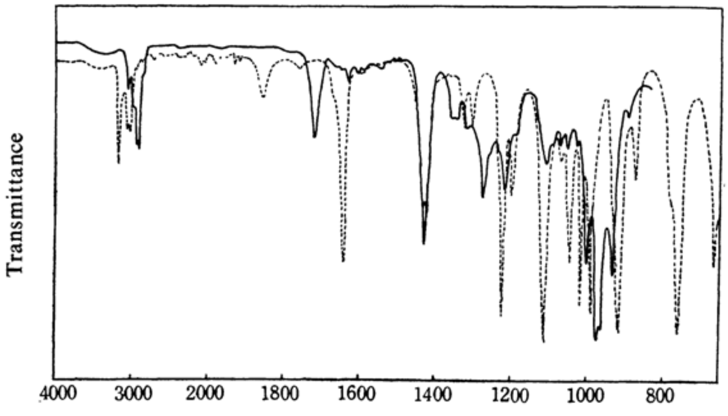


Fig. 1. Infrared spectra: (a) solid line, polymer obtained by benzoyl peroxide in CCl_4 paste; (b) dotted line, 1, 1-dichloro-2-vinylcyclopropane.

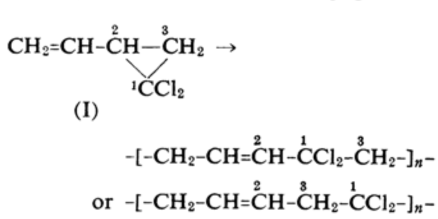
cases a trace of a solid product was obtained. When, however, benzoyl peroxide or α, α'-azobisisobutyronitrile was used as a catalyst, a polymeric product was obtained. For instance, when the bulk polymerization of I was carried out by benzoyl peroxide (5% wt.) for 40 hr. at 80°C, a crude polymer (with an average molecular weight* of about 1000) was obtained in a 36% yield. The curde polymer was dissolved in benzene, purified by pouring the solution into a large excess of methanol, and dried in vacuo. The purified polymer was powdery white, it melted at 70°C, its molecular weight* was about 7000, and its reduced viscocity was 0.025 (measured on a solution of 0.037 g. of polymer in 100 ml. of benzene at 30°C).

The chlorine content of the polymer (48.18 %) was found to be comparable with that of the monomer (calcd. 51.76%). Therefore, almost no dehydrochlorination or dechlorination took place in the polymerization process. The near-infrared spectrum of the polymer had no absorption band at 1.63 μ that might be assigned to the 1, 1-dichlorocyclopropane ring. The infrared spectra of I and the polymer obtained by benzoyl peroxide are shown in Fig. 1. In the spectrum of the polymer, the absorption bands of the cyclopropane ring (1020 cm^{-1}) and of the end vinyl group (990 cm^{-1}, 910 cm^{-1}) almost disappeared and that of the trans-double bond (965 cm^{-1}) was observed. Three peaks, 1720 cm^{-1}, 1270 cm^{-1}, and 1110 cm^{-1}, might be due to those of the benzoate group, which is an initiator fragment attached to the polymer's end. The presence of this end group was confirmed by the fact that, in the infrared spectrum of the hydrolysis product of the polymer, these absorption bands were absent. The polymer obtained by the use of α, α'-azobisisobutyronitrile had the absorption band of the immonium group (1800 cm^{-1}) in place of that of the benzoate group.

The infrared spectrum of unreacted monomer was in agreement with that of I.

On the other hand, 1, 1-dichloro-2-ethylcyclopropane gave no polymer when radical catalysts were used.

These facts might suggest that the polymerization of I mainly occurs by opening both the double bond and the cyclopropane ring, as is shown in the following scheme. This scheme is similar to those that have been proposed for the 1, 4-polymerization of conjugated dienes.



(I)

$$-[-CH_2-CH{=}\overset{2}{C}H-\overset{1}{C}Cl_2-\overset{3}{C}H_2-]_n-$$

$$\text{or } -[-CH_2-CH{=}\overset{2}{C}H-\overset{3}{C}H_2-\overset{1}{C}Cl_2-]_n-$$

Further details of such polymerization results and of the polymer structure will soon be published.

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