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Radical Isomerization Polymerization of 1,1-Dicyclopropylethylene

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Radical Isomerization Polymerization of 1,1-Dicyclopropylethylene

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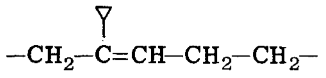
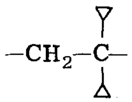
SUMMARY

The polymerization of 1, 1-dicyclopropylethylene with radical (ABIN) and cationic ($AlEtCl_2$) initiators has been investigated. The structure of the polymers was elucidated by IR and NMR spectroscopy. These studies indicated that the major repeat unit of the polymer obtained by radical initiator is



$$-CH_2-\overset{\triangledown}{C}=CH-CH_2-CH_2-$$

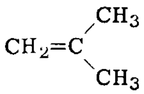
suggesting a ring-opening isomerization polymerization mechanism, whereas that produced with cationic initiator is the unrearranged



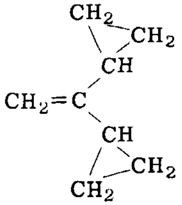
$$-CH_2-\underset{\triangle}{\overset{\triangledown}{C}}-$$

unit.

In the course of our studies on isomerization polymerization (for a review see [1]) we became interested in the polymerization of 1, 1-dicyclopropylethylene, an analogue of isobutylene, the polymerization of which has been studied in detail by numerous workers:



$CH_2{=}C(CH_3)_2$



We have polymerized 1, 1-dicyclopropylethylene by cationic catalyst ($AlEtCl_2$ in dry methyl chloride at −35 and −100°C) and by radical initiator (azobisisobutyronitrile, neat, at ~50°C). These conventional polymerization techniques have also been used by previous workers, notably by Ketley et al. [2], who polymerized this monomer by $AlBr_3$, and by Takahashi [3], who was the first to use both cationic and free-radical initiators for the polymerization of various related monomers. The structure of the polymers obtained was investigated by IR and NMR spectroscopy.

In our hands the cationic polymerization of 1, 1-dicyclopropylethylene (Aldrich Chemical Company) occurred at an appreciable rate even at −100°C. Thus about 1.4×10^{-5} mole of $AlEtCl_2$ produced a 42.8% conversion in a 1.53 M monomer solution. The $\overline{M}_n$ of this white brittle powdery polymer (by VPO) was 5323 and its softening range was between 55 and 69°C. The polymer prepared at −35°C (32.9% conversion) was also a white powdery product of $\overline{M}_n = 3448$ and softening range 47-61°C. In contrast, the azobisisobutyronitrile initiated polymerization proceeded extremely slowly: 0.5 mole % ABIN dissolved in 1 g of monomer and stirred at 50°C under nitrogen for 35 days yielded 0.141 g (14.1%) of soft solid, most likely an oligomer.

The IR spectra were determined on films cast from CS_2 solution with a Perkin-Elmer 521 spectrophotometer, and the NMR spectra were obtained with polymers in CCl_4 solution on a Varian A-60 instrument. Among the cationically polymerized materials, that prepared at −100°C was examined intensively; however, no significant differences were found by spectroscopy between this product and that prepared at −35°C.

Figure 1 shows the IR spectra of the cationic (I) and free-radical (II) polymer. The bands at 3070, 1012, and 820 cm^{-1} in I and at 3075, 1010, and 812 cm^{-1} in II are characteristic of the cyclopropyl group [4]. However, there are significant differences between the spectra both in the presence and absence of peaks and in their relative intensities. An important difference between the spectra is the presence in II of the medium-intensity band at 1650 cm^{-1}, indicating a C=C bond and the virtual absence of a band at that position in I. This suggests that considerable rearrangement has taken place during polymerization of II and very little with I. These data are supported by the NMR evidence.

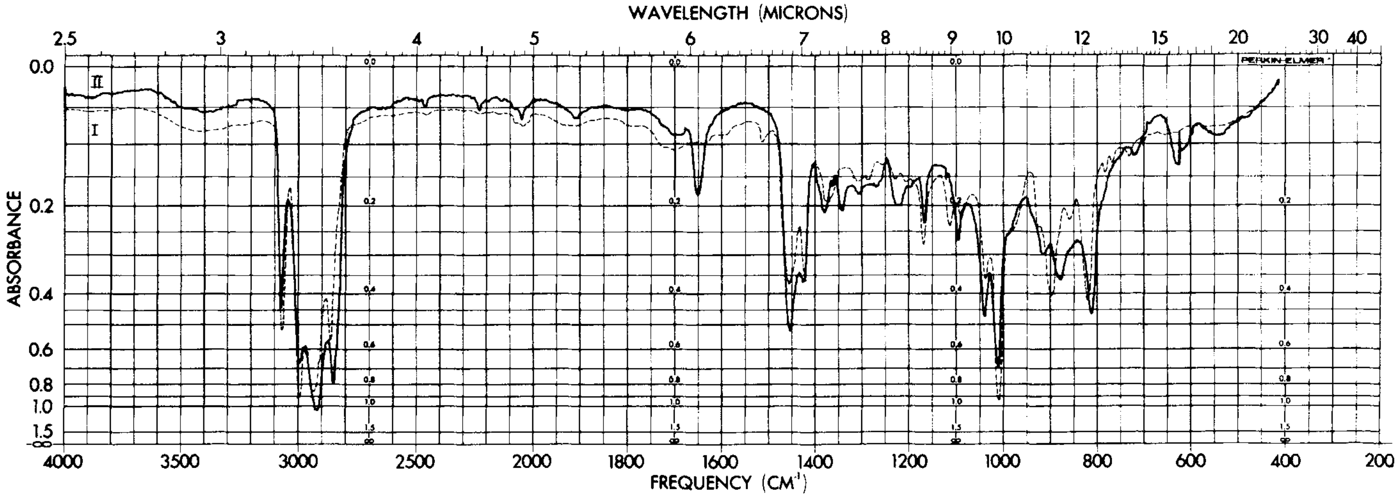


Fig. 1. IR spectra of poly(1, 1-dicyclopropylethylenes).

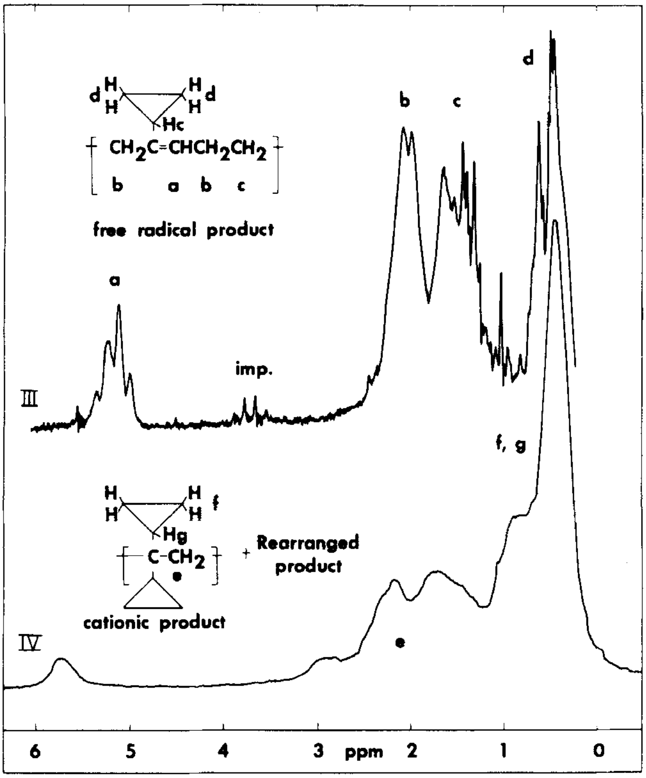
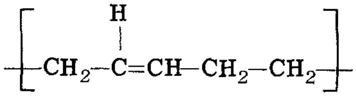


Fig. 2. NMR spectra of poly(1, 1-dicyclopropylethylenes).

As indicated in Fig. 2, the spectrum of the cationic product (IV) shows an intense multiplet peak centered near 0.5 ppm for the protons of the cyclopropyl groups and only a low intensity olefinic multiplet at about 5.7 ppm $\left(\mathrm{C}{=}\mathrm{C}\overset{\mathrm{H}}{\diagup}\right)$ to indicate the presence of a minor amount of rearranged 1, 5-product [1]. In the free-radical product (III), however, the intensity of the cyclopropyl protons is greatly diminished with a corresponding enhancement in the intensity of signals for proton groups assigned to allylic methylene protons (1.6-2.4 ppm) and "saturated" methylene + allylic cyclopropyl (5.2 ppm) protons.

The latter signal is a pair of overlapping triplets (confirmed by a 100-MHz spectrum) assigned to the chemically shifted cis and trans forms of the 1, 5 product. These signals are in an approximately 60:40 ratio, indicating that neither one of the possible geometric isomers is favored. Its position upfield at about 5.2 ppm is in agreement with its position in the fully rearranged polyvinylcyclopropane [3]:



$$\left[-CH_2-\overset{\overset{H}{|}}{C}=CH-CH_2-CH_2- \right]$$

Apparently this proton experiences a differential long-range anisotropic effect between the "pure" free-radical polymer, in which there is one repeating rearranged monomer unit, and the cationic product, in which this unit is interspersed among the large majority of rearranged units.

From a calculation based on the relative areas of the assigned proton groups it was determined that the free-radical product III contains >90% rearranged material, while the cationically prepared product IV is a mixture of 70-75% unrearranged and 25-30% rearranged polymer units. Evidently, our results with the cationic polymer are in complete accord with those of Ketley et al. [2], who postulate 73% unrearranged and 27% rearranged structures.

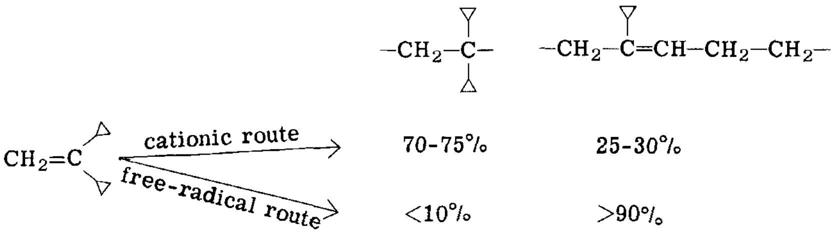
The infrared results are in agreement with these data. Thus CS_2 solutions of polymers obtained by $AlEtCl_2$ and ABIN catalysts, respectively, were prepared and the relative intensities of the 3075-cm^{-1} band were measured. The intensity of the 3070-cm^{-1} band in I is 1.8 times that of the 3075-cm^{-1} band in II, indicating that if II is totally rearranged, then only about 20% of I had rearranged.

It is of interest to note the spectra of the two polymers in the region 800-830 cm^{-1}. The strong peak at 822 cm^{-1} in I is assigned to the cyclopropyl group. There is a significant 10-cm^{-1} shift in the position of this band (to 812 cm^{-1}) in II, which is almost certainly associated with the cyclopropyl group of II now being located directly on the double bond. The out-of-plane deformation band of the trisubstituted double bond is probably located at the same frequency.

The location of the band due to the C=C stretching vibration at 1650 cm^{-1} is also of interest, for this is some 10-20 cm^{-1} lower than normal for a double bond of this type [4]. Its shift is probably due to the conjugative effect of the cyclopropyl group with the double bond to which it is directly attached.

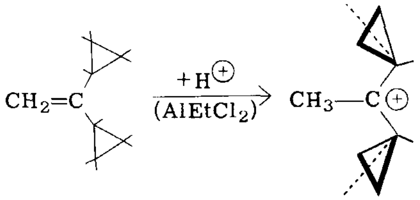
These findings are also in over-all agreement with the results of Takahashi [3], who found in polymers of vinylcyclopropane, isopropenylcyclopropane, and 1-methyl-1-vinylcyclopropane, in general, rearranged structures with free-radical initiators and rearranged units with $SnCl_4$.

On the basis of this analysis the structure of poly(1, 1-dicyclopropylethylene) is determined by the nature of the initiator used:

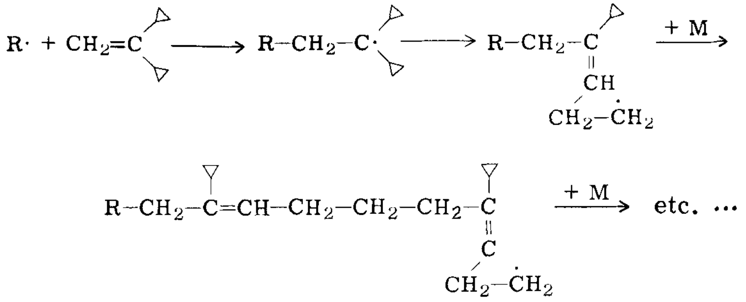


This finding is surprising, as we would expect isomerization to occur during a cationic process rather than in the course of a radical one. However, on closer examination our results can be readily interpreted.

The methyldicyclopropyl cation, which is expected to form on protonation of the 1, 1-dicyclopropylethylene monomer by the cationic catalyst, is most likely unusually stable because of resonance interaction of the carbonium ion center with the two cyclopropyl groups. This ion will exist preferentially in the bisected arrangement:



This bisected arrangement permits a conformation which represents minimum steric interference with the addition of the ion to the monomer. As it is known that the tertiary cyclopropyl cation can solvolyze without rearrangement [5], it is conceivable that under polymerization conditions the above strongly stabilized tertiary cation does not rearrange or rearranges only to a small extent. In contrast, the tertiary cyclopropyl free radical will exhibit far less interaction with and stabilization by the cyclopropyl groups. There will be less tendency for restricted rotation of the cyclopropyl groups and therefore far more steric interaction in the addition to monomer step. This steric interaction can be avoided by reaction in the form of the (stabilized?) homoallylic radical:



It is interesting that cationically polymerized (i.e., largely unrearranged) poly(1, 1-dicylopropylethylene) is a powdery solid. Closely related polymers of 1, 1-dimethylethylene (isobutylene) and 1, 1-methylethyl ethylene synthesized under similar conditions are rubbers and soft solids, respectively. Apparently due to the presence of the cyclopropyl rings in poly(1, 1-dicyclopropylethylene), the backbone of the polymer becomes rigid and the stiff chains give rise to powdery products. 1, 1-Diphenylethylene, because of the bulky phenyl groups, yields only dimers and cannot be polymerized to high polymers.

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