The Rearrangement Polymerization of Propenylbenzene: A Reinvestigation

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In a previous paper[1] the present authors studied the rearrangement polymerization of propenylbenzene, which had been proposed by Staudinger,[2] and reported a set of confirmative data. However, further study has revealed that the propenylbenzene used, which had been prepared by thermal cracking of ethylbenzyl acetate at 500°C,[3] contained a small impurity (ca. 5%), and that this impurity even in a minute quantity deeply influences the course of polymerization.

The impurity was, therefore, concentrated by preparative gas chromatography and identified with indene by a comparison of its infrared spectrum with that of an authentic sample.

Since indene is a monomer with a high cationic polymerizability, the presence of indene in propenylbenzene of a low activity influences the polymerization of propenylbenzene a great deal. Thus, i) the residual monomer, which was recovered after the initial polymerization (about 20% conversion) with a mild catalyst, BF_3Et_2O, is found to contain no indene. This means that indene has been consumed at an early stage of polymerization. ii) The initial rate of polymerization became larger upon the addition of a small amount of indene to pure propenylbenzene. iii) The initial polymer obtained with a BF_3Et_2O catalyst using an indene-containing propenylbenzene yielded a methanol-insoluble polymer of a comparatively high molecular weight, as was reported in the previous paper. On the other hand, pure propenylbenzene yielded only a methanol-soluble polymer of a low molecular weight. Many differences are observed between the two polymers in infrared and NMR spectra. While the former shows a very weak CH_3 band at 2960 cm^{-1} and a strong CH_2 band at 2925 cm^{-1}, and the ratio of the number of methyl protons to that of aromatic protons is found to be 0.26, the latter has a strong CH_3 band and a comparatively weak CH_2 band, and the ratio of methyl protons to aromatic protons is nearly 0.6, which corresponds to the theoretical value for polypropenylbenzene polymerized by a 1,2-opening. When a strong cationic initiator, such as BF_3, is used, the effect of the presence of a small amount of indene is masked by the rapid production of a large amount of polypropenylbenzene.

Table I shows a gas chromatographic analysis of relative amounts of impurities contained in samples of propenylbenzene prepared by three different methods.

In order to examine the existence of rearrangement polymerization in more detail, the polymerization was carried out under various conditions, including Staudinger's system. When toluene was used as a solvent, as in the case of Staudinger's original work, the resulting viscous polymer appeared to contain toluene residues ($\tau=7.7$). This complicated the NMR analysis and made the apparent ratio of methyl protons ($\tau\sim9.2$) to aromatic protons considerably lower than the theoretical value (0.4—0.5). When *n*-heptane or methylene chloride was used as the solvent and boron fluoride or titanium(IV) chloride as the initiator, the resulting polymers showed a ratio of methyl to aromatic protons of about 0.6, indicating

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[1] S. Murahashi, S. Nozakura, K. Tsuboshima and Y. Kotake, This Bulletin, 37, 706 (1964).

[2] H. Staudinger and E. Dreher, *Ann.*, 517, 73 (1935).

[3] C. G. Overberger and D. Tanner, *J. Am. Chem. Soc.*, 77, 369 (1955).

TABLE I. PROPENYLBENZENE PREPARED BY DIFFERENT METHODS

Method of preparation	Allylbenzene %[a]	Propenylbenzene cis %	Propenylbenzene trans %	Indene %
Thermal cracking of ethylbenzyl acetate³⁾	5.4	20.2	66.3	8.1
Dehydrochlorination of ethylbenzyl chloride with pyridine¹⁾	0	1.5	98.5	0
Catalytic dehydration of ethylbenzyl alcohol[b]	4.7	30.5	64.8	0

a) Relative composition was calculated based on peak area of gas chromatogram.
b) Dehydration was carried out at about 300°C in a stream of N_2 using alumina as catalyst.

no sign of rearrangement during polymerization.[4]

The confirmative results reported in the previous paper must, therefore, be corrected; there was contamination by indene, which led the authors to a misunderstanding of the polymer structure.

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[4] Recently Kennedy stated a similar negative observation in a review article. J. F. Kennedy and A. W. Langer, Jr., *Fortschr. Hochpolym. Forsch.*, 3, 523 (1964).