*The Rearrangement Polymerization of Propenylbenzene**

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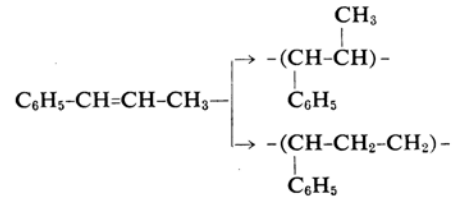
Propenylbenzene belongs to a family of 1, 2-disubstituted ethylenes which are generally reluctant to homopolymerize by means of a radical mechanism.[1] Little information has been reported on the cationic polymerization of the monomer.

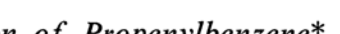
In 1935 Staudinger and Dreher observed the cationic polymerization of propenylbenzene when boron trifluoride was used as an initiator.[2] Their close examination of the polymeric product by thermal degradation and viscometric measurements led them to conclude that the chemical structure of the polymer is not the expected one I but structure II.



$$C_6H_5\text{-}CH{=}CH\text{-}CH_3 \begin{cases} \rightarrow -(\underset{C_6H_5}{CH}\text{-}\overset{CH_3}{CH})- & \text{I} \\ \rightarrow -(\underset{C_6H_5}{CH}\text{-}CH_2\text{-}CH_2)- & \text{II} \end{cases}$$

The occurrance of structure II would, however, involve, in the intermediate stage, an intramolecular hydrogen shift from the primary carbon to the secondary one, a phenomenon which is surprising and contrary to the usual observation on the isomerization of a cation.[3] Although a similar unusual rearrangement during polymerization was reported, without detailed proof, to occur in the polymerization of isobutylene by a Ziegler-type catalyst,[4] it has recently been disproved by Bacskai and Lapporte.[5]

More recently, 3-methylbutene-1 was polymerized by Kennedy and Thomas at a low temperature with a cationic catalyst to give a rearranged polymer III, which involves a normal hydrogen shift from the tertiary to the secondary carbon.[6]



$$CH_2{=}CH\text{-}\underset{CH_3}{\overset{CH_3}{CH}} \longrightarrow -(CH_2\text{-}CH_2\text{-}\underset{CH_3}{\overset{CH_3}{C}})_n- \qquad \text{III}$$

Thus, Staudinger's result presents an example of a rather peculiar type of polymerization reaction, and it seemed worthwhile to reinvestigate it in detail. The present paper will study the chemical structure of polypropenylbenzene by infrared spectroscopy and will also study the effect of reaction conditions on the polymer structure.

Experimental

Monomers. — Propenylbenzene was prepared by the method of Overberger and Tanner[7] through the thermal decomposition of α-ethylbenzyl acetate (b. p. 56.5∼63°C 10 mmHg, n_D^{25} 1.5473). The propenylbenzene was found by gas chromatography to consist of 74% trans-isomer and 26% cis-isomer; it was used for polymerization without separation.

Allylbenzene was prepared according to the method of Hershberg from allyl bromide and

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* Paper I in a series on "The Polymerization of Internal Olefins."

1) T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, New York (1952), p. 49.

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

3) E. S. Gould, "Mechanism and Structures in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York (1959), p. 449.

4) A. V. Topchiev et al., *Doklady Akad. Nauk S. S. S. R.*, **111**, 121 (1956).

5) R. Bacskai and S. J. Lapporte, *J. Polymer Sci.*, Part A, **1**, 2225 (1963).

6) J. P. Kennedy and R. M. Thomas, *Makromol. Chem.*, **53**, 28 (1962).

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

phenylmagnesium bromide.[8] B. p. 67.5~69.5°C/35 mmHg.

Catalysts.—Boron trifluoride was prepared when required by the thermal decomposition of phenyldiazonium borofluoride, and it was freed from fluorobenzene by passing it through a dry ice-acetone trap.

Boron trifluoride complexes were prepared by passing a calculated amount of boron trifluoride gas through an appropriate amount of a donor compound, after which it was subjected to vacuum distillation. $BF_3 \cdot 2H_2O$, b. p. 29.0°C/0.33 mmHg; $BF_3 \cdot 2CH_3COOH$, b. p. 138~139°C; $BF_3 \cdot 2CH_3OH$, b. p. 34.0~34.8°C/1.5 mmHg; $BF_3 \cdot (CH_3)_2O$, b. p. 126~127°C.

The other metal halides were commercial products and were used without further purification.

Solvents.—All the solvents used were purified according to the usual method[9] and were stored over a molecular sieve.

The Polymerization of Propenylbenzene.—Polymerization was carried out in a 50 ml. flask under a slight positive pressure of dry nitrogen, with occasional gentle shaking. Solvent and monomer were placed in the flask, which was then flushed with a stream of nitrogen, and the catalyst was injected through a rubber cap using a hypodermic syringe. The fluctuation of temperature of bath was kept at ±1°C. Polymerization was stopped by adding a mixture of concentrated aqueous ammonia and methanol, and the contents of the flask were poured into a large excess of methanol (250 ml.). The precipitated polymer was separated from the mother liquor by filtration through a sintered glass filter of medium porosity, and was weighed after drying as the methanol-insoluble part of the polymer. An aliquot of the filtrate was iodometrically titrated for unreacted monomer using a standard bromate-bromide solution. The remainder of the filtrate was evaporated in vacuo and dissolved in benzene. The benzene solution was washed with dilute aqueous hydrochloric acid and then water, dried with calcium chloride, and evaporated again in vacuo to give the methanol-soluble part of the polymer.

The Polymerization of Allylbenzene.—Allylbenzene (2 g.) was polymerized at 50°C for 48 hr. in a sealed tube using a Ziegler catalyst, which was composed of 6 ml. of heptane, $TiCl_4$ (monomer/Ti=10) and $Al(i\text{-}C_4H_9)_3$ (Al/Ti=1.2).[10] The catalyst was prepared under the refluxing of *n*-heptane.[11] The yield of the polymer was 24%. The polymer was extracted with hot benzene, using a modified Soxhlet apparatus for 15 hr., 32.5% of the total polymer being insoluble (softening pt. 170~210°C).

Molecular Weight. — The molecular weight of the polymers was determined cryoscopically in benzene.

Infrared Spectra.—The infrared spectra of the polymers were obtained in the state of polymer films when possible, in KBr disks, or sometimes in thin liquid films, using a Nihon Bunko DS 402G grating spectrophotometer.

Results and Discussion

The Infrared Spectra of Polypropenylbenzene. —There are two structural possibilities for polypropenylbenzene. One is structure I, resulting from the normal opening of the double bond, and the other is the rearranged structure, II, as has been suggested by Staudinger. In fact, the infrared spectra of polypropenylbenzene obtained show considerable differences in the 2850~2960 cm^{-1} region and in the 1450~1500 cm^{-1} region according to the polymerization conditions.

Figure 1 shows the infrared spectra of the methanol-insoluble part of two polymers obtained by using borontrifluoride as the catalyst at room temperature in toluene and borontrifluoride etherate, at 0°C in toluene. The latter have a very weak absorption of the CH_3 degenerated stretching mode at 2960 cm^{-1} and of the CH_3 symmetric stretching mode at 2870 cm^{-1}, showing a very small methyl-group content. On the other hand, the former BF_3-polymer showed much more intensive absorptions at these two wave numbers, indicating a higher methyl-group content. These differences in spectra correspond to the structural

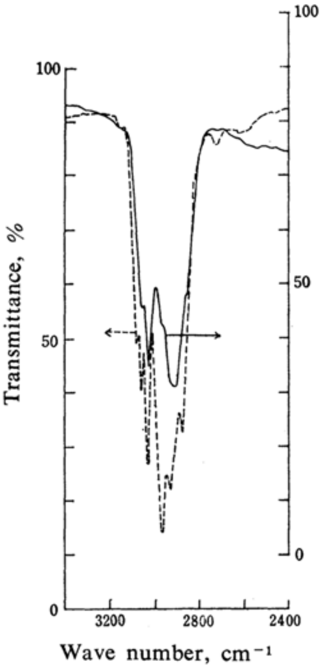

Fig. 1. IR-Spectra of polypropenylbenzene.
—— Polymerized with BF_3Et_2O at 0°C
---- Polymerized with BF_3 at −78°C

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[8] E. B. Hershberg, *Helv. Chim. Acta*, **17**, 351 (1934).

[9] A. Weissberger et al., "Organic Solvents," 2nd. Ed., Interscience Publisher Inc., New York (1955).

[10] G. F. D'Alelio, *J. Polymer Sci.*, **45**, 83 (1960); G. Pregaglia and M. Binaghi, ibid., **51**, s61 (1961).

[11] S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, This Bulletin, **32**, 1094 (1958).

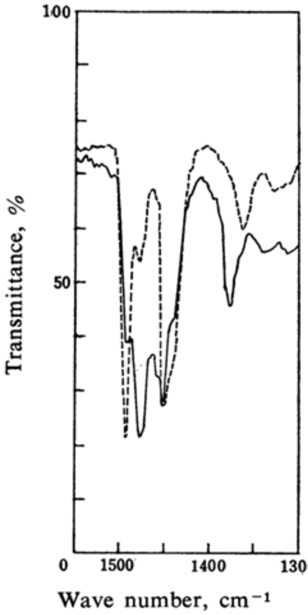
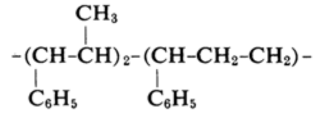


Fig. 2. Comparison of IR spectra of polypropenylbenzene and polyallylbenzene.
—— Polypropenylbenzene prepared with $BF_3 \cdot Et_2O$ at 0°C
---- Polyallylbenzene prepared with Ziegler catalyst

change from I to II, and it was concluded that the BF_3-polymer is relatively rich in structure I and that the $BF_3 \cdot Et_2O$-polymer is rich in structure II. Thus, the authors hereafter will use the ratio of optical densities at 2960 and 2925 cm^{-1}, $D(CH_3/CH_2)$, as a measure of the methyl to the methylene ratio and, hence, of the ratio of structual units I to II in the polymer.* A definite numerical correlation between the values of $D(CH_3/CH_2)$ and the ratio of the structural units, I/II, has not yet been established. Also, we do not have a standard polymer specimen which has either the pure structural unit I or the pure II. However, there is one example which suggests the correspondence between these two values. Poly-α-methylstyrene of high molecular weight has one methyl group and one methylene group, the ratio of methyl and methylene being unity, and the observed value of $D(CH_3/CH_2)$ was 0.7. In the case of polypropenylbenzene, the value, unity, of the methyl/methylene ratio corresponds to the following structural ratio:


$$-(\underset{C_6H_5}{CH}-\overset{CH_3}{CH})_2-(\underset{C_6H_5}{CH}-CH_2-CH_2)-$$

Thus, polypropenylbenzene with the $D(CH_3/CH_2)$ value of 0.7 would correspond to a polymer having a 1/3 rearranged structure II and 2/3 normal structure I, as has been indicated above.

There is one more possible structure of the polymer, the structural unit of which is that of polyallylbenzene. This possibility can not be excluded since the existence of an isomerization equilibrium has been reported between allylbenzene and propenylbenzene under some favorable conditions.[13] A comparison was made between the infrared spectra of the BF_3 etherate polymer and polyallylbenzene, which had been prepared with a Ziegler catalyst (Fig. 2). The spectra showed little difference in the CH stretching region, but there was a remarkable difference in the 1450~1495 cm^{-1} region. The band at 1495 cm^{-1} characteristic of polyallylbenzene is absent in the rearranged polymer. In addition, the residual propenylbenzene after the polymerization was found by gas chromatography to contain no detectable amount of allylbenzene. Therefore, the possibility of the existence of the polyallylbenzene structural unit in the present polymers could be excluded.

It should be noted that, when using $D(CH_3/CH_2)$ as a measure of the polymer structure, we did not take account of the structure of the polymer ends, which would have contributed considerably to the $D(CH_3/CH_2)$ values when the molecular weight was very low. Accordingly, the $D(CH_3/CH_2)$ of the methanol-soluble parts (oligomers) of the polymers is not listed in the present data.

A Comparison of Various Catalysts. — Two groups of catalysts were tested. One group is metal halides, which are considered to need water as a co-catalyst (Table I). The other group is boron trifluoride complexes with definite chemical compositions (Table II). Higher yields of total polymer were obtained with metal halide catalysts, especially with such strong Friedel-Crafts-type catalysts as boron fluoride, aluminum bromide and titanium tetrachloride, than with boronfluoride complexes. Boron fluoride complexes exhibited moderate catalytic action. Some metal halides gave higher yields of polymer at −78°C than at 0°C, while all the boronfluoride complexes showed a better yield at 0°C than at −78°C.

Fractions of the methanol-isoluble part are

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* The ratio of optical densities at 2960/2850 cm^{-1} is usually used to estimate the ratio of methyl and methylene groups.[12] In our cases, however, the absorption at 2850 cm^{-1} is invariably very weak and is considered unsuitable for the measurement.

12) For example, H. V. Drushell and F. A. Iddings, *Anal. Chem.*, **35**, 28 (1963).

13) L. Bateman, *J. Chem. Soc.*, **1951**, 2283.

TABLE I. POLYMERIZATION OF PROPENYLBENZENE WITH METAL HALIDE CATALYSTS
Monomer (trans 74%) 1 ml.; solvent 4 ml.;
Catalyst/monomer mole ratio=1/20; 4 hr.

Catalyst	Solvent	Polymer yield, %[b]	Methanol-insoluble part			
			Yield, %	$D(CH_3/CH_2)$	Soft. pt., °C	Mol. wt.
0°C						
BF_3[a]	Toluene	73.3	12.1	0.57	143∼154	1100
BF_3[a]	*n*-Heptane	20.1	9.6	1.31	113∼121	670
$AlBr_3$[c]	Toluene	72.1	3.5	1.41	135∼145	980
$TiCl_4$[c]	Toluene	32.1	3.6	0.29	160∼170	710
$FeCl_3$	Toluene	22.2	4.8	0.29	156∼165	—
Et_2AlCl	Toluene	(3.4)	—	—	—	—
$SnCl_4$	Toluene	(0.9)	trace	—	—	—
VCl_4	Toluene	(2.0)	0	—	—	—
−78°C						
BF_3[a]	Toluene	31.2	21.2	1.50	127∼134	850
BF_3[a]	*n*-Heptane	(8.9)	5.4	0.15	188∼197	2900
$AlBr_3$[c]	Toluene	83.4	11.1	1.75	135∼145	710
$TiCl_4$[c]	Toluene	55.6	13.3	0.50	160∼175	1200
$FeCl_3$	Toluene	(10.3)	5.8	0.18	170∼177	2700
Et_2AlCl	Toluene	(8.6)	—	—	—	—
$SnCl_4$	Toluene	(6.4)	2.1	0.27	182∼188	—
VCl_4	Toluene	(4.7)	trace	—	—	—

a) BF_3 gas was saturated.
b) Yields in parenthes are values obtained by bromate-bromide titration of the residual monomer.
c) Monomer contains 78% of the trans-isomer.

TABLE II. POLYMERIZATION OF PROPENYLBENZENE WITH BF_3 COMPLEXES
Monomer (trans 74%) 1 ml.; solvent toluene 4 ml.;
catalyst/monomer mole ratio=1/20; 4 hr.

Catalyst	Polymer yield, %[a]	Methanol-insoluble part				
		Yield, %	$D(CH_3/CH_2)$	Soft. pt. °C	Mol. wt.	Unusual IR
0°C						
$BF_3 \cdot 2CH_3OH$	(16.1)	9.6	0.51	150∼160	2000	1095 cm^{-1}, ether
$BF_3 \cdot 2CH_3COOH$	(13.5)	10.4	0.37	153∼164	2400	1230, 1740 cm^{-1}, ester
$BF_3 \cdot 2H_2O$	(10.8)	trace	—	—	—	
$BF_3 \cdot (CH_3)_2O$	(9.6)	8.6	0.23	168∼175	2100	1090 cm^{-1}, ether
$BF_3 \cdot (C_2H_5)_2O$	9.9	8.1	0.17	155∼166	1600	1090 cm^{-1}, ether
−78°C						
$BF_3 \cdot 2CH_3OH$	(8.1)	3.6	0.30	172∼186	—	1095 cm^{-1}, ether
$BF_3 \cdot 2CH_3COOH$	—	trace	—	—	—	
$BF_3 \cdot 2H_2O$	(4.9)	0	—	—	—	
$BF_3 \cdot (CH_3)_2$	—	trace	—	—	—	
$BF_3 \cdot (C_2H_5)_2O$	1.2	0.7	0.17	102∼113	—	1090 cm^{-1}, ether

a) Yields in parenthes are values obtained by bromate-bromide titration of the residual monomer.

generally smaller in amount with BF_3 complexes than with metal halides. There is a sharp contrast between the two groups of catalysts in the effect of the polymerization temperature on the molecular weights of the resulting polymers. Metal halides yielded a higher fraction of the insoluble polymer at −78°C than at 0°C, while the BF_3-complexes showed reverse results.

Among all the catalysts tested, the milder catalysts generally gave polymers with the smaller value of (CH_3/CH_2) and, hence, the larger proportion of rearrangement during polymerization.

It is interesting to note here that there were observed some unusual absorptions in the infrared spectra of the polymers obtained with the borontrifluoride complexes (Table II, the last column). These absorptions are considered to come from the terminal groups of the polymer, probably being incorporated into the polymers by a termination reaction with

TABLE III. EFFECT OF TEMPERATURE ON THE POLYMERIZATION OF PROPENYLBENZENE WITH BF_3 ETHERATE

Monomer (trans 74%) 1 ml.; solvent, toluene 4 ml.; catalyst/monomer mole ratio=1/20; 4 hr.; temperature ±1°C

Temp., °C	Polymer yield, %	Methanol-insoluble part			
		Yield, %	$D(CH_3/CH_2)$	Soft. pt., °C	Mol. wt.
−78	1.2	0.7	0.17	102∼113	−
−60	2.4	1.7	0.11	118∼137	−
−40	6.6	4.5	0.14	155∼165	1600
0	9.9	8.1	0.17	155∼166	1600
20	9.8	6.3	0.12	152∼165	1600
40	12.5	3.6	0.13	145∼154	−

"gegen" ions or initiator molecules.* Another unusual infrared band to be noted is the one observed around 800 cm^{-1} (which is not shown here) in polymers obtained with borontrifluoride in *n*-heptane at 0°C as well as at −78°C. This band may possibly be assigned to the occurrence of *p*-disubstituted benzene which originates from the *p*-substitution of the benzene ring by the growing cation in a termination reaction or during the propagation step. This assignment needs further experimental verification, however.

The Effect of the Polymerization Temperature. —The polymerization ofp ropenylbenzene with BF_3 etherate was carried out in toluene at temperatures from −78 to 40°C (Table III and Fig. 3). The total yields polymer increased with a rise in the temperature. However, the methanol-insoluble part showed a maximum at about 0°C and rapidly decreased thereafter while at the same time the yield of the methanol-soluble low polymer fractions increased rapidly above 0°C. Correspondingly, the Arrhenius plot of the total yield (Fig. 4) showed a break, giving an activation energy of 1.2 kcal./mol. at the high temperature region and 4.3 kcal./mol. at the low temperature region. The phenomenon seems to indicate that there is some change in the mechanisms of polymerization processes between below and above 0°C.

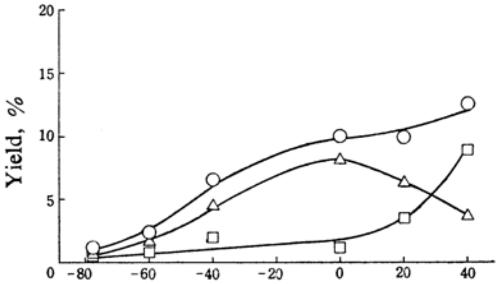

Fig. 3. Effect of temperature on polymerization of propenylbenzene with BF_3 etherate.
○ Total polymer
△ The methanol-insoluble part
□ The methanol-soluble part

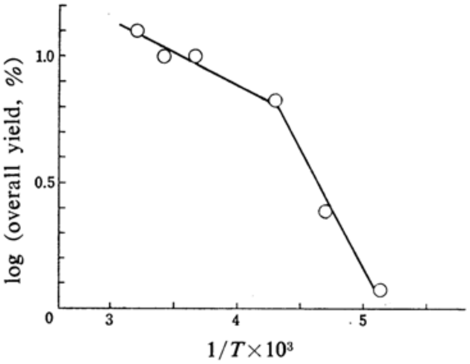

Fig. 4. Effect of polymerization temperature on overall yield of polypropenylbenzene (BF_3Et_2O catalyst).

Although the temperature of the polymerization had a marked effect on the rate of polymerization as well as on the molecular weight, it had no appreciable effect on $D(CH_3/CH_2)$ (Fig. 5). Hence, it is suggested that the activation energy of the normal propagation is nearly equal to that of the rearrangement propagation.

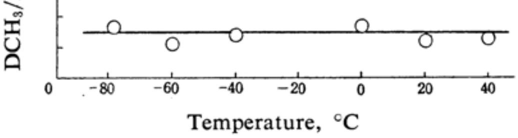

Fig. 5. Effect of polymerization temperature on the chemical structure of polypropenylbenzene (BF_3Et_2O catalyst).

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* In a preliminary experiment, there was observed less than a first-order dependence of the polymerization rate on the initiator concentration, especially at high initiator concentrations. In addition, the molecular weight was found to decrease with increasing initiator concentrations. These facts appear to suggest qualitatively the existence of a termination or a transfer reaction with initiator molecules.

TABLE IV. EFFECT OF DIELECTRIC CONSTANTS OF SOLVENTS ON THE POLYMERIZATION OF PROPENYLBENZENE WITH BF_3 ETHERATE

Monomer (trans 74%) 1 ml.; solvent 4 ml.;
catalyst/monomer mole ratio=1/20; 4 hr. at 0°C

Solvent	Dielectric constant	Yield, %	Methanol-insoluble part			
			Yield, %	$D(CH_3/CH_2)$	Soft. pt., °C	Mol. wt.
CCl_4	2.3	11.5	6.1	0.36	159∼167	—
$C_6H_5CH_3$	2.4	9.9	8.1	0.17	155∼166	1600
$CHCl_3$	5.2	9.2	5.2	0.33	167∼177	2100
CH_2Cl_2	9.9	12.7	8.7	0.52	160∼168	1900
$(CH_2Cl)_2$	10.7	13.6	8.4	0.66	153∼164	1600

The Effect of the Solvents. — The influence of the dielectric constants of the solvents was studied at 0°C using BF_3-etherate as a catalyst, as is shown in Table IV. The total yields of polymer and those of the methanol-insoluble part were observed to increase slightly with the increasing polarity of the solvents (Fig. 6). The $D(CH_3/CH_2)$ value increased remarkably, showing that the rearrangement in the propagation became unfavorable with the increasing polarity of the solvent (Fig. 7).

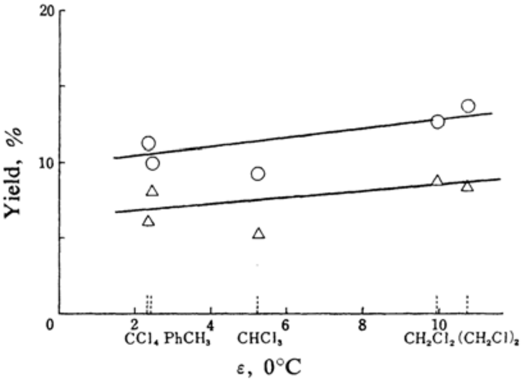


Fig. 6. Effect of dielectric constants of solvents on overall yield of polypropenylbenzene (BF_3Et_2O catalyst).
○ Total polymer
△ The methanol-soluble part

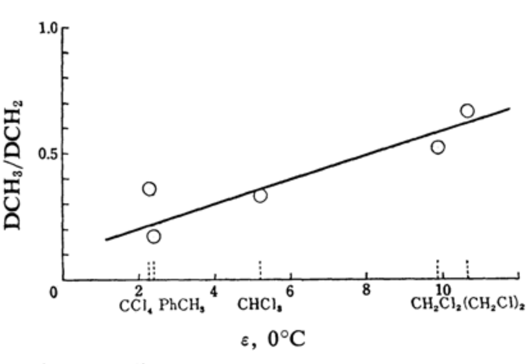
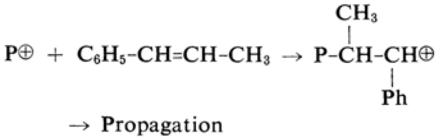


Fig. 7. Effect of dielectric constants of solvents on chemical structure of polypropenylbenzene (BF_3Et_2O catalyst).

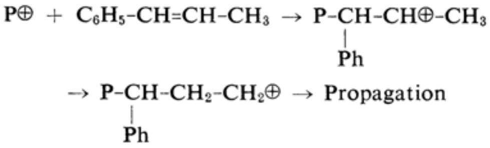
The molecular weight of the resulting polymer, on the other hand, appears to decrease with the increasing dielectric constants of the solvents, except for the case of the toluene solvent, where a molecular termination on the aromatic ring may play some role. The decrease of the molecular weight with the increasing polarity of the solvent may be explained as due to a termination reaction which is favored by the polar medium.

Discussion of the Reaction Mechanism.—It has clearly been shown that a variety of "gegen" ions influenced the polymerization of propenylbenzene, i. e., the structure of the resulting polymer as well as the overall rate and the molecular weight. The facts may, as a whole, be interpreted in terms of ion pairs of growing ends. The rearrangement polymerization was found to be favored by mild initiators. Among the catalysts examined, BF_3-etherate showed the better results for the rearrangement polymerization.

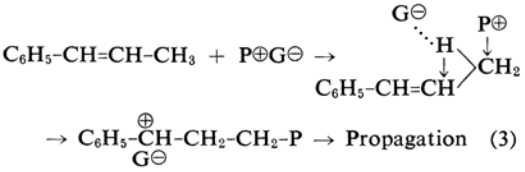
Propagation.—The characteristic features of a propagation reaction using BF_3-etherate as a catalyst may be summarized as follows: (i) $D(CH_3/CH_2)$ does not change with a change in the temperature of polymerization, indicating that the activation energy for the usual propagation is nearly equal to that of the rearrangement. (ii) $D(CH_3/CH_2)$ increased markedly with an increase in the dielectric constants of the solvents; in other words, the rearrangement propagation is favored in a less-ionizing medium. This suggests that the growing species may be more intimate ion pairs in the rearrangement propagation than in the usual propagation. Propagation with the usual opening of double bonds (I) will proceed according to Scheme 1, the resonance stabilization of the α-alkylbenzyl cation being the determining factor for the attacking position of the growing cation. This reaction does not seem to need the strong cooperation of "gegen" ions and, hence, will be favored by highly-ionizing solvents. On the other hand, for the rearrangement polymerization two alternative mechanisms, 2 and 3, have to be considered. Mechanism 2 involves two unfavorable steps, i. e., the prevalent formation of the more unstable secondary carbonium ion instead of the more stable α-alkylbenzyl cation, and the subsequent hydrogen transfer from primary to secondary carbon, which is also energetically unfavorable. Mechanism 3 seems more plausible for the rearrangement propagation. The methyl hydrogen of propenylbenzene would have an acidic nature. The "gegen" ion of the growing ion pair will assist in loosening the proton from the methyl group, and at the same time the growing carbonium ion will make an electrophillic attack on the methyl carbon. The proton will then be transfered to the adjacent double bond. Thus, the growing ion pair cooperates in the push-pull mechanism, and so highly-ionizing solvents will retard the reaction, making the contribution of the rearrangement propagation relatively smaller than the usual propagation in polar media.



$$P^{\oplus} + C_6H_5\text{-}CH{=}CH\text{-}CH_3 \rightarrow P\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}\underset{\underset{Ph}{|}}{C}H^{\oplus} \rightarrow \text{Propagation} \qquad (1)$$

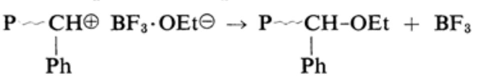


$$P^{\oplus} + C_6H_5\text{-}CH{=}CH\text{-}CH_3 \rightarrow P\text{-}\underset{\underset{Ph}{|}}{C}H\text{-}CH^{\oplus}\text{-}CH_3 \rightarrow P\text{-}\underset{\underset{Ph}{|}}{C}H\text{-}CH_2\text{-}CH_2^{\oplus} \rightarrow \text{Propagation} \qquad (2)$$

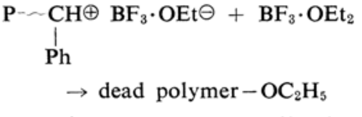


$$C_6H_5\text{-}CH{=}CH\text{-}CH_3 + P^{\oplus}G^{\ominus} \rightarrow \rightarrow C_6H_5\text{-}\overset{\oplus}{\underset{G^{\ominus}}{C}}H\text{-}CH_2\text{-}CH_2\text{-}P \rightarrow \text{Propagation} \qquad (3)$$

Termination.—In the polymers obtained using boron trifluoride complexes as catalysts, some infrared absorption bands characteristic of the initiator fragments have been observed (Table II). This appears to indicate that the termination reaction with "gegen" ions (4) (self termination) or with an initiator (5) seems to play an important role.



$$P\sim\underset{\underset{Ph}{|}}{C}H^{\oplus}\ BF_3\cdot OEt^{\ominus} \rightarrow P\sim\underset{\underset{Ph}{|}}{C}H\text{-}OEt + BF_3 \qquad (4)$$



$$P\sim\underset{\underset{Ph}{|}}{C}H^{\oplus}\ BF_3\cdot OEt^{\ominus} + BF_3\cdot OEt_2 \rightarrow \text{dead polymer}-OC_2H_5 \qquad (5)$$

Reaction 5 may actually be considered to be a reaction between the growing ion pair and the ionized initiator molecule $BF_3\cdot OEt^{\ominus}\ Et^{\oplus}$. The concentrations of the ion pairs are usually fairly small compared to the concentration of total initiators and will increase in polar media. Thus, reaction 5 might be accelerated in a polar solvent, resulting in a decrease in the molecular weight of the polymer (Table IV.) Self-termination reaction 4 is a reaction between opposite-charged ions leading to neutral compounds, and so will be accelerated in non-polar media. The Arrhenius plot, as we have observed, of the polymerization of propenylbenzene by borontrifluoride etherate (Fig. 4) is composed of two straight lines, with a break at about 0°C. The activation energy above 0°C is lower (1.2 kcal./mol.) than that below 0°C (4.3 kcal./mol.). On the other hand, the activation energies for two kinds of propagation reactions (usual and rearrangement) are shown to be nearly equal over the temperature range examined (Fig. 5). Therefore, if we assume only one kind of initiation reaction, we would have to consider at least two kinds of termination reaction, with different activation energies. The termination reaction with a higher activation energy should be predominant at higher temperatures, thus resulting in a smaller overall activation energy at higher temperatures. The authors do not have any evidence at present to show whether these two kinds of termination reactions correspond to the termination schema 4, 5 and/or to others. At any rate, this termination reaction may be at least partly responsible for the existence of a maximum in the yield of the methanol-insoluble polymer, that is, a rapid decrease in the molecular weight of the total polymer at high temperatures (above 0°C). Chain transfer processes are also to be considered in interpreting the decrease in the molecular weight in polymerizations at high temperatures. Kinetic studies are being undertaken in this respect.

Summary

1) Propenylbenzene has been found to polymerize by a cationic mechanism in two ways. Both the structure $-(CHPh{-}CH(CH_3))_n-$ (I) resulting from the usual opening of the double bond and the structure $-(CHPh{-}CH_2{-}CH_2)-$ (II) resulting from the rearrangement along the backbone chain of the resultant polymer occur.

2) The relative ratio of structures I/II has been pursued using the ratio of infrared absorptions, CH_3/CH_2, as a measure.

3) The rearrangement polymerization is generally preferred by mild catalysts, such as BF_3-etherate, while the polymerization to I has been found to predominate in polymerization with BF_3.

4) On the basis of the observed effect of reaction variables on the rate of polymerization and on the I/II ratio, a propagation mechanism has been proposed which includes the "gegen" ion attack on the methyl hydrogen of propenylbenzene.

5) Termination reaction by a "gegen" ion or an initiator has been shown to be important in polymerization catalyzed by BF_3-complexes.

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Added in Proof

During further experiments, the authors have found that the propenylbenzene used in the experiments contains about 5% unknown impurity. They can not at present exclude the possibility that the rearrangement under consideration would have been more or less modified by the existence of this impurity. Experiments for the clarification of this point is in progress.