Monomer-isomerization polymerization: 29. Monomer-isomerization polymerization of allyl phenyl ether with cationic catalyst

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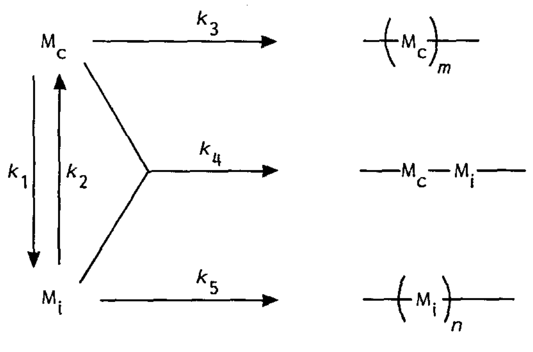
Polymerizations of allyl phenyl ether (APhE) and its isomers, 2-allylphenol (2APhOH), 2-propenyl phenyl ether (PrPhE), 2-propenylphenol (2PrPhOH) and 2-methyldihydrobenzofuran (MDBF), were studied with $BF_3 \cdot OEt_2$ catalyst. 2APhOH, PrPhE and 2PrPhOH polymerized without monomer isomerization, and MDBF did not give a polymer. When the polymerization of APhE was carried out above 40°C, it gave a solid polymer. The polymer obtained from APhE was found to be very similar to that from 2APhOH, and an *in situ* monomer isomerization of APhE to 2APhOH was observed. These results indicated that APhE underwent monomer-isomerization polymerization with $BF_3 \cdot OEt_2$ catalyst, i.e. APhE first isomerized to APhOH before polymerization, and then the APhOH gave a polymeric material. From the analysis of the resulting polymers, it was found that the polymerization of APhE and 2APhOH proceeded predominantly via polyalkylation to the aromatic ring.

(Keywords: monomer-isomerization polymerization; cationic catalyst; allyl phenyl ether; 2-allylphenol; isomer; alkylation)

INTRODUCTION

Polymerizations of vinyl monomers usually proceed via an opening of the double bond without any rearrangement of the monomer structure. If monomers have isomers that are able to polymerize, the general scheme for polymerization of the monomers can be expressed as follows:



Here M_c is charged monomer, M_i is its isomer produced by isomerization, and k_i ($i = 1$ to 5) indicates the rate constant of each reaction. The ratios of M_c to M_i in the resulting polymer depend on the rates of each reaction.

We have reported that many 2-olefins such as 2-butene and 4-methyl-2-pentene undergo monomer-isomerization polymerization through a coordination mechanism to give polymers consisting of the respective 1-olefin units[1–11]. From these works, the conditions that induce the monomer-isomerization polymerization of 2-olefins with Ziegler–Natta catalysts are summarized as follows: (1) Isomerization from M_c to M_i takes place easily. (2) Among the isomers, M_i has a high selectivity and reactivity for polymerization. (3) M_c does not participate in the polymerization of M_i.

Hence, if the above conditions are satisfied, monomer-isomerization polymerization is expected to take place by other polymerization mechanisms. However, a few examples are found in the literature[12–20].

In radical polymerization, dialkyl maleates were reported to undergo monomer-isomerization radical polymerization to yield polymers consisting of dialkyl fumarate units in the presence of both 2,2′-azobisisobutyronitrile (AIBN) and amines such as morpholine[12,13]. The hydrogen transfer polymerization of 3-butenamide, accompanying monomer isomerization to 2-butenamide in the presence of t-BuOK, is an example of anionic monomer-isomerization polymerization[14].

In the field of cationic polymerization, it was reported that α-pinene is polymerized with $AlCl_3$ catalyst accompanying isomerization to limonene prior to polymerization, but the occurrence of monomer isomerization was not clear[15]. In the polymerization of allylbenzene (AB) with cationic catalyst, the isomerization to propenylbenzene (PB) was observed, and the newly formed PB also participates in polymerization[16]. Higashimura and coworkers[17,18] found that 2-ethyl-1,3-butadiene, methylenecyclohexane and methylenecyclopentane undergo monomer-isomerization oligomerization by a superacid catalyst such as CF_3SO_3H.

Yip *et al.*[19,20] reported that the polymerization of allyl phenyl ether (APhE) with $BF_3 \cdot OEt_2$ catalyst in bulk gave a polymer consisting of 2-allylphenol (2APhOH) units. They asserted that the rearrangement to 2APhOH took place in the propagation step. However, the compositions of the residual monomers recovered after the polymerization were not analysed. On the other hand, Claisen rearrangement of APhE is known to be induced by heat to yield 2APhOH[21], and a similar reaction

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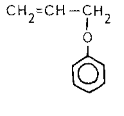
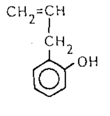
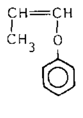
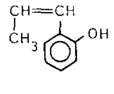
proceeds easily in the presence of Lewis acids even at room temperature[22,23].

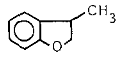
On the basis of the above consideration, a monomer-isomerization polymerization of APhE is expected to take place with adequate cationic catalysts. To clarify these points, we carried out the polymerization of APhE and its isomers, 2-allylphenol (2APhOH), 2-propenyl phenyl ether (PrPhE), 2-propenylphenol (2PrPhOH) and 2-methyldihydrobenzofuran (MDBF). The results obtained are described in this article. The formulae of the isomers are shown below:


APhE


2APhOH


PrPhE


2PrPhOH


MDBF

EXPERIMENTAL

Materials

APhE was synthesized by the reaction of phenol with allyl bromide in the presence of potassium carbonate[21]. The yield was 84.6%, and the purity after purification was 99.8%. 2APhOH was obtained by utilizing the Claisen rearrangement of APhE at 190°C[21]. The yield was 81.4%, and the purity was 98.9% after purification. 2PrPhOH was prepared by isomerization of 2APhOH in the presence of KOH in dimethylsulphoxide; yield 20%, purity 99.5%. The synthesis of PrPhE was carried out according to the procedure of Price *et al.*[24] by the isomerization of APhE with t-BuOK catalyst in DMSO at room temperature; yield 91.9%, purity 96.1%. MDBF was also prepared by refluxing 2APhOH with acetic acid in the presence of aqueous hydrobromic acid; yield 48.7%, purity 99.2%[21].

$BF_3 \cdot OEt_2$, $SnCl_4$ and $TiCl_4$ (commercially available reagents) were used after distillation, and H_2SO_4 was used without further purification. AIBN and benzoyl peroxide (BPO) were used after recrystallization. Solvents and other reagents were used after purification by standard methods.

Table 1 Polymerization of APhE and its isomers with $BF_3 \cdot OEt_2$ catalyst in bulk[a]

Monomer	Temp. (°C)	Time (h)	Yield (%)	Monomer isomerization observed[b]
APhE	0	48	0.0	Isomerization to 2APhOH
APhE	60	1	69.6	Isomerization to 2APhOH
2APhOH	0	48	73.2	None
2APhOH	60	1	95.3	None
PrPhE	0	24	49.9	None
PrPhE	60	1	60.4	None
2PrPhOH[c]	0	48	99.8	None
2PrPhOH	60	1	96.2	None
2MDBF	60	3	0.0	None

[a] Polymerization conditions: $[BF_3 \cdot OEt_2] = 0.37$ mol l^{-1}, monomer = 2.0 ml
[b] Determined by gas chromatography
[c] Polymerization was carried out in CH_2Cl_2: $[2PrPhOH] = 3.6$ mol l^{-1}

Polymerization procedure

The polymerizations were carried out in a sealed glass tube, with shaking, in a thermostat for a given time. Isomer distribution after polymerization was analysed by gas chromatography (Apiezon grease-L on Chromosorb-AWA 60/80 mesh column (3 mm × 2.5 m) at 120°C). The polymer yield was determined by gravimetry.

Characterization of the polymer

The structure of the resulting polymers was checked by their i.r. and ^1H n.m.r. (JEOL GX-400) spectra. G.p.c. measurements were carried out at 38°C by using polystyrene gel columns (Toso RE-8000), and tetrahydrofuran was used as eluent.

RESULTS AND DISCUSSION

Polymerization of APhE and its isomers with $BF_3 \cdot OEt_2$

Table 1 shows the results of polymerizations of APhE, 2APhOH, PrPhE, 2PrPhOH and MDBF with $BF_3 \cdot OEt_2$ catalyst. Although APhE did not polymerize at 0°C, it gave a polymer at 60°C. On the other hand, 2APhOH, PrPhE and 2PrPhOH polymerized even at 0°C, but MDBF did not give a polymer. From this table, the polymerization reactivity for these monomers can be expressed by the following order: 2PrPhOH $\geqslant$ 2APhOH > PrPhE > APhE > MDBF = 0. It is noted that the polymerization of APhE was slower than that of 2APhOH. In the polymerization of APhE, 2APhOH was detected in the unreacted monomer recovered after the reaction, but the polymerizations of 2APhOH, PrPhE and 2PrPhOH were found to proceed without any monomer isomerization.

All resulting polymers are yellow or brown powders, and some properties of these polymers are summarized in *Table 2*. The solubility and softening point of the polymers obtained from APhE were in agreement with

Table 2 Some properties of the resulting polymers

	Polymer						
	Solubility[a]						
Monomer	CH_3OH	C_6H_6	n-C_6H_{14}	S.p.[b] (°C)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	Appearance
APhE	○	○	○	72–76	700	2.15	Powder
2APhOH	○	○	○	70–74	590	1.70	Powder
PrPhE	●	○	○	109–113	600	1.70	Powder
2PrPhOH	○	○	●	121–124	950	1.92	Powder

[a] (○) soluble, (●) insoluble
[b] Softening point
[c] Determined by g.p.c.

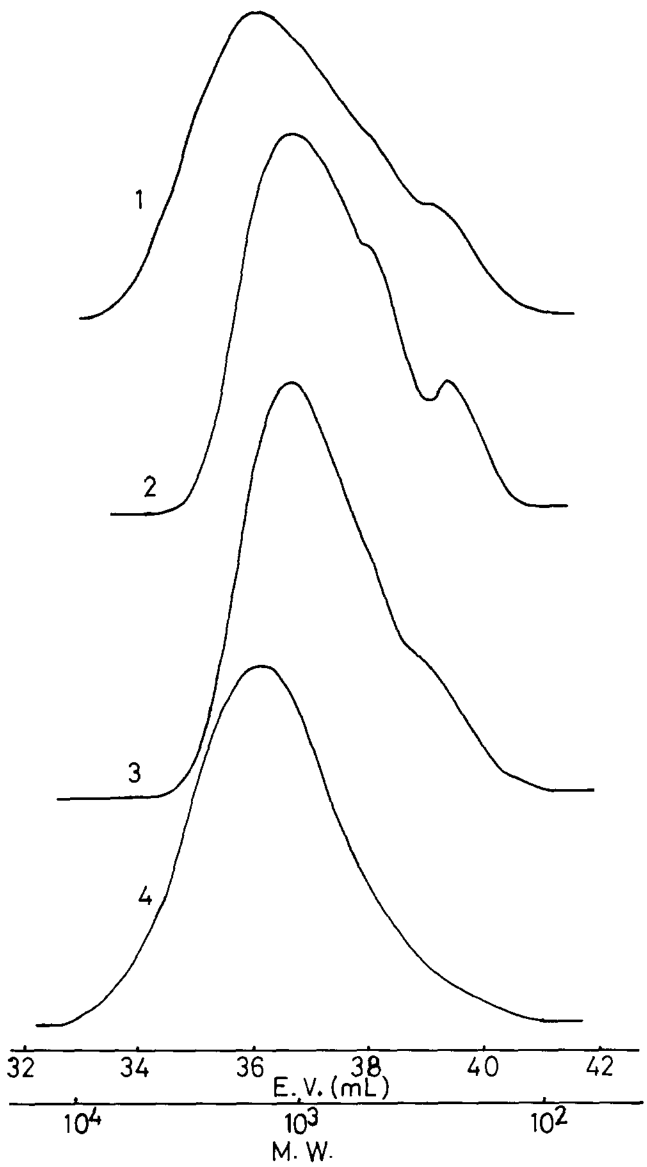


Figure 1 G.p.c. elution curves for the polymers obtained from (1) APhE, (2) APhOH, (3) PrPhE and (4) 2PrPhOH with $BF_3 \cdot OEt_2$ catalyst

those from 2APhOH. From the g.p.c. elution curves depicted in *Figure 1*, the molecular weights of these polymers at 60°C were found to be low, and the calculated molecular weights and distributions are listed in *Table 2*.

If the polymer obtained from APhE bears hydroxyl groups, it can be transformed to ester groups by reacting with acid chlorides such as acetyl chloride. To clarify this point, the polymer was allowed to react with acetyl chloride. As a result, introduction of ester groups and disappearance of hydroxyl groups were identified by i.r. spectra.

From these findings, we supposed that the polymers obtained from APhE have the same structure as those from 2APhOH. To elucidate the polymer structure, we analysed them by means of i.r. and ^1H n.m.r. spectroscopy.

I.r. spectra of the polymers obtained from these monomers are shown in *Figure 2*. In contrast to the polymers obtained from PrPhE and 2PrPhOH, the polymer obtained from APhE gave an i.r. spectrum indistinguishable from that from 2APhOH. For the polymer obtained from APhE, an absorption band appeared at 3400 cm^{-1} due to a hydroxyl group and a 1,2-disubstituted benzene, respectively, along with the disappearance of absorption at 755 cm^{-1} due to a monosubstituted benzene. Further, for both polymers obtained from APhE and 2APhOH, distinct absorption bands due to methyl group (1380 cm^{-1}) and 1,2,4-trisubstituted benzene (890 cm^{-1}) were observed. If both monomers are polymerized via a conventional opening of the double bond, such absorption bands would not appear.

To confirm these points, ^1H n.m.r. measurements were carried out, and the spectra obtained are depicted in *Figure 3*. Although the structure of the polymers formed from APhE and 2APhOH is likely to be very complex, both polymers gave basically the same spectra. On the other hand, the spectra of the polymers obtained from PrPhE and PrPhOH are distinguishable from those from APhE and APhOH.

In accordance with the i.r. spectra, in both polymers obtained from APhE and 2APhOH, the presence of methyl ($\delta = 0.8$–1.4 ppm) and hydroxyl groups ($\delta = 4.8$ ppm) was confirmed by ^1H n.m.r. spectroscopy. If the polymerization proceeds simply via a conventional opening of double bonds, the ratio of aromatic to aliphatic protons should be unity for APhE and 0.5 for 2APhOH, respectively. However, the ratios were found to be 0.52 and 0.43 for the polymers obtained from APhE and 2APhOH, respectively. Judging from the strong resonance of the methyl group, the polymers are formed via other routes, presumably polyalkylation.

Taking the previously reported results for the polym-

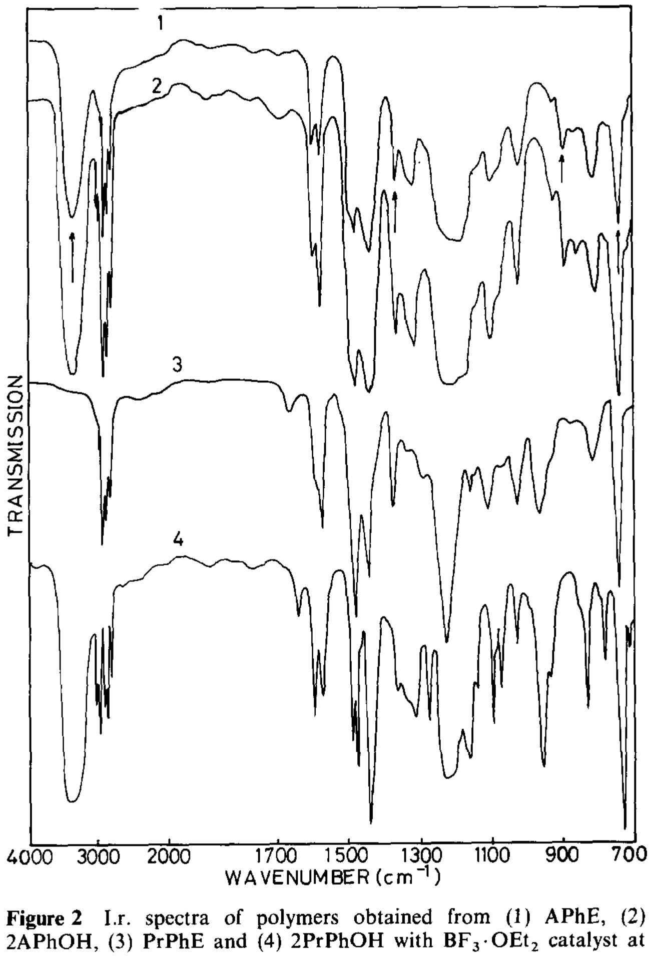


Figure 2 I.r. spectra of polymers obtained from (1) APhE, (2) 2APhOH, (3) PrPhE and (4) 2PrPhOH with $BF_3 \cdot OEt_2$ catalyst at 60°C

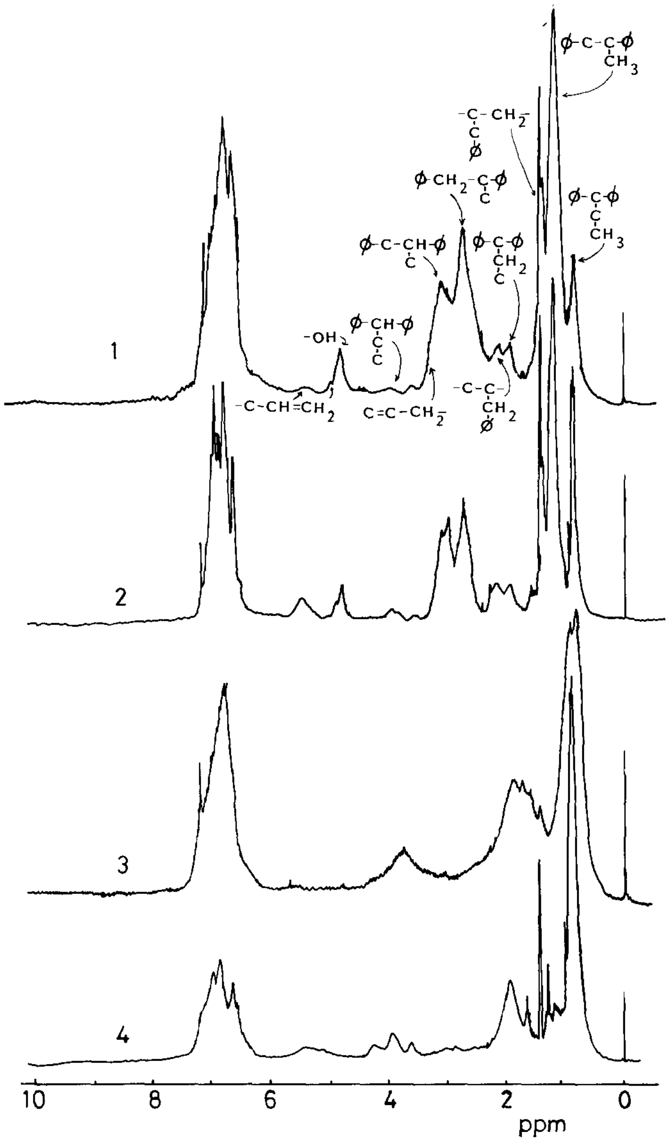
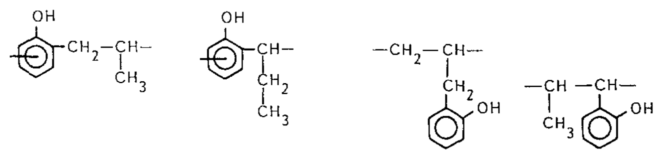


Figure 3 ^1H n.m.r. spectra of polymers obtained from (1) APhE, (2) 2APhOH, (3) PrPhE and (4) 2PrPhOH with $BF_3 \cdot OEt_2$ catalyst at 60°C

erization of AB into consideration[25–29], the following four repeat units can be assumed:



I II III IV

The peaks at 1.2, 2.8 and 3.1 ppm can be assigned, respectively, to CH_3, CH_2 and CH in structure **I**; and the peaks at 0.9, 1.9 and 3.7 ppm are also assigned to CH_3, CH_2 and CH in structure **II**, respectively. Further, the peaks at 1.4 and 2.2 ppm would be due to structure **III**. In the polymerization of AB, poly(PB) is reported to be produced via a monomer isomerization[25]. However, the monomer isomerization to 2PrPhOH was not observed in the polymerization of APhE and 2APhOH, so that structure **IV** may be excluded. The peaks at 3.2, 4.8 and 5.5 ppm would be assigned to allyl groups attached to the aromatic ring.

Although other small peaks indicate that some side-reactions took place, all the main peaks could be assigned. Hence, we deduced that polyalkylation is predominant in the polymerization reaction. The ratio of *ortho* to *para* in the alkylation could not be determined, but we believe that 1,2,4-trisubstituted benzene structure would mainly be formed, as suggested by the i.r. spectra of the polymers and by the reactivity of the hydroxyl group in the aromatic ring of 2APhOH. From areas of the proton peaks, the compositions of **I**, **II** and **III** were estimated to be 68%, 17% and 15% for APhE, and 62%, 22% and 18% for 2APhOH, respectively.

In the resonance of aromatic protons, the pattern of APhE was a little different from that of 2APhOH. If the aromatic ring in the repeat unit has a trisubstituted benzene structure, the ratio of aromatic to aliphatic protons should be 0.42, which is consistent with that for 2APhOH estimated to be 0.43. The ratio in APhE (0.52) is higher than the expected value for the alkylated structure, suggesting that the polymer from APhE contains a disubstituted benzene structure besides the trisubstituted one. Since the molecular weights of polymers were low, as listed in *Table 2*, the disubstituted benzene can affect the resonance pattern of aromatic protons. In the rearrangement of APhE catalysed by Lewis acid, a small amount of 4-allylphenol (4APhOH) in addition to 2APhOH was reported to form[20]. However, alkylation of the aromatic ring in 4APhOH yields a trisubstituted benzene structure that is indistinguishable from that from 2APhOH.

Thus, the difference in the patterns of aromatic resonance between APhE and 2APhOH would be attributed to the occurrence of alkylation of APhE in the polymerization of APhE.

The polymerization of allyl vinyl ether with $BF_3 \cdot OEt_2$ catalyst is reported to proceed with opening of the double bond of the vinyl group, and the allyloxy group did not participate in the polymerization[30]. Similarly, the allyloxy group in APhE would not take part in the propagation.

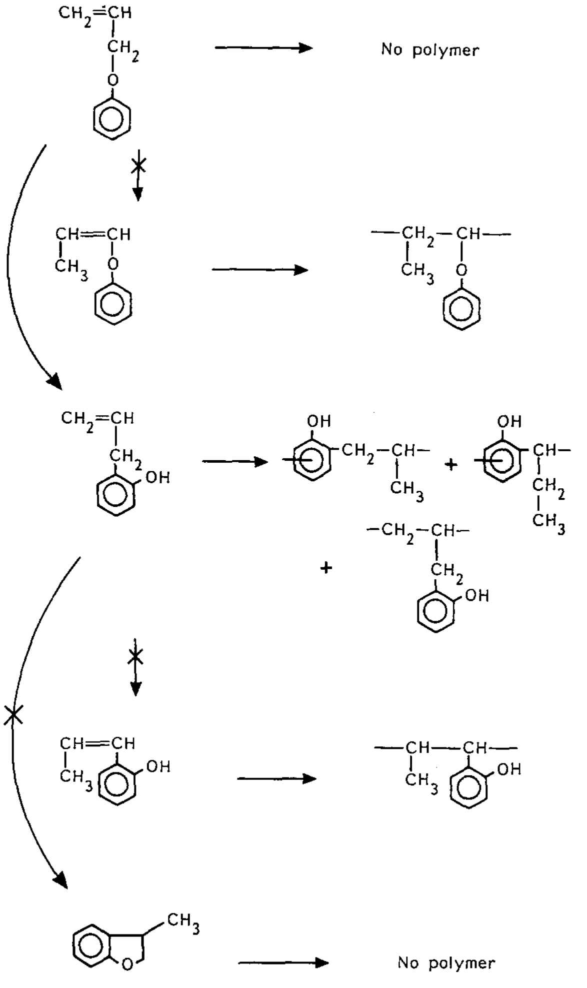
From evidence gathered, it is apparent that APhE underwent monomer-isomerization polymerization with $BF_3 \cdot OEt_2$ catalyst, i.e. APhE isomerizes first to 2APhOH prior to polymerization and then 2APhOH gives polymers. The polymerization proceeds mainly via polyalkylation to the aromatic ring, and a conventional double bond opening also takes place. In the alkylation the isomerization of initial secondary to benzylic carbonium ion was also observed as a part of the propagation. Consequently, the polymerization of APhE with $BF_3 \cdot OEt_2$

Table 3 Monomer-isomerization polymerization of APhE with $BF_3 \cdot OEt_2$ catalyst in bulk[a]

Temp. (°C)	Time (h)	Yield (%)	Composition of monomers after polymerization (%)[b] APhE	2APhOH
0	48.0	0.0	96.3	3.7
0	720	0.0	–	–
40	15.0	51.3	38.2	61.8
60	0.2	Trace	94.3	5.7
60	1.0	71.6	34.8	65.2

[a] Polymerization conditions: $[BF_3 \cdot OEt_2] = 0.37$ mol l^{-1}, APhE = 2 ml
[b] Determined by gas chromatography

can be expressed as follows:



(—✕→ Reaction did not proceed with $BF_3 \cdot OEt_2$ catalyst)

Effect of temperature

Table 3 shows the results for the effect of temperature on the polymerization of APhE with $BF_3 \cdot OEt_2$ catalyst. When the polymerization was carried out at 0°C for a prolonged time, no monomer-isomerization polymerization took place. Since polymerization of 2APhOH takes place easily at 0°C, this is attributed to the fact that the isomerization of APhE to 2APhOH hardly occurred. However, above 40°C the isomerization of APhE to 2APhOH was observed with a fairly high rate and monomer-isomerization polymerization was also induced.

Effect of solvent

The monomer-isomerization polymerization of APhE with $BF_3 \cdot OEt_2$ catalyst was examined in various solvents, and the results are shown in *Table 4*. The polymer yields in solution polymerization were lower than that in bulk. When aromatic solvents were used, new products in addition to APhE and 2APhOH were observed in the unreacted monomers recovered after polymerization. These products are likely to be formed by the alkylation of the aromatic ring in the solvents used.

Effect of initiators

Table 5 shows the results of the polymerization of APhE with various initiators. $SnCl_4$ and $TiCl_4$ catalysts gave viscous materials, and the catalytic activities were found to be lower than that of $BF_3 \cdot OEt_2$ catalyst.

With H_2SO_4 catalyst, a viscous polymer was obtained, and MDBF along with 2APhOH was also observed in the unreacted monomers after the polymerization. Namely, APhE was first isomerized to 2APhOH prior to the polymerization, and then a part of the 2APhOH polymerizes and the other part takes part in intramolecular cyclization to form MDBF. With radical initiators, APhE neither gave a polymer nor underwent monomer isomerization.

Table 4 Monomer-isomerization polymerization of APhE with $BF_3 \cdot OEt_2$ catalyst in various solvents at 60°C[a]

			Composition of monomers after polymerization (%)[b]		
Solvent	Time (h)	Yield (%)	APhE	2APhOH	Others
Toluene	3.0	6.3	54.0	28.5	17.5
Anisole	3.0	Trace	50.4	38.0	11.6
CH_2Cl_2	3.0	23.6	56.8	39.4	3.9
$C_2H_5NO_2$	1.0	Trace	91.8	8.8	0.2

[a] Polymerization conditions: $[BF_3 \cdot OEt_2] = 0.12$ mol l^{-1}, APhE = 4 ml, solvent = 4 ml
[b] Determined by gas chromatography

Table 5 Polymerization of APhE with various initiators[a]

				Composition of monomers after polymerization (%)[b]		
Initiator (mol l^{-1})	Temp. (°C)	Time (h)	Yield (%)	APhE	2APhOH	Others
$SnCl_4$ (0.04)	60	4.0	5.3	90.7	6.6	2.7[d]
$TiCl_4$ (0.43)	60	4.0	9.9	–	–	–
$ZnCl_2$ (0.34)	60	1.0	0.0	100.0	0.0	0.0
H_2SO_4 (0.93)	60	1.0	29.3	45.0	8.4	46.5[e]
AIBN[c] (0.008)	80	4.0	0.0	100.0	0.0	0.0
BPO[c] (0.005)	80	24.0	1.2	–	–	–

[a] Polymerized in bulk: monomer = 4.0 ml
[b] Determined by gas chromatography
[c] Polymerized in benzene
[d] Phenol was detected
[e] MDBF was detected

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