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Polymerization and Isomerization of Allylbenzene and Propenylbenzene*1

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In order to clarify the relationship between the isomerization and polymerization of α- and β-olefins by various types of catalysts, the isomerizations of allylbenzene and propenylbenzene during their polymerizations were studied. In the presence of cationic catalysts ($AlBr_3$, $BF_3O(C_2H_5)_2$, *etc*), neither the polymerization nor the isomerization of allylbenzene was observed, but propenylbenzene was found to be polymerized without the isomerization of the monomer to give a solid polymer which consisted substantially of a 1,2-structure, plus a minor unit of an isomerized structure. In the cases of the Natta catalysts [$TiCl_3$-$Al(C_2H_5)_3$, $Al/Ti \geq 2$], allylbenzene could easily be polymerized to a high-molecular-weight polymer with a 1,2-structure. During this polymerization, both positional and geometrical isomerizations of the unreacted monomer were observed, indicating that the propenylbenzene obtained from the isomerization did not participate in the polymerization of allylbenzene. It was also found that the polymerization and the positional isomerization of propenylbenzene by these catalysts did not occur.

In previous papers[1-3] it has been shown that some β-olefins, such as butene-2, pentene-2, and hexene-2, can be homopolymerized by the Natta catalyst to give high-molecular-weight polymers with a recurring unit of the corresponding α-olefins. As to the mechanism of the polymerization, it has been concluded that β-olefins were isomerized first to the corresponding α-olefins, which have less steric hindrance, and were then polymerized as α-olefins through a coordinated anionic mechanism. In such cases, it is characteristic that the isomerization of the unreacted monomer is observed, but that of a growing anion to give more stable anion species does not occur during the polymerization.

On the other hand, Kennedy and his co-workers[4] discovered and developed the isomerization polymerization of some branched α-olefins by cationic catalysts at lower temperatures. In this case, the isomerization of a growing cation, which is accompanied by a hydride shift to give a more stable carbonium ion, must occur during the polymerization, while no isomerization of the unreacted monomer is observed.

In order to clarify the relationship between the polymerization and isomerization of α-and β-olefins by various types of catalysts, we attempted to investigate the isomerizations of allylbenzene and propenylbenzene during their polymerizations in the present study. The polymerization of these

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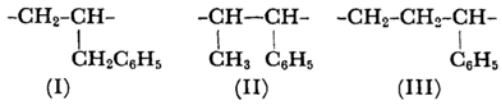
1) A. Shimizu, T. Otsu and M. Imoto, *J. Polymer Sci.*, **3B**, 449 (1965).

2) A. Shimizu, T. Otsu and M. Imoto, *ibid.*, **3B**, 1031 (1965).

3) T. Otsu, A. Shimizu and M. Imoto, *ibid.*, **4A**, 1579 (1966).

4) J. P. Kennedy, *Fortschr. Hochpolym. Forsch.*, **3**, 508 (1964).

monomer is expected to give polymers with the following three types of recurring units:

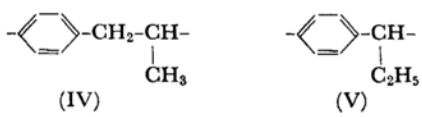


(I) (II) (III)

In 1935, Staudinger and Dreher[5] reported that, in the presence of boron trifluoride as a catalyst, propenylbenzene was polymerized to give a polymer with the structure III, but not the structure II. However, this experiment was reexamined in 1944 by Müller *et al.*[6] and the presence of a CH_3-C bond in the resulting polymer was established, negating Staudinger's findings.

Recently Murahashi, Nozakura, and their coworkers[7] found that propenylbenzene could be polymerized by a cationic mechanism to give the polymer with the structures II and III, and that the isomerization polymerization to the structure III was preferred by less acidic catalysts such as $BF_3O(C_2H_5)_2$, while the polymerization to the structure II was predominant with the BF_3 catalyst. They also reported that allylbenzene was polymerized by the BF_3 catalyst in methylene chloride at $-78°C$ to give a polymer which was somewhat different from the conventional polyallylbenzene I and polypropenylbenzene II. Similar results were independently reported by Kennedy.[8]

More recently, Murahashi, Nozakura, and their coworkers[9] pointed out that the polymer obtained by the cationic polymerization of allylbenzene contained the following two types of recurring units, IV and V:



(IV) (V)

Experimental

Materials. The allylbenzene was prepared according to the procedure of Hershberg[10] by the reaction of allyl bromide with phenylmagnesium bromide; bp 60—61°C/27 mmHg, n_D^{20} 1.5144 (lit.[11]; n_D^{20} 1.5135 for the cis-isomer). From the gas chromatographic analysis (4-m tricresyl phosphate column), it was found that this compound was 97.5% pure.

The propenylbenzene was prepared by the procedure described by Overberger and Saunder[12] through the thermal decomposition of ethylphenylcarbinol; bp 71—74°C/27 mmHg, n_D^{20} 1.5505 (lit.[13]: n_D^{25} 1.5480 for the trans-isomer). This propenylbenzene was 99.1% pure and was found by gas chromatography to consist of 86.9% trans-isomers and 13.1% cis-isomers.

The boron trifluoride - diethyl etherate used as a catalyst was distilled under reduced pressure; bp 126—127°C. The metal halides, titanium tetrabutoxide, and aluminum alkyls were commercially obtained, and were used without further purification.

The *n*-heptane was purified by washing it thoroughly with concentrated sulfuric acid, followed by washing with distilled water until it was neutral, whereupon it was distilled over metallic sodium.

Polymerization Procedure. Cationic polymerizations by the $AlBr_3$ or $BF_3O(C_2H_5)_2$ catalyst were carried out in a sealed glass tube in methylene chloride or in toluene. The charging of the required amounts of reagents into the tube was performed in a dry nitrogen atmosphere.

Coordinated anionic polymerizations were also carried out by charging as follows: to a hard glass tube containing a given amount of titanium trichloride or vanadium trichloride in *n*-heptane, there was added, through a rubber cap using a hypodermic syringe, the required amount of a *n*-heptane solution of aluminum alkyl in a dry nitrogen atmosphere. The catalyst mixture thus obtained was aged for an hour at room temperature, after which the monomer was charged into this tube and the tube was sealed off.

After polymerization in a thermostat for a given period, the tube was opened and the unreacted monomer was recovered and its isomer distribution determined by gas chromatography. The contents of the tube were then poured into a large amount of a hydrochloric acid - isopropyl alcohol mixed solution in order to precipitate the polymer formed. The conversion was calculated from the weight of the dry polymer obtained.

Characterization of the Polymer. The infrared spectra of the resulting polymers were obtained on KBr disks or in thin liquid films. The ratio in the optical density of the band at 2960 to that at 2925 cm^{-1}, $D(CH_3/CH_2)$, was used as a measure of the methyl-to-methylene ratio, *i. e.*, the ratio of the structural units of II to I, or of II to III, in the polymer.[7]

The obtaining solid polymer was extracted with hot toluene, and its crystallinity was expressed by the amount of the insoluble fraction in hot toluene.

Results

Cationic Polymerization with $AlBr_3$ or $BF_3O(C_2H_5)_2$ Catalyst. The results obtained in the polymerization of allylbenzene and propenylbenzene by the $AlBr_3$ or $BF_3O(C_2H_5)_2$ catalyst are shown in Table 1, in which the isomer distribution of the recovered monomer after polymerization and the ratio of the optical densities, $D(CH_3/CH_2)$, of the resulting polymers are also indicated.

5) H. Staudinger and E. Dreher, *Ann.*, **517**, 73 (1935).
6) A. Müller, L. Toldy and Z. Racz, *Ber.*, **77**, 77 (1944).
7) S. Murahashi, S. Nozakura, K. Tsuboshima and Y. Kotake, This Bulletin, **37**, 706 (1964).
8) J. P. Kennedy, *J. Polymer Sci.*, **2A**, 5171 (1964).
9) S. Murahashi, S. Nozakura, Y. Kotake and T. Okamoto, Presented at the 14th Annual Meeting of the Polymer Society of Japan, May, 1965; Preprint, p. 66.
10) E. B. Hershberg, *Helv. Chim. Acta*, **17**, 352 (1934).
11) K. C. Frisch, *J. Polymer Sci.*, **41**, 359 (1959).
12) C. G. Overberger and J. H. Saunders, *Org. Synthesis*, **28**, 31 (1949).
13) C. G. Overberger, D. Tanner and E. M. Pearce, *J. Am. Chem. Soc.*, **80**, 4566 (1958).

TABLE 1. RESULTS OF CATIONIC POLYMERIZATION OF ALLYLBENZENE (AB) AND PROPENYLBENZENE (PB) WITH $AlBr_3$, OR $BF_3O(C_2H_5)_2$ CATALYST

Monomer	Temp. °C	Time hr	Conversion %	$D(CH_3/CH_2)$	Isomer distribution of monomer recovered after polymerization[a]		
					AB	*cis*-PB	*trans*-PB
$AlBr_3$ catalyst: $[AlBr_3]=7.7$ mmol/l in methylene chloride[b]							
AB	−78	458	0	—	100.0	0.0	0.0
AB	10—15	434	0	—	100.0	0.0	0.0
PB	−78	458	0.3	—	0.0	12.4	87.6
PB	10—15	434	0.1	—	0.0	12.8	87.2
$BF_3O(C_2H_5)_2$ catalyst: $[BF_3O(C_2H_5)_2=65.9$ mmol/l in bulk[c]							
AB	10—15	240	0.1	—	100.0	0.0	0.0
PB	10—15	240	8.6[d]	1.21	0.0	11.4	88.6
PB	0	71[e]	4.9[f]	1.00	0.0	12.0	88.0

a) Determined by gas chromatography. Values are wt%.
b) [Monomer]=2.63 mol/l.
c) [Monomer]=7.62 mol/l.
d) Colorless solid polymer having mol wt of 720 (Mechrolab vapor pressure osmometer).
e) [Monomer]=1.51 mol/l in toluene.
f) Colorless solid polymer.

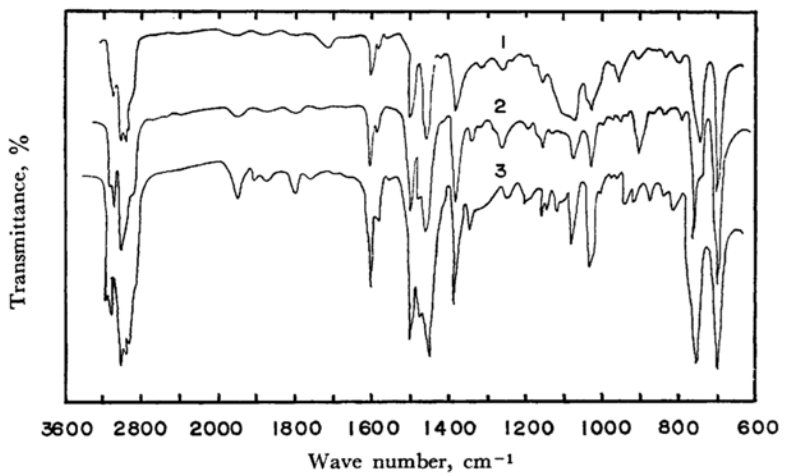


Fig. 1. Infrared spectra of polypropenylbenzene (film).
(1) Polymer obtained with $BF_3 \cdot O(C_2H_5)_2$ catalyst, (2) polymer obtained with $C_2H_5AlCl_2$-$TiCl_3$ catalyst, (3) polymer obtained with $TiCl_3$ catalyst.

As can be seen from this table, allylbenzene was neither polymerized nor isomerized by these catalysts during the reaction. However, propenylbenzene was polymerized by the $BF_3O(C_2H_5)_2$ catalyst, without the isomerization of the monomer, thus giving a colorless solid polymer which was soluble in benzene. The infrared spectrum of the obtaining polymer is shown in Fig. 1, where the $D(CH_3/CH_2)$ value was 1.00—1.21, indicating that the methylene group is present in the backbone of this polymer.

Polymerization with Catalyst Systems Containing $TiCl_3$. The results of the polymerization of allylbenzene by the catalyst systems of $TiCl_3$ alone and of $TiCl_3$-organoaluminum compounds are summarized in Table 2. By the addition of $TiCl_3$ alone, allylbenzene was found to be hardly polymerized at all and to be isomerized to propenylbenzene, giving a colorless viscous polymer. In its infrared spectrum, shown in Fig. 2, this polymer showed $D(CH_3/CH_2)$ values of 0.91—1.11, unmistakably confirming the presence of a methyl group attached to the backbone of this polymer.

In the presence of the binary systems of $TiCl_3$ and organoaluminum compounds, allylbenzene was readily polymerized to a solid polymer containing no methyl group ($D(CH_3/CH_2)=0$), as is indicated in Fig. 2. The polymer yields were found to depend upon the kind of organoaluminum compounds

TABLE 2. RESULTS OF POLYMERIZATION OF ALLYLBENZENE (AB) WITH THE CATALYST SYSTEMS CONTAINING $TiCl_3$ IN *n*-HEPTANE AT 80°C
$[TiCl_3]=50$ mmol, $[AB]=3.0$ mol/*l*

Catalyst system	Al/Ti molar ratio	Time hr	Conversion %	Toluene-insoluble polymer		$D(CH_3/CH_2)$	Isomer distribution of monomer recovered after polymerization		
				wt, %	mp, °C		AB	*cis*-PB	*trans*-PB
$TiCl_3$[a]	0	46	0.3	—	—	—	95.8	1.1	3.1
	0	158	2.4	—	—	1.11	89.0	1.3	9.7
$TiCl_3$-$Al(C_2H_5)_3$	0.5	3.5	20.1	48.3	208—211	0	98.3	0.0	1.7
	1	3.5	41.9	—	—	0	97.0	0.0	3.0
	2	3.5	49.7	52.7	211—216	0	91.2	1.6	7.2
	4	3.5	43.0	44.6	208—210	0	83.6	3.1	13.3
$TiCl_3$-$Al(C_2H_5)_2Cl$	2	7.5	12.7	—	175—181[b]	0	99.9	0.0	0.1
$TiCl_3$-$Al(C_2H_5)Cl_2$	2	24	20.4	0	50— 56	1.08	98.1	0.0	1.9
	2	68[c]	52.4	0	51— 58[d]	1.07	99.5	0.0	0.5
$TiCl_3$-$Al(i\text{-}C_4H_9)_3$	2	3.5	38.1	—	—	0	93.5	0.0	6.5

a) $[TiCl_3]=100$ mmol/*l*, $[AB]=1.0$ mol/*l*.
b) Determined for the unextracted polymer.
c) Polymerized at 10—15°C.
d) Mol wt was 1080.

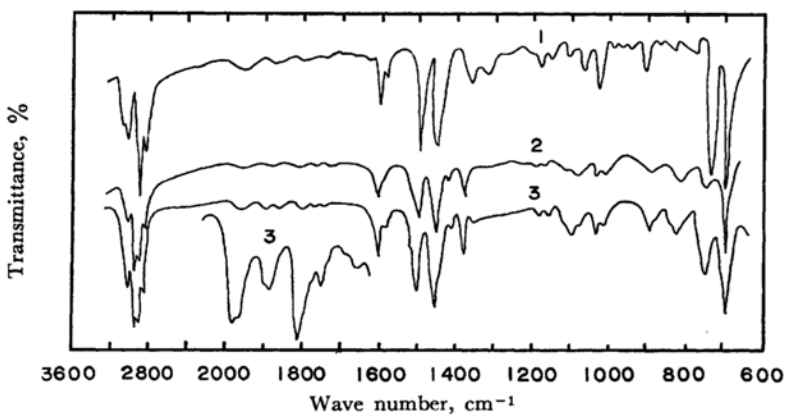


Fig. 2. Infrared spectra of polyallylbenzene (film).
(1) Polymer obtained with $(C_2H_5)_3Al$-$TiCl_3$ catalyst, (2) polymer obtained with $TiCl_3$ catalyst, (3) polymer obtained with $C_2H_5AlCl_2$-$TiCl_3$ catalyst.

and also on the Al/Ti molar ratios in the catalyst systems, indicating that the polymerization rate decreased with an increase in the cationic character of the catalyst systems (*i. e.*, from $Al(C_2H_5)_3$ to $Al(C_2H_5)Cl_2$ in the organoaluminum component, and from 2 to 0 in the Al/Ti molar ratio), while the $D(CH_3/CH_2)$ values in the resulting polymers increased from zero to 1.08 (see Fig. 2). In the case of the $TiCl_3$-$Al(C_2H_5)_3$ catalyst, it was also found that the positional isomerization of allylbenzene to propenylbenzene after the polymerization was accelerated upon an increase in the Al/Ti molar ratio.

Table 3 shows the results of the polymerization of propenylbenzene by these catalyst systems. It can be seen in this table that the polymerization of propenylbenzene by the $TiCl_3$ catalyst was observed, giving a yellowish oily product but without any positional isomerization to allylbenzene. This product was confirmed to be a dimer of propenylbenzene by a molecular-weight determination; it was showed an absorption band characteristic of the methylene group, *i. e.*, $D(CH_3/CH_2)=1.10$—1.33 (Fig. 1).

TABLE 3. RESULTS OF POLYMERIZATION OF PROPENYLBENZENE (PB) WITH THE CATALYST SYSTEMS CONTAINING $TiCl_3$ IN *n*-HEPTANE AT 80°C
$[TiCl_3]=50$ mmol/*l*, $[PB]=3.0$ mol/*l*

Catalyst system	Al/Ti molar ratio	Time hr	Conversion %	$D(CH_3/CH_2)$	Isomer distribution of monomer recovered after polymerization, wt%		
					AB	*cis*-PB	*trans*-PB
$TiCl_3$[a]	0	46	44.9[b]	1.10	0.0	4.3	95.7
	0	158	74.9	1.33	0.0	0.0	100.0
$TiCl_3$-$Al(C_2H_5)_3$	0.5	48	0	—	0.0	8.5	91.5
	2	48	0	—	0.0	4.1	95.9
$TiCl_3$-$Al(C_2H_5)_2Cl$	2	48	0	—	0.0	11.6	88.4
$TiCl_3$-$Al(C_2H_5)Cl_2$	2	48	21.4[c]	∞	0.0	12.5	87.5
$TiCl_3$-$Al(i\text{-}C_4H_9)_3$	2	48	0	—	0.0	7.5	92.5

a) $[TiCl_3]=100$ mmol/*l*, $[PB]=1.0$ mol/*l*.
b) Molecular weight of this polymer was 270.
c) Molecular weight of this polymer was 840.

TABLE 4. RESULTS OF POLYMERIZATION OF ALLYLBENZENE (AB) AND PROPENYLBENZENE (PB) WITH THE CATALYST SYSTEMS CONTAINING VCl_3 IN *n*-HEPTANE AT 80°C
$[VCl_3]=50$ mmol/*l*, [Monomer]$=3.0$ mol/*l*

Catalyst system	Al/Ti molar ratio	Monomer	Time hr	Conversion %	$D(CH_3/CH_2)$	Isomer distribution of monomer recovered after polymerization, wt%		
						AB	*cis*-PB	*trans*-PB
VCl_3	0	AB	158[a]	0	—	100.0	0.0	0.0
	0	PB	46[b]	0	—	0.0	12.7	87.3
VCl_3-$Al(C_2H_5)_3$	2	AB	0.5	20.1[c]	0	100.0	0.0	0.0
	2	PB	48	0	—	0.0	12.1	87.9
VCl_3-$Al(i\text{-}C_4H_9)_3$	2	AB	1.0	13.5	0	100.0	0.0	0.0
	2	PB	48	0	—	0.0	12.0	88.0

a) $[VCl_3]=93.1$ mmol/*l*, $[AB]=1.24$ mol/*l*.
b) $[VCl_3]=89.7$ mmol/*l*, $[PB]=1.50$ mol/*l*.
c) This polymer contained 36.4% of insoluble fraction (mp 212—215°C) in hot toluene.

TABLE 5. RESULTS OF POLYMERIZATION OF ALLYLBENZENE (AB) AND PROPENYLBENZENE (PB) WITH THE CATALYST SYSTEMS CONTAINING $Ti(OC_4H_9)_4$ IN *n*-HEPTANE AT 80°C
$[Ti(OC_4H_9)_4]=50$ mmol/*l*, Al/Ti$=3.0$, [Monomer]$=3.0$ mol/*l*

Catalyst system	Monomer	Time hr	Conversion %	$D(CH_3/CH_2)$	Isomer distribution of monomer recovered after polymerization, wt%		
					AB	*cis*-PB	*trans*-PB
$Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$	AB	24	5.9	0	65.9	6.6	27.5
	PB	48	1.1	0.94	0.0	3.6	96.4
$Ti(OC_4H_9)_4$-$Al(C_2H_5)_2Cl$	AB	24	0.6	0	99.8	0.0	0.2
	PB	48	0.7	—	0.0	12.9	88.1
$Ti(OC_4H_9)_4$-$Al(C_2H_5)Cl_2$	AB	24	0.7	—	100.0	0.0	0.0
	PB	48	0.1	—	0.0	12.9	88.1

In these binary catalyst systems, the geometrical cis-trans isomerization of propenylbenzene was observed, accelerating with a nincrease in the Al/Ti molar ratio, but no positional isomerization occurred. A solid polymer which has no absorption band for the methylene group was obtained when only the $C_2H_5AlCl_2$-$TiCl_3$ catalyst was used. These isomerizations and polymerizations were dependent on the cationic character of the catalyst system, as are those of allylbenzene.

Polymerization with Catalyst Systems Containing VCl_3. Table 4 shows the results of the polymerization of allylbenzene and propenylbenzene by the binary catalyst systems of VCl_3. As can be seen from this table, no isomerization occurred in any case. Allylbenzene was polymerized by VCl_3-trialkylaluminum catalysts to give a solid polymer whose infrared spectrum indicated no absorption band for the methyl group in the polymer.

Polymerization with Catalyst Systems Containing $Ti(OC_4H_9)_4$. The results of the polymerization of allylbenzene and propenylbenzene by the binary catalyst systems of $Ti(OC_4H_9)_4$ are summarized in Table 5, in which the isomerization of the monomer during the reaction and the $D(CH_3/CH_2)$ values of the resulting polymers are also shown. In these cases, both the isomerization and the polymerization were observed to be dependent upon the cationic character of the catalyst systems used. A viscous polymer from allylbenzene and an oily product from propenylbenzene were obtained by the use of the $Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$ catalyst.

Discussion

As can be seen from Table 1, neither the polymerization nor the isomerization of allylbenzene was observed in the presence of the $AlBr_3$ catalyst or the $BF_3O(C_2H_5)_2$ catalyst. However, propenylbenzene was found to be polymerized by the latter catalyst to give a solid polymer whose molecular weight was 720. Although the infrared spectrum of the produced polymers showed intense absorption bands due to the methyl group at 2960, 2878, and 1380 cm^{-1}, weak absorption bands due to the methylene group were also observed at 2925 and 755 cm^{-1}, indicating that this polymer consisted of the structure II, with a minor unit of the I or III structure. In view of the results shown in Table 1 (no isomerization of the monomer takes place during the reaction), the participation of the allylbenzene isomerized from propenylbenzene to give the structual unit I was not considered in this polymerization. Although the isomerization of a growing cation of propenylbenzene leading to the structual unit III was considered, it might be impossible to find a driving force to cause this type of isomerization to proceed, as has been pointed out by Kennedy[8] and Murahashi *et al.*[14] No other evidence for the presence of such isomerized structures was obtained, and the possible mechanism for its production is also uncertain at the present time. Figure 1 shows that the structural unit IV in this polymer was not present.

No isomerizations of the monomer were observed in the polymerizations of allylbenzene and propenylbenzene by catalyst systems containing VCl_3. On the other hand, both isomerizations from allylbenzene to propenylbenzene and from *cis*-propenylbenzene to *trans*-propenylbenzene occurred in the presence of the catalyst systems including $TiCl_3$; these isomerizations were found to be accelerated upon increase in the Al/Ti molar ratio (*i. e.*, an increase in the anionic nature of the catalyst system). These results were in agreement with those observed in the isomerization of butene-2 by the same catalyst systems.[3]

However, the positional isomerization from propenylbenzene to allylbenzene did not occur in the polymerization of propenylbenzene by any of the catalyst systems used. This fact leads to the conclusion that the high-molecular-weight polyallylbenzene (I) from propenylbenzene is not obtained in the presence of the Natta catalyst, just as in the polymerization of butene-2 with isomerization to butene-1.[3] The experimental results coincided with this conclusion.

From Tables 1—4, it is clear that the polymerization activities of allylbenzene toward the Natta catalysts decrease greatly with a decrease in the Al/Ti molar ratio and with an increase in the substitution of the chloride component in organoaluminum compounds of the catalyst systems (*i. e.* an increase in the cationic nature). On the other hand, the polymerization of propenylbenzene was observed when the cationic nature of the catalyst systems used increased, and the resulting polymers were low in molecular weight.

As is shown in Fig. 2, the infrared spectra of the polyallylbenzene obtained through a coordinated anionic mechanism by the Natta catalysts showed a strong absorption band for the methylene group at 2925 cm^{-1}, but none for the methyl group. This result indicates that allylbenzene is polymerized by an ordinary anionic 1,2-addition mechanism to give a high-molecular-weight polymer with the non-isomerized structure (I). In this case, it is clear that propenylbenzene does not participate in the polymerization of allylbenzene, just as in the production of polybutene-1 from butene-2.[3]

Figure 2 shows, however, that the infrared spectra of the polymers obtained from allylbenzene by the $TiCl_3$-$Al(C_2H_5)Cl_2$ or $TiCl_3$ catalyst, which might induce cationic polymerization, showed the absorption bands characteristic of the methyl group

14) S. Murahashi, S. Nozakura, K. Tsuboshima and Y. Kotake, This Bulletin, **38**, 157 (1965).

of 2960, 2878, and 1380 cm^{-1}, that of the methylene group at 2925 cm^{-1}, and those of substituted benzene at 1700—2000 and 830 cm^{-1}. Accordingly, it can be concluded that the polymer is obtained not only by an ordinary 1,2-addition mechanism of allylbenzene and of the propenylbenzene which is isomerized from it, but also by the Friedel-Crafts-type addition mechanism[9] of a growing cation to the benzene nuclei of the monomer or of the polymer, leading to the recurring units, IV and V.

In the presence of the $TiCl_3$-$Al(C_2H_5)Cl_2$ catalyst, it was found that propenylbenzene is readily polymerized, giving a heptamer whose infrared spectrum showed a absorption band for the methyl group, but none for the methylene group or for substituted benzene, suggesting that this catalyst induces the cationic polymerization by an ordinary 1,2-addition mechanism, thus giving a polymer with the structure II.