Cationic Polymerization of Phenylbutadienes. 6. Cationic Polymerization of Methylphenyl-1,3-butadienes

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ABSTRACT: The reactivities of methylphenyl-1,3-butadienes in cationic polymerization and the microstructures of the resulting polymers were investigated. The cationic homopolymerizations of methylphenyl-1,3-butadienes were carried out using various catalysts in methylene chloride and toluene. 1-Phenyl-1,3-pentadiene was shown to be the most reactive monomer in the homopolymerizations of phenylbutadienes. The polymerizations of 1-phenyl-1,3-pentadiene and 1-methyl-, 3-methyl-, and 4-methyl-2-phenyl-1,3-butadienes proceeded with 1,4-propagation. 3-Methyl-1-phenyl-1,3-butadiene gave polymers predominantly of 1,4-type whereas polymers of 1-methyl- and 2-methyl-1-phenyl-1,3-butadienes had mainly the microstructure of 3,4-type. The olefinic double bonds in the polymers were a little consumed during polymerization. The relative reactivities of methylphenyl-1,3-butadienes toward a styryl cation decreased in the following order: 3-methyl-1-phenyl-1,3-butadiene > 1-methyl-1-phenyl-1,3-butadiene > 4-methyl-2-phenyl-1,3-butadiene > 2-methyl-1-phenyl-1,3-butadiene > 1-phenyl-1,3-pentadiene > 1-methyl-2-phenyl-1,3-butadiene > 3-methyl-2-phenyl-1,3-butadiene. From the findings that 1-phenyl-1,3-pentadiene was 0.69 times as reactive as 1-phenyl-1,3-butadiene whereas the reactivity of 1-methyl-2-phenyl-1,3-butadiene was 1.6 times greater than that of 2-phenyl-1,3-butadiene, the attack of propagating styryl cation on 1-phenyl-1,3-butadienes may be considered to take place through a similar transition state to that of styrene. On the other hand, the attack of the styryl end on 2-phenyl-1,3-butadienes involved a more restricted intermediate than that of 1-phenyl-1,3-butadiene in order to diminish the steric hindrance of the methyl group in the transition state. The effects of solvent and temperature on the copolymerization of 2-chloroethyl vinyl ether with 3-methyl-1-phenyl-1,3-butadiene were examined. The relative reactivity of 3-methyl-1-phenyl-1,3-butadiene increased in methylene chloride relative to toluene and using $SnCl_4$·TCA rather than using BF_3OEt_2. This fact can be explained in terms of selective solvation of the propagating end by a more polar monomer in a nonpolar solvent. Temperature effect was little except for the BF_3OEt_2–toluene system. These results were interpreted by Fontana–Kidder's mechanism on propagation.

In preceding papers, the authors have investigated the cationic polymerization of phenyl-1,3-butadienes[2–5] and the initiation reaction of phenyl-1,3-butadienes with triphenylmethyl stannic pentachloride.[6] It has been described that the initiation rate constant decreased according to the following order: 1-phenyl-1,3-butadiene > 2-phenyl-1,3-butadiene > 1,1-diphenyl-1,3-butadiene > 1,2-diphenyl-1,3-butadiene > 2,3-diphenyl-1,3-butadiene ≫ 1,4-diphenyl-1,3-butadiene. This order has been explained in terms of the stability of allylic cations formed by the attack of trityl cation except for 1,4-diphenyl-1,3-butadiene.

We next studied the cationic polymerizability of methylphenyl-1,3-butadienes and the microstructures of the resulting polymers in the comparison with that of monophenyl-1,3-butadienes. It is well-known that the reactivity of monomers and the microstructure of the resulting polymers vary with an introduction of methyl group as a result of the electronic and the steric effects of methyl group. In general, the radical homopolymerizations of α,β-disubstituted olefins occur with difficulty since steric hindrance between β-substituents of the propagating end and the incoming monomer exists in the transition state for radical propagation.[7] However, the polymerization of α,β-disubstituted olefins readily proceeds by a cationic mechanism.[8–13] On the other hand, the cationic polymerizability of vinyl monomers is remarkably increased by an introduction of a methyl group onto the α-carbon of the monomers as are the case of isobutene and α-methylstyrene.[14] The change of reactivity may be the result of an increase of π-electron density on the β-carbon and the stability of the resulting carbonium ion by electron donation of the methyl group.

In the present paper, the effect of a methyl group on the cationic polymerization of methylphenyl-1,3-butadienes will be discussed in terms of the electronic and the steric effects in relation to the position in which it was introduced. A transition state for propagation of the cationic polymerization of phenyl-1,3-butadienes will also be discussed in detail on the basis of the effect of the methyl substituent.

Experimental Section

Materials. *trans*-1-Phenyl-1,3-butadiene (1-PB) and 2-phenyl-1,3-butadiene (2-PB) were synthesized as described before.[2,3] 1-Methyl-1-phenyl-1,3-butadiene (1-Me-1-PB) and 4-methyl-2-phenyl-1,3-butadiene (4-Me-2-PB) were synthesized from 4-phenylpentene-2-one[15] formed by acetylation of α-methylstyrene, followed by the reduction with sodium borohydride and the subsequent dehydration with potassium bisulfate, bp 56–58 °C (2 mm). As this crude monomer was a mixture of 1-Me-1-PB (40%) and 4-Me-2-PB (60%) according to gas chromatography, they were separated from the mixture by fractional distillation through a spinning band column. 2-Methyl-1-phenyl-1,3-butadiene (2-Me-1-PB)[16] was prepared from the corresponding diazonium salt and isoprene through Meerwein arylation and subsequent dehydrochlorination, bp 89 °C (12 mm). 3-Methyl-1-phenyl-1,3-butadiene (3-Me-1-PB),[17] 1-phenyl-1,3-pentadiene (1-PPD),[17] 1-methyl-2-phenyl-1,3-butadiene (1-Me-2-PB),[18] and 3-phenylisoprene (3-Me-2-PB)[19] were prepared by the Grignard reagents with benzalacetone, cinnamic aldehyde, propiophenone, and acetone, followed by hydration and subsequent dehydration, respectively. The boiling points of these monomers were as follows: 3-Me-1-PB, 83–85 °C (7 mm); 1-PPD, 101 °C (12 mm); 1-Me-2-PB, 73–76 °C (13 mm); 3-Me-2-PB, 80–85 °C (23 mm). ^{1}H NMR spectrum showed that 1-PPD was composed of the isomeric mixture (cis,trans/trans,trans = 45/55). According to gas chromatographic data, the purities of these monomers except for 1-Me-1-PB and 4-Me-2-PB were more than 98%, and those of 1-Me-1-PB and 4-Me-2-PB were 80 and 89%, respectively, because isomer was involved.

Styrene, α-methylstyrene, 2-chloroethyl vinyl ether (CEVE), and the solvents were commercially obtained and purified by the usual methods. $SnCl_4$ and BF_3OEt_2 were distilled into small glass ampules. Acetyl perchlorate ($AcClO_4$) was synthesized by the reaction of silver perchlorate with acetyl chloride in methylene chloride.[20] WCl_6 and trichloroacetic acid (TCA) of the best grade commercially available were used without further purification.

Procedures. Polymerization was carried out under a dry nitrogen atmosphere in an Erlenmeyer flask equipped with a three-way stopcock. Concentration of the water in the system was ca. 5×10^{-4} M.

Table I
Polymerization of Phenylbutadienes Using Various Catalysts[a]

	Conversion, %					
	Methylene chloride				Toluene	
	$SnCl_4 TCA$	$AcClO_4$	WCl_6	BF_3OEt_2	$SnCl_4 TCA$	WCl_6
1-PB	55.6	38.4	78.9	11.9 (38.1)[b]	37.8	71.1
2-Me-1-PB	97.5		99.0		85.5	99.0
3-Me-1-PB	71.0	86.8	96.7	5.8	34.9	58.8
1-PPD	97.9	100	100	(82.3)	97.5	100
2-PB	95.7	95.5	93.6	1.1 (31.6)	8.7	73.0
1-Me-2-PB	68.4		56.8	(0.9)	0.8	13.0
3-Me-2-PB	55.1	38.1	23.0	(6.6)	16.4	17.0

	No. average molecular weight					
	Methylene chloride				Toluene	
	$SnCl_4 TCA$	$AcClO_4$	WCl_6	$SnCl_4 OEt_2$	$SnCl_4 TCA$	WCl_6
1-PB	2 500	2 200	2200	(2 300)	3 800	2600
2-Me-1-PB	2 600		2900		2 500	2300
3-Me-1-PB	6 900	7 000	7900	8 100	8 200	6600
1-PPD	13 900	10 400	9600	(10 200)	11 000	9800
2-PB	Gel	2 700	7300	(3 200)	3 200	2900
1-Me-2-PB	5 400		4700			4000
3-Me-2-PB	2 700	2 500	2200	(2 500)	2 700	2600

[a] Polymerization conditions: $[M]_0 = 5 \times 10^{-3}$ M; temperature = — 78°C; time = 20 min. [b] Data for the polymerization carried out at 0°C.

The rate of consumption of a monomer was determined by measuring the concentration of residual monomer by gas chromatography. Monomer reactivity ratios were calculated by Ezrielev's method.[21] The equilibrium constant of π-complex between iodine and monomer was determined by UV spectra in isooctane at 30 °C. The number-average molecular weight of polymers was measured in benzene solution by using a Hitachi 115 osmometer. ^1H NMR spectrum was measured in carbon tetrachloride solution at 60 MHz on a Hitachi R-20B spectrometer.

Results and Discussion

Cationic Homopolymerization of Methylphenyl-1,3-butadienes. The results of the cationic homopolymerization of methyl-substituted phenyl-1,3-butadienes, using the various catalysts in methylene chloride and toluene, are listed in Table I. The conversions shown in Table I indicate that the homopolymerizability of phenyl-1,3-butadienes using $SnCl_4$·TCA in methylene chloride decreased according to the following order: 1-PPD ≥ 2-Me-1-PB > 2-PB > 3-Me-1-PB > 1-Me-2-PB > 1-PB > 3-Me-2-PB. Although the conversion was dependent on the kind of catalyst, 1-PPD was shown to be the most reactive monomer among these phenyl-1,3-butadienes. It is strange that the conversion of 1-PPD possessing a methyl group on the terminal carbon in the butadienyl framework is higher than that of 1-PB since the rate of the cationic polymerization of β-methylstyrene is much less than that of styrene. The reason for this finding will be discussed in a later section.

The order of the activity of catalysts in the polymerization of methyl-1-phenyl-1,3-butadiene series except for 1-PB in methylene chloride decreased as follows:

$$WCl_6 > AcClO_4 > SnCl_4{\cdot}TCA \gg BF_3OEt_2$$

The order in the case of 2-PB derivatives was as follows:

$$SnCl_4{\cdot}TCA > AcClO_4 > WCl_6 \gg BF_3OEt_2$$

In general, the rate of initiation of 1-PB derivatives was much larger than that of 2-PB derivatives.[6] The reason why the order of the activity of catalyst in the polymerization of methyl-1-phenyl-1,3-butadiene series was different from that of methyl-2-phenyl-1,3-butadiene series may be ascribed to the initiation reaction.

In a nonpolar solvent such as toluene, the polymerization rate depends on the ionic character of propagating end in addition to the initiation. The conversion of WCl_6 in comparison with that for $SnCl_4$·TCA in toluene suggests that an ion pair of the propagating end formed from WCl_6 might be looser than that formed from $SnCl_4$·TCA. The same result that WCl_6 was more active than $SnCl_4$·TCA in nonpolar solvent was also observed in the cationic polymerization of styrene.[22]

The polymers obtained by using these catalysts were benzene-soluble polymers except that a partial gelled poly(2-PB) was obtained by $SnCl_4$·TCA in methylene chloride. It has already been shown that a monomer chain transfer reaction frequently occurred during the cationic polymerization of phenyl-1,3-butadienes.[2,3] The finding that the molecular weights of poly(2-Me-1-PB) and poly(3-Me-2-PB) were smaller than those of poly(1-PPD) and poly(3-Me-1-PB) suggests that the monomer chain transfer which produces an indene derivative by cyclization of the growing end is a dominant reaction governing the molecular weight of polymers. The molecular weight of the polymers obtained by using these catalysts in toluene was the same as that in methylene chloride. Therefore, a chain transfer reaction to toluene, such as observed in the polymerization of styrene using $SnCl_4$,[23] did not occur in the cases of phenyl-1,3-butadienes because of the greater stabilization of the propagating end compared to that of the styryl cation.

Microstructure of Poly(methylphenyl-1,3-butadiene)s. The microstructures of the polymers obtained in Table I were determined by NMR analysis. Figure 1 shows the representative NMR spectra of the polymers, and the results of the microstructure of the polymers are listed in Table II. As reported in the preceding paper,[2] the polymerization of 1-PB proceeded predominantly with 3,4-propagation regardless of the kind of catalyst and solvent. However, 1-PPD, that is, a monomer introduced with a methyl group onto the 4-position carbon of 1-PB, was shown to propagate completely in the fashion of 1,4-type. Although the charge distribution of the propagating end of 1-PPD is considered to be similar to that of 1-PB, a steric hindrance between the propagating end of 1-PPD and the methyl group of the approaching monomer might force 1-PPD to propagate in a 1,4-fashion.

Table II
Microstructure of Poly(phenylbutadienes)[a]

	NMR proton ratio				% microstructure[b]		
		Olefinic H					
Polymer	Phenyl	1,4	3,4	Others[c]	1,4	3,4	Cyclization of 3,4
Poly(1-Me-1-PB)	5.00	0.14	0.80	6.13	7	93	13
Poly(2-Me-1-PB)	5.00	0.29	0.62	6.32	29	71	9
Poly(3-Me-1-PB)	5.00	0.82	0.32	5.86	82	18	2
Poly(1-PPD)	5.00	1.99	0.00	5.00	100	0	0
Poly(1-Me-2-PB)	5.00	1.00	0.00	6.00	100	0	0
Poly(3-Me-2-PB)	5.00	0.00	0.00	6.95	100	0	0
Poly(4-Me-2-PB)	5.00	0.98	0.00	5.94	100	0	0

[a] Polymers obtained by using $SnCl_4$·TCA in methylene chloride at −78 °C. [b] The loss of olefinic double bonds was assumed to be based on a cyclization of the 3,4-type. [c] Signals in the range of τ 7.0 to 9.5 ppm.

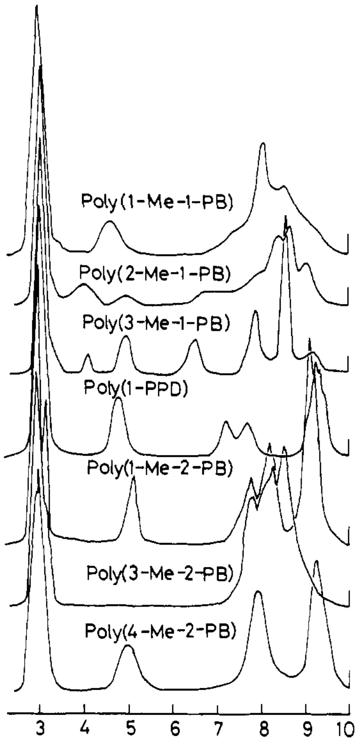


Figure 1. NMR spectra of poly(methylphenylbutadiene)s obtained using $SnCl_4$·TCA in methylene chloride at −78 °C.

Poly(3-Me-1-PB) was mostly 1,4-structure. The polymerization proceeded with 3,4-propagation to an extent of about 20% in spite of the attack by tertiary carbonium ion. The microstructure of poly(3-Me-1-PB) obtained by using the various catalysts did not change within errors of the analysis of NMR spectra. The NMR spectra of poly(1-PPD) and poly(3-Me-1-PB) show that the olefinic double bonds in these polymers were not cyclized during polymerization since the ratio of the content of olefinic double bonds to that of phenyl groups did not decrease relative to theoretical value.

On the other hand, the olefinic double bonds of poly(1-Me-1-PB) and poly(2-Me-1-PB) obtained by $SnCl_4$·TCA were shown to isomerize to saturated bonds to the extent of about 10% by the analysis of the NMR spectra of the polymers. If the loss of the olefinic double bonds is ascribed to the cyclization of 3,4-units in analogy with poly(1-PB), the polymerization of 2-Me-1-PB proceeded predominantly by 3,4-propagation. Poly(1-Me-1-PB) is also shown to consist of 3,4-polymer.

As described in the preceding report,[3] the polymerization of 2-PB proceeded with 1,4-propagation. 1-Methyl-, 3-methyl-, and 4-methyl-2-phenyl-1,3-butadienes also gave polymers of the 1,4-type regardless of the kind of catalyst and solvent. No olefinic proton signal assigned to 1,2- or 3,4-polymerization was observed in the NMR spectra of poly(methyl-2-phenyl-1,3-butadiene)s. None of the cyclized polymers were obtained from these monomers.

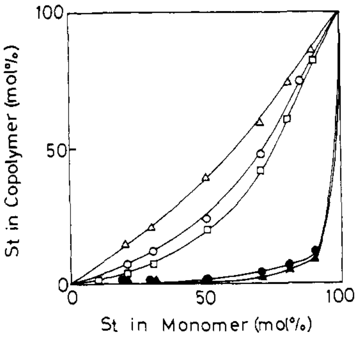


Figure 2. Composition curves for the copolymerizations of styrene (St) with 1-phenylbutadienes using $SnCl_4$·TCA in methylene chloride at −78 °C: (○) 1-PB; (●) 1-Me-1-PB; (△) 2-Me-1-PB; (▲) 3-Me-1-PB; (□) 1-PPD.

The above data suggest that the steric hindrance of substituents plays an important role in determining the microstructure of poly(methylphenyl-1,3-butadiene)s. Furthermore, the olefinic double bonds in their polymers were little cyclized on account of the steric interference of substituents in comparison with those of poly(monophenyl-1,3-butadiene)s.

Cationic Copolymerization of Styrene with Methylphenyl-1,3-butadienes. The cationic copolymerizations of styrene with methyl-substituted 1-phenyl-1,3-butadienes were carried out in order to study quantitatively the effect of a methyl group on the reactivity of these monomers in their cationic polymerizations. Figure 2 shows the copolymer composition curves; the monomer reactivity ratios calculated from these data are listed in Table III. As can be seen in Table III, the relative reactivity of 1-PB derivatives toward a styryl cation in methylene chloride decreased in the following order: 3-Me-1-PB > 1-Me-1-PB ≫ 1-PB > 2-Me-1-PB > 1-PPD > St. This higher reactivity of methyl-1-phenyl-1,3-butadienes than that of styrene can be ascribed to greater stability of the resulting cations than that of styryl cation. The products of r_1 and r_2 were always greater than unity in the copolymerization performed. The reason may be ascribed to the difference between the stability of styryl cation and that of allylic cation.

The above order can be interpreted on the basis of the electronic and the steric effects of a methyl group introduced onto 1-PB in attacking of a styryl cation. An introduction of

Table III
Monomer Reactivity Ratios in the Copolymerizations of Phenylbutadienes[a]

M_1	M_2	r_1	r_2	$1/r_1$
St[b]	1-PB[c]	0.60 ± 0.09	3.58 ± 0.34	1.67
St	1-PB[d]	0.77 ± 0.08	3.50 ± 0.39	1.30
St	1-Me-1-PB	0.04 ± 0.02	65.91 ± 3.25	33
St	2-Me-1-PB	0.62 ± 0.04	1.57 ± 0.09	1.49
St	3-Me-1-PB	0.03 ± 0.02	92.60 ± 1.65	40
St	1-PPD	0.87 ± 0.05	7.57 ± 0.18	1.15
St	1-PPD[d]	0.61 ± 0.03	4.92 ± 0.11	1.64
α-MeSt[b]	3-Me-1-PB	0.19 ± 0.11	6.02 ± 0.63	5.26
St	2-PB[e]	1.70 ± 0.04	0.98 ± 0.04	0.59
St	2-PB[d]	1.83 ± 0.03	0.90 ± 0.05	0.54
St	1-Me-2-PB	1.04 ± 0.05	1.18 ± 0.08	0.95
St	1-Me-2-PB[d]	0.63 ± 0.04	1.61 ± 0.11	1.59
St	3-Me-2-PB	1.60 ± 0.04	0.72 ± 0.04	0.63
St	4-Me-2-PB	0.11 ± 0.06	26.51 ± 1.75	9.09
1-PB	1-PPD	2.04 ± 0.09	0.60 ± 0.05	0.49
1-PB	1-PPD[d]	2.21 ± 0.07	0.53 ± 0.03	0.45
2-PB	1-Me-2-PB	1.01 ± 0.03	1.05 ± 0.04	0.99

[a] Using $SnCl_4$·TCA in methylene chloride at −78 °C. [b] St = styrene; α-MeSt = α-methylstyrene. [c] See ref 4. [d] Using $SnCl_4$·TCA in toluene at −78 °C. [e] See ref 5.

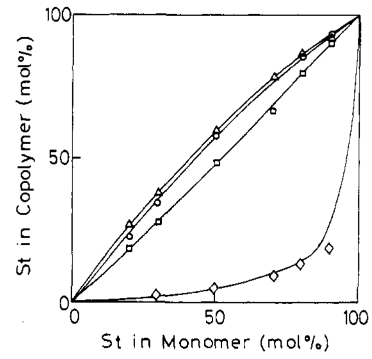


Figure 3. Composition curves for the copolymerizations of styrene (St) with 2-phenylbutadienes using $SnCl_4$·TCA in methylene chloride at −78 °C: (○) 2-PB; (□) 1-Me-2-PB; (△) 3-Me-2-PB; (◇) 4-Me-2-PB.

a methyl group on the 1-, 2-, and 3-carbons of 1-PB must enhance the stability of the resulting allylic cations more than that of allylic cation formed from 1-PB because of the hyperconjugation of methyl group.

From the values of r_1 shown in Table III, it is calculated that 3-Me-1-PB is 40 times as reactive as styrene toward a styryl cation and 5 times as reactive as α-methylstyrene toward an α-methylstyryl cation. It is also calculated that introduction of a methyl group on the 1-carbon of 1-PB increased the reactivity by a factor of about 20. Hence, 1- and 3-Me-1-PB are shown to be about 20 times as reactive as 1-PB toward these carbonium ions. The reason for this finding may be explained in terms of enhanced π-allyl conjugation of cinnamyl cation by methyl group. The reactivity of α-methylstyrene was reported to become 4–10 times greater than that of styrene in the cationic copolymerization of styrene with α-methylstyrene.[24]

A methyl group on the 2-position carbon of 1-PB was not effective for the enhancement of the reactivity of 1-PB toward a styryl cation. The methyl group linked on the central carbon of allylic cation is not so useful as a terminal methyl group for the stabilization by allylic resonance. Furthermore, neither cisoid nor transoid conformation of the allylic cation obtained from 2-Me-1-PB is planar. Therefore, the low reactivity of 2-Me-1-PB can be ascribed to low stability of the resulting cinnamylic cation.

The reactivity of 1-PPD toward a styryl cation in methylene chloride was less than that of 1-PB; the introduction of a methyl group made 1-PPD 0.69 times as reactive as 1-PB. A decrease of reactivity due to methyl group was observed in the cationic copolymerization of styrene with β-methylstyrene.[25] The value of r_2 in the copolymerization of styrene with 1-PPD suggests that the steric hindrance between the 1-PPD propagating end and incoming 1-PPD is small compared with that in the propagation of β-methylstyrene. This is consistent with the finding that 1-PPD propagates in a 1,4-manner in order to avoid the steric interference. The 3,4-unit of 1-PPD was observed to a small extent, ca. 10%, in the NMR spectrum of the copolymer of styrene with 1-PPD. Therefore, 1-PPD can proceed to a little extent with 3,4-propagation when the steric interference is not so important as the homopolymerization of 1-PPD.

The cationic copolymerizations of styrene with 2-PB derivatives were carried out in methylene chloride. Figure 3 shows the copolymer composition curves; the monomer reactivity ratios are listed in Table III. In the copolymerization of styrene with 2-PB, the relative reactivity of 2-PB has been reported to be less than that of styrene.[5] As shown in Table III, the reactivity of 1-Me-2-PB toward a styryl cation was much greater than that of 2-PB; a methyl group enhanced the reactivity 1.6 times as much as the corresponding unsubstituted one, which is in contrast to that of 1-PPD. Such result was observed in the transition state for propagation involving the steric hindrance of less importance.[9-11] These findings suggest that the attack of styryl cation on 1-Me-2-PB involves a more restricted intermediate than that of 1-PPD in order to diminish the steric hindrance of methyl group in the transition state.

The reactivity of 3-Me-2-PB was almost the same as that of 2-PB. The reason seems to be similar to that of the case of 2-Me-1-PB. The reactivity of 4-Me-2PB was nine times as reactive as that of styrene toward a styryl cation; therefore, it is calculated that the reactivity of 2-PB was increased 15-fold by introducing a methyl group onto 4-carbon. It was recognized from the values of r_1 that a terminal methyl group of allylic cation remarkably enhances its stability. Consequently, the relative reactivity of 2-PB series toward a styryl cation decreased in the following order: 4-Me-2-PB > 1-Me-2-PB > 3-Me-2-PB > 2-PB.

The solvent effect on the copolymerizations of styrene with 1-PPD and 1-Me-2-PB was investigated; the results are shown

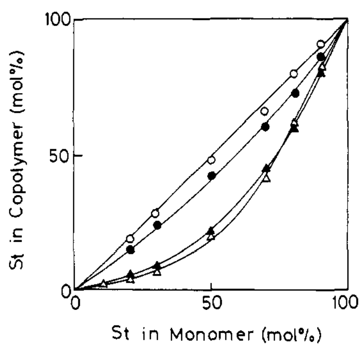
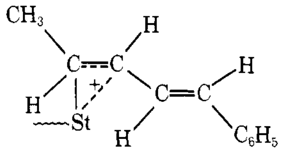


Figure 4. Solvent effect on the copolymerizations of styrene (St) with 1-PPD and 1-Me-2-PB using $SnCl_4$·TCA at −78 °C: St-1-PPD, (△) methylene chloride, (▲) toluene; St-1-Me-2-PB, (○) methylene chloride, (●) toluene.

in Figure 4 and Table III. When styrene was used as a reference comonomer, the reactivity of 1-PPD was less than that of 1-PB in methylene chloride whereas the reverse was true in toluene. This phenomenon may be explained on the basis of tightness of the ion pair of the propagating end which increased as the solvent polarity decreased. As the propagating end of styrene is suggested to be an ion pair in nonpolar solvent, styryl cation may be considered to attack through the transition state for propagation which diminishes the steric hindrance of the terminal methyl group of 1-PPD. It has been suggested by the ring-substituent effects of 1- and 2-phenylbutadienes that the styryl cation attacks the monomer through a cyclic carbonium ion intermediate. It is considered in methylene chloride that the transition state involves a weak interaction between the vacant orbital of styryl cation and the occupied orbital of 3-carbon as represented by model I. However, the interaction increased in toluene in comparison with that in methylene chloride. Therefore, unsymmetrical α,β-attack of styryl cation as shown by model II will be suggested for the transition state of propagation in toluene.



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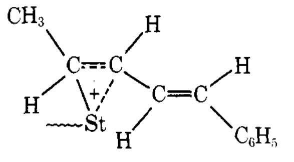

II

The relative reactivity of 1-Me-2-PB toward 2-PB was also greater in toluene than in methylene chloride. Therefore, 2-PB is suggested to proceed by way of unsymmetrical cyclic carbonium ion intermediate in attack of styryl cation in methylene chloride though the steric hindrance between the styryl cation and the terminal methyl group on 2-PB derivatives is small in comparison with that of 1-PB derivatives.

From the results obtained in this section, the effect of methyl group on reactivity of phenylbutadienes in methylene chloride may be summerized as follows.

(I) When the methyl group was introduced onto the 4-position carbon of 1-PB, the reactivity became 0.69 times greater than that of 1-PB toward a styryl cation. However, a methyl group introduced onto the 1-carbon of 2-PB enhanced the reactivity to the extent of 1.6 times as compared to 2-PB.

(II) When the methyl group was linked onto the 1- or 3-carbon of 1-PB, the reactivity became about 20 times greater than that of 1-PB. Similarly, the reactivity of 4-Me-2-PB increased by a factor of 15 in comparison with 2-PB.

(III) When the methyl group was introduced onto γ-carbon numbered from the terminal carbon attacked by a styryl cation, the reactivity was almost the same as that of the corresponding unsubstituted one.

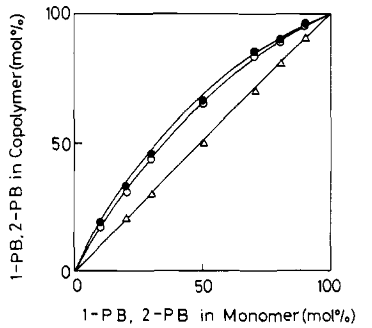

Figure 5. Effect of methyl group on the composition curves for the copolymerizations between phenylbutadienes using $SnCl_4$·TCA at −78 °C: 1-PB-1-PPD, (○) methylene chloride, (●) toluene; 2-PB-1-Me-2-PB, (△) methylene chloride.

Furthermore, these results may offer us the following information. The order of the reactivity of phenyl-1,3-butadienes to the attacking cation is consistent with that of the reactivity of the resulting allylic cations except for having large steric hindrance. It is concluded from the magnitude of the steric effect of methyl group that the attack of styryl cation on 1-PB derivatives takes place through a similar transition state to that of styrene. On the other hand, the attack of styryl cation on 2-PB derivatives involves a more restricted intermediate than that of 1-PB derivatives.

Copolymerization between Phenylbutadienes. The reactivity of phenyl-1,3-butadienes toward an allylic cation was investigated for comparison with that toward a styryl cation (Figure 5 and Table III). It is shown that 1-PPD was 0.45–0.60 times as reactive as 1-PB toward both the 1-PB propagating end and the 1-PPD one. The solvent effect on the monomer reactivity ratios was small. NMR spectra of copolymers showed that the polymerization of 1-PB proceeded predominantly with 3,4-propagation whereas that of 1-PPD proceeded with 1,4-propagation. The steric effect in the attack of the 1-PPD propagating end on a monomer was the same as that in the attack of the 1-PB propagating end.

However, the overall reaction rate of the copolymerization of 1-PB with 1-PPD increased with an increase of 1-PPD content in the feed, although the reactivity of 1-PPD is less than that of 1-PB in the copolymerization. The homopolymerizability of 1-PPD was also greater than that of 1-PB, as described in the foregoing section. In the preceding paper,[6] the authors showed that the initiation reaction of 1-PB was rapid. Therefore, the reason why the increase of 1-PPD content in the feed leads to an increase of the overall reaction rate cannot be explained in terms of increase of the concentration of propagating species. The cationic homopolymerization of 1-PPD using $SnCl_4$·TCA in methylene chloride proceeded completely with 1,4-propagation but that of 1-PB in similar conditions proceeded with 3,4-propagation to the extent of about 90%. These facts may suggest that the rate of 1,4-propagation of the 1-PPD propagating end is much faster than that of 3,4-propagation of the 1-PB propagating end.

In the electrophilic reactions of 1-PB, the products were almost exclusively 3,4-adducts.[25] However, a small amount of 1,4-polymer unit was observed in poly(1-PB) in cationic polymerization. Since it is reasonable from the electrophilic reactions of 1-PB that the concentration of the 1,4-type propagating species is very low compared to that of the 3,4-type propagating species, the fact will support that the rate constant of 1,4-propagation is much greater than that of 3,4-propagation.

In the copolymerization of 2-PB with 1-Me-2-PB, the in-

Table IV
Monomer Reactivity Ratios in the Copolymerizations of CEVE (M_1) with 3-Me-1-PB (M_2)

Catalyst	Solvent	Temp, °C	r_1	r_2	r_1r_2
BF_3OEt_2	Toluene	−78	4.20 ± 0.26	0.39 ± 0.05	1.63
BF_3OEt_2	Toluene	0	6.15 ± 0.23	0.20 ± 0.06	1.24
BF_3OEt_2	MC[a]	−78	1.03 ± 0.16	1.92 ± 0.32	1.98
BF_3OEt_2	MC	0	1.37 ± 0.10	1.71 ± 0.16	2.35
$SnCl_4$·TCA	Toluene	−78	1.48 ± 0.13	1.09 ± 0.12	1.61
$SnCl_4$·TCA	Toluene	0	1.85 ± 0.15	1.01 ± 0.14	1.88
$SnCl_4$·TCA	MC	−78	0.68 ± 0.18	3.97 ± 0.66	2.71
$SnCl_4$·TCA	MC	0	0.68 ± 0.09	4.78 ± 0.38	3.25

[a] MC = methylene chloride.

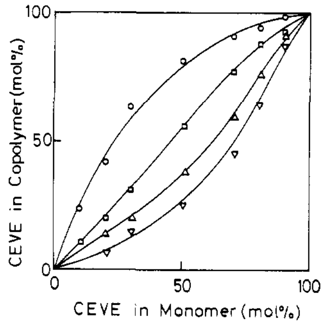

Figure 6. Composition curves for the copolymerization of CEVE with 3-Me-1-PB at −78 °C: (○) BF_3OEt_2–toluene; (□) $SnCl_4$·TCA–toluene; (△) BF_3OEt_2–methylene chloride; (▽) $SnCl_4$·TCA–methylene chloride.

troduction of a methyl group did not decrease the reactivity (Figure 5 and Table III). This result was also observed in the attack of a styryl cation on 1-Me-2-PB. Therefore, the steric effect on the methyl group in 1-Me-2-PB was smaller than that on the methyl group in 1-PPD in attacks of both styryl cation and allylic cation. This fact may be due to the difference of the modes on the transition state for propagation.

Copolymerization of 2-Chloroethyl Vinyl Ether with 3-Methyl-1-phenyl-1,3-butadiene. It is well-known that vinyl ether is a highly reactive monomer because of the electron donation of the alkoxy group in cationic polymerization.[27] In this series, phenyl-1,3-butadienes have been shown to be highly reactive monomers. The copolymerization of CEVE with 3-Me-1-PB was carried out in order to obtain further information on structure and reactivity of monomer in cationic polymerization. This is a copolymerization between structurally dissimilar monomers.

Figure 6 shows the effects of catalyst and solvent on the copolymer composition curves. Evidently, the copolymer composition was remarkably affected by the kind of solvent and catalyst. The monomer reactivity ratios are listed in Table IV. The relative reactivity of 3-Me-1-PB toward a CEVE propagating end increased according to the following order: BF_3OEt_2–toluene < $SnCl_4$·TCA–toluene < BF_3OEt_2–methylene chloride < $SnCl_4$·TCA–methylene chloride. Therefore, the reactivity of 3-Me-1-PB was greater in methylene chloride than in toluene and using $SnCl_4$·TCA than using BF_3OEt_2. This finding can be explained in terms of selective solvation to propagating end by a more polar monomer in a nonpolar solvent proposed by Overberger et al.[28]

In order to know the extent of the formation of π-complex between propagating end and phenylbutadienes, iodine was chosen as a model compound of a propagating end. The equilibrium constant K in eq 1 was determined from eq 2, i.e., Benesi–Hildebland's equation[29] under a large excess of monomer concentration.

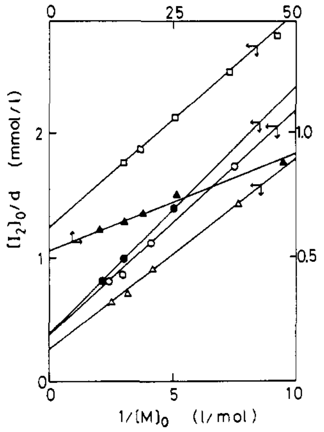

Figure 7. The relationship between $[I_2]/d$ and the reciprocal concentration of phenylbutadiene: (□) 1-PPD; (▲) 3-Me-2-PB; (●) styrene; (○) 1-PB; (△) 3-Me-1-PB.

$$I_2 + M \overset{K}{\rightleftharpoons} I_2\cdot M \qquad (1)$$

$$[I_2]_0/d_i = (\textstyle\sum K_i)/K_i\epsilon_i + 1/(K_i\epsilon_i[M]) \qquad (2)$$

where d_i, ϵ_i, K_i, $[I_2]_0$, and [M] represent absorbance, molar extinction coefficient, equilibrium constant of i-complex, initial concentration of iodine, and monomer concentration, respectively. The fact is, only a summation of equilibrium constants, ΣK_i of π-complexes of iodine with butadiene chain, phenyl ring, and so forth can be calculated from the experimental data. The data were plotted in Figure 7. It is reasonable under the conditions shown in Figure 7 that eq 2 can be applied in all phenylbutadienes used. The values of ΣK_i calculated from the intercept and slope of the straight line by using eq 2 are listed in Table V. The equilibrium constant of π-complex between iodine and 3-Me-1-PB was the same order as that of styrene but the value was much less than that of CEVE. As a carbonium ion was solvated selectively by CEVE in nonpolar solvent, therefore, the increase of CEVE concentration near the propagating end favors the increase of CEVE unit in copolymer. As BF_3OEt_2 is a weaker catalyst compared to $SnCl_4$·TCA, the separation of counterion from a propagating end by a polar monomer will be more important than the case of $SnCl_4$·TCA.

The temperature effect of this copolymerization by using these catalysts and solvents was examined. Figure 8 shows the composition curves for the copolymerization of CEVE with 3-Me-1-PB carried out at 0 °C; the monomer reactivity ratios are listed in Table V. A little temperature effect was observed except for the BF_3OEt_2–toluene system. This is very different from the copolymerization of CEVE with styrene where a large temperature effect was observed.[31]

Table V
Equilibrium Constant of π-Complex between Iodine and Monomer[a]

Monomer	λ, nm	ΣK, l/mol
1-PB	330	2.1
1-PPD	375	7.2
3-Me-1-PB	370	1.7
3-Me-2-PB	325	68.2
Styrene	302	2.0 (1.4)[b]
CEVE	275	(8.3)
IsoButyl vinyl ether	272	(41)

Activation parameters calculated from the monomer reactivity ratios are listed in Table VI. The result that vinyl ether is, in general, more reactive than styrene derivatives has been explained in terms of large entropy though the former is less reactive than the latter in terms of enthalpy.[31] The addition reaction of triphenylmethyl cation to 1-PB[6] and the copolymerization of styrene with 1-PB[4] suggest the similar interpretation as vinyl ether leads to 1-phenyl-1,3-butadienes. As can be expected from these facts, the difference of activation enthalpy of addition between two monomers was small except in the BF_3OEt_2–toluene system. The activation entropy of diene addition in toluene was more negative than that of CEVE in toluene but vice versa in methylene chloride. The entropy difference was the greatest in the BF_3OEt_2–toluene system or in the $SnCl_4$·TCA–methylene chloride system but was small under other conditions.

In general, propagation reaction in cationic polymerization may be assumed to be subdivided into the following two elementary reactions shown in eq 3, i.e., the formation of π-complex between propagating end and monomer, and the subsequent step changed from π-complex into σ-bond formation by the attack of the propagating end to a monomer.[32]

$$P_n^+ A^- + M \underset{\text{step 1}}{\overset{K}{\rightleftharpoons}} (P_nM)^+ A^- \underset{\text{step 2}}{\overset{k}{\longrightarrow}} P_{n+1}^+ A^- \qquad (3)$$

It has been assumed that a rate-determining step of the propagation reaction of styrenes is step 1 but that of vinyl ethers is step 2 because of the difference in stability of propagating end.[31,33] On the other hand, it is reasonable that step 2 is the rate-determining step in attacking of 3-Me-1-PB propagating end using $SnCl_4$·TCA onto a monomer in methylene chloride since the propagating end is highly stabilized by allylic resonance. Therefore, activation-entropy difference, −4.0 eu, between CEVE and 3-Me-1-PB toward a 3-Me-1-PB propagating end in the $SnCl_4$·TCA–methylene chloride system may be considered to be the entropy difference in step 2. This result leads to the assumption that diene is more reactive than vinyl ether in terms of entropy when the allylic cation attacks these monomers in the rate-determining step 2. However, step 1 may be considered to contribute to the rate-determining step as the polymerization conditions give a tight ion pair in the order of BF_3OEt_2–methylene chloride > $SnCl_4$·TCA–toluene > BF_3OEt_2–toluene. Activation entropy is considered to be more negative in step 1 than in step 2 since the total number of reacting molecules changed in step 1. Evidently, vinyl ether, which has a large solvating power, is favorable for the formation of π-complex in step 1. Consequently, the reactivity of 3-Me-1-PB decreased in terms of entropy under a tight ion-pair condition.

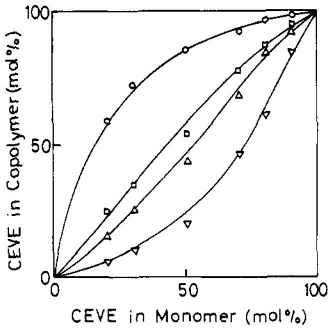

Figure 8. Composition curves for the copolymerization of CEVE with 3-Me-1-PB at 0 °C: (○) BF_3OEt_2–toluene; (□) $SnCl_4$·TCA–toluene; (△) BF_3OEt_2–methylene chloride; (▽) $SnCl_4$·TCA–methylene chloride.

The activation enthalpy of CEVE was larger than that of 3-Me-1-PB except for the $SnCl_4$·TCA–methylene chloride system. These data suggest that the activation enthalpy increased in the order of styrene < phenylbutadienes < vinyl ethers. In Fontana-Kidder's mechanism shown in eq 3, the enthalpy term will depend predominantly on the second step. Accordingly, the above order may be parallel to the importance of step 2 in the rate-determining step.

The products of r_1 and r_2 in the range of 1–3 were obtained in the copolymerizations of CEVE with 3-Me-1-PB and were in contrast with the large value obtained in the copolymerization of CEVE with styrenes.[31] The same values were also obtained in the copolymerization of styrene with phenyl-1,3-butadienes.[5] These results can be explained by the facts that phenyl-1,3-butadiene resembles styrene regarding nonpolar monomer and there is a parallel point between phenyl-1,3-butadiene and vinyl ether concerning the high stability of the resulting cation.

Acknowledgment. The authors are indebted to Mr. M. Wada for his skilled technical assistance.

Table VI
Activation Parameters of Monomer Reactivity Ratios

Monomer pair M_1–M_2	Catalyst	Solvent	$\Delta H^{\ddagger}_{11} - \Delta H^{\ddagger}_{12}$, kcal/mol	$\Delta H^{\ddagger}_{21} - \Delta H^{\ddagger}_{22}$, kcal/mol	$\Delta S^{\ddagger}_{11} - \Delta S^{\ddagger}_{12}$, cal/deg	$\Delta S^{\ddagger}_{21} - \Delta S^{\ddagger}_{22}$, cal/deg	Ref
CEVE-3-Me-1-PB	BF_3OEt_2	MC[a]	0.39	0.16	2.0	−0.5	This work
CEVE-3-Me-1-PB	BF_3OEt_2	Toluene	0.52	0.91	2.8	4.1	This work
CEVE-3-Me-1-PB	$SnCl_4$·TCA	MC	0.00	−0.25	−0.8	−4.0	This work
CEVE-3-Me-1-PB	$SnCl_4$·TCA	Toluene	0.30	0.10	2.3	0.4	This work
CEVE-α-Methylstyrene	$SnCl_4$·TCA	MC	1.9	0.53	9.5	2.6	31
CEVE-α-Methylstyrene	$SnCl_4$·TCA	Toluene	0.77	0.19	6.3	2.5	31
Styrene-1-PB	$SnCl_4$·TCA	MC	−0.66	−0.33	−4.4	−4.2	5

[a] MC = methylene chloride.

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Cationic Polymerization of Alkyl-1,3-butadienes

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ABSTRACT: The polymerizations of 1- and 2-alkyl-1,3-butadienes, including methyl, ethyl, isopropyl, and *tert*-butyl groups as the alkyl group, were carried out using various cationic catalysts in methylene chloride. The polymerization rate using both $SnCl_4$·TCA and WCl_6 decreased with an increase in the bulkiness of the alkyl group in contrast with $AcClO_4$ and BF_3OEt_2. The nature of the polymers obtained by $SnCl_4$·TCA, WCl_6, and BF_3OEt_2 varied from rubberlike to white powder except that oily oligomers of 2-*tert*-butyl-1,3-butadiene formed. The reactions of 1-isopropyl-, 1-*tert*-butyl-, and 2-alkyl-1,3-butadienes with $AcClO_4$ produced only methanol-soluble oligomers. The content of 1,4-structure of poly(1-alkyl-1,3-butadiene)s decreased as the bulkiness of the substituent increased. The NMR spectra of the oligomers obtained by $AcClO_4$ suggested that a proton elimination in the monomer transfer reaction was governed by Saytzeff's rule. The reactivities of 1- and 2-alkyl-1,3-butadienes toward a styryl cation decreased with an increase in the bulkiness of alkyl group.

It has been known that the linear conjugated dienes could be polymerized readily by both Friedel–Crafts catalysts and Lewis acids. However, there is little information available on the cationic polymerization of alkyl-1,3-butadienes compared with other polymerizations, i.e., radical, anionic, and coordination polymerizations, since the side reactions such as cyclization and cross-linking frequently make the information on the polymer structure uncertain.

The authors have already reported studies of the cationic polymerization of monophenyl-1,3-butadienes,[2–5] diphenyl-1,3-butadienes,[6] and methylphenyl-1,3-butadienes[7] that make clear the relationship between the structure and the reactivity of phenyl-1,3-butadienes. The results obtained in the above polymerizations are summarized as follows:

(i) 1-Phenyl-[2] and 2-phenyl-1,3-butadienes[3] are highly reactive monomers, and the former gave polymers predominantly of 3,4-type, whereas the latter polymerized with 1,4-propagation. (ii) About half of the olefinic double bonds of these polymers were consumed by cyclization. The cyclized polymer of 1-phenyl-1,3-butadiene may have a fused cyclohexane ring and that of 2-phenyl-1,3-butadiene may have a hydrophenanthrene structure. (iii) In the cationic polymerization of diphenyl-1,3-butadienes,[6] only oligomers were obtained because of steric hindrance of the phenyl ring. (iv) The relative reactivities of 1-phenyl-1,3-pentadiene and 3-methyl-1-phenyl-1,3-butadiene toward 1-phenyl-1,3-butadiene were analogous to the tendency of β-methyl- and α-methylstyrenes, whereas the reactivity of 1-methyl-2-phenyl-1,3-butadienes has been enhanced 1.6 times compared to that of 2-phenyl-1,3-butadiene, in the $SnCl_4$·TCA–methylene chloride system at −78 °C.[7] (v) Steric hindrance of substituents plays an important role in determining the microstructure of poly(methylphenyl-1,3-butadiene)s. The olefinic double bonds in their polymers were little cyclized on account of the steric interference of substituents.

In this paper, the authors investigated the cationic polymerizabilities of alkyl-1,3-butadienes and the structure of polymers obtained and compared the results with those ob-