Cationic Polymerization of Phenylbutadienes. V. Cationic Copolymerization of Monophenyl-1,3-butadienes

Kan-ichi HASEGAWA and Ryuzo ASAMI

Department of Synthetic Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466, Japan.

ABSTRACT: To obtain information about the transition state for the cationic polymerization of monophenylbutadienes, the ring-substituent and the temperature effects on the copolymerizability were investigated. Judging from the magnitude of the ρ^+ values for the copolymerizations of styrene with ring-substituted 1- and 2-phenylbutadienes, it is suggested that the propagation of monophenylbutadiene proceeds through the transition state which involves an cyclic carbonium ion intermediate. The same interpretation could be applied for the attack of a cinnamyl-type cation onto monophenylbutadiene. The reactivity of monomers toward a styryl cation decreased according to the following order: 1-phenylbutadiene > styrene > 2-phenylbutadiene. The lower reactivity of 2-phenylbutadiene in comparison with styrene may be ascribed to the enthalpy increase which overweighs the entropy increase in the transition state.

KEY WORDS   1-Phenylbutadiene / 2-Phenylbutadiene / Ring-Substituent Effect / Temperature Effect / Transition State /

In a previous paper,[1] the authors reported the cationic copolymerization of 1-phenyl-1,3-butadiene (1-PB) with olefinic monomers such as isobutene, styrene, and α-methylstyrene. The reactivities of these monomers toward a 1-PB propagating end in methylene chloride decreased in the following order: α-methylstyrene > 1-PB > isobutene > styrene. This order has been explained in terms of the nucleophilicity of the monomers and the stability of the resulting cations.

In general, the kinetic feature of the propagation depends on the steric and the electronic effects of both the monomer and the propagating end. In addition, the propagation rate is sensitively influenced by a slight difference of the geometrical structures for the transition state.

In this work, the transition state for the cationic polymerization of monophenylbutadienes will be discussed on the basis of the reactivity difference in the copolymerization.

EXPERIMENTAL

Materials

1-PB and 2-phenyl-1,3-butadiene (2-PB) were prepared as described in previous papers.[2,3]

1-*p*-Methylphenyl-1,3-butadiene (*p*-CH$_3$-1-PB) and 1-*p*-chlorophenyl-1,3-butadiene (*p*-Cl-1-PB) were synthesized from the corresponding benzaldehydes by the same method as 1-PB. 1-*m*-Chlorophenyl-1,3-butadiene (*m*-Cl-1-PB) was synthesized by Meerwein arylation between butadiene and the corresponding diazonium salt, and subsequent dehydrochlorination by potassium hydroxide.[4] These monomers were all trans isomers. Ring-substituted-2-phenyl-1,3-butadienes including *p*-methoxy, *p*-methyl, and *p*-chloro groups were prepared from the corresponding acetophenones and vinylmagnesium bromide by Grignard reaction and subsequent dehydration by potassium bisulfate. The boiling points of these monomers were as follows: *p*-CH$_3$-1-PB 87°C (7 mm); *p*-Cl-1-PB 98°C (7 mm); *m*-Cl-1-PB 100°C (8 mm); *p*-CH$_3$O-2-PB 76°C (4 mm); *p*-CH$_3$-2-PB 61—62°C (7 mm); *p*-Cl-2-PB 67—69°C (5 mm). The purities of these monomers were more than 99% according to gas chromatography. Styrene, β-methylstyrene, catalysts, and methylene chloride were purified in the usual manners. Trichloroacetic acid (TCA) was used as the cocatalyst of stannic chloride (SnCl$_4$) without further purification. An equimolar mixture of SnCl$_4$ and TCA was used
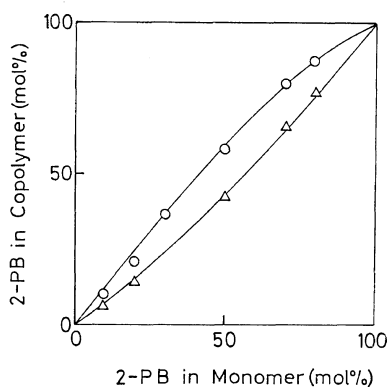
to start the copolymerization.

Procedures

Copolymerization was carried out in an Erlenmeyer flask equipped with a three-way cock under a dry nitrogen atmosphere. After suitable time intervals, an aliquot amount of the copolymerization solution was withdrawn with a syringe into methanol, which contained a small amount of aqueous ammonia solution in order to stop the copolymerization. The copolymer compositions were determined by measuring the residual monomers by means of gas chromatography. The monomer reactivity ratios were calculated by Ezrielev's method.[5]

RESULTS AND DISCUSSION

Figure 1 shows the result of the cationic copolymerization of 2-PB with styrene; the monomer reactivity ratios are listed in Table I.

Figure 1. Copolymer composition curves for the copolymerizations of 2-PB with styrene by $SnCl_4 \cdot$ TCA in methylene chloride: $[M]_0 = 0.50 \, mol/l$; $\bigcirc$, 0°C; $\triangle$, −78°C.

The ratios of the reactivity of 2-PB to that of styrene toward a styryl cation, by using $SnCl_4 \cdot$ TCA, were about 0.6 at −78°C and 0.9 at 0°C. The relative reactivity of 2-PB toward a 2-PB propagating end increased upon raising the temperature. A similar temperature effect was observed in the copolymerization of 1-PB with styrene in polar solvents such as nitroethane and methylene chloride.[1] From the activation parameters determined using the monomer reactivity ratios in the temperature range from −78 to 0°C, 2-PB is shown to be less reactive than styrene in the enthalpy term but more reactive in the entropy one (Table II). The reactivity of monomers toward a styryl cation decreased in the following order: 1-PB > styrene > 2-PB. This order may not be explained in terms of the stability of the resultant cation. The lower reactivity of 2-PB in comparison with styrene may be ascribed to the enthalpy increase which overweighs the entropy increase in the transition state. When a styryl cation attacks on 1- and 2-phenylbutadienes, the values of these activation enthalpies are almost the same order, but the value of the activation entropy of 2-PB is smaller than that of 1-PB. This difference in the entropy term may be due to a difference of number of modes for the transition state.

The ring-substituent effect on the cationic copolymerization of phenylbutadienes was investigated in methylene chloride at 0°C, using boron trifluoride etherate as a catalyst and styrene as a reference monomer. Figures 2 and 3 show the copolymerizations of styrene with 1- and 2-phenylbutadienes, respectively. The monomer reactivity ratios are summarized in Table III. The reactivity of phenylbutadiene was increased by introducing an electron-donat-

Table I. Monomer reactivity ratios in the copolymerization of 2-PB(M_1) with styrene, β-methylstyrene, and 1-PB(M_2)[a]

M_2	Temp, °C	r_1	r_2	$r_1 \times r_2$	$1/r_1$
Styrene	0	1.70 ± 0.09	1.07 ± 0.04	1.82	0.59
Styrene	−78	0.98 ± 0.04	1.70 ± 0.04	1.66	1.02
β-Methylstyrene	0	1.67 ± 0.15	0.05 ± 0.05	0.08	0.60
β-Methylstyrene	−78	1.07 ± 0.11	0.42 ± 0.07	0.44	0.93
1-PB	0	0.50 ± 0.02	1.43 ± 0.04	0.72	2.00
1-PB	−78	0.42 ± 0.08	2.09 ± 0.13	0.88	2.38

[a] Catalyst, $SnCl_4 \cdot$ TCA; solvent, methylene chloride.

Table II. Activation parameters of monomer reactivity ratios

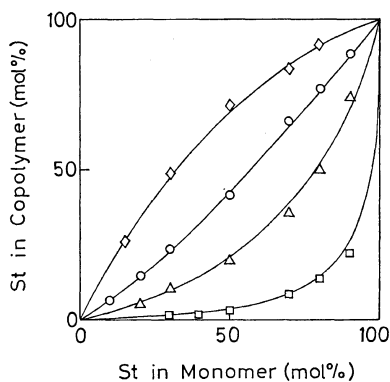| Monomer pair, M₁—M₂	$\Delta H_{11}^{\neq} - \Delta H_{12}^{\neq}$, kcal/mol	$\Delta H_{21}^{\neq} - \Delta H_{22}^{\neq}$, kcal/mol	$\Delta S_{11}^{\neq} - \Delta S_{12}^{\neq}$, cal/deg	$\Delta S_{21}^{\neq} - \Delta S_{22}^{\neq}$, cal/deg
Styrene—1-PB	−0.66	−0.33	− 4.4	−4.2
Styrene—2-PB	−0.63	−0.75	− 2.2	−3.8
1-PB—2-PB	−0.52	−0.24	− 1.2	0.5
β-Methylstyrene—2-PB	−2.89	−0.61	−16.5	−3.2
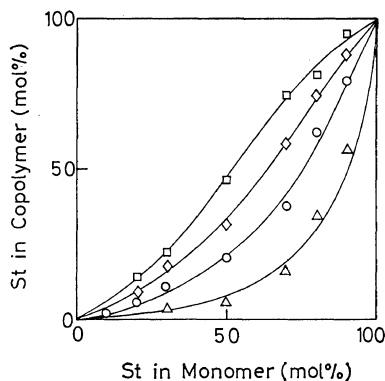
Figure 2. Copolymer composition curves for the copolymerizations of styrene with ring-substituted 1-PB by BF₃OEt₂ in methylene chloride at 0°C: □, *m*-Cl; ◇, *p*-Cl; ○, H; △, *p*-CH₃.

Figure 3. Copolymer composition curves for the copolymerizations of styrene with ring-substituted 2-PB by BF₃OEt₂ in methylene chloride at 0°C: ◇, *p*-Cl; ○, H; △, *p*-CH₃; □, *p*-OCH₃.

Table III. Monomer reactivity ratios in the copolymerizations of styrene (M₁) with ring-substituted phenylbutadienes (M₂)[a]

M₂	r_1	r_2	$1/r_1$
p-CH₃-1-PB	0.18±0.11	12.38±2.26	5.56
1-PB	0.60±0.13	5.30±0.47	1.67
p-Cl-1-PB	0.98±0.10	2.87±0.24	1.02
m-Cl-1-PB	2.07±0.32	2.30±0.45	0.48
p-CH₃O-2-PB	0.06±0.05	40.09±4.39	17.24
p-CH₃-2-PB	0.30±0.05	4.02±0.25	3.33
2-PB	0.92±0.03	1.62±0.04	1.09
p-Cl-2-PB	2.06±0.14	0.45±0.07	0.49

[a] Catalyst, BF₃OEt₂; solvent, methylene chloride; temp, 0°C.

method. The ring-substituent effects of phenyl-butadienes toward a styryl cation in the BF₃OEt₂—methylene chloride-0°C system were as follows.

1-PB: $\rho^+ = -1.51$, $r = 0.993$, $s = 0.064$

2-PB: $\rho^+ = -1.67$, $r = 0.994$, $s = 0.092$

where ρ^+, r, and s represent the reaction constant, the correlation coefficient, and the standard deviation, respectively. These ρ^+ values were less negative than that of the hydro-chlorination of 1-PB ($\rho^+ = -2.98$)[6] or that of the cationic polymerization of styrene ($\rho^+ = -2.03$).[7] Judging from the ring-substituent and the deuterium isotope effects, Izawa, *et al.*,[6] have concluded that the hydrochlorination of 1-PB proceeds through a transition state which is close to an intermediate allylic cation and that the relatively low absolute value of −2.98 compared with the hydration of styrene ($\rho^+ = -3.58$)[8] must be due to the effective delocalization of a positive charge by allylic conjugation. In protonation, therefore, the allylic resonance decreased the ring-substituent effect by a factor of about 0.8.

ing substituent, such as methyl and methoxy groups. The log $(1/r_1)$ obtained from the copolymerizations was plotted against Brown's σ^+ and the plots gave two straight lines (Figure 4). The ρ^+ values were obtained from the slopes of the Hammett plots by the least-squares
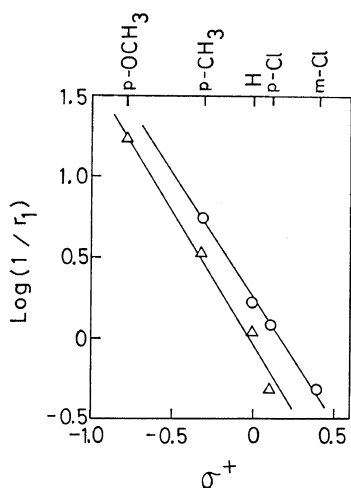
Figure 4. Plots of $\log(1/r_1)$ against σ^+ in the copolymerizations of styrene with 1- and 2-phenylbutadienes: ○, ring-substituted 1-PB; △, ring-substituted 2-PB.

In the case of styrene, the absolute value of ρ^+ (−2.03) for the cationic polymerization is much smaller than that $(\rho^+ = -4.21)^9$ for bromination which involves the transition state of an open benzilic carbonium ion. This value is very close to that of the sulfenyl chloride addition $(\rho = -2.41 - -2.29)^{10}$ which has been well established to occur with the formation of a cyclic episulfonium ion intermediate for a transition state by Kharasch, et al. Therefore, it is suggested that the transition state of the propagation of the cationic polymerization of styrene also involves a cyclic intermediate, as the case of the addition of sulfenyl chloride.[11] A positive charge localized on the olefinic carbons at a cyclic carbonium ion intermediate in the transition state would be responsible for the low ring-substituent effect.

In the case of 1-PB, it has already been shown from the result of ^{13}C NMR that the inductive effect of the ring substituent was missing 20~30% on carbon 4 of 1-PB on which an electrophilic attack took place after crossing the 1,2 double bond.[12] Therefore, the ρ^+ value (−1.51) obtained in the cationic copolymerization of styrene with ring-substituted 1-PB, which is 0.74 times as high as in the case of styrene (−2.03), suggests a similar transition state for both cases

of 1-PB and styrene, that is, the cyclic carbonium ion between the attacking styryl cation and the π-orbital on the 3,4 double bond of 1-PB. Ishida, et al.,[13] have reported the ρ^+ value (−1.50) for the copolymerization of 1-PB with ring-substituted 1-PB. In this case it is also reasonable to consider a similar cyclic carbonium ion as the intermediate in the transition state.

The same interpretation could be applied for the copolymerization of styrene with ring-substituted 2-PB. The magnitude of the ρ^+ value (−1.67) suggests that the cyclic carbonium ion is between the styryl cation and the 2-PB derivatives, and that a small part of the positive charge will be delocalized on the phenyl group in the transition state compared with that of the cinnamyl-type cation.

However, we cannot choose whether the transition state is a symmetrical intermediate in which the vacant orbital of the styryl cation overlaps equivalently occupied orbitals of α,β-carbons of the monomer or an asymmetrical one. The authors will discuss the transition state for the propagation of phenylbutadienes in further detail in the next paper on the cationic polymerization of methylphenylbutadienes.[14]

The cationic copolymerization of 2-PB with β-methylstyrene was carried out in order to obtain information on the reactivity of the 2-PB propagating end (Figure 5 and Table I). β-Methylstyrene was 0.9—1.0 times as reactive as styrene in attacking the 2-PB propagating end.
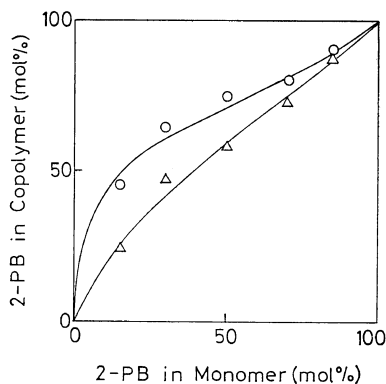
Figure 5. Copolymer composition curves for the copolymerizations of 2-PB with β-methylstyrene by SnCl$_4$·TCA in methylene chlroride: ○, 0°C; △, −78°C.

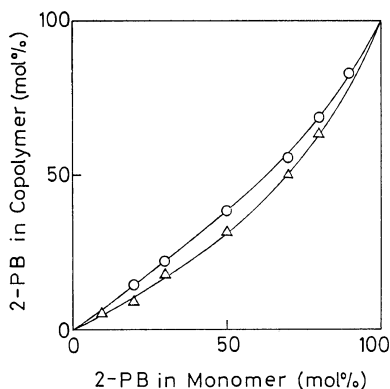**Figure 6.** Copolymer composition curves for the copolymerizations of 2-PB with 1-PB by SnCl₄· TCA in methylene chloride: ○, 0°C; △, −78°C.

Mizote, et al.,[15] reported that the reactivity of β-methylstyrene toward a styryl cation was about a half of that of styrene. Therefore, a 2-PB propagating end may attack β-methylstyrene through a more bridged carbonium ion than a styryl cation does, since the steric interaction between 2-PB propagating end and β-methylstyrene was less than that between the styryl cation and β-methylstyrene. On the other hand, the reactivity of β-methylstyrene decreased considerably because of the large steric hindrance of the β-methyl group.

The copolymerization of 1-PB and 2-PB was carried out in methylene chloride, using SnCl₄· TCA (Figure 6). In this copolymerization, the reactivity difference between the two monomers was smaller than that expected in the copolymerization of styrene with phenylbutadienes: namely, the relative reactivity of 2-PB toward 1-PB increased compared with that toward a styryl cation. This result may be explained as follows: since the ring-substituent effect has already suggested that a styryl cation attacks 2-PB through the following model (A), the overlap between the lowest vacant orbital of the cation and the highest occupied orbital of 2-PB will increased as the bond length of the double bond of the monomer becomes as short as possible. However, if a cinnamylic cation attacks 2-PB through model (B), it is favorable

that the carbon—carbon double bond of the monomer is long in order to give a much greater overlap. The length of the olefinic double bond of phenylbutadiene is greater than that of styrene because of a long conjugation. Therefore,
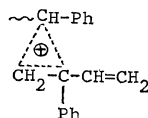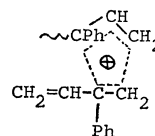
Model (A)   Model (B)

the relative reactivity of 2-PB toward an allylic cation is greater than that expected in the copolymerization of styrene with phenylbutadienes.

REFERENCES

1. R. Asami, K. Hasegawa, N. Asai, I. Moribe, and A. Doi, *Polymer J.*, **8**, 74 (1976).
2. R. Asami, K. Hasegawa, and T. Onoe, *ibid.*, **8**, 43 (1976).
3. R. Asami and K. Hasegawa, *ibid.*, **8**, 67 (1976).
4. "Organic Syntheses" Coll. IV, N. Rabjohn Ed., John Wiley & Sons, Inc., New York, N.Y., 1963, p 727.
5. A. I. Ezrielev, E. L. Brokhina, and E. S. Roskin, *Vysokomol. Soedin.*, **11**, 1670 (1969).
6. K. Izawa, T. Okuyama, T. Sakagami, and T. Fueno, *J. Amer. Chem. Soc.*, **95**, 6752 (1973).
7. J. P. Kennedy in "Copolymerization," G. E. Ham, Ed,, Interscience, New York, N.Y., 1964, p 308.
8. W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4272 (1964).
9. J. H. Polston and K. Yates, *ibid.*, **91**, 1483 (1969).
10. W. L. Orr and R. Kharash, *ibid.*, **78**, 1201 (1956).
11. T. Okuyama, N. Asami, and T. Fueno, *Bull. Chem. Soc. Japan*, **43**, 3553 (1970).
12. T. Masuda, M. Otsuki, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1385 (1974).
13. H. Ishida and I. Yamaji, *Kobunshi Ronbunshu*, **32**, 357 (1975).
14. K. Hasegawa and R. Asami, to be published.
15. A. Mizote, T. Tanaka, T. Higashimura, and S. Okamura, *J. Polym. Sci., Part A*, **3**, 2567 (1965).