Cationic Polymerization of Phenylbutadienes. IV. Cationic Copolymerization of *trans*-1-Phenyl-1,3-butadiene with Olefinic Monomers*

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ABSTRACT: The copolymerization of 1-phenylbutadiene with olefinic monomers was performed by using isobutene, styrene, and α-methylstyrene as comonomers catalyzed by BF_3OEt_2 or $SnCl_4$-trichloroacetic acid. From the monomer reactivity ratios in these copolymerizations in methylene chloride, the following order of the reactivities of the monomers is indicated: α-methylstyrene > 1-phenylbutadiene > isobutene > styrene > isoprene > butadiene. This order of the reactivities will be explained by the stability of the cations formed from the monomers and by the nucleophilicity of the monomers. In the copolymerization of 1-phenylbutadiene with styrene catalyzed by BF_3OEt_2, the reactivity of 1-phenylbutadiene increased with increasing the polarity of the solvent in the order of nitroethane > methylene chloride > toluene. The temperature effect on the copolymerization was also recognized in such polar solvent as nitroethane. These results and the block character in the copolymerization of 1-phenylbutadiene with isobutene were interpreted on the basis of the two-step theory of propagation.

KEY WORDS   1-Phenylbutadiene / Isobutene / Styrene / α-Methylstyrene / Solvent Effect / Temperature Effect /

In the preceding papers,[1,2] we have already reported the kinetic results in the cationic homopolymerization of phenylbutadienes and the microstructure of the polymer obtained.

For this paper, the cationic copolymerization of 1-phenylbutadiene with nonpolar olefinic monomers was studied in order to make clear the relation between the reactivity and the structure of the monomer. Isobutene, styrene, and α-methylstyrene were selected as representative olefinic monomers. Monomer reactivity ratios were determined in several solvents and at different temperatures to study the solvent effect and the temperature effect in these cationic copolymerizations. We will discuss the reactivity of phenylbutadiene in cationic polymerization in comparison with that of other diene and vinyl monomers.

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EXPERIMENTAL

Materials

1-Phenylbutadiene (1-PB) was synthesized as described in the preceding paper[1] and the purity of the monomers was more than 99% according to gas chromatography. Styrene, α-methylstyrene, isobutene, catalysts, and solvents were used as commercially available, and purified by conventional methods.

Procedures

Copolymerization of 1-PB with olefinic monomers was carried out by a technique using a high vacuum system. All monomers and solvents were completely dried by use of calcium hydride. Copolymers were precipitated by an addition of excess methanol from the solutions and dried in vacuum. The composition of the copolymers was determined by UV analysis in most cases, except that of α-methylstyrene. The following values were used for the molar extinction coefficients at 255 nm

$\varepsilon(\text{P-1-PB}) = 8500$, $\varepsilon(\text{P-styrene}) = 350$,

$\varepsilon(\text{P-isobutene}) = 0$,

The NMR analysis of the copolymer was also used to confirm the composition obtained by UV analysis. In the case of α-methylstyrene, the composition of the copolymers was determined from the monomer concentrations remaining, by means of gas chromatography.

RESULTS AND DISCUSSION

Cationic Copolymerization of 1-Phenylbutadiene with Isobutene

The copolymerization of 1-PB with isobutene was carried out using BF_3OEt_2 as catalyst at 0°C in methylene chloride. The copolymer obtained was analyzed by UV spectroscopy in its tetrahydrofuran solution. The experimental data are summarized in Table I and the composition of copolymers are plotted in Figure 1. The monomer reactivity ratios were determined by the intersection method. The values of r_1 and r_2 calculated in this study were compared with those obtained by other workers in Table II. In the copolymerization of isobutene with conjugated dienes, the reactivity of the diene monomer occurred in the following order, according to Table II.

$$1\text{-PB} > \text{cyclopentadiene} > \text{isobutene}$$
$$> \text{isoprene} > \text{butadiene}$$
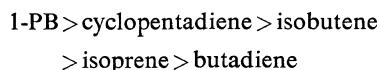
1-PB was considered to be incorporated most easily in copolymers of isobutene, whereas butadiene was included in such copolymers only slightly. This high reactivity of 1-PB might be
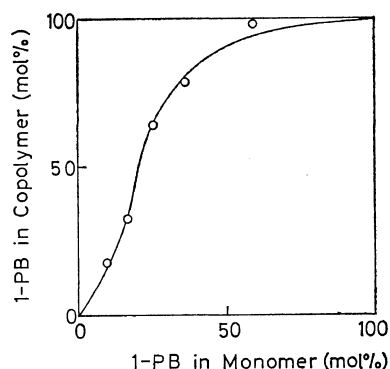

Figure 1. Composition curve for the copolymerization of 1-PB with isobutene by BF_3OEt_2 in methylene chloride at 0°C.

explained by the stabilization of a cation derived from the monomer. Although the copolymers of isobutene with cyclopentadiene and isoprene have been reported to be random copolymers, the copolymer of 1-PB with isobutene was shown to be rather a block copolymer from the high value of the product of r_1 and r_2, *i.e.*, $r_1 \times r_2 = 10$.

The two-step theory based on selective solvation has been already proposed for cationic copolymerization by Imanishi, *et al.*,[6] and others.[8] According to this theory the propagation in cationic polymerization includes the two steps of the formation of a π-complex and the bond formation between the propagating ends and the monomers; then the propagation steps are written as follows
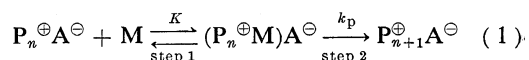
$$P_n^{\oplus}A^{\ominus} + M \underset{\text{step 1}}{\overset{K}{\rightleftharpoons}} (P_n^{\oplus}M)A^{\ominus} \xrightarrow[\text{step 2}]{k_p} P_{n+1}^{\oplus}A^{\ominus} \quad (1)$$

Table I. Copolymerization of 1-PB with isobutene in methylene chloride

Run no.	1-PB, mol/l	Isobutene, mol/l	f_1,[a] mol%	BF_3OEt_2, mmol/l	Time, hr	Yield, %	F_1,[b] mol%	Color[c]	Appearance of polymer
1	0	0.824	0	132	121	8.2	0	Colorless	Rubberlike
2	0.078	0.719	9.7	45.6	7	7.2	17.1	Lemon yellow	Rubberlike
3	0.121	0.600	16.8	53.2	24	9.6	32.3	Yellow	Glassy
4	0.160	0.423	25.6	76.9	5	13.1	64.0	Yellow	White powder
5	0.232	0.325	36.4	44.2	4	29.9	78.1	Orange	White powder
6	0.282	0.194	59.3	47.2	6	45.2	98.5	Reddish orange	White powder
7	0.299	0	100	11.8	24	90.0	100	Reddish orange	White powder

[a] 1-PB fraction in monomer feed.

[b] 1-PB units in copolymer.

[c] Color observed in the course of copolymerization.

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The block character shown in the copolymerization of 1-PB with isobutene would be considered to be explicable on the basis of the above theory. The unstable propagating end formed from isobutene is thought to be very reactive and therefore the rate of polymerization will be controlled by the π-complex formation step, step 1, so that isobutene, which is more nucleophilic than 1-

PB,[9] is favorable to π-complex formation, and hence more included in the copolymers. On the other hand, the growing end of 1-PB is so stable that the rate of polymerization will be determined at the step of bond formation, step 2; therefore the more reactive monomer, 1-PB, is quite copolymerized.

In the copolymerization of isobutene with

Table II. Summary of monomer reactivity ratios for copolymerization of isobutene (M_1) with another monomer (M_2)

M_2	r_1	r_2	Catalyst	Solvent	Temp, °C	Reference
Butadiene	43	~0	$AlEtCl_2$	CH_3I	-100	3
Butadiene	115 ± 15	~0.01	$AlCl_3$	CH_3I	-100	4
Isoprene	2.17	0.5	$AlEtCl_2$	CH_3I	-100	3
Isoprene	2.5 ± 0.5	0.4 ± 0.1	$AlCl_3$	CH_3I	-100	4
1-PB	1.1 ± 0.3	9.8 ± 3.0	BF_3OEt_2	CH_2Cl_2	0	This work
Cyclopentadiene	0.73 ± 0.17	1.86 ± 0.20	BF_3OEt_2	CH_2Cl_2	-78	5
Cyclopentadiene	0.60 ± 0.15	4.5 ± 0.5	BF_3OEt_2	$C_6H_5CH_3$	-78	5
Styrene	0.37 ± 0.07	2.41 ± 0.12	$TiCl_4$	$n\text{-}C_6H_{14}$	-78	6
Styrene	4.48 ± 0.28	1.08 ± 0.07	$TiCl_4$	CH_2Cl_2	-78	6
Styrene	1.70	0.3	$TiCl_4$	CH_2Cl_2	-78	7
α-Methylstyrene	0.3	1.7	$TiCl_4$	CH_2Cl_2	-78	7

Table III. Solvent effect on copolymerization of 1-PB with styrene using BF_3OEt_2 at 0°C.

Run no.	1-PB, mol/l	Styrene, mol/l	f_1,[a] mol%	BF_3OEt_2, mmol/l	Time, hr	Solvent	Yield, %	F_1,[b] mol%
11	0	1.010	0	29.1	0.25	$C_6H_5NO_2$	32.4	0
12	0.203	0.719	22.0	20.7	0.5	$C_6H_5NO_2$	32.9	67.8
13	0.358	0.514	41.1	18.7	0.25	$C_6H_5NO_2$	10.6	86.0
14	0.438	0.498	46.8	19.4	0.5	$C_6H_5NO_2$	33.8	86.1
15	0.534	0.393	57.6	21.1	0.25	$C_6H_5NO_2$	14.9	96.5
16	0.765	0.225	77.3	20.7	0.25	$C_6H_5NO_2$	20.7	99.8
17	0.952	0	100	28.0	0.25	$C_6H_5NO_2$	51.6	100
21	0	0.288	0	28.5	48	CH_2Cl_2	70.9	0
22	0.078	0.423	15.6	56.3	0.5	CH_2Cl_2	15.6	33.1
23	0.121	0.355	25.4	58.0	0.5	CH_2Cl_2	12.0	49.0
24	0.174	0.280	38.4	48.8	0.5	CH_2Cl_2	8.3	70.1
25	0.230	0.195	54.2	47.6	1	CH_2Cl_2	10.1	80.6
26	0.280	0.113	71.3	57.2	1	CH_2Cl_2	8.2	91.2
27	0.299	0	100	11.8	24	CH_2Cl_2	90.0	100
31	0	0.808	0	42.5	92	$C_6H_5CH_3$	8.8	0
32	0.157	0.644	19.6	48.8	1	$C_6H_5CH_3$	3.9	39.0
33	0.266	0.503	35.6	77.0	2.5	$C_6H_5CH_3$	11.8	54.5
34	0.384	0.404	48.7	46.2	1	$C_6H_5CH_3$	15.7	67.7
35	0.524	0.258	67.0	48.3	1	$C_6H_5CH_3$	9.4	84.5
36	0.649	0.154	80.8	65.6	1	$C_6H_5CH_3$	24.5	91.0
37	0.805	0	100	46.1	1.5	$C_6H_5CH_3$	32.3	100

[a] 1-PB fraction in monomer feed.
[b] 1-PB units in copolymer.

linear conjugated dienes, it has been known that the rates and the molecular weights of the copolymer decreased in the order of the dienes' ability to form a more stable allyl cation.[10,11] The molecular weight of the copolymer of 1-PB with isobutene was of the same order as the homopolymer of 1-PB. Therefore, monomer chain transfer will be the dominant reaction governing the molecular weight of the copolymer.

The color that had been seen in the course of copolymerization of 1-PB with isobutene is indicated in the 9th column of Table I. The same color has also been observed in the copolymerization of 1-PB with styrene; these colors could be ascribed to the propagating species in the copolymerizations, as was described in the homopolymerization of 1-PB in the preceding paper.[1]

Cationic Copolymerization of 1-Phenylbutadiene with Styrene and α-Methylstyrene

The copolymerization of 1-PB (M_1) with styrene (M_2) was carried out in nitroethane, methylene chloride, and toluene as solvents using BF_3OEt_2 as the catalyst. These copolymerizations were performed with a high-vacuum technique. The composition of the white powder copolymers obtained was determined by UV and NMR spectroscopy. The composition of these copolymers are listed in Table III and the composition curves are shown in Figure 2. The relative reactivity of 1-PB increased slightly with an in-

crease in the polarity of solvent, *i.e.*, in the order of nitroethane > methylene chloride > toluene. This solvent effect on the copolymerization could be explained by the two-step interpretation described in the preceding section as eq 1. The growing ends of both 1-PB and styrene are stabilized with conjugation. Therefore, it is reasonable that the ion pairs of the propagating ends are more ionized and solvated in polar solvents than in nonpolar solvents and the rate of propagation will be determined by the step of bond formation, step 2 of eq 1. Consequently, 1-PB, which produces a more stable cation than
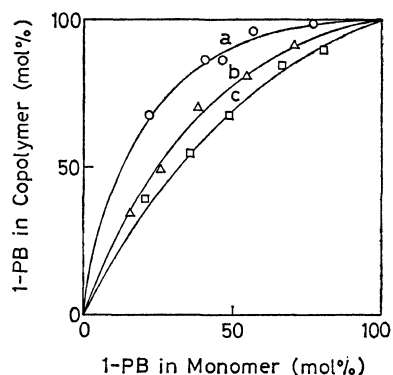

Figure 2. Composition curves for the copolymerization of 1-PB with styrene by BF_3OEt_2 at 0°C: solvent, a(○), nitroethane; b(△), methylene chloride; c(□), toluene.

Table IV. Temperature effect on copolymerization of 1-PB with styrene using BF_3OEt_2 in nitroethane

Run no.	1-PB, mol/l	Styrene, mol/l	f_1,[a] mol%	BF_3OEt_2, mmol/l	Time, hr	Temp, °C	Yield, %	F_1,[b] mol%
11	0	0.935	0	28.8	1.8	−40	9.6	0
12	0.204	0.717	22.0	19.2	18	−40	19.5	53.0
13	0.344	0.512	40.2	19.1	18	−40	5.0	78.9
16	0.752	0.231	76.5	21.1	18.2	−40	9.7	93.0
17	0.788	0.216	78.4	19.4	18	−40	9.7	95.9
18	0.887	0	100	27.8	15	−40	19.2	100
21	0	0.996	0	29.2	1.5	−78	11.6	0
22	0.208	0.736	22.0	20.3	1.5	−78	5.4	45.5
23	0.342	0.509	40.2	21.4	1.5	−78	1.4	70.3
24	0.451	0.422	51.7	22.4	1.0	−78	5.7	70.4
25	0.569	0.406	58.4	19.8	1.5	−78	2.3	80.0
26	0.781	0.224	77.7	21.0	1.0	−78	3.7	85.4
27	0.632	0	100	32.6	1.0	−78	19.0	100

[a] 1-PB fraction in monomer feed.
[b] 1-PB units in copolymer.

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styrene, will be selected by the growing end more preferentially than styrene.

The effect of temperature on the copolymerization of 1-PB with styrene were investigated in nitroethane and in toluene in the range of temperatures from −78 to 30°C. The results obtained in nitroethane and toluene are shown in Tables IV and V and Figures 3 and 4, respec-

Table V. Temperature effect on copolymerization of 1-PB with styrene using BF_3OEt_2 in toluene

| Run no.	1-PB, mol/l	Styrene, mol/l	f_1,[a] mol%	BF_3OEt_2, mmol/l	Time, hr	Temp, °C	Yield, %	F_1,[b] mol%
11	0	0.808	0	42.5	21.4	30	17.9	0
12a	0.157	0.644	19.6	48.8	0.4	30	7.2	42.0
12b	0.164	0.609	21.2	49.5	0.2	30	3.8	45.1
13a	0.266	0.537	33.1	43.0	0.4	30	11.7	61.0
13b	0.254	0.505	33.5	53.7	0.2	30	7.0	58.3
14	0.384	0.404	48.7	46.2	0.4	30	17.3	69.0
15	0.524	0.258	67.0	48.3	0.4	30	24.7	87.1
16a	0.610	0.159	79.3	49.0	0.5	30	41.1	94.4
17	0.805	0	100	46.1	1.2	30	69.1	100
21	0	0.808	0	42.5	141.6	−40	2.4	0
22	0.157	0.644	19.6	48.8	20.5	−40	3.5	37.0
23	0.266	0.537	33.1	43.0	23.5	−40	3.1	58.0
24	0.384	0.404	48.7	46.2	18.5	−40	4.0	64.3
25	0.524	0.258	67.0	48.3	18.0	−40	6.9	80.2
26	0.610	0.159	79.3	49.0	18.1	−40	10.4	89.0
27	0.805	0	100	46.1	94.7	−40	43.0	100
31	0	0.808	0	42.5	141.9	−78	0.8	0
32	0.157	0.644	19.6	48.8	69.5	−78	1.9	37.0
33	0.261	0.486	34.9	56.6	192.0	−78	4.8	55.5
34	0.384	0.404	48.7	46.2	24.5	−78	9.2	61.3
35a	0.524	0.258	67.0	48.3	25.0	−78	4.8	75.3
35b	0.510	0.259	66.3	51.9	144.0	−78	3.1	80.1
36	0.610	0.159	79.3	49.0	24.5	−78	4.7	85.0
37	0.805	0	100	46.1	140.2	−78	10.6	100

[a] 1-PB fraction in monomer feed.
[b] 1-PB units in copolymer.
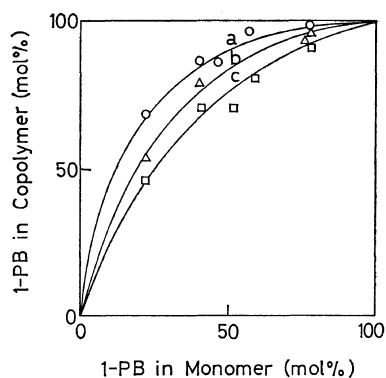
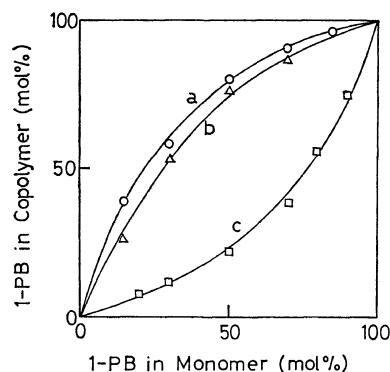**Figure 3.** Composition curves for the copolymerization of 1-PB with styrene by BF_3OEt_2 in nitroethane: Temp, a(○), 0°C; b(△), −40°C; c(□), −78°C.
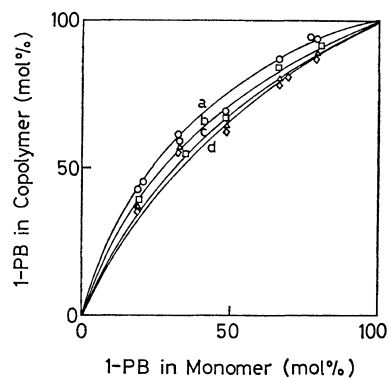
Figure 4. Composition curves for the copolymerization of 1-PB with styrene by BF_3OEt_2 in toluene: Temp, a(○), 30°C; b(□), 0°C; c(△), −40°C; d(◇), −78°C.

**Table VI.** Monomer reactivity ratios in the copolymerization of 1-PB (M_1) with styrene derivatives

M_2	Solvent	Catalyst	Temp, °C	r_1	r_2
Styrene	$C_2H_5NO_2$	BF_3OEt_2	0	7.35 ± 3.05	0.34 ± 0.13
Styrene	$C_2H_5NO_2$	BF_3OEt_2	-40	5.55 ± 1.25	0.46 ± 0.13
Styrene	$C_2H_5NO_2$	BF_3OEt_2	-78	3.03 ± 0.47	0.60 ± 0.09
Styrene	CH_2Cl_2	BF_3OEt_2	0	5.30 ± 0.47	0.60 ± 0.13
Styrene	$C_6H_5CH_3$	BF_3OEt_2	30	3.70 ± 0.53	0.58 ± 0.09
Styrene	$C_6H_5CH_3$	BF_3OEt_2	0	3.30 ± 0.42	0.66 ± 0.13
Styrene	$C_6H_5CH_3$	BF_3OEt_2	-40	2.98 ± 0.40	0.70 ± 0.10
Styrene	$C_6H_5CH_3$	BF_3OEt_2	-78	2.60 ± 0.60	0.74 ± 0.08
Styrene	CH_2Cl_2	$SnCl_4\cdot TCA$	0	4.55 ± 0.22	0.37 ± 0.06
Styrene	CH_2Cl_2	$SnCl_4\cdot TCA$	-78	3.58 ± 0.34	0.60 ± 0.09
α-Methylstyrene	CH_2Cl_2	$SnCl_4\cdot TCA$	-78	3.12 ± 0.18	0.29 ± 0.04

tively. In nitroethane the reactivity of 1-PB increased with increasing temperature, whereas in toluene this effect was shown to be much less. This temperature effect on the composition of copolymers in the polar solvent could not be explained by the change of the nature of growing ion-pairs, but rather explained by the higher activation enthalpy of 1-PB compared to that of styrene in the addition reaction. This fact will be supported by the result that the activation enthalpy of 1-PB was larger than that of styrene in the initiation with triphenylmethyl stannic pentachloride in the preceding paper.[12] Similar results noting that the high-reactive monomer is more incorporated than the low-reactive one as the temperature is raised in a cationic copolymerization have been reported in other studies.[13,14] The monomer reactivity ratios were calculated for the above data by means of the intersection method and are summarized in Table VI. The copolymerization of 1-PB with styrene and α-methylstyrene was performed in methylene chloride by using $SnCl_4\cdot$trichloroacetic acid ($SnCl_4\cdot$TCA) as the catalyst. The composition curves obtained are shown in Figure 5 and the monomer reactivity ratios calculated are listed in Table VI. The result of copolymerization of 1-PB with styrene coincided with that previously reported by Higashimura, et al.,[15] and that shown in Table VI, where BF_3OEt_2 was used as the catalyst. The copolymerization of 1-PB with α-methylstyrene has been shown to be an ideal copolymerization, $r_1\times r_2=1$, that is, the relative reactivity of the monomer was independent of the propagating ends.

Figure 5. Composition curves for the copolymerizations of 1-PB with styrene and α-methylstyrene by $SnCl_4\cdot TCA$ in methylene chloride: a($\bigcirc$), styrene, 0°C; b($\triangle$), styrene, -78°C; c($\square$), α-methylstyrene, -78°C.

As a summary of Tables II and VI, the relative reactivities of monomers against the 1-PB propagating end in the cationic copolymerization are shown to decrease according the following order.

α-methylstyrene $>$ 1-PB $>$ isobutene $>$ styrene

$>$ isoprene $>$ butadiene
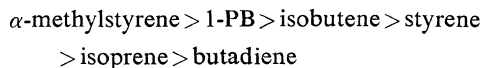
This order might be explained in terms of the stabilization of carbonium ions formed and the nucleophilicity of the monomers.

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