Cationic Copolymerization of Styrene with Indene or α-Methylstyrene Catalyzed with Boron Trifluoride Etherate under an Electric Field[1]

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ABSTRACT: The influence of an electric field on the cationic copolymerization of styrene (M_1) with indene (M_2) or α-methylstyrene (M_2) was investigated. The copolymerizations were enhanced in the presence of the field. The field increased the styrene contents in the copolymers; that is, r_1 increased and/or r_2 decreased. These results could successfully be accounted for in terms of the field-facilitated dissociation of growing chain ends, which was earlier suggested for the field accelerating effect on ionic homopolymerizations.

In previous papers,[2-9] the effect of an electric field on various kinds of polymerization systems has been investigated. The field was found to increase the rates of ionic polymerizations in general, whereas radical polymerizations were not affected.[2] It has tentatively been proposed that the field-facilitated dissociation of ion pairs at growing chain ends (the second Wien effect[10]) may be responsible for the accelerating effect, on the assumption that the propagation rate constant of free ions is much larger than that of ion pairs. This interpretation has most clearly been substantiated by the experimental fact that the over-all propagation rate constants of living anionic polymerization of styrene were also increased in the presence of the electric field.[9] On the other hand, for cationic systems, the interpretation lacked clear support because of the intricate mechanism of this type of polymerizations.

Thus it is interesting to investigate the effect of an electric field on the cationic *copolymerization.* It is generally admitted that monomer reactivity ratios depend only on the rates of propagation and not on the rates of initiation, termination, and other elementary processes.

When styrene was cationically copolymerized with indene[11] or α-methylstyrene[12] (both are more reactive monomers than styrene), the styrene content in the copolymer was found to increase as the dielectric constant of the medium or the strength of the catalyst increased. These results indicate that the difference in the reactivities of monomers becomes smaller in the more free ionic copolymerization systems. Since both increasing the dielectric constant and applying the high electric field can result in enhancement of the ionic dissociation, it would be expected that, in the presence of the electric field, the styrene content in the copolymer increases. We report, in the present paper, the experimental study of the copolymerizations of styrene with indene or with α-methylstyrene by boron trifluoride etherate as a catalyst in ethylene dichloride (DCE) or nitrobenzene (NB) as the solvent.

Experimental Section

Materials. DCE (reagent grade) (500 g) was washed with five to ten 100-ml portions of concentrated sulfuric acid (reagent grade) until the acid layer was colorless, washed with three 100-ml portions of water and three 100-ml portions of 5% sodium hydroxide solution, and finally with five to ten 100-ml portions of water until neutral, dried over calcium chloride for 1 week, then over Drierite, and fractionally distilled off calcium hydride under a nitrogen atmosphere, bp 83.0–83.5°. NB (reagent grade) (500 g) was washed with five 100-ml portions of 5% sodium hydroxide solution and five to ten 100-ml portions of water until neutral, dried over calcium chloride for 1 week, then over Drierite, and fractionally distilled at reduced pressure in a nitrogen atmosphere, bp 74–75° (6 mm). Styrene (chemically pure) (500 g) was washed with three 100-ml portions of 5% sodium bisulfite solution, then with five 100-ml portions of sodium hydroxide solution and five to ten 100-ml portions of water until neutral, and dried over calcium chloride, Drierite, and calcium hydride. The dried monomer was distilled off calcium hydride at reduced pressure in a nitrogen atmosphere just before use, bp 41–42° (17 mm). Indene (chemically pure) (250 g) was stirred with 200 ml of 6 *N* hydrogen chloride solution for about 12 hr, washed with three 100-ml portions of water, stirred with 200 ml of 5% sodium hydroxide solution for 12 hr, and then extracted with 250 ml of *n*-hexane. The organic layer was washed with three 100-ml portions of water and then dried over anhydrous sodium sulfate. The *n*-hexane was removed from the solution under nitrogen. From the residue, indene was fractionally distilled at reduced pressure in a nitrogen atmosphere. The monomer thus obtained was dried over calcium hydride and distilled again at reduced pressure in a nitrogen atmosphere just before use, bp 55.5–56.0 (9 mm). α-Methylstyrene (reagent grade) was distilled at reduced pressure in a nitrogen atmosphere after drying over Drierite for 20 hr, bp 53.0–53.5 (15 mm).

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(1) This article is part X of "Ionic Polymerization under an Electric Field." Part IX appeared in *J. Phys. Chem.*, **71**, 3711 (1967).

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(5) I. Sakurada, N. Ise, and Y. Hayashi, *J. Macromol. Sci.*, **A1**, 1039 (1967).

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(10) M. Wien, *Ann. Physik.*, **83**, 327 (1927); *Physik. Z.*, **28**, 834 (1927).

(11) A. Mizote, T. Tanaka, and T. Higashimura, *Kobunshi Kagaku*, **23**, 239 (1966); P. Sigwalt, *J. Polym. Sci.*, **52**, 15 (1961).

(12) A. V. Tobolsky and R. J. Boundreau, *ibid.*, **51**, S-53 (1961).

TABLE I
ANALYTICAL CONDITIONS OF UNCONSUMED MONOMER BY GAS CHROMATOGRAPHY

System	Column	Temp, °C	Helium flow rate, cc/min
Styrene–indene–DCE	Polyethylene glycol 4000/C-22 (40 ~ 60 mesh) (1 :4 in weight) 2.25 m × 3 mm	154	20
Styrene–indene–NB	Silicone D.C. 550/Celite 545 (80 ~ 100 mesh) (3 :7 in weight) 2.25 m × 3 mm	144	30
Styrene–α-methylstyrene–DCE	Polyethylene glycol 4000/124 C-22 (40 ~ 60 mesh) (1 :4 in weight) 1.5 m × 3 mm	124	25

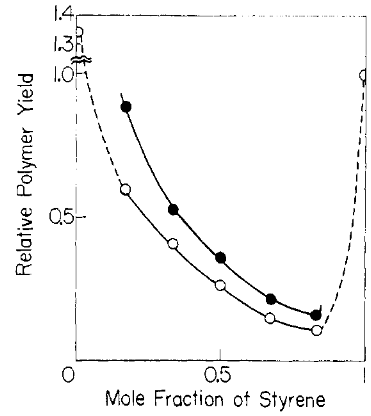

Figure 1. Relative polymer yield and monomer composition in the styrene–indene copolymerizations: total monomer concentration, 20 vol %; [BF$_3$OEt$_2$]$_0$, 2.6 × 10^{-3} mol/l.; solvent, DCE, 0°; polymerization time, 30 min; ○, 0 kV/cm; ●, 0.33 kV/cm.

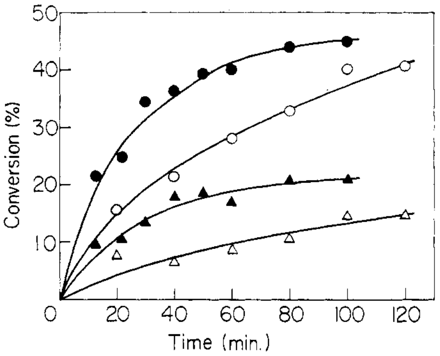

Figure 2. Time-conversion curves of the styrene–indene copolymerizations: solvent, DCE, 20°; [styrene]$_0$, 0.90 mol/l., [indene]$_0$, 0.87 mol/l.; [BF$_3$OEt$_2$]$_0$, 2.6 × 10^{-3} mol/l.; △, styrene, 0 kV/cm; ▲, styrene, 0.33 kV/cm; ○, indene, 0 kV/cm; ●, indene, 0.33 kV/cm.

Commercially available boron trifluoride etherate (BF$_3$-OEt$_2$) was distilled under a nitrogen atmosphere, bp 125–126°.

Apparatus and Procedures. The copolymerizations were carried out in a glass vessel with a neck of 20 cm long. A pair of parallel plate platinum electrodes (area, about 2 cm^2, 3 cm apart, with cell constant 1 cm^{-1}) was sealed into the bottom of the vessel. In a drybox, the monomer and solvent were transferred into the polymerization vessel by using a syringe, and the mixture was brought in a thermostat controlled within 0.1°. After 30 min, a small amount of a catalyst solution of a known concentration was added into the mixture from the top of the neck by using a syringe and shakened vigorously. The electrode terminals were then quickly connected with a high (dc) voltage source. Usually, the total volume of the polymerizing solution was 15 ml, covering completely the electrode surface. The monomer concentration was determined by gas chromatography. The control copolymerizations were carried out in the same way as with the electric field.

The copolymer yield was determined gravimetrically; after a definite time of polymerization, the polymerizing solution was poured into 100 ml of methanol, and the precipitated polymer was filtrated, washed with methanol, and dried at 40° *in vacuo* to a constant weight. The monomer conversion was determined by measuring the unconsumed monomers by gas chromatography; the copolymerization was stopped by pouring 0.3 ml of the polymerizing solution into 1.5 ml of methanol. The resultant solution (10 μl) was analyzed by gas chromatography. Standard mixtures of various compositions of the monomers and the solvents were analyzed as control experiment in order to determine the relationship between mole ratio and relative signal intensity. The apparatus used was a GCG-550T with a thermal conductivity detector, Yanagimoto Mfg. Co., Kyoto, Japan. The packings used were all the products of this company and are given in Table I with the operating conditions. The columns were conditioned at a temperature of 10° higher than the expected operating temperature overnight with the same carrier gas flow rate as at the operating condition. After lowering the temperature, the sample was analyzed.

The copolymer composition was determined by the infrared spectroscopic method employed by Mizote, *et al.*,[11] using peaks at 3025 cm^{-1} (CH) and 1475 cm^{-1} (C=C in indene). The spectrum was taken with a DS-402G spectrophotometer of Japan Spectroscopic Co., Tokyo, Japan.

Results

Styrene (M$_1$)–Indene (M$_2$). In Figure 1, the ratios of polymer yields in the copolymerization and in the homopolymerization of styrene are plotted against the monomer composition. The homopolymerization of styrene was carried out at a monomer concentration of 20 vol % and without electric field. Obviously, the polymer yield increases in the copolymerization by the application of the electric field as was the case in the homopolymerization.[5,8] The polymer yield decreases abruptly with an addition of a small quantity of indene to styrene, and through a minimum, increases with increasing fraction of indene. From this behavior, it appears that there exist cross-termination reactions in the present system of styrene and indene, as was earlier suggested.[13]

In Figure 2 are shown the time-conversion curves for the copolymerizations in approximately equimolar mixtures of styrene and indene in DCE at 20°. The conversions were obtained by determining the amounts of unconsumed monomers gas chromatographically.

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(13) K. Saotome and M. Imoto, *Kobunshi Kagaku*, **15**, 373 (1958).

As is seen from the figure, the conversions of both monomers in the presence of the field are larger than those in its absence. As in the case of the homopolymerizations,[5,8] the rate of polymerization with the field is seen to be larger than that without the field. This result is in accord with the results shown in Figure 1, which were obtained by the gravimetric method.

Figure 3 is a plot of the conversion of styrene *vs.* that of indene at the same experimental condition as shown in Figure 2. It is clear that the styrene conversion in the presence of the field is larger than that in the absence of the field at a given conversion of indene. This result indicates that the styrene content of the copolymers obtained in the presence of the field is larger than that in the absence of the field.

In Figure 4 are shown copolymer compositions (solvent, DCE, 0°), which were determined by the infrared spectroscopy. The conversions of the copolymers analyzed were below 7%. Obviously the styrene contents in the copolymers in the presence of the field are larger than those without the field. This result is in accord with that shown in Figure 3, which was obtained by determining the unconsumed monomers gas chromatographically.

The degree of polymerization of the copolymers ($\bar{P}_n$) was conveniently determined viscometrically in benzene solution at 30°, using the following equation derived for polyindene[14]

$$[\eta] = 1.31 \times 10^{-4} \times \bar{M}_n^{0.75}$$

The $\bar{P}_n$ value obtained was always smaller than that ($\bar{P}_n'$) calculated by using viscosity-molecular weight equations for polystyrene. It may be said, therefore, that the correct value of the degree of polymerization of the copolymers is not smaller than $\bar{P}_n$. We further note that the $\bar{P}_n$ values of the copolymers produced from an approximately equimolar mixture in DCE at 20° were 46 and 48 at conversions of 10 and 46%, respectively. This implies that the $\bar{P}_n$ value did not depend on conversion. The $\bar{P}_n$ values of the copolymers obtained in DCE at 0° without electric field were 86, 53, and 52, at mole fractions of styrene of 0.17, 0.51, and 0.82, respectively. In the presence of an electric field of 0.33 kV/cm, the respective $\bar{P}_n$ values were 95, 54, and 54. These values show that the conversion relation (shown in Figure 3) and the copolymer composition (demonstrated in Figure 4) can be regarded as a true reflection of the propagation reaction. It is interesting to note that the $\bar{P}_n$ value slightly increased with the field at the low mole fraction of styrene. This is in line with our previous observation that the electric field increased the degrees of polymerization of polyindene[8] whereas it did not change those of polystyrene.[5]

TABLE II
SUMMARY OF MONOMER REACTIVITY RATIOS OF STYRENE (M_1) AND INDENE (M_2)
(TOTAL MONOMER CONCENTRATION, 20 VOL %)

Solvent (dielectric constant at 25°)	Temp, °C	Field strength, kV/cm	Monomer reactivity ratio r_1	r_2
NB (35)	10[a]	0	0.5	1.8
		0.33	0.7	1.7
	20[a]	0	0.3	2.7
		0.33	0.5	2.3
DCE (10)	0[b]	0	0.3 ± 0.1	3.0 ± 0.1
		0.33	0.5 ± 0.3	2.3 ± 0.3
	20[a]	0	0.3	3.3
		0.33	0.4	2.5

[a] Monomer reactivity ratios were determined by using eq 1 from time-conversion curves. [b] Monomer reactivity ratios were determined by the intersection method.

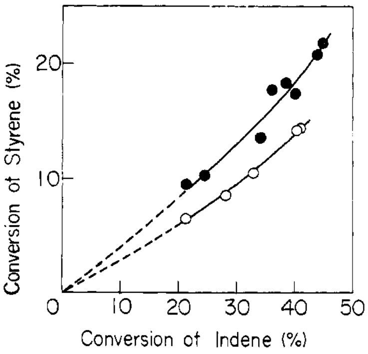

Figure 3. Conversions of monomers in the styrene-indene copolymerizations. Polymerization conditions are the same as in Figure 2: ○, 0 kV/cm; ●, 0.33 kV/cm.

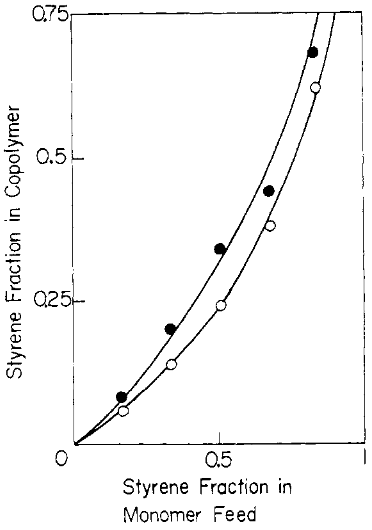

Figure 4. Copolymer composition in the sytrene-indene copolymerizations: solvent, DCE; catalyst, BF_3OEt_2; total monomer concentration, 20 vol %, 0°; ○, 0 kV/cm; ●, 0.33 kV/cm.

The monomer reactivity ratios obtained under various polymerization conditions are summarized in Table II. The monomer reactivity ratios in DCE at 0° were determined by the intersection method, plots of which are shown in Figure 5, and others were determined from time-conversion curves. In determining the monomer reactivity ratios from the time-conversion curves, a form[15] of the copolymer equation given in eq 1 was used for small conversion increments (below 10%)

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[14] A. Mizote, T. Tanaka, and T. Higashimura, *Kobunshi Kagaku*, 23, 78 (1966).

[15] This form of the equation was reported by one of the authors (I. S.) at a polymer symposium held by the High Polymer Society of Japan in 1944.

$$[M_1]/[M_2] - 1/\alpha = r_1(1/\alpha)([M_1]/[M_2]) - r_2 \quad (1)$$

where α is given by the equation

$$\alpha = (d[M_1]/d[M_2])/([M_1]/[M_2]) \quad (2)$$

As is seen from the table, r_1 values increase and/or r_2 values decrease with the application of the field; in other words, the apparent reactivity of styrene is enhanced by the field. It should be noted that the changes of the monomer reactivity ratios with rising temperature are opposite to those with the field. Thus, it is concluded that the Joule heat is not responsible for the changes of the reactivity ratios observed under the field.

TABLE III

COMPARISON OF MONOMER CONVERSION AND POLYMER YIELD[a]

Expt no.	Temp, °C	Field strength, kV/cm	Yield, g Obsd	Yield, g Calcd[b]
2M13	20	0	0.97	1.07
2M14		1.33	1.28	1.42
1M14	10	0	0.89	0.94
1M7		1.33	0.99	1.00

[a] Polymerization condition: $[St]_0/[\alpha\text{-MSt}]_0$, 1.17; total monomer concentration, 20 vol %; total volume, 10 ml; polymerization time, 70 min; $[BF_3OEt_2]_0$, 2.7×10^{-4} mol/l. [b] The yield values were calculated from the unconsumed monomer concentration determined by the gas chromatographic method.

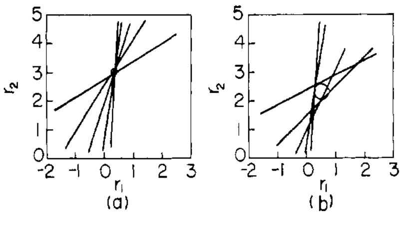

Figure 5. Determination of monomer reactivity ratios: (a) 0 kV/cm; (b) 0.33 kV/cm. Polymerization conditions are the same as in Figure 4.

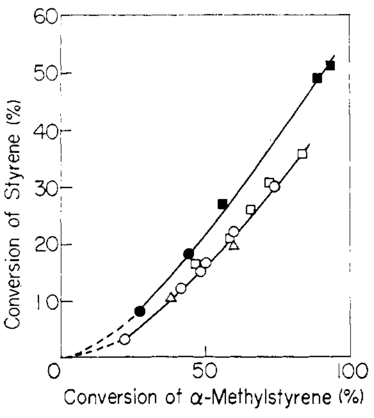

Figure 6. Conversions of monomers in the styrene–α-methylstyrene copolymerizations: solvent, DCE; catalyst, BF_3OEt_2; $[\text{styrene}]_0$, 0.89 mol/l.; $[\alpha\text{-methylstyrene}]_0$; 0.76 mol/l.; △, 5°, 0 kV/cm; ▲, 5°, 1.33 kV/cm; ○, 10°, 0 kV/cm; ●, 10°, 1.33 kV/cm; □, 20°, 0 kV/cm; ■ 20°, 1.33 kV/cm.

It is also seen that less reactive styrene can be incorporated more easily into the copolymer with increasing dielectric constant of the solvent, which is in agreement with the results reported by Mizote, *et al.*[11]

Styrene (M_1)–α-Methylstyrene (M_2). In Table III, the polymer yields determined gravimetrically are compared with the yield values calculated from the concentrations of the unconsumed monomers determined gas chromatographically. Good agreement between the two methods should be noted. It is seen that the field increases the polymer yields, that is, the rates of copolymerization.

Figure 6 is a plot of conversions of styrene *vs.* those of α-methylstyrene for the copolymerizations of an approximately equimolar mixture, which were determined gas chromatographically. The figure indicates that conversions are not largely affected by temperature. This shows that the monomer reactivity ratios are practically insensitive toward temperature between 5 and 20°. It is again obvious from Figure 6 that the conversion of styrene increases by the application of the field at a given conversion of α-methylstyrene, the styrene content in the copolymers increases with the field as in the case of the styrene–indene systems. From the time-conversion curves obtained at 20°, the monomer reactivity ratios were determined by using eq 1[16] and the following values were obtained: 0 kV/cm, $r_1 = 0.2$, $r_2 = 3.0$; 1.33 kV/cm, $r_1 = 0.2$, $r_2 = 2.5$.

Discussion

As is seen from the results mentioned in the preceding sections, the monomer reactivity ratios are changed by the application of an electric field, causing an increase in the styrene content in copolymers. Obviously the changes of the monomer reactivity ratios with the field are not due to the Joule heat.

Generally, the monomer reactivity ratios are determined almost exclusively by competition between different kinds of monomers in the propagation reactions and are independent of rates of other elementary reactions. Thus, it is most reasonable to consider that the influence of an electric field on the propagation reactions caused the observed changes of the monomer reactivity ratios.

In ionic polymerizations, gegenion may influence on the propagation reactions; that is, the dissociation of ion pairs at growing ends is considered to play an important role in the propagation reactions, or in determining the monomer reactivity ratios. The dissociation of ion pairs at growing ends may depend on solvents and catalysts. Many investigations to verify the effects of solvents and catalysts on the monomer reactivity ratios have already been done. Mizote, *et al.*,[11] have reported that the styrene content in the copolymers increases with increasing dielectric constant of the solvent in the copolymerization of styrene and indene. They explained their results in terms of preferential solvation of the growing chain ends by the

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(16) It is not accurate to use this equation when the propagation step of one of two monomers (in this case, α-methylstyrene) is reversible. However, this procedure seems to be useful for understanding of the qualitative effect of an electric field on the copolymerization.

more polar monomer (indene) in nonpolar solvent. According to Tobolsky, *et al.*,[12] in the case of styrene–α-methylstyrene copolymerization catalyzed by titanium tetrachloride, the styrene content in the copolymers has increased with increasing dielectric constant of the solvent. This result, however, is inconsistent with the concept of preferential solvation, because the solvating power of styrene is larger than that of α-methylstyrene.[17] Thus it would appear that the solvent effect should be accounted for in terms of factors other than the preferential solvation. In the present paper, we propose again that the dissociation of the growing chain ends is sensitively influenced by the solvent and outer disturbances, which in turn has effects on the monomer reactivity ratio and the rate of polymerization. It has been earlier proposed for the field-accelerating effects of the ionic polymerization rates that the field-facilitated dissociation of ion pairs at growing chain ends may be responsible, on the assumption that the propagation rate constant of free ions (k_p'') is much larger than that of ion pairs (k_p').[2–9] According to the proposed mechanism, an apparent propagation rate constant (k_{pij}^{ap}) is expressed as

$$k_{pij}^{ap} = \alpha_i k_{pij}'' + (1 - \alpha_i)k_{pij}' \qquad (3)$$

Here, the subscript of k_{pij} denotes that the terminal group of growing chain ends is a monomer i and that the attacking monomer is a monomer j, and α_i is a degree of dissociation of the ion pairs at growing ends with monomer i as the terminal. With an application of an electric field, α_i increases (the second Wien effect[10]). A monomer reactivity ratio r_i is expressed by using eq 3 as

$$r_i = \frac{k_{pii}^{ap}}{k_{pij}^{ap}} = \frac{\alpha_i k_{pii}'' + (1 - \alpha_i)k_{pii}'}{\alpha_i k_{pij}'' + (1 - \alpha_i)k_{pij}'} \qquad (4)$$

When α_i increases, r_i (expressed by eq 4) varies as follows: (a) if $k_{pij}''/k_{pii}'' < k_{pij}'/k_{pii}'$, r_i increases; (b) if $k_{pij}''/k_{pii}'' > k_{pij}'/k_{pii}'$, r_i decreases.

The experimental findings show that r_1 increased and/or r_2 decreased with an application of an electric field. Since it would be well that both α_1 and α_2 increase with the field, the conditions a and b can be expressed as follows: (a′) r_1 increases when $k_{p12}'/k_{p11}' > k_{p12}''/k_{p11}''$ (>1); (b′) r_2 decreases when $k_{p21}'/k_{p22}' < k_{p21}''/k_{p22}''$ (<1). The inequality with respect to the numeral 1 indicates that the monomer reactivity of the monomer 2 is greater than that of the monomer 1 regardless of the type of growing chain ends. The condition a′ and b′ can simply be expressed as

$$\frac{k_{pi2}'}{k_{pi1}'} > \frac{k_{pi2}''}{k_{pi1}''} \ (>1) \qquad (5)$$

Equation 5 implies that the selectivity of growing ends for more reactive monomer (M_2) rather than less reactive monomer (M_1) becomes smaller as the reactivity of growing ends increases, as is generally accepted,[18] because free ions are generally considered to be more reactive than ion pairs.[19] This explanation seems to agree with the concept that the monomer reactivity ratios become unity with increasing reactivity of growing ends.[12]

The effects of solvent and catalyst on the reactivity ratios mentioned in the previous sections and reported by Mizote, *et al.*,[11] or Tobolsky, *et al.*,[12] may also be accounted for with eq 5. As the dielectric constant of solvent and the activity of catalyst increase, the dissociation constant of ion pairs at growing ends (that is, the degree of dissociation) increases. As mentioned above, an increase in the degree of dissociation of ion pairs at growing ends with solvent and catalyst can cause similar changes in r_i as in the case of the field application, as far as k_{pii}''/k_{pii}' and k_{pij}''/k_{pij}' vary in the same direction with changing solvent and catalyst and specific ion–solvent interactions (such as the preferential solvation) are absent.

In the styrene (M_1)–indene (M_2) systems r_1 increased with the field. This result is considered to show that the dissociation of ion pairs at the growing ends, terminal group of which is from styrene, is enhanced by the field. It has been reported that the field has no effect on the homopolymerization of styrene by BF_3OEt_2 in nitrobenzene.[5] The result of the homopolymerization seems to be apparently inconsistent with that of the copolymerization, but may be explained as follows: as described in the previous paper,[8] the field effect on the rate of polymerization decreases as k_p''/k_p' becomes smaller, when an increase of the degree of dissociation with the field is given. So, one of the simplest explanations of the effect on the hompolymerization of styrene with BF_3OEt_2 in nitrobenzene is that k_p''/k_p' may be considered to be fairly small. On the other hand, the field increases the rate of homopolymerization of indene by BF_3OEt_2 in nitrobenzene.[8,20] The difference in the effects of the field on the two monomer systems seems to indicate that the following relation (eq 6) holds for styrene (M_1)–indene (M_2).

$$\frac{k_{p11}''}{k_{p11}'} < \frac{k_{p22}''}{k_{p22}'} \qquad (6)$$

Combining eq 5 and 6, we obtain the following relation

$$\frac{k_{p21}''}{k_{p21}'} > \frac{k_{p22}''}{k_{p22}'} > \frac{k_{p11}''}{k_{p11}'} > \frac{k_{p12}''}{k_{p12}'} \ (>1) \qquad (7)$$

Generally, more reactive monomer forms less reactive growing end.[21] Therefore, eq 7 implies that the ratio of the reactivities of free ions and of ion pairs (k_p''/k_p') becomes smaller as growing ends become more reactive

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[17] N. Kano, K. Ikeda, A. Gotoh, T. Higashimura, and S. Okamura, *Makromol. Chem.*, **86**, 200 (1965).

[18] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 162.

[19] For example, D. N. Battacharrya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965); H. Hostalka and G. V. Schulz, *Polym. Lett.*, **3**, 175, 1043 (1965).

[20] The specific role of nitrobenzene on styrene–BF_3OEt_2 may be excluded in the light of the field effect on the indene–BF_3OEt_2–nitrobenzene. Furthermore, by gas chromatography, we could find no products which might be produced electrolytically from nitrobenzene under the experimental conditions described in the present paper.

[21] For example, T. Higashimura, Y. Imanishi, T. Yonezawa, K. Fukui, and S. Okamura, *Polymer*, **3**, 167 (1962).

($k_{p12}''/k_{p12}' < k_{p22}''/k_{p22}'$).[22] Furthermore this is also the case as attacking monomers become more reactive ($k_{p12}''/k_{p12}' < k_{p11}''/k_{p11}'$).

In summary, we state that the rate of the copolymerization can be increased by the field and the increase is due to the field-facilitated dissociation of growing chain ends. Furthermore, the monomer reactivity ratios can be changed; the less reactive monomer can be more easily incorporated into the copolymers in the presence of the field than in its absence. This finding is also explainable in terms of the shift of the dissociation state by the field.

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(22) It cannot presently be concluded whether this interpretation is of a wide validity. Some data available now on living anionic polymerizations do not agree with this interpretation. However, the values of the rate constants reported for the living systems vary from author to author, evidently on the basis of the experimental difficulty.

The Diffusion of Radioactively Tagged *n*-Hexadecane and *n*-Dodecane through Rubbery Polymers. Effects of Temperature, Cross-Linking, and Chemical Structure

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ABSTRACT: The diffusion of *n*-hexadecane (cetane) and *n*-dodecane, tagged in the terminal position by C^{14}, has been studied in trace amounts ($<0.2\%$) by the thin smear method of Moore and Ferry in the following rubbery polymers: natural rubber, styrene–butadiene random copolymer (23.5% styrene by weight), several styrene–butadiene block copolymers, polyisobutylene, polydimethylsiloxane, and twelve polybutadienes with different microstructures, including 97% *cis*, 91.5% vinyl, 67% *trans*, and approximately half-*cis*, half-*trans*. The samples included uncross-linked polymers and samples cross-linked by dicumyl peroxide, sulfur, tetramethylthiuram disulfide, and (for polydimethylsiloxane) high-energy electrons. The diffusion coefficients (D) for the two penetrants were approximately in inverse proportion to their molecular lengths in several polymers. The diffusion of cetane showed the following behavior. (a) The apparent activation energy for diffusion at 25°, from the temperature dependence of D, was close to that for viscoelastic relaxation in most polymers but in natural rubber was smaller. (b) At 25°, D in different polymers covered a 2600-fold range from polydimethylsiloxane ($\log D = -5.80$, units square centimeters per second) to polyisobutylene ($\log D = -9.22$). With two exceptions, it followed the equation $\log D = A_d - (1/2.303f)$, where f is the fractional free volume derived from the temperature dependence of viscoelastic relaxation. For the polybutadienes, $\log D$ ranged from -6.34 (high *cis*) to -9.03 (high vinyl); it decreased slightly with increasing *trans* content at constant low vinyl. (c) Increasing cross-linking generally diminished D slightly. For natural rubber cross-linked by dicumyl peroxide, the change could be attributed to a decrease in free volume as proposed by Mason. (d) In styrene–butadiene block copolymers, D decreased with increasing styrene content but was larger than in a random copolymer with the same composition. The translational friction coefficient of cetane, ζ_1, calculated as kT/D, was similar in magnitude for most polymers to the monomeric friction coefficient ζ_0 calculated by matching viscoelastic data to the Rouse theory. A simple diffusion measurement may therefore serve to estimate the friction coefficient and hence the time and frequency scale of viscoelastic properties.

Diffusion of small molecules in concentrated polymer solutions and in essentially undiluted rubbery polymers has been studied to provide information about local segmental motions of the macromolecules.[1-9] The interpretation is simplest if the experiment corresponds to self-diffusion, as in the application of spin–echo nuclear magnetic resonance[4,7] or the use of a radioactively tagged solvent in a solution of constant composition.[1,5,6] An alternative is to use a radioactively tagged penetrant in trace amounts, so that its concentration remains very small during the course of the diffusion. This method (the "thin smear" method of Moore and Ferry[5]) has been employed in the present study to determine the diffusion coefficient of *n*-hexadecane (cetane) in a wide variety of rubbery polymers of different chemical structures and different degrees of cross-linking, together with some more fragmentary data on *n*-dodecane. The dependence of diffusion coefficient on temperature, cross-linking, and chemical structure is interpreted in terms of free volume, and the friction coefficients for translational motion of the penetrant molecules are compared with those of the polymer chains themselves derived from viscoelastic measurements.

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