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Polymerization Thermodynamics of *N*-Phenylmaleimide and Its Copolymerizations with Styrene and Phenyl Vinyl Sulfide

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ABSTRACT: Equilibrium polymerization of *N*-phenylmaleimide (PMI) was studied in *N*,*N*-dimethylformamide (DMF) with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator to determine the ceiling temperatures and the equilibrium monomer concentrations. The values for enthalpy (ΔH) and entropy changes (ΔS) of the polymerization were found to be $\Delta H = -36.9$ kJ/mol and $\Delta S = -86.1$ J/K·mol, respectively. Its copolymerization with styrene (St) took place in an alternating fashion irrespective of PMI monomer concentration. On the other hand, its copolymerization with phenyl vinyl sulfide (PVS) was found to change in copolymerization fashion from random to alternating depending upon the PMI monomer concentration. The difference in the copolymerization behavior between PMI–St and PMI–PVS systems was reasonably explained in terms of our proposed mechanism of an alternating copolymerization and the order in general reactivity: St > PMI > PVS.

Introduction

In general it is said that 1,1-disubstituted ethylenes are more reactive in their polymerization than 1-substituted ethylenes, while 1,2-disubstituted ethylenes are less reactive probably owing to steric interference in their substituents to lose homopolymerizability[1] except for compounds such as vinylene carbonate,[2] fumarates,[3] and maleimides.[4] As to maleimides, the homopolymer of *N*-phenylmaleimide (PMI) with high molecular weight was obtained in *N*,*N*-dimethylformamide (DMF) with a radical initiator such as 2,2′-azobis(isobutyronitrile) (AIBN).[5] Its copolymerizations with vinyl acetate[6] and styrene (St)[7] were carried out in benzene at 60 °C to obtain monomer reactivity ratios, $r_1 = 0.66$, $r_2 = 0.02$ and $r_1 = 0.13$, $r_2 = 0.05$, respectively, where M_1 refers to PMI. The Q and e values of PMI were evaluated as $Q = 0.74$ and $e = 1.75$ from the monomer reactivity ratios for the former system. Moreover, a living type of anionic polymerization of PMI took place with alkali-metal *tert*-butoxide in THF.[8]

Polymerization kinetics of PMI have not been studied in detail and its thermodynamics were not reported in any literature.

In this paper polymerization kinetics of PMI in DMF with AIBN as an initiator was investigated to determine thermodynamic parameters for the polymerization of PMI. Furthermore, radical copolymerizations of PMI with St and phenyl vinyl sulfide (PVS) were carried out in DMF under two PMI monomer concentrations, above and below its equilibrium monomer concentration, in order to look into the influence of PMI monomer concentration on copolymerization behavior. The copolymerization behaviors gave additional support to the mechanism of an alternating copolymerization as proposed previously.[9]

Experimental Section

Materials. *N*-Phenylmaleimide (PMI) was recrystallized from hexane and dried under reduced pressure. Phenyl vinyl sulfide (PVS) was prepared according to the method of Hopkin and Fuchs.[10] Styrene (St) was washed with 2% aqueous sodium hydroxide solution and water, dried over barium oxide, stirred with calcium hydride at room temperature for 6 h, and then distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure. Benzophenone was recrystallized from methanol.

Determination of Polymerization Rate. Given amounts of PMI, DMF as a solvent, AIBN as an initiator, and benzophenone as a reference compound for HPLC analysis were placed in an ampule, which was degassed completely by the freeze–thaw method (repeated three times) and sealed. The ampule was set in a bath thermostated at 40, 50, 60, or 70 °C for the time of polymerization and then opened. The reaction mixture was poured into an excess of a mixture of acetonitrile and water (7/3 by volume) to give a turbid mixture, which was filtered with a membrane filter (Fluoropore Type FP-100) to remove the polymer. The filtrate was subjected to HPLC analysis, which was performed on Toso CCPE and UV-8011 instruments (column, ODS-80 T_M; eluent, $CH_3CN/H_2O/AcOH/NEt_3$ (70/30/0.2/0.2); flow rate, 0.8 mL/min; UV detector, 245 nm) to determine the concentration of unreacted PMI from the relative peak area ratio of PMI to benzophenone as a reference compound.

Hydrolysis of PMI in Aqueous Acetonitrile Solution. A 1-mL aliquot of 4.0×10^{-2} M PMI solution in 70% aqueous acetonitrile and 1 mL of 4.0×10^{-4} M benzophenone solution in 70% aqueous acetonitrile were added to 100 mL of 70% aqueous acetonitrile. The resulting solution was kept at 25 °C and aliquots were subjected to HPLC at regular intervals. The concentration of maleanilic acid, as a hydrolysis product of PMI, was determined from the relative peak area ratio of maleanilic acid to benzophenone.

Copolymerization Procedure. Given amounts of PMI, St, or PVS as a comonomer, DMF as a solvent, and AIBN as an initiator were placed in an ampule, which was degassed completely by the freeze–thaw method (repeated three times) and sealed. The ampule was placed in a bath thermostated at 50 or 60 °C for the time of polymerization and then opened. The reaction mixture was poured into an excess of methanol to precipitate the copolymer. For purification, the copolymer obtained was dissolved in a small amount of dichloromethane and the resulting solution was poured into an excess mixture of hexane and isopropyl ether (1/2 by volume) to precipitate the copolymer again. This procedure was twice repeated. The copolymer was dried under reduced pressure to constant weight.

Copolymer composition was established by elemental analysis. Number-average molecular weight ($\bar{M}_n$) of the copolymer was determined by gel permeation chromatography (GPC) using standard polystyrenes as references and tetrahydrofuran (THF) as an eluent without further correction.

Results and Discussion

Equilibrium Polymerization of PMI. At the beginning, the measurement of polymerization rate (R_p) of PMI in DMF was carried out by a gravimetric method. After

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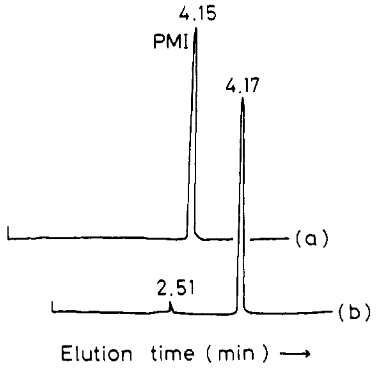

Figure 1. HPLC chromatograms of PMI in 70% aqueous acetonitrile standing for (a) 5 min and (b) 2 h.

given times of polymerization the reaction mixture were poured into an excess of methanol to deposit polymeric materials, which were washed repeatedly with methanol and dried under reduced pressure until of constant weight. However, the data obtained were not reproducible because of the low extent of polymerization due to the very small amounts of polymeric materials.

Alternatively, R_p was determined by a method using HPLC as described in the Experimental Section. The requirements for an internal reference compound for this method were as follows: (1) it had to be unreactive to free-radical species, (2) it had to be soluble in the polymerization medium, (3) it could not be volatile, (4) it had to have a different retention time from that of PMI, and (5) it had to have as large an extinction coefficient as possible to allow the amount of it to be less compared to that of PMI. It was found that benzophenone is the most preferred among several candidates such as dioctyl phthalate, diethyl phthalate, *m*-dicyanobenzene, diphenylcarbonate, and methyl phenylacetate.

In order to look at the hydrolysis of PMI in 70% aqueous acetonitrile as HPLC eluent, 4.0×10^{-4} M PMI in the solvent was kept at 25 °C for 5 min and for 2 h and these two samples were subjected to HPLC analysis. The 5-min sample chromatogram exhibited only one peak at a retention time of 4.15 min due to PMI, but that of the 2-h sample had an additional small peak at a retention time of 2.51 min, as shown in Figure 1. Authentic maleanilic acid[11] obtained in the reaction of maleic anhydride with aniline was found to have the same retention time in HPLC analysis as that of the additional peak. It was concluded therefore that PMI is subject to hydrolytic reaction to give maleanilic acid when it is allowed to stand in 70% aqueous acetonitrile for a long time. The rate of the hydrolytic reaction of PMI in the solvent at 25 °C was determined by a method similar to that for determining the polymerization rate of PMI, using benzophenone as an internal reference compound. The relationship of ln ([PMI]/[PMI]$_0$) versus time as shown in Figure 2 gave a pseudomonomolecular reaction rate constant of 1.0×10^{-3} h^{-1}, meaning that the hydrolytic reaction of PMI in the solvent at the temperature of the HPLC measurement takes place at so slow rate as to be negligible.

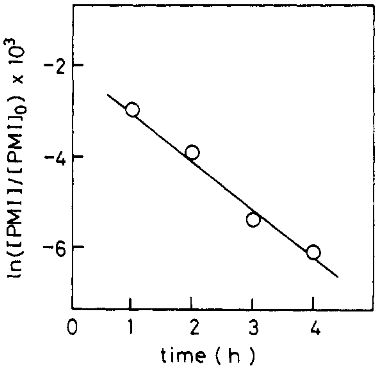

Figure 2. Plot of ln ([PMI]/[PMI]$_0$) versus time of hydrolysis of PMI in 70% aqueous acetonitrile at 25 °C. [PMI] = 4.0×10^{-4} mol/L.

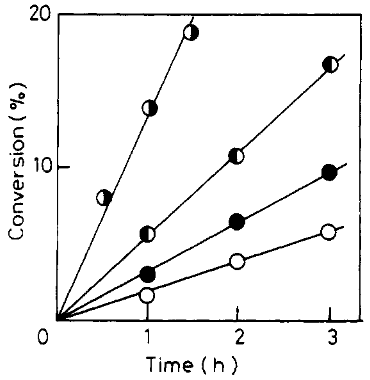

Figure 3. Time–conversion curves for the polymerization of PMI at various temperatures. Key: 40 (○), 50 (●), 60 (◐), and 70 (◑) °C. [PMI] = 0.43 mol/L; [AIBN] = 6.7 10^{-3} mol/L.

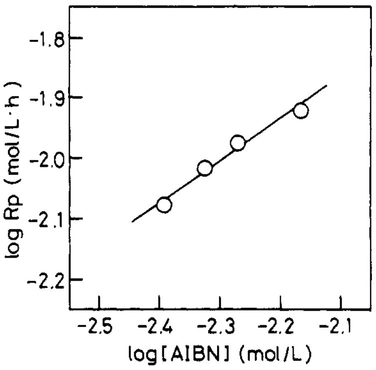

Figure 4. Relationship of log R_p versus log [AIBN] for the polymerization of PMI at 60 °C. [PMI] = 0.32 mol/L.

Time–conversion curves for the polymerizations of PMI at 40, 50, 60, and 70 °C are shown in Figure 3. It was found that the conversions increased linearly with time at each temperature of polymerization. A log–log plot of R_p versus concentration of AIBN gave a straight line with a slope of 0.73, as shown in Figure 4. This value for the dependence of R_p on initiator is close to the corresponding value of 0.8 reported by Yamada et al.,[5] who explained the high dependence on initiator above a slope of 0.5 in terms of the delay of bimolecular termination due to occlusion of the PMI polymer radicals in the polymer because poly(PMI) is sparingly soluble in DMF. Although this polymerization of PMI in DMF was carried out at a much lower monomer concentration, about one-seventh of that for Yamada's experiment,[5] and it took place in a transparent liquid state at low conversion stage, the deviation from the square-root rule for dependence of R_p on initiator was observed as well. At the moment there is no good explanation other than those of Yamada et al.

A log-log plot of R_p versus monomer concentration ([PMI]) at 60 °C is shown in Figure 5. In the range of monomer concentrations above 0.16 mol/L, this plot was found to be a straight line with a slope of unity, whereas in the range of monomer concentrations below 0.16 mol/L, it greatly deviated from the straight line, the less the concentration the steeper the slope. In the monomer concentration region above 0.16 mol/L, a first-order dependence of R_p on monomer held as well as conventional radical polymerization, while in the low monomer con-

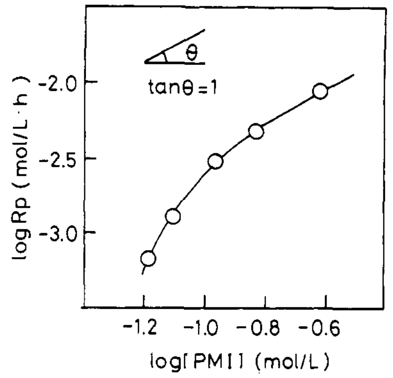

Figure 5. Relationship of log R_p versus log [PMI] for the polymerization of PMI at 60 °C. [AIBN] = 6.7 × 10^{-3} mol/L.

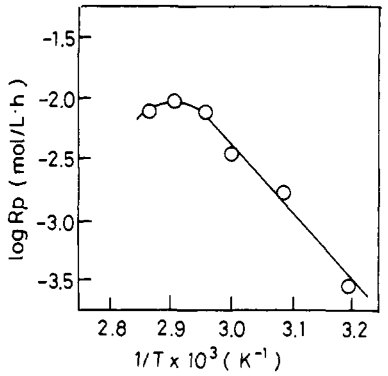

Figure 6. Arrhenius plot for the polymerization of PMI. [PMI] = 0.089 mol/L.

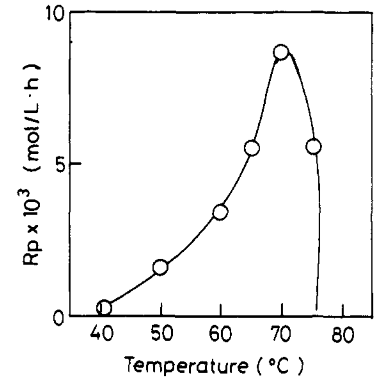

Figure 7. Plot of R_p versus T for the polymerization of PMI. [PMI] = 0.089 mol/L.

centration region below 0.16 mol/L, it no longer held well and the higher order dependence of R_p on monomer was observed.

A so-called Arrhenius plot of log R_p versus the reciprocal of absolute temperature of polymerization ($1/T$) at a monomer concentration of 0.089 mol/L gave a straight line in the range of temperatures below 65 °C, as shown in Figure 6. Its slope allowed us to estimate the activation energy of polymerization to be 93.0 kJ/mol. On the other hand, a large deviation from the straight line was observed in the temperature range above 65 °C. Eventually, R_p decreased with temperature in the temperature range above 70 °C. The relationship of R_p versus polymerization temperature at a monomer concentration of 0.089 mol/L is shown in Figure 7. R_p was found to increase with temperature in a temperature region below 70 °C, whereas it decreased sharply with temperature above 70 °C, and extrapolation of the plot to the rate of zero gave a ceiling temperature of about 76 °C, above which no polymerization takes place. Both polymerization behaviors suggested a great contribution of depolymerization to polymerization of PMI at low monomer concentration and at high temperature. It was concluded therefore that polymerization of PMI is a typical equilibrium polymerization.

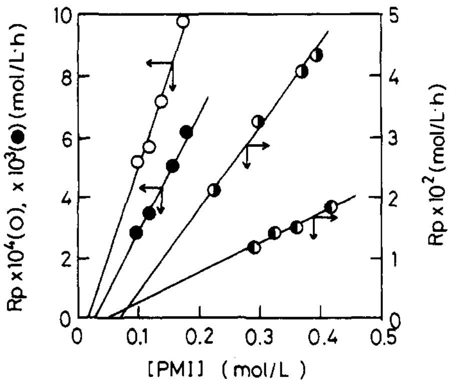

Figure 8. Plots of R_p versus [PMI] for the polymerization of PMI at various temperatures. Key: 40 (○), 50 (●), 60 (◐), and 70 (◑) °C. [AIBN] = 6.7 × 10^{-3} mol/L.

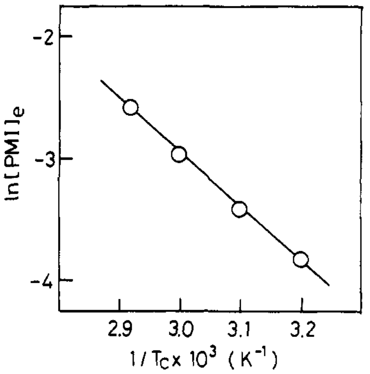

Figure 9. Plot of ln $[PMI]_e$ versus $1/T_c$ for the polymerization of PMI.

Table I
Equilibrium Monomer Concentration of PMI

T, °C	$10^3\ 1/T$	$10^2\ [PMI]_e$, mol/L	T, °C	$10^3\ 1/T$	$10^2\ [PMI]_e$, mol/L
40	3.19	2.2	60	3.00	5.2
50	3.10	3.4	70	2.92	7.7

Equilibrium monomer concentration was determined according to the method of Vofsi and Tobolsky.[12] Polymerization rates of PMI were plotted against monomer concentration at 40, 50, 60, and 70 °C to give straight lines at the respective polymerization temperature as shown in Figure 8, where extrapolation of the plots to the rate of zero allowed us to estimate values for an equilibrium monomer concentration ($[PMI]_e$) at the respective polymerization temperatures, as summarized in Table I.

The relationship between $[PMI]_e$ and a reciprocal of ceiling temperature ($1/T_c$) was given by the equation[13]

$$\ln [PMI]_e = \Delta H/RT_c - \Delta S/R \qquad (1)$$

where ΔH and ΔS are an enthalpy change and an entropy change for polymerization, respectively, and R is the gas constant. It was found, from the linear relationship between ln $[PMI]_e$ and $1/T_c$ as shown in Figure 9, that the values of ΔH and ΔS are −36.9 kJ/mol and −86.1 J/K·mol, respectively. log–log plots of R_p versus effective monomer concentration ([PMI] − $[PMI]_e$) at 40, 50, 60, and 70 °C gave straight lines with slopes of unity for the whole monomer concentration range, as shown in Figure 10. Therefore, the polymerization rate of PMI was given by

Table II
Copolymerizations of PMI with St in DMF at 50 °C

	monomer feed						copolymer compn				
							anal, %				
run	PMI (M_1), mg	St (M_2), mg	PMI, mol %	DMF, mL	time, h	conv, %	H	C	N	PMI,[a] mol %	$\bar{M}_n/10^5$ [b]
					[PMI] = 0.17 mol/L[c]						
1	88.6	479.3	10.0	2.3	0.3	1.2	5.27	75.30	5.07	50.3	4.5
2	89.1	216.6	19.9	2.6	0.3	1.0	5.07	75.41	5.21	52.1	3.2
3	87.8	128.9	29.1	2.8	1	4.0	5.45	75.46	5.41	54.8	2.3
4	85.3	84.0	37.9	2.9	1	2.5	5.34	75.27	5.52	56.4	2.5
5	88.2	54.1	49.5	2.9	1	7.2	5.44	76.72	5.67	58.6	2.1
6	89.5	36.3	59.7	2.9	2.5	9.0	5.84	76.93	5.79	60.2	1.5
					[PMI] = 0.03 mol/L[d]						
7	11.9	63.7	10.1	2.1	2.5	5.4	5.27	75.84	4.99	49.2	0.65
8	11.6	27.9	20.0	2.1	5	13.6	5.71	76.09	5.14	51.2	0.70
9	11.6	16.1	30.2	2.1	6	15.0	5.60	75.68	5.58	57.2	0.23
10	47.9	43.7	39.7	9.5	4	11.1	5.49	76.50	5.52	57.2	0.08
11	48.3	29.4	49.7	9.5	7	12.2	5.41	76.05	5.62	57.8	0.10
12	59.9	25.0	59.0	11.5	26	4.3	5.35	75.81	5.67	58.6	0.06

[a] Calculated from N%. [b] Determined by GPC. [c] AIBN, 1 mg. [d] AIBN, 4 mg.

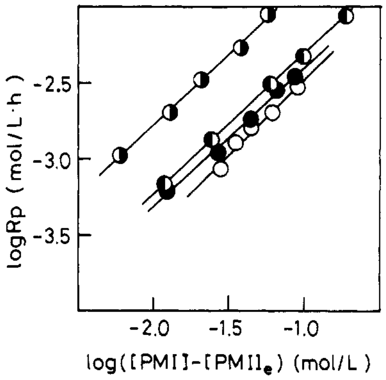

Figure 10. log-log plots of R_p versus [PMI] - $[PMI]_e$ for the polymerization of PMI. [AIBN] = 6.7 × 10^{-3} mol/L.

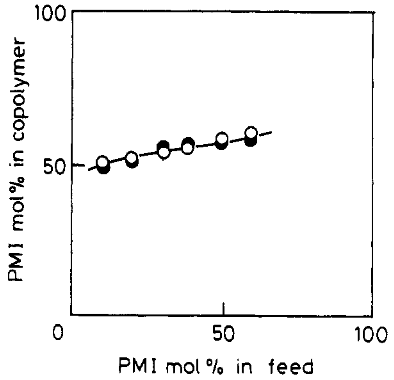

Figure 11. Copolymerization composition curves of PMI with St at 50 °C. Key: (○) [PMI] = 0.17 mol/L; (●) [PMI] = 0.03 mol/L.

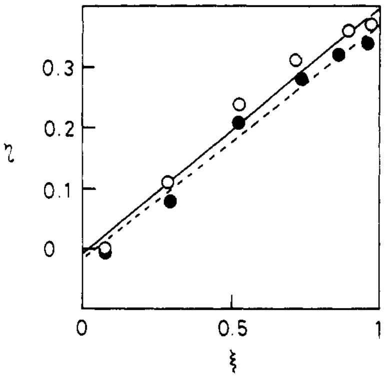

Figure 12. Kelen–Tüdős plots of the copolymerization of PMI with St at 50 °C. Key: (○) [PMI] = 0.17 mol/L; (●) [PMI] = 0.03 mol/L.

the equation

$$R_p = k[\text{AIBN}]^{0.73}([\text{PMI}] - [\text{PMI}]_e)^{1.0} \qquad (2)$$

where k is an apparent rate constant of polymerization. It was concluded, therefore, that polymerization of PMI is conventionally explained in terms of elementary reaction processes such as initiation, propagation, and termination plus depolymerization except for the square-root rule for dependence of R_p on initiator.

Copolymerization of PMI with St. Copolymerization of PMI (M_1) with St (M_2) were carried out in DMF at 50 °C for two PMI monomer concentrations, 0.17 and 0.03 mol/L. The former monomer concentration is higher than its equilibrium monomer concentration at 50 °C ($[PMI]_e$ = 0.034 mol/L), while the latter is a little bit lower. The results are summarized in Table II, and the composition diagrams are shown in Figure 11. The results were successfully treated according to the cross-section[14] and the Kelen–Tüdős[15] methods to obtain the monomer reactivity ratios (MRRs). The Kelen–Tüdős plots for both systems gave straight lines as shown in Figure 12, indicating that the copolymerization conform to the conventional terminal model equations of Mayo[14] and Lewis and of Alfrey and Goldfinger.[16] The MRRs obtained were r_1 = 0.36 ± 0.15, r_2 = 0.01 ± 0.01 at a monomer concentration of 0.17 mol/L and r_1 = 0.34 ± 0.15, r_2 = 0.01 ± 0.01 at a monomer concentration of 0.03 mol/L. Both systems gave similar MRRs with a fairly high tendency of alternation.

Copolymerization of PMI with PVS. Phenyl vinyl sulfide (PVS) (Q = 0.34, e = −1.4) was selected from the table of Young[17] as a preferable comonomer, which would be as polar as St and also less conjugative (lower in general reactivity) than St. The copolymerizations of PMI (M_1) with PVS (M_2) were carried out in DMF at 60 °C under two PMI monomer concentrations, 0.26 and 0.05 mol/L, respectively above and a little bit below its equilibrium monomer concentration of 0.052 mol/L at 60 °C. The results of the copolymerizations are summarized in Table III, and their composition diagrams are shown in Figure 13, where it was observed that the copolymerization at the high PMI monomer concentration took place in a random fashion while that at the low PMI monomer concentration did so in an alternating fashion. The results of the

Table III
Copolymerization of PMI with PVS in DMF at 60 °C

	monomer feed						copolymer compn				
							anal, %				
run	PMI (M_1), mg	PVS (M_2), mg	PMI, mol %	DMF, mL	time, h	conv, %	H	C	N	PMI,[a] mol %	$\bar{M}_n/10^4$ [b]
					[PMI] = 0.26 mol/L[c]						
1	35.2	244.3	10.2	0.6	0.2	5.1	4.12	67.50	3.46	31.0	18
2	35.0	108.0	20.3	0.7	0.2	2.9	4.76	68.41	4.66	45.0	13
3	69.6	126.9	30.1	1.3	0.2	3.7	4.63	67.34	4.97	49.0	13
4	70.7	81.4	40.6	1.4	1	5.1	4.53	67.64	5.38	54.5	11
5	103.4	54.0	60.1	2.1	1.5	6.0	4.30	66.78	6.02	63.6	4.5
6	173.2	58.7	69.9	3.6	1.5	5.8	4.29	67.58	6.58	72.4	4.5
7	174.8	34.9	79.8	3.6	1.5	8.5	4.13	66.77	6.96	78.7	4.0
					[PMI] = 0.05 mol/L[d]						
8	36.0	226.1	11.1	4.0	2	12.7	4.51	68.92	4.77	46.4	6.5
9	53.8	164.1	20.5	5.0	2	12.9	4.94	69.90	5.16	51.4	4.3
10	104.4	123.9	39.9	11.9	22	10.9	4.88	69.32	5.46	55.6	3.5
11	105.4	81.7	50.3	12.0	22	6.7	4.51	68.92	5.36	54.1	3.2
12	104.6	54.3	60.2	12.0	22	4.7	4.44	68.84	5.59	57.4	3.0
13	103.5	34.4	70.3	12.0	72	4.1	4.37	67.89	5.70	59.0	3.2

[a] Calculated from N%. [b] Determined by GPC. [c] AIBN, 2 mg. [d] AIBN, 7 mg.

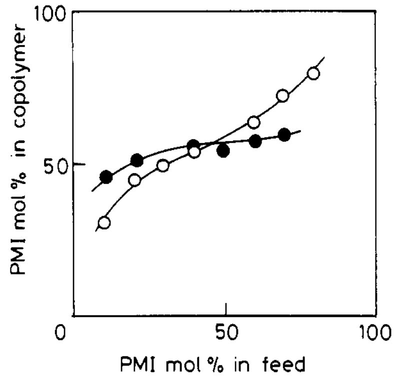

Figure 13. Copolymerization composition curves of PMI with PVS at 60 °C. Key: (○) [PMI] = 0.26 mol/L; (●) [PMI] = 0.05 mol/L.

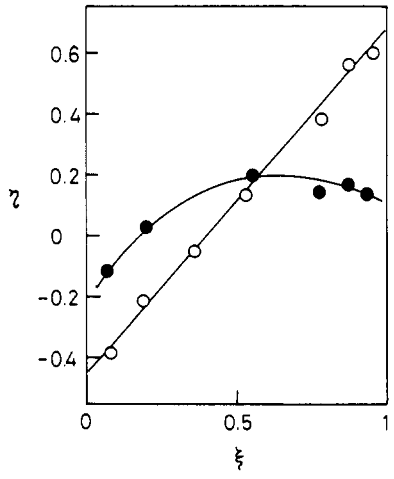

Figure 14. Kelen–Tüdös plots of the copolymerization of PMI with PVS at 60 °C. Key: (○) [PMI] = 0.26 mol/L; (●) [PMI] = 0.05 mol/L.

copolymerizations were analyzed according to the Kelen–Tüdös method, as shown in Figure 14. Copolymerization at the high monomer concentration gave a plot of a straight line, indicating that it obeys the copolymerization composition equation of the terminal model to allow us to calculate MRRs as $r_1 = 0.69 \pm 0.20$ and $r_2 = 0.07 \pm 0.04$. On the other hand, that of the low monomer concentration gave a curve of a convex shape instead of a straight line, indicating that it no longer obeys the equation of the terminal model. From a cross-section method MRRs were roughly obtained to be $r_1 = 0.2 \pm 0.5$ and $r_2 = 0.03 \pm 0.1$, carrying unavoidable, large uncertainty owing to the large deviation from the copolymerization composition equation of the terminal model.

When the PMI monomer concentration was changed from the high to the low, it was found that r_1 values remarkably decreased to almost one-third but r_2 values remained almost constant. Conceivably, the decrease in r_1 values let the copolymerization fashion change from random to alternating.

Alfrey and Price's Q and e values for PMI were calculated from MRRs of the copolymerization of PMI with PVS under the high PMI monomer concentration (0.26 mol/L) to be $Q = 0.43$ and $e = 0.34$. The Q and e values for PMI appear to be in a fairly good agreement with those from the copolymerization of PMI with vinyl acetate because the product of MRRs, $r_1 \times r_2$, (0.048) for the copolymerization of PMI with PVS under the high PMI monomer concentration is not as small as the corresponding one (0.013) for the copolymerization of PMI with vinyl acetate.

Change of Copolymerization Fashion and Mechanism of Alternating Copolymerization. Regardless of PMI monomer concentration with respect to its equilibrium monomer concentration, the copolymerization of PMI with St always took place in almost alternating fashion. On the other hand, the copolymerization fashion of PMI with PVS was found to be seriously dependent upon the PMI monomer concentration. In the case where PMI monomer concentration was above its equilibrium monomer concentration, it took place in a random fashion, whereas when PMI monomer concentration was below that, it took place in an alternating fashion. This difference between the copolymerization of PMI with St and that of PMI with PVS can be explained in terms of a general reactivity between PMI and St or PVS.

If PMI were much higher in general reactivity than a comonomer, it would add to the polymer radical with a terminal PMI unit at much higher rate than the comonomer, depending upon a combination of a general reactivity and polarity factor in the case of a PMI monomer concentration above its equilibrium monomer concentration, but PMI would not have to add to it in the case of a PMI monomer concentration below its equilibrium one. This change would let the copolymerization fashion change with PMI monomer concentration with respect to its equilibrium monomer concentration, as in the case of the copolymerization of PMI with PVS.

If PMI were lower in general reactivity than a comonomer, PMI would not be able to add to the polymer radical with a terminal PMI unit at a rate comparable to the comonomer even in the case where the PMI monomer concentration was above or below its equilibrium monomer concentration. After all, only a small change of the copolymerization fashion with a change of the PMI monomer concentration with respect to its equilibrium monomer concentration would have to be observed. This change is the case of the copolymerization of PMI with St.

Under the condition that St and PVS have to be similarly electron donating in polarity, it can be mentioned therefore that PMI is less electron donating in general reactivity than St but higher than PVS. In other words, the monomer pair of PMI and PVS allows us to observe the change of copolymerization fashion with PMI monomer concentration with respect to its equilibrium monomer concentration.

Previously, the same change in copolymerization fashion was found in the copolymerizations of equilibrium-polymerizable, electron-accepting quinodimethanes such as 7,8-dibenzoyl-7,8-dicyano-1,4-quinodimethane (BzCQ) and 7,8-bis(butoxycarbonyl)-7,8-dicyano-1,4-quinodimethane (BCQ) with St when the monomer concentration of the quinodimethane monomer was changed depending upon the equilibrium monomer concentration. Moreover, it was pointed out in the studies of alternating terpolymerizations[18,19] that the monomer reactivity in alternating copolymerization is controlled exclusively by its polar effect, different from that of a conventional random copolymerization, which is supposed to be controlled by a balanced combination of general reactivity and polar effects. Also, it was found, in the study of a linear free energy relationship in the copolymerization of BzCQ and BCQ with para-substituted styrenes,[20] that the nature of the cross-propagation step in which styrenes add to the polymer radical with a terminal quinodimethane unit changes from a balanced combination of general reactivity and polar effects to an unbalanced polar lowered effect when the quinodimethane monomer concentration is lowered close to its equilibrium monomer concentration. From those findings a new concept on the mechanism of an alternating copolymerization was proposed:[9] In the copolymerization of the more reactive, equilibrium-polymerizable, electron-accepting monomer (Q) with electron-donating St, there had to be three predominant propagations to consider:

$$\mathrm{Q} + \mathrm{St} \xrightarrow{k_{12}} \mathrm{St} \tag{3}$$

$$\mathrm{Q} + \mathrm{Q} \xrightarrow{k_{11}} \mathrm{Q} \tag{4}$$

$$\mathrm{St} + \mathrm{Q} \xrightarrow{k_{21}} \mathrm{Q} \tag{5}$$

When Q loses homopolymerizability due to the participation of depolymerization, the polymer radical with the terminal Q unit, which is considered as very stable and unreactive, barely undergoes cross propagation with St with great assistance from strong polar (charge-transfer) interaction between the two reacting species. This step is considered to take place at a very slow rate in view of reaction energetic theory and to be the rate-determining process of the whole alternating copolymerization. The polymer radical with a terminal St unit reacts more readily with Q in view of general reactivity and polar effects.

In conclusion, in the case of the copolymerization of PMI and St, where St has a higher general reactivity than PMI, its fashion has not been changed with PMI monomer concentration with respect to its equilibrium monomer concentration. It is conceivable that the cross propagations of eqs 3 and 4 take place much more readily under the strong support of polar effects between PMI and St. Conversely, in the case of the copolymerization of PMI and PVS, where PMI has a higher general reactivity than PVS, it is obvious that the copolymerization fashion was changed from random to alternating when the PMI monomer concentration was changed from above to below that of the equilibrium monomer concentration. This change in the copolymerization fashion and the difference in the change between the two cases can be explained in terms of the new concept[9] of the mechanism of alternating copolymerization as proposed previously, and they could be regarded as providing additional evidence for the new concept.

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Registry No. PMI, 941-69-5; St, 100-42-5; (NPMI)(St) (copolymer), 26316-43-8; (NPMI)(PVS) (copolymer), 134879-87-1; PVS, 1822-73-7.