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Free Radical Copolymerizations of N-Arylmaleimides

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Free Radical Copolymerizations of N-Arylmaleimides.

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ABSTRACT

The free radical copolymerization of methyl acrylate (MA) with N-phenylmaleimide (NPMI) and N-p-tolylmaleimide (NPTMI) at 75°C in cyclohexanone solution initiated by AIBN was studied. The copolymer composition has been calculated from the nitrogen content estimated by the micro-Kjeldahl's method and by NMR spectral studies. The reactivity ratios have been calculated by Mayo and Lewis, Fineman and Ross, Kelen and Tüdös, and Joshi and Joshi methods. Q and e values of NPMI and NPTMI were also calculated. Since the reactivity ratios are the measure of distribution of monomer units in a copolymer chain, the values obtained are compared and discussed.

INTRODUCTION

Copolymerization of various monomers to obtain properties that could not be obtained via homopolymerization has been going on, and the effect of copolymerization on some properties has only recently been understood. Knowledge of the copolymerization process is of considerable interest since it provides information on the reactivity

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of several growing species toward a monomer as well as the reactivity ratios of a series of monomers against a reference radical.

For the present study N-phenylmaleimide (NPMI) and N-p-tolylmaleimide (NPTMI) were selected to copolymerize with methyl acrylate (MA), a widely used monomer in the field of modern plastic technology. Some reports on the synthesis of copolymers of MA with N-alkyl- and N-arylmaleimides and their thermal behavior are available [1-3]. When the maleimide unit, which has a rigid structure, is introduced into a flexible vinyl polymer chain, the intra- and intermolecular interactions, which differ from those of homopolymers, are expected to play an important role on the properties of the copolymers.

EXPERIMENTAL

Monomers, Initiator, and Solvent

NPMI and NPTMI were synthesized in two stages according to the method developed by Searle [4]. After recrystallization from carbon tetrachloride, NPMI and NPTMI gave yellow needles, mp 89 and 148°C, respectively. Methyl acrylate was freed from inhibitor by washing it thrice with 2% sodium hydroxide solution followed by several washings with distilled water. It was then dried over anhydrous sodium sulfate before being used in copolymerization.

AIBN was purified by crystallization from methanol thrice. Cyclohexanone was purified by drying overnight under anhydrous sodium sulfate followed by fractional distillation.

Copolymerization

The free radical solution copolymerization method was adopted for the synthesis of copolymers of different compositions using AIBN (9.146×10^{-5} mol) as an initiator and cyclohexanone as the solvent for both copolymer system. Copolymerization was carried out up to about 10% conversion of the monomers in a nitrogen atmosphere. The copolymers were precipitated out in methanol, filtered, and washed with methanol. The copolymers having the lower and higher imide contents were thrice purified in MEK/CH_3OH and cyclohexanone/CH_3OH systems, respectively, and dried in vacuum at 30°C.

Copolymer Analysis

Copolymer compositions were calculated on the basis of the nitrogen contents of the copolymers estimated by the micro-Kjeldahl's method, and the integrator height units for the aromatic (7.2-7.6 ppm)

TABLE 1. Experimental Data for the Copolymers (PM) [MA (M_1) copolymerized with NPMI (M_2)]. Solvent cyclohexanone (60 mL), time 40 min, initiator AIBN, 75 ± 0.5°C

Copolymer	Mole fraction of NPMI in the monomer feed (F_2)	Conversion (%)	N in the copolymer (wt%)	Mole fraction of NPMI in the copolymer	
				From % N, f_2	By NMR, f_2
PM-1	0.1383	11.19	2.4227	0.1752	0.1784
PM-2	0.3006	8.84	3.8980	0.3160	0.3199
PM-3	0.4930	13.21	4.858	0.4275	0.4210
PM-4	0.7190	9.82	5.5134	0.5152	0.5110
PM-5	0.8548	7.465	6.0560	0.5965	0.5901

TABLE 2. Experimental Data for the Copolymers (PTM) [MA (M_1) copolymerized with NPTMI (M_2)]. Solvent cyclohexanone (60 mL), time 20 min, initiator AIBN, 75 ± 0.5°C

Copolymer	Mole fraction of NPTMI in the monomer feed (F_2)	Conversion (%)	N in the copolymer (wt%)	Mole fraction of NPTMI in the copolymer	
				From % N, f_2	By NMR, f_2
PTM-1	0.100	14.17	1.6176	0.1125	0.1173
PTM-2	0.300	11.42	3.7083	0.3110	0.3146
PTM-3	0.500	12.18	4.6820	0.4296	0.4252
PTM-4	0.700	7.92	5.4439	0.5507	0.5564
PTM-5	0.900	5.206	5.9426	0.6390	0.6363

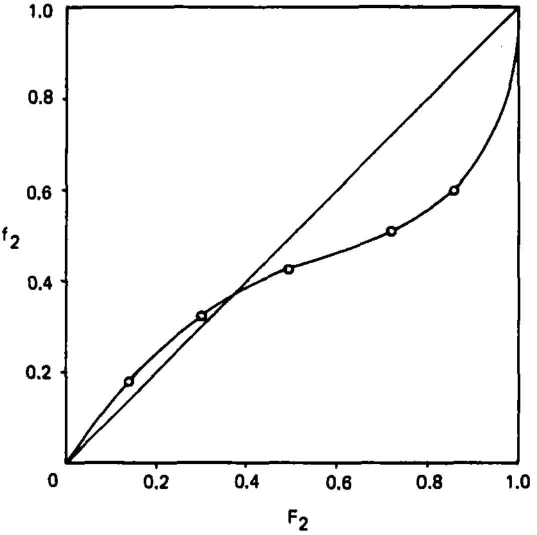


FIG. 1. Copolymer composition curve of N-phenylmaleimide (M_2) and methyl acrylate (M_1) in cyclohexanone at 75° C.

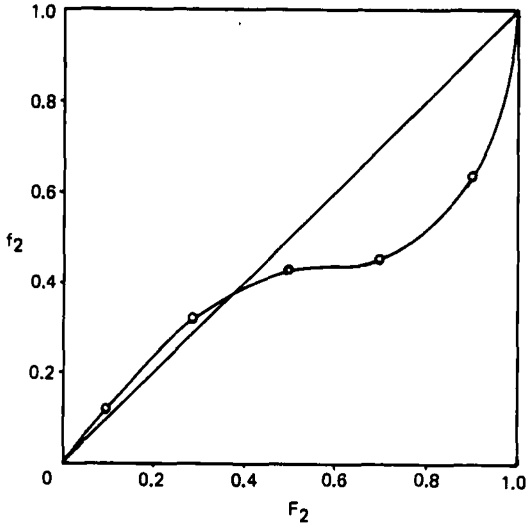


FIG. 2. Copolymer composition curve of N-p-tolylmaleimide (M_2) and methyl acrylate (M_1) in cyclohexanone at 75° C.

TABLE 3. Copolymerization Parameters for MA (M_1)-N-Arylmaleimides (M_2) Systems

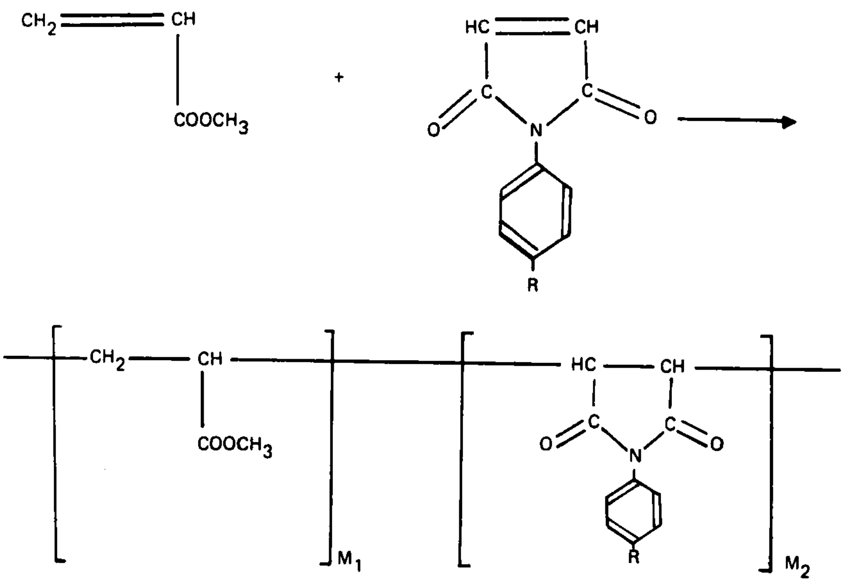
	PM		PTM		
Method	r_1	r_2	r_1	r_2	Refs.
ML	0.57	0.12	0.65	0.165	This paper
FR	0.53	0.10	0.625	0.175	This paper
FR	0.86	0.72	0.83	1.26	2
KT	0.5532	0.1049	0.6249	0.1554	This paper
JJ	0.5553	0.1148	0.6546	0.1946	This paper
	Q_2[a]	e_2[a]	Q_2[a]	e_2[a]	
	2.090	2.2872	1.68	2.1270	This paper

[a] To calculate Q and e values, r_1 and r_2 due to the KT method are used.

and methoxy (3.6-3.7 ppm) ^1H peaks in the NMR spectra were recorded on a Varian EM390 NMR spectrometer in $CDCl_3$. The polymerization conditions and copolymer compositions are shown in Tables 1 and 2. The relationships between F_2, the initial molar fractions of imide in the monomer feed, and f_2, the molar fractions of imide in the copolymers, are shown in Figs. 1 and 2. The monomer reactivity ratios r_1 and r_2 were calculated using the ML [5], FR [6], KT [7], and JJ [8] methods. Q and e values for NPMI and NPTMI were also calculated using the Alfrey-Price [9] Q-e scheme. The r_1, r_2, Q_2, and e_2 values obtained are summarized in Table 3.

RESULTS AND DISCUSSION

Copolymerization of MA with N-arylmaleimides is represented by the formula shown on the following page. Using the copolymer composition data of NMR, the reactivity ratios were determined by different methods [ML (Fig. 3, Tables 4 and 5), FR (Fig. 4, Table 6), KT (Fig. 5, Table 7), and JJ], and they are found to be nearly the same within experimental limits. The copolymer composition against monomer feed composition is represented in Figs. 1 and 2. From these data it is established that the dependence of the two parameters has the specific features of systems with $r_1 < 1$ and $r_2 < 1$, with an azeotropic point at 0.35 mol fraction of N-arylmaleimide in the monomer feed. The values of $r_{NPMI} = 0.11$ and $r_{NPTMI} = 0.17$ are low,



R = H; –CH_3.

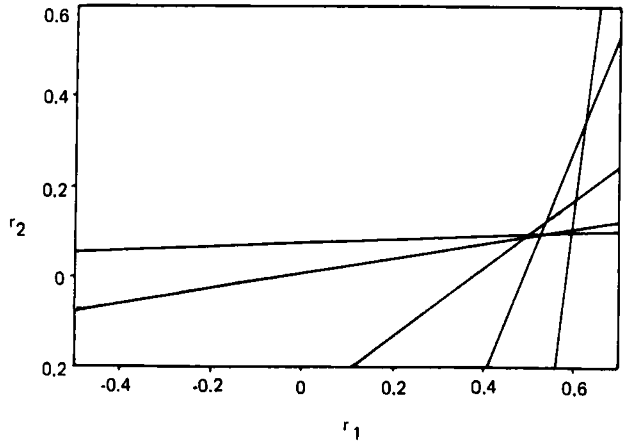


FIG. 3. Graphical solution of ML (Mayo and Lewis) equation for MA/NPMI copolymerization in cyclohexanone at 75°C. (Plots of r_1 versus r_2.)

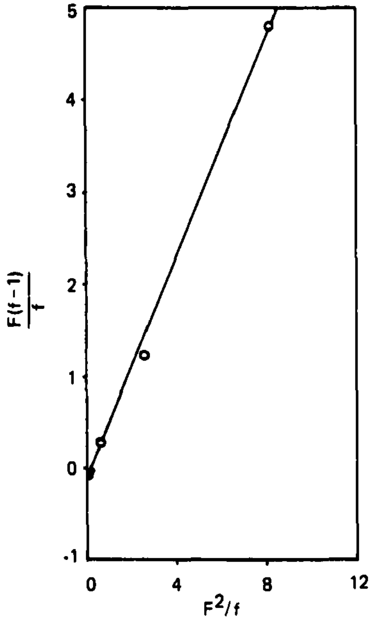


FIG. 4. Application of FR (Fineman and Ross) equation for determination of reactivity ratios r_1 and r_2. Plot of F^2/f versus $F(f - 1)/f$ for MA/NPMI copolymerization in cyclohexanone at 75° C.

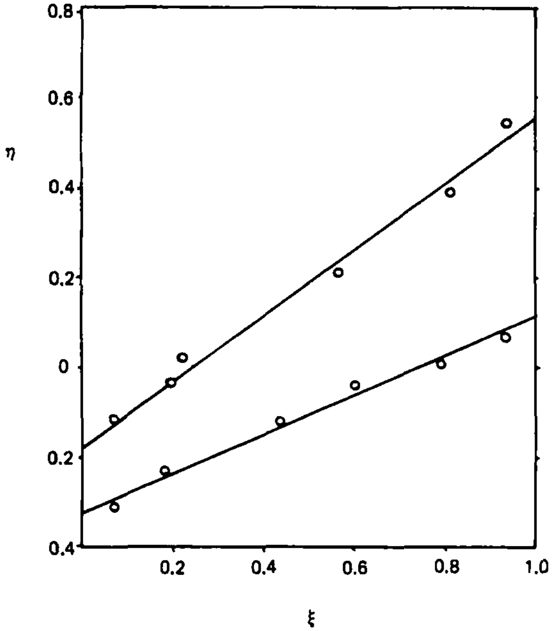


FIG. 5. Application of KT (Kelen and Tudos) equation for determination of r_1 and r_2 (plots of η versus ξ) for MA/NPMI copolymerization in cyclohexanone at 75° C.

TABLE 4. Reactivity Ratios by the ML Method[a] [MA (M_1) and NPMI (M_2)]. Arbitrary Values of r_2 for Selected Values of r_1 Which Range from 0.6 to -0.4

	r_2				
r_1	PM-1	PM-2	PM-3	PM-4	PM-5
0.6	0.1755	0.3019	0.1758	0.1103	0.0992
0.4	-1.4811	-0.2104	0.0226	0.0788	0.0910
0.2	-3.1377	-0.7228	-0.1305	0.0473	0.0827
0.0	-4.7944	-1.2352	-0.2836	0.0158	0.0744
-0.2	-6.4510	-1.7477	-0.4368	-0.0156	0.0661
-0.4	-8.1077	-2.2601	-0.5900	-0.0470	0.0578

[a] Data based on copolymer composition by NMR spectra.

TABLE 5. Reactivity Ratios by the ML Method[a] [MA (M_1) and NPTMI (M_2)]. Arbitrary Values of r_2 for Selected Values of r_1 Which Range from 0.6 to -0.4

	r_2				
r_1	PTM-1	PTM-2	PTM-3	PTM-4	PTM-5
0.6	-1.3456	0.2370	0.1835	0.2472	0.0962
0.4	-3.4084	-0.2627	0.03562	0.2011	0.0919
0.2	-5.6512	-0.7625	-0.1123	0.1550	0.0875
0.0	-7.8040	-1.2623	-0.2602	0.1089	0.0832
-0.2	-9.9567	-1.7631	-0.4082	0.0629	0.0789
-0.4	-12.1095	-2.2619	-0.5561	0.0168	0.0746

[a] Data based on copolymer composition by NMR spectra.

TABLE 6. Reactivity Ratios by the FR Method[a] [MA (M_1) and N-arylmaleimides (M_2) System]

Copolymer number	PM		PTM	
	F(f - 1)/f	F_2/f	F(f - 1)/f	F_2/f
1	4.7944	8.2832	7.8040	10.7639
2	1.2353	2.5620	1.2623	2.4990
3	0.2837	0.7658	0.2602	0.7397
4	-0.0159	0.1574	-0.1089	0.2303
5	-0.0744	0.0413	-0.0832	0.0216

[a] Data based on copolymer composition by NMR spectra.

TABLE 7. Reactivity Ratios by the KT Method[a] [MA (M_1) and N-arylmaleimides (M_2) System]

Copolymer	M_1-M_2 system[b]		M_2-M_1 system[c]	
	η	ξ	η	ξ
PM-1	0.5404	0.9339	-0.3165	0.0660
PM-2	0.3924	0.8139	-0.2297	0.1860
PM-3	0.2099	0.5667	-0.1229	0.4332
PM-4	0.0213	0.2118	0.0125	0.7881
PM-5	-0.1187	0.0660	0.0695	0.9339
PTM-1	0.6939	0.9571	-0.3345	0.0428
PTM-2	0.4234	0.8382	-0.2041	0.1617
PTM-3	0.2129	0.6053	-0.1027	0.3946
PTM-4	-0.1529	0.3233	0.0737	0.6766
PTM-5	-0.1653	0.0428	0.07997	0.9571

[a] Data based on copolymer composition by NMR spectra.

[b] α = 1.7079 and 2.0739 for PM and PTM, respectively. r_2/α = 0.3239 and 0.3018 for PM and PTM, respectively.

[c] α = 0.5855 and 0.4821 for PM and PTM, respectively. r_2/α = 0.1792 and 0.3223 for PM and PTM, respectively, (Intercept r_2/α values based on the least-squares procedure.)

indicating the higher reactivity of the poly(N-arylmaleimide) growing species toward the MA radical than toward the same type of radical, which would result in an alternating copolymer chain. The same type of alternation has been noticed in the copolymerization of N-phenylmaleimide with styrene [10], and for MA with isobutyl vinyl sulfide [11], methyl vinyl sulfide [12], N-vinyl carbazole [13], and 2-methyl-5-vinylpyridine [14]. The r_1 and r_2 values for the two series of copolymers are summarized in Table 3 together with values from the literature. The Q_2 and e_2 values of NPMI and NPTMI were calculated using the Alfrey-Price equation. The r_1 and r_2 values came from the KT method by assuming the values of MA given by other authors. The Q and e values are large, similar to the case of the styrene/NPMI [10] system which has abnormal values. The positive and higher e values agree with the fact that these maleimides have electron-poor double bonds due to neighboring carbonyl groups.

SUMMARY AND CONCLUSIONS

In this investigation MA was copolymerized with N-arylmaleimides by using free-radical initiators. Conversion was limited to about 10%. A wide range of initial monomer feed ratios was chosen to give equal weightage to both monomers.

The reactivity ratios for both systems have been evaluated by using the ML, FR, KT, and JJ methods. Since reactivity ratios indicate the distribution of monomer units in a polymer chain, this can aid in choosing the desired composition of copolymers of specific end-use requirements.

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