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RADICAL COPOLYMERIZATION OF N-[(3-DIMETHYLAMINO)PROPYL] ACRYLAMIDE (OR METHACRYLAMIDE) WITH METHYL ACRYLATE (OR METHACRYLATE)

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ABSTRACT

The radical copolymerization of N-[(3-Dimethylamino)-propyl] acrylamide (DMAPAA) or N-[(3-Dimethylamino)-propyl] methacrylamide (DMAPMA) with methyl acrylate (MA) or methyl methacrylate (MMA) was carried out in benzene using 2,2'-azobisisobutyronitrile as initiator at 60°C. The copolymer compositions were estimated by elemental microanalysis and the monomer reactivity ratios were determined by Fineman-Ross, Mayo-Lewis, and Kelen-Tudos methods, respectively. The ratios calculated by Kelen-Tudos method were found as follows: $r_1=0.69$ and $r_2=0.22$ for MA/DMAPAA system, $r_1=0.48$ and $r_2=0.63$ for MA/DMAPMA system, $r_1=1.68$ and $r_2=0.38$ for MMA/DMAPAA system, $r_1=1.36$ and $r_2=0.31$ for MA/DMAPMA system, respectively. The Q and e values of DMAPAA, DMAPMA were also calculated by using the Alfrey-Price equation.

INTRODUCTION

N-[(3-Dimethylamino)-propyl] acrylamide (DMAPAA) and N-[(3-Dimethylamino)-propyl] methacrylamide (DMAPMA) are derivatives of acrylamide. In recent years, these monomers containing an amide and an amine

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group, have become well known as important agents for practical applications. Since these N-substituted acrylamides and their polymers could be dissolved in both organic and aqueous solutions, they are found in various applications, such as in coating materials[1], hydrogels[2,3], permeation or separation membranes[4,5], ion exchange membranes[6], coagulant or flocculating agents for waste water or solid/liquid separation[7,8] biology and biochemistry[9,10], electroconductive organgels[11], nonlinear optical films[12], etc. The polymerization and copolymerization behaviors of DMAPAA and DMAPMA have been investigated, and many interesting results have been found[6,13,14,15]. This paper describes the determination of reactivity ratios of DMAPAA or DMAPMA in the copolymerization with methyl acrylate(MA) or methyl methacrylate(MMA) in an organic solution, respectively. The Alfrey-Price Q and e values were also calculated and some comparing results are briefly discussed.

EXPERIMENTAL

Materials: DMAPAA and DMAPMA were prepared in our laboratory by the reactions of 3-dimethylaminopropylamine with acryloyl and methacryloyl chloride, respectively. The products were distilled under reduced pressure and collected the fraction at 112-113 ^{O}C/133.3Pa and 108-110 ^{O}C/133.3Pa respectively. MMA and MA were washed with 5% aqueous sodium hydroxides to remove the inhibitor and purified by reduced pressure distillation. 2,2'-Azobisisobutyronitrile(AIBN) and solvent benzene were purified by conventional methods. All other agents were used as received.

Copolymerization: Free-radical copolymerization of MMA or MA with DMAPAA or DMAPMA in benzene at 60 ^{O}C were carried out in a sealed tube. The amounts of the monomers in various ratios (20mmol in total), 0.25% (on the basis of total monomer moles) of AIBN and 25 ml of benzene were placed in a tube. The tube was sealed after degassing by repeated freezing and thawing cycles. Polymerization were carried out at 60 ^{O}C about 2h, then the reaction mixture was poured into a large amount of ether or n-hexane with vigorous stirring to precipitation the copolymer. The copolymer was further purified by precipitation from a chloroform/ethanol solution into an excess of hexane, then the copolymer was filtered and dried in vacuum to constant weight. The conversion was around 10%.

TABLE 1. Experimental data for the MA(M_1)/DMAPAA(M_2) copolymers

Mole fraction MA in feed (f_1)	Nitrogen content(%)	Conv. (%)	Mole fraction MA in copolymer (F_1)	$F^{a.)}$	$G^{b.)}$	$\xi^{c.)}$	$\eta^{d.)}$
0.20	12.87	7.03	0.416	0.088	-0.101	0.051	-0.058
0.30	12.76	7.47	0.422	0.251	-0.158	0.132	-0.083
0.40	10.29	7.83	0.574	0.330	0.172	0.167	0.087
0.50	10.82	12.42	0.544	0.838	0.162	0.337	0.065
0.60	9.09	13.18	0.638	1.277	0.649	0.436	0.222
0.70	7.46	14.06	0.718	2.138	1.417	0.564	0.374

a.): $F=(f_1/f_2)^2(F_1^{-1}-1)$ b.): $G=-(f_1/f_2)(F_1^{-1}-2)$, c.): $\xi=F/(\alpha+F)$, d.): $\eta=G/(\alpha+F)$ ($\alpha=1.65$)

The copolymer compositions were determined by the elemental analysis of copolymers, which was performed with a Heraeus CHN-Rapid Microanalyzer. The monomer reactivity ratios were calculated by using the Fineman-Ross[16], Mayo-Lewis[17], and Kelen-Tudos[18]methods, and the Q, e values of DMAPAA and DMAPMA were calculated by using the Alfrey-Price equation[19].

RESULTS AND DISCUSSION

Copolymerization of MA and DMAPAA or DMAPMA system: The data of copolymerization are shown in TABLES 1, 2. The reactivity ratios are determined from Fineman-Ross plots (Fig.1) and Kelen-Tudos plots (Fig.2) by the "line of best fit" method, respectively, and the corresponding correlation coefficients(R) are noted at the bottom of the figures. The values of r_1 and r_2 are compiled in TABLE 3, and for comparison the reactivity ratios obtained from Mayo-Lewis method are listed as well. The copolymeization curves are given in Fig.3. There are crossover points as shown in Fig.3. In this case, each polymeric radical prefers to cross-propagation, i.e. addition of the other monomer to the propagating radical, and the reactivity ratios are less than unity.

Copolymerization of MMA and DMAPAA or DMAPMA system: The results are shown in TABLES 4, 5. The reactivity ratios calculated from Fineman-Ross

TABLE 2. Experimental data for the MA(M_1)/DMAPMA(M_2) copolymers

Mole fraction MA in feed (f_1)	Nitrogen content(%)	Conv. (%)	Mole fraction MA in copolymer (F_1)	F[a.)]	G[b.)]	ξ[c.)]	η[d.)]
0.30	13.09	10.36	0.337	0.361	-0.415	0.196	-0.226
0.40	12.18	7.33	0.410	0.640	-0.293	0.302	-0.138
0.50	11.51	11.72	0.461	1.169	-0.169	0.442	-0.064
0.60	10.26	8.38	0.544	1.886	0.243	0.561	0.072
0.70	9.29	9.01	0.604	3.570	0.804	0.707	0.159
0.80	6.28	9.76	0.737	5.710	2.573	0.794	0.358

a.): $F=(f_1/f_2)^2(F_1^{-1}-1)$ b.): $G=-(f_1/f_2)(F_1^{-1}-2)$, c.): $\xi=F/(\alpha+F)$, d.): $\eta=G/(\alpha+F)$ ($\alpha=1.48$)

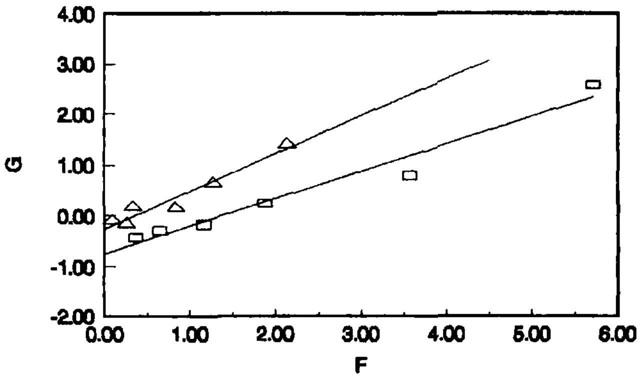

Fig. 1 Fineman-Ross plots of copolymerization of MA(M_1) with DMAPAA or DMAPMA(M_2)

(Δ) MA/DMAPAA system (R=0.9711)

(□) MA/DMAPMA system (R=0.9816)

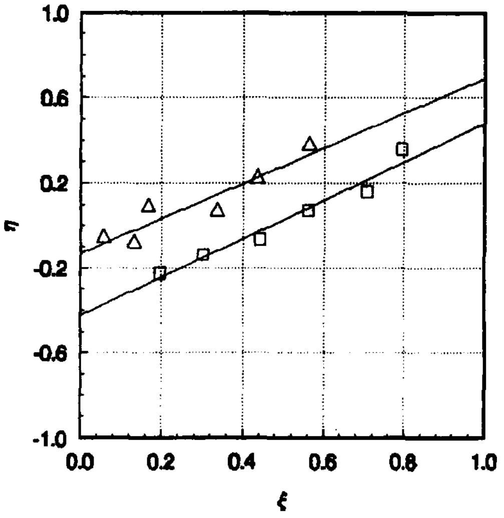

Fig.2 Kelen-Tudos plots of copolymerization of MA(M_1) with DMAPAA or DMAPMA(M_2)

(Δ) MA/DMAPAA system (R=0.9338)

(□) MA/DMAPMA system (R=0.9791)

TABLE 3. Reactivity ratios of various monomers calculated by different methods

M_1	M_2	r_1			r_2		
		FR[a.)]	ML[b.)]	KT[c.)]	FR[a.)]	ML[b.)]	KT[c.)]
MA	DMAPAA	0.74	0.62±0.10	0.69	0.25	0.19±0.10	0.22
MA	DMAPMA	0.54	0.51±0.04	0.48	0.74	0.64±0.04	0.63
MMA	DMAPAA	1.65	1.71±0.08	1.68	0.36	0.39±0.08	0.38
MMA	DMAPMA	1.38	1.60±0.06	1.36	0.33	0.40±0.06	0.31

a.): by Fineman-Ross Method b.): by Mayo-Lewis Method c.): by Kelen-Tudos Method

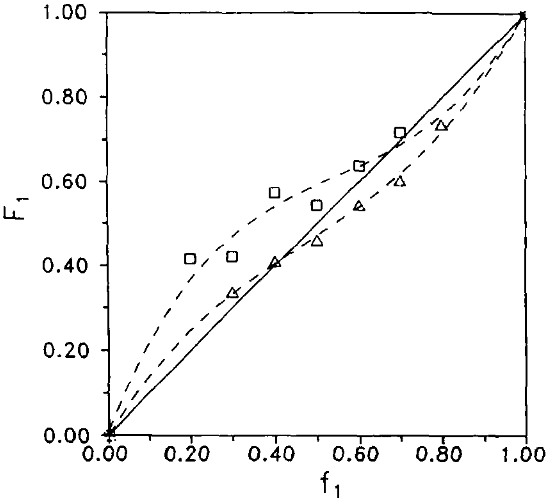

Fig.3 Copolymerization composition curves for the system MA(M_1) with DMAPAA or DMAPMA(M_2) in benzene at 60°C
(□) MA/DMAPAA system (Δ) MA/DMAPMA system

TABLE 4. Experimental data for the MMA(M_1)/DMAPAA(M_2) copolymers

Mole fraction MMA in feed(f_1)	Nitrogen content(%)	Conv. (%)	Mole fraction MMA in copolymer (F_1)	$F^{a.)}$	$G^{b.)}$	$\xi^{c.)}$	$\eta^{d.)}$
0.30	11.62	10.67	0.459	0.217	-0.077	0.248	-0.088
0.40	9.44	7.47	0.584	0.317	0.192	0.325	0.197
0.50	8.02	9.76	0.659	0.519	0.481	0.441	0.408
0.60	6.11	8.16	0.751	0.745	1.003	0.531	0.714
0.70	4.97	10.69	0.803	1.338	1.760	0.670	0.881
0.80	3.27	11.23	0.875	2.286	3.429	0.776	1.164

a.): $F=(f_1/f_2)^2(F_1^{-1}-1)$ b.): $G=-(f_1/f_2)(F_1^{-1}-2)$, c.): $\xi=F/(\alpha+F)$, d.): $\eta=G/(\alpha+F)$ ($\alpha=0.66$)

TABLE 5. Experimental data for the MMA(M_1)/DMAPMA(M_2) copolymers

Mole fraction MMA in feed(f_1)	Nitrogen content(%)	Conv. (%)	Mole fraction MMA in copolymer (F_1)	F a.)	G b.)	ξ c.)	η d.)
0.30	10.85	11.67	0.468	0.209	-0.059	0.131	-0.037
0.40	9.28	3.51	0.568	0.338	0.160	0.196	0.093
0.50	7.94	7.40	0.646	0.548	0.452	0.283	0.234
0.60	6.39	8.58	0.728	0.841	0.940	0.378	0.421
0.70	5.01	9.58	0.795	2.024	1.732	0.593	0.508
0.80	3.22	14.45	0.875	2.286	3.429	0.622	0.934

a.): $F=(f_1/f_2)^2(F_1^{-1}-1)$ b.): $G=-(f_1/f_2)(F_1^{-1}-2)$, c.): $\xi=F/(\alpha+F)$, d.): $\eta=G/(\alpha+F)$ ($\alpha=1.39$)

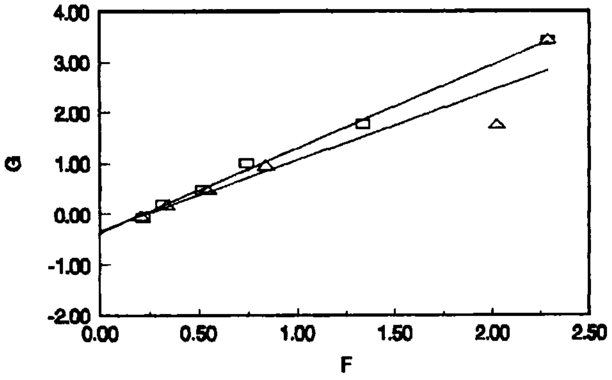

Fig.4 Fineman-Ross plots of copolymerization of MMA(M_1) with DMAPAA or DMAPMA(M_2)

(□) MMA/DMAPAA system (R=0.9981)

(Δ) MMA/DMAPMA system (R=0.9447)

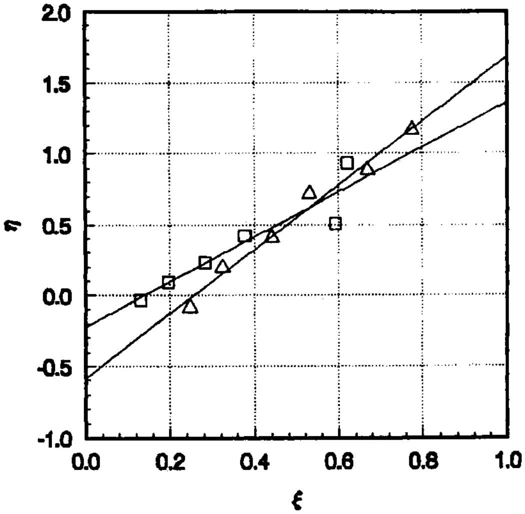

Fig.5 Kelen-Tudos plots of copolymerization of MMA(M_1) with DMAPAA or DMAPMA(M_2)

(Δ) MMA/DMAPAA system (R=0.9913)

(□) MMA/DMAPMA system (R=0.9348)

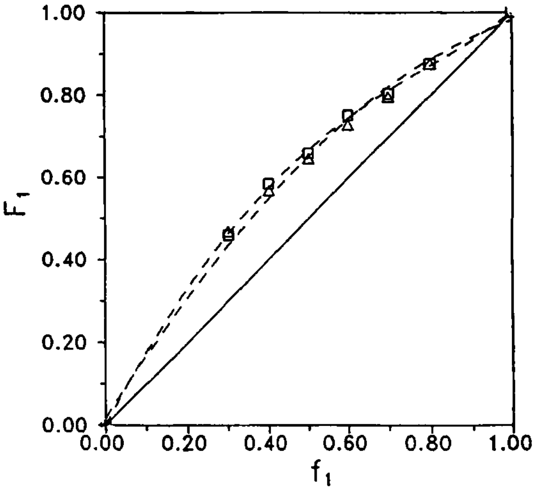

Fig.6 Copolymerization composition curves for the system MMA(M_1) with DMAPAA or DMAPMA(M_2) in benzene at 60°C

(□) MMA/DMAPAA system (Δ) MMA/DMAPMA system

TABLE 6. Copolymerization parameters of various monomers in benzene at 60°Ca)

M_1	M_2	r_1	r_2	$r_1 r_2$	Q_2	e_2	ref.
MA	DMAPAA	0.69	0.22	0.15	0.27	-0.73	found
MMA		1.68	0.38	0.64	0.36	-0.27	found
St		1.63	0.46	0.75	0.40	-0.26	[20]
MVKb)		1.18	0.38	0.46	0.32	-0.24	[20]
AAmc)		0.95	0.47	0.45	0.33	-0.15	[21]
MA	DMAPMA	0.48	0.63	0.30	0.46	-0.45	found
MMA		1.36	0.31	0.42	0.40	-0.53	found
VPhd)		3.30	0.23	0.76			[22]

a): $Q_1=0.45$, $e_1=0.64$ for MA and $Q_1=0.78$, $e_1=0.40$ for MMA are used[23].
To calculate Q and e values, r_1 and r_2 due to the KT method are used.

b): MVK: methyl vinyl ketone (in dioxane at 60°C)

c): AAm: acrylamide (in water at 40°C, pH=6.1)

d): VPh: 9-vinylphenanthrene (in tetrahydrofuran at 60°C)

plots (Fig.4) and Kelen-Tudos plots (Fig.5) are also shown in TABLE 3, together with the results by using Mayo-Lewis method. The corresponding copolymeization curves are summarized in Fig.6. It can be found that both curves are above the diagonal in Fig.6, in this case, the methyl methacrylate propagating radical preferentially adds MMA itself and produces a copolymer with mostly MMA sequences. A comparison of the reactivity ratios of DMAPAA and DMAPMA interestingly shows no significant differences.

Copolymerization Parameters: The Q, e values of DMAPAA and DMAPMA monomers, which are estimated from Alfrey-Price equaton, are summarized in TABLE 6, together with some parameters of the literature results. It is well known that the reactivity ratios are strongly influenced by the type of comonomer and the polymerization medium, and the different results can be found by different methods. Therefore, there is a disagreement in the Q, e values of DMAPAA and DMAPMA as shown in TABLE 6.

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