Copolymerization of N-Acryloylpiperidine with Acrylic Acid, Methyl Methacrylate, and Styrene

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ABSTRACT

Low conversion copolymerizations of N-acryloylpiperidine (NAPi)
(monomer-1) were conducted with each of the co-monomers , acrylic acid (AA) ,
methyl methacrylate (MMA) and styrene (ST) in benzene at 60°C using AIBN as
initiator. The copolymer compositions were determined by elemental analyses.
The monomer reactivity ratios were calculated by the Fineman-Ross, the Kelen-
Tudos and the Mayo-Lewis graphical procedures. The derived reactivity ratios (r_1,
r_2) are (0.535, 0.81), (0.223, 1.293) and (0.247, 1.51) for NAPi/AA, NAPi/MMA
and NAPi/ST systems respectively. Relative reactivities of various monomers in
cross-propagation reactions involving NAPi-terminated polymer radicals were
compared and discussed.

INTRODUCTION

N-Cycloalkyl acrylamides are known to exhibit a wide range of reactivities.
Detailed studies on the kinetics of homopolymerization in bulk [1,2] and in
solution [3-5] have shown that the homopolymerizabilities of these monomers
depend on the size of the N-cycloalkyl ring and the presence of electron-
withdrawing groups adjacent to the nitrogen. These factors which influence the
extent of interaction of the nitrogen lone-pair with the acryloyl π-system are

believed [1] to be responsible for the enhanced reactivities of N-acryloyl pyrrolidone and N-acryloyl succinimide [3] (due to the presence of carbonyl groups adjacent to nitrogen) and of N-(meth)acryloyl aziridines [6,7] (due to the highly strained aziridine ring).

Despite this widespread activity, there have been few reports [1,3,5,8] on the copolymerization of these monomers and in some cases, the reported reactivity ratios of the same monomer-co-monomer system showed conflicting values [3,5].

In connection with our previous work [4] on the radical polymerization of N-acryloyl piperidine (NAPi), we now report on the copolymerization of NAPi with acrylic acid (AA), methyl methacrylate (MMA) and styrene (ST).

EXPERIMENTAL

Materials :

N-acryloyl piperidine (NAPi) was prepared by the reaction of acryloyl chloride and piperidine as described previously [4]. All other monomers and the initiator, 2,2'-Azobisisobutyronitrile (AIBN) were obtained from Fluka (Switzerland). Acrylic acid (AA) was dried over anhydrous magnesium sulfate (MgSO$_4$) and vacuum distilled immediately prior to the copolymerization experiment. Styrene (ST) and methyl methacrylate (MMA) were freed from the inhibitor by shaking with 10% w/v aqueous NaOH. After washing with water they were treated as indicated above for AA. 2,2'-Azobisisobutyronitrile (AIBN) was recrystalized from methanol.

Copolymerization :

Copolymerizations of NAPi with AA, MMA and ST were carried out using AIBN as the initiator and benzene as the solvent at 60°C in sealed tubes under vacuum. The glass tubes were charged with the prescribed amounts of monomers, AIBN (1.0×10^{-3} mol dm^{-3}) and benzene. The total molar composition of the monomer mixture was maintained at 3.5 mol dm^{-3} while the feed ratio was varied. The mixtures were degassed by successive freeze-pump-thaw cycles. The tubes were then sealed under vacuum and placed in a constant temperature bath at 60 ± 0.1°C. After the requisite time (< 10% conversion) the copolymers were precipitated in petroleum ether (b.p. 40-60°C). The precipitates were filtered off, dissolved again in benzene and reprecipitated in petroleum ether prior to drying to constant weight in vacuum at 40°C. Copolymer compositions were determined by elemental analysis (N%). The results are summarized in Table 1.

Table 1.   The copolymerization of NAPi (M_1) with AA, MMA and ST in benzene at 60°C. AIBN is used as the initiator at a concentration of 1.0×10^{-3} mol dm^{-3}.

Test No.	NAPi (M_1) - AA (M_2)			NAPi (M_1) - MMA (M_2)			NAPi (M_1) - ST (M_2)		
	initial feed f_1[a]	copolymer N%	F_1[b]	initial feed f_1[a]	copolymer N%	F_1[b]	initial feed f_1[a]	copolymer N%	F_1[b]
1	0.1991	3.40	0.2090	0.1996	1.91	0.1442	0.1999	1.68	0.1304
2	0.2984	4.45	0.2910	0.2998	2.68	0.2071	0.3000	2.33	0.1840
3	0.3999	5.15	0.3518	0.4000	3.48	0.2755	0.2964	2.46	0.1950
4	0.4999	6.39	0.4734	0.4990	4.34	0.3530	0.3999	3.35	0.2719
5	0.5941	7.31	0.5789	0.6000	5.16	0.4309	0.5000	4.23	0.3518
6	0.6000	7.33	0.5814	0.6942	5.88	0.5028	0.5993	4.63	0.3894
7	0.6999	7.89	0.6528	-	-	-	0.6930	5.53	0.4772
8	0.7987	7.98	0.6649	-	-	-	0.7930	6.42	0.5687

[a] f_1 is the mole fraction of monomer-1 (NAPi) in the initial feed ; $f_2 = 1 - f_1$

[b] F_1 is the mole fraction of monomer-1 (NAPi) in the copolymer ; $F_2 = 1 - F_1$

RESULTS AND DISCUSSION

Reactivity Ratios :

The reactivity ratios r_1 and r_2 of the copolymerization of NAPi (monomer-1) with each of the co-monomers AA, MMA and ST were determined using the Mayo-Lewis [9], Fineman-Ross [10] and Kelen-Tudos [11] graphical procedures for the data given in Table 1. For mathematical details of these procedures, the original papers [9-11] should be consulted. The plots are not reproduced here. The results of the reactivity ratios are given in Table 2. With these values of r_1 and r_2, the variation of the instantaneous mole fraction F_1 of NAPi in copolymer (at low conversion) with mole fraction f_1 of NAPi in the initial feed may be calculated using the following copolymer composition equation [9] :

$$F_1 = (r_1f_1^2 + f_1f_2) / (r_1f_1^2 + 2f_1f_2 + r_2f_2^2) \qquad (1)$$

Figure 1 shows the copolymer composition curves for NAPi/AA, NAPi/MMA and NAPi/ST systems. The theoretical curves (solid lines in Figure 1) calculated by means of equation (1) follow closely the experimental copolymer composition data. An azeotropic composition is possible when r_1 and r_2 are both greater than 1 or both less than 1. This condition is fulfilled in the NAPi/AA system since r_1 and r_2 are both less than unity. The corresponding azeotropic feed composition f_1(az.) is given by :

$$f_1 (az.) = (1 - r_2)/(2 - r_1 - r_2) \qquad (2)$$

A value of 0.29 is obtained for f_1 (az.) in the NAPi/AA system.

The higher values of r_2 as compared with r_1 in NAPi/MMA and NAPi/St systems and to a lesser extent in NAPi/AA system (Table 2), indicate that the resulting copolymers may contain large blocks of monomer-2 units interspersed by NAPi units. Within the terminal model the rate constant k_{ij} of cross-propagation reflecting the relative reactivity of monomer-j towards a given polymer radical-i may be calculated from reactivity ratios ($k_{12} = k_{11}/r_1$; $k_{21} = k_{22}/r_2$). In absence of reliable data on the absolute rate constants of propagation of NAPi (k_{11}) at the conditions employed here, comparisons were made on the basis of reactivity ratios alone (Table 2) which revealed that the relative reactivities of various co-monomers towards NAPi-terminated polymer radical (based on $1/r_1$ values) follow the order: MMA $\approx$ ST > AA.

The higher reactivities of MMA and ST towards NAPi-terminated polymer radical may be attributed to the extra-stabilities of the growing polymer radicals resulting

Table 2. Monomer reactivity ratios for the copolymerization of NAPi with AA, MMA and ST.

Procedure	NAPi (M_1) - AA (M_2)		NAPi (M_1) - MMA (M_2)		NAPi (M_1) - ST (M_2)	
	r_1	r_2	r_1	r_2	r_1	r_2
Fineman - Ross	0.56	0.84	0.22	1.32	0.25	1.53
Kelen - Tudos	0.51	0.78	0.19	1.26	0.25	1.50
Mayo - Lewis	-[a]	-[a]	0.26	1.31	0.24	1.50
Average values	0.535	0.81	0.223	1.293	0.247	1.51
	±0.025	±0.03	±0.035	±0.03	±0.005	±0.035

[a] The Mayo-Lewis intersection method for the NAPi/AA system afforded comparable values, but with large uncertainties and were excluded from the table.
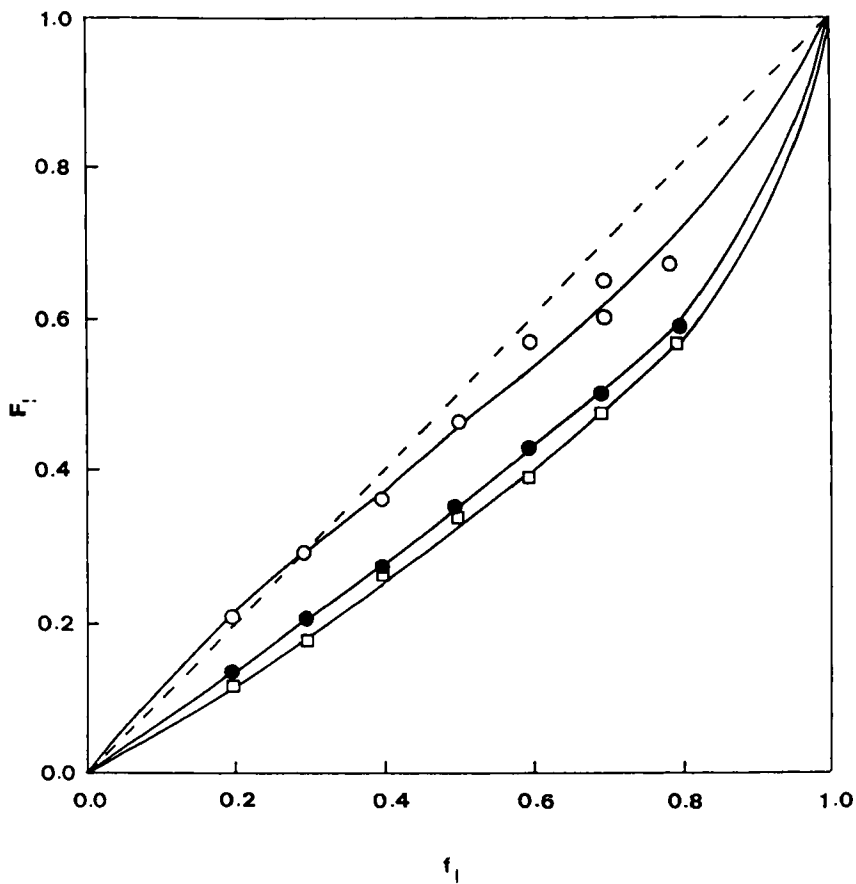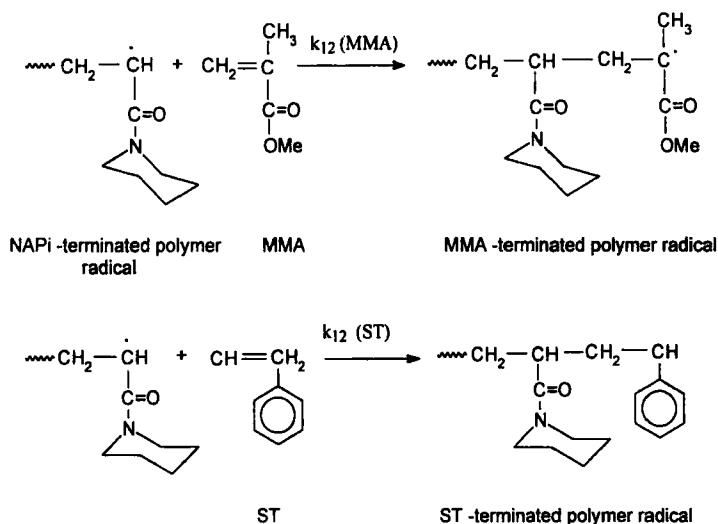
Figure 1. Copolymer composition curves. Experimental data are represented by :
(o) - NAPi/AA system ; (•) - NAPi/MMA system and (□) - NAPi/ST
system. Solid lines represent theoretical curves calculated from the
copolymer composition equation and the relevant reactivity ratios.

from hyperconjugation of the α-methyl group in MMA and conjugation involving the phenyl group in ST respectively as represented by the following reactions.

NAPi -terminated polymer   MMA   MMA -terminated polymer radical
        radical

ST   ST -terminated polymer radical

Additionally, comparisons of $1/r_2$ values for various systems (Table 2) revealed that the reactivity of NAPi monomer towards various polymer radicals is highest towards AA-terminated polymer radical compared with MMA-terminated and ST-terminated polymer radicals.

Q-e values :

The Q-e scheme is sometimes used for predictive purposes despite its well-documented shortcomings [12]. The determination of a reliable set of parameters (Q and e) for a given monomer requires copolymerization with a series of standard monomers of known Q and e values . At present, few reports [1,8] are available on copolymerizations involving NAPi. Yamada and coworkers [1] obtained the values Q = 0.28 and e = -0.17 for NAPi based on bulk copolymerization with styrene. Using these values for NAPi and the relevant literature values [13] for the other monomers investigated here, we have calculated the following values of (r_1, r_2): NAPi/AA (0.21, 1 .99); NAPi/MMA (0.34, 2.10) and NAPi/ST (0.31, 2.16). Apart from NAPi/AA system, the calculated reactivity ratios, though slightly overestimated, are in reasonable accord with observed values (Table 2).

The present values of reactivity ratios (Table 2) were used to calculate values of Q and e. These values were averaged to give Q = 0.46 and e = -0.22. In both sets of Q-e values, the parameter Q has a value (0.28-0.46) within the range of a resonance

stabilized monomer. Although the present set of Q-e values gave improved reactivity ratios compared with that of Yamadaandcoworkers[1], clearly more reactivity ratios involving NAPi are required to determine definite values of Q and e for this monomer.

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