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COPOLYMERS OF *N*-ACRYLOYL-*N*′-METHYL PIPERAZINE AND METHYL METHACRYLATE: SYNTHESIS AND DETERMINATION OF MONOMER REACTIVITY RATIOS

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Abstract—Copolymers of *N*-acryloyl-*N*′-methylpiperazine (AcrNMP) and methyl methacrylate (MMA) were synthesized in 1,4-dioxane using benzoyl peroxide as initiator at 70 ± 1°C. The copolymers were analyzed by FTIR spectroscopy. The monomer reactivity ratios were determined by the methods of Fineman–Ross (F–R) and Kelen–Tüdös (K–T), yielding the results r_1 (AcrNMP) = 0.552 and r_2 (MMA) = 1.074 by the F–R method and $r_1 = 0.466$ and $r_2 = 0.980$ by the K–T method. The latter r values in turn yielded $Q = 0.56$ and $e = -0.49$ for AcrNMP. © 1997 Elsevier Science Ltd

INTRODUCTION

Interest in multifunctional synthetic polymers or copolymers is steadily increasing because of their possible uses as macromolecular catalysts [1–4], macromolecular drugs [5, 6] etc. Polymers containing amino groups have been widely investigated for their various potential applications in the field of biomedical materials [7–9] and as constituents of drug delivery systems [10, 11]. Amino polymers containing piperazine moieties have also been studied for their interesting properties and potential applications [12–15]. We have previously reported [16] the synthesis of copolymers of *N*-acryloyl-*N*′-methylpiperazine (AcrNMP) and methyl methacrylate (MMA, Scheme 1) and their application for Hg(II) detection by anodic stripping voltammetry. In this paper, we report the copolymerization behavior of AcrNMP and MMA in solution, and the determination of the monomer reactivity ratios.

EXPERIMENTAL

Materials

MMA (Riedel-de-Haën) was distilled at reduced pressure under nitrogen and stored in the refrigerator. 1,4-Dioxane (Merck) was freshly distilled under nitrogen over metallic sodium. Benzoyl peroxide (Merck) was purified by dissolving in a small amount of chloroform, followed by precipitation in *n*-hexane. Diethyl ether and *n*-hexane, both from Merck were used as received.

Synthesis

Copolymerization of AcrNMP with MMA. AcrNMP was synthesized by the method described previously [16]. For copolymerizations, the monomers AcrNMP and MMA in various proportions but with the total weight maintained at ~3 g and the initiator benzoyl peroxide (0.5 wt% based on the total weight of the monomers) were dissolved in 25 ml of freshly distilled dioxane. The contents of the flask was degassed three times by freeze–thaw cycles and sealed under vacuum. Polymerizations were carried out at 70 ± 1°C for periods ranging from 30 min to 1 hr. Each polymer was precipitated in *n*-hexane, washed repeatedly in diethyl ether and dried in vacuum at 75°C for 12 hr. For the determinations of reactivity ratios, the polymer conversions were always less than 10% and, in most cases, were less than 5%.

Instrumentation

IR spectra were recorded by a Perkin–Elmer 1725-X Fourier Transform IR (FTIR) spectrometer.

RESULTS AND DISCUSSION

All the copolymers were soluble in chloroform. Although the homopolymer of AcrNMP were soluble in water [16], most of the copolymers were insoluble in water, but they swelled to extents depending on the content of AcrNMP in the copolymers. Attempts to determine the ratios of monomers in the copolymer using ^{1}H NMR spectroscopy were not successful because of the overlapping of the signals (spectrum not shown). However, the compositions of the copolymer could be conveniently determined from their IR spectra. The IR spectra of three copolymers are shown in Fig. 1. It can be seen that the two carbonyl absorptions at 1728 and 1636 cm^{-1} for the two monomeric units, MMA and AcrNMP, respectively, were fairly well separated. Hence, the compositions of the copolymers were determined by analyzing the relative intensities of the carbonyl absorptions of the two monomers. Homopolymers of MMA and AcrNMP were used as the model compounds for the determination of the molar extinction coefficients of the carbonyl absorptions at 1728 and 1635 cm^{-1}, respectively. Various concentrations of the homopolymers in chloroform were prepared and their absorbances were measured using a liquid cell with a pathlength of 0.5 mm. The molar extinction coefficients calculated for the two carbonyl

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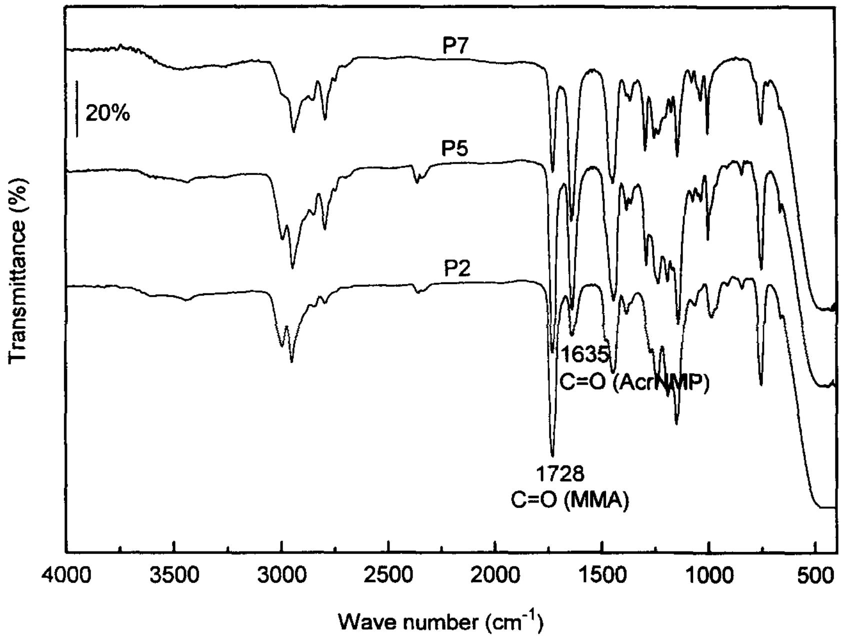


Fig. 1. IR spectra of copolymers of AcrNMP with MMA films on NaCl window. Mole fractions of AcrNMP in the feed: P2, 0.139; P5, 0.395; P7, 0.716.

absorptions were $\epsilon_{1728} = 300 \pm 19$** dm^3 mol^{-1} cm^{-1} and $\epsilon_{1635} = 330 \pm 13$** dm^3 mol^{-1} cm^{-1}. Having found the molar extinction coefficients, the ratio of the monomer units in the copolymer was calculated from the intensities of the absorptions, using equation (1):

$$[\mathrm{MMA}]/[\mathrm{AcrNMP}] = (A_{1728}/A_{1635})(\epsilon_{1635}/\epsilon_{1728}). \quad (1)$$

In the cases where there was slight overlapping of the two absorptions, deconvolution treatment were first performed using Perkin–Elmer FTIR software. The results are presented in Table 1.

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of AcrNMP and MMA were evaluated by the methods of both Fineman–Ross (F–R) [17] and Kelen–Tüdös (K–T) [18]. Using the F–R equation [equation (2)]:

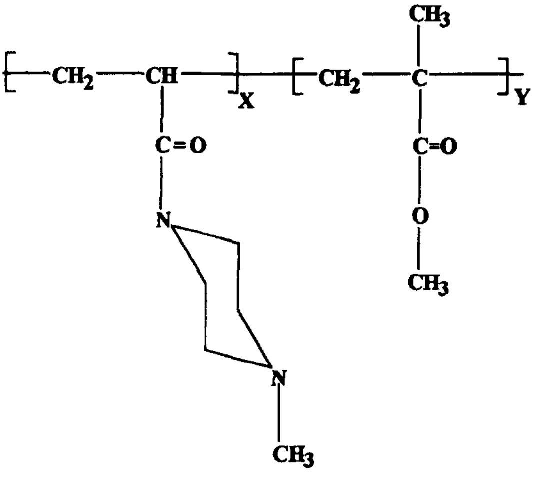
$$f(F-1)/F = r_1(f^2/F) - r_2, \quad (2)$$

where subscript 1 denotes AcrNMP and subscript 2 denotes MMA, and $F = F_1/F_2$ and $f = f_1/f_2$. The linear plot of $f(F-1)/F$ vs f^2/F is shown in Fig. 2 and leads to $r_1 = 0.552 \pm 0.023$ and $r_2 = 1.074 \pm 0.082$.

The monomer reactivity ratios were also calculated using the method of K–T [18] according to equation (3):

$$\eta = [r_1 + (r_2/\alpha)]\xi - [r_2/\alpha], \quad (3)$$

where η and ξ are functions of the molar ratios of the monomers in the copolymer and in the feed; α is any arbitrary denominator having any positive value, but chosen so as to give a more homogeneous distribution of the date along the η–ξ axis. The values of r_1 and r_2 could be obtained from the linear plot of η vs ξ. Thus, r_1 is the value of η when $\xi = 1$ and the intercept of the straight line $\eta = -r_2/\alpha$. The K–T as well as the F–R parameters obtained are given in Table 2. The value of $\alpha = 0.8456$ was calculated from $\alpha = (H_{\min} \times H_{\max})^{1/2}$, by substituting the minimum and the maximum value of H for an even distribution of the data points. The plot of η against ξ is shown in Fig. 3, which gives $r_1 = 0.466 \pm 0.078$ and $r_2 = 0.980 \pm 0.024$. Using the values of r_1 and r_2 by the K–T method and $Q = 0.78$, $e = 0.40$ for MMA [19] two sets of Q–e values were obtained for AcrNMP: (i) $Q = 0.56$, $e = -0.49$ and (ii) $Q = 1.1$, $e = 1.3$. The first set of values is chosen because these values compared reasonably well with $Q = 0.41$ and $e = -0.26$ for *N*,*N*-dimethyl acrylamide, a tertiary amide considered similar to AcrNMP.



Scheme 1

**Standard deviation of five determinations.

Table 1. Copolymerizations of AcrNMP with MMA for the determination of reactivity ratios

	Mole fraction of monomer in feed		IR Absorbance (cm^{-1})		Mole fraction of monomer in copolymer	
Copolymer	AcrNMP (f_1)	MMA (f_2)	AcrNMP	MMA	AcrNMP (F_1)	MMA (F_2)
P1	0.0721	0.9261	0.0839	1.0533	0.0702	0.9299
P2	0.1394	0.8574	0.1289	0.7656	0.1332	0.8668
P3	0.2177	0.7822	0.1349	0.4897	0.2016	0.7984
P4	0.3018	0.6982	0.1710	0.5711	0.2713	0.7287
P5	0.3945	0.6055	0.3999	0.7361	0.3305	0.6695
P6	0.5993	0.4004	0.5821	0.5214	0.5043	0.4957
P7	0.7157	0.2843	0.4667	0.2796	0.6039	0.3961
P8	0.8497	0.1503	0.5798	0.1478	0.7807	0.2192

Table 2. Fineman–Ross and Kelen–Tüdös parameters for the copolymerization of AcrNMP with MMA in dioxane at 70 ± 1°C

		F–R parameters		K–T parameters	
$f = f_1/f_2$	$F = F_1/F_2$	$G = f(F-1)/F$	$H = f^2/F$	$\eta = G/(\alpha + H)$	$\xi = H/(\alpha + H)$
0.0779	0.0755	− 0.9539	0.0804	− 1.0301	0.0868
0.1626	0.1537	− 0.8953	0.1720	− 0.8799	0.1690
0.2783	0.2525	− 0.8239	0.3067	− 0.7150	0.2662
0.4323	0.3723	− 0.7289	0.5019	− 0.5410	0.3725
0.6515	0.4937	− 0.6681	0.8597	− 0.3918	0.5042
1.4968	1.0173	0.0255	2.2023	0.0084	0.7226
2.5174	1.5246	0.8662	4.1567	0.1732	0.8310
5.6534	3.5616	4.0661	8.9738	0.4141	0.9139

The higher reactivity of MMA can be explained on the basis of π-electron availability and the radical stability. In the case of AcrNMP, the electron-withdrawing carbonyl group reduces the electron density around the double bond, thus making it less available for attack by free radicals. For the monomer MMA, though the −*I* effect of the carbonyl is operative so reducing the reactivity, the hyperconjugation of the methyl group and the presence of a pair of electrons on the methoxy oxygen atom may have compensated for the polarization of the carbonyl group, hence rendering the double bond more available for the free radical attack [20, 21].

CONCLUSION

Copolymers of AcrNMP with MMA of various compositions were synthesized in solution by free radical polymerization using benzoyl peroxide as initiator. The copolymer compositions were determined by FTIR spectroscopy. The reactivity ratios were determined by both the F–R and K–T methods,

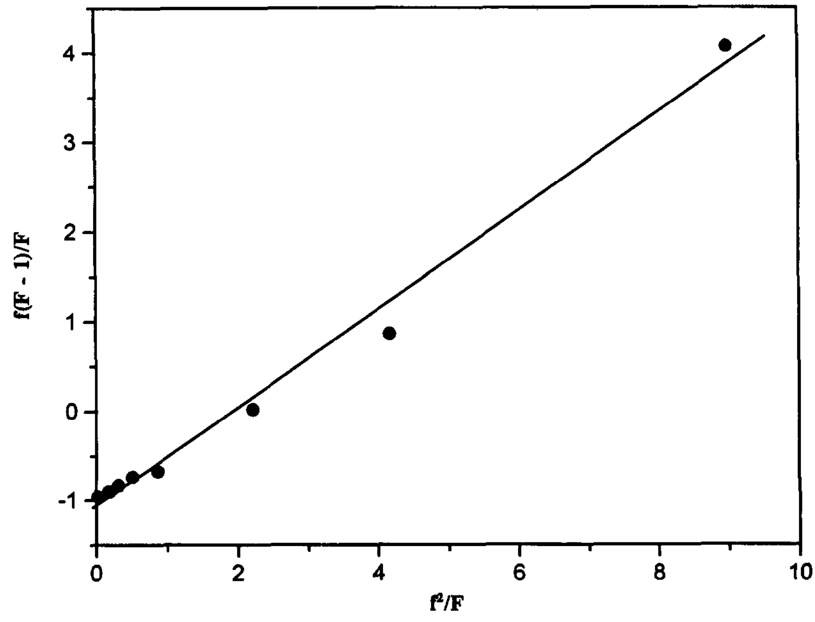


Fig. 2. Fineman–Ross plot for the free radical copolymerization of AcrNMP with MMA.

and the two methods yielded comparable results. It was found that AcrNMP was less reactive than MMA.

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