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Solvent Effect on Acrylamide with Methylmethacrylate and Ethylmethacrylate Copolymer—Synthesis and Characterization

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Free radical copolymerisation of acrylamide (A) with methyl methacrylate (MM) and ethylmethacrylate (EM) have been carried out using 2,2′-azo-bis-isobutyronitrile (AIBN) at 60°C using dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and dioxane as solvents. The copolymers AMM and AEM were characterized by IR and ^{1}H–NMR studies. The reactivity ratios (r) of the copolymers were determined by YBR method. The effect of solvent on these copolymerizations has been discussed.

INTRODUCTION

Saini *et al.*[1, 2], studied the free radical copolymerization of acrylamide (A) and methacrylamide (M) with methylmethacrylate (MM) in solvents like dioxane and ethanol having different dielectric constants. The experimental data clearly shows a strong solvent influence on these copolymerizations. This prompted us to study the effect of solvent on AMM and AEM copolymers. The present paper deals with synthesis and characterization of AMM and AEM copolymers in solvents like dimethyl formamide, dimethyl sulfoxide and dioxane.

EXPERIMENTAL

The detail of the experimental procedure was given in our earlier publications[3, 4]. The compositions of the AMM and AEM copolymers formed with varying feed compositions are determined by nitrogen estimation and are given in Table 1. These data are used for the evaluation of the reactivity ratios of copolymers by YBR method[5]

RESULTS AND DISCUSSION

The infrared spectra of copolymers of acrylamide with methyl methacrylate and ethylmethacrylate showed that the characteristic strong absorption bands at 2980, 1740, 1680 and 1460 cm^{-1} correspond to methylene —CH stretching, >C=O stretching in ester, >C=O stretching in amide and —OCH$_3$ stretching vibrations respectively and 3550–3200 cm^{-1} is due to —NH— stretching vibrations. The appearance of absorption bands corresponding to ester and amide is the evidence for the formation of copolymer.

The ^{1}H-NMR spectrum of AMM copolymer showed that methoxy protons of methyl methacrylate appear at δ 3–7, β-methylene protons appeared near δ 2.0, α-methyl protons appeared at δ 1.0. Amide protons of acrylamide appeared at δ 5.6–6.6. For AEM copolymer β-methylene and methine protons appear in the region of δ 1.2–2.3, α–methylene protons and —CH_3 group protons of alkyl part of ester appear in the region of δ 0.9–1.7 and amide protons of acrylamide appear at δ 5.0–7.2, —OCH_2 protons of EM appear at δ 3.7–4.3. The above ^{1}H-NMR spectral evidence confirms the formation of copolymer.

Reactivity Ratios

Most procedures for evaluating reactivity ratios involve the experimental determination of the copolymer compositions for several different comonomer feed compositions. The compositions of the AMM and AEM copolymers formed with varying feed compositions are determined by nitrogen estimation and are given in Table-1 for three solvents. These data are used for evaluation of reactivity ratios of AMM and AEM copolymers by YBR method[5].

TABLE-1
COPOLYMERIZATION OF ACRYLAMIDE WITH METHYL AND ETHYL METHACRYLATES IN DIFFERENT SOLVENTS

Copolymers	Mole fraction of A in feed [M_2]	N%	Mole fraction of A in copolymer [M_2]
	Solvent : DMSO		
AMM_1	0.401	2.165	0.1478
AMM_2	0.467	2.932	0.1974
AMM_3	0.532	3.654	0.2426
AMM_4	0.601	4.135	0.2721
AMM_5	0.667	4.657	0.3034
	Solvent : Dioxane		
AEM_1	0.372	3.542	0.2604
AEM_2	0.493	5.516	0.3844
AEM_3	0.538	6.061	0.4164
AEM_4	0.574	6.517	0.4435
AEM_5	0.649	7.162	0.4784
	Solvent : dimethyl sulfoxide		
AEM_1	0.372	1.010	0.0836
AEM_2	0.493	1.280	0.1027
AEM_3	0.538	1.911	0.1478
AEM_4	0.574	2.216	0.1794
AEM_5	0.649	2.748	0.2073
	Solvent : dimethyl formamide		
AMM_1	0.466	3.150	0.211
AMM_2	0.532	3.890	0.261
AMM_3	0.600	4.850	0.319
AMM_4	0.666	5.400	0.351
AMM_5	0.735	6.450	0.412

YBR Method

The linear Mayo-Lewis equation can be written in a symmetrical form as follows:

$$\frac{F_1}{F_2} = \frac{f_1}{f_2}\,\frac{[(r_1 f_1 + f_2)]}{[(r_2 f_2 + f_1)]}$$

where

$F_1 = 1 - F_2$ = mole fraction of monomer M_1 in the copolymer.

$f_1 = 1 - f_2$ = mole fraction of monomer M_1 in the initial monomer mixture

r_1 and r_2 are the relativity ratios for monomers M_1 and M_2 respectively.

The symmetrical equations for calculating r_1 and r_2 are as follows:

$$r_1 = (A_2C_1 + nC_2)/(A_1A_2 - n^2)$$
$$r_2 = (A_1C_2 + nC_1)/(A_1A_2 - n^2)$$

where n = no of points.

$$A_1 = \sum_{i=1}^{n} \frac{x_i}{k_i}; \qquad A_2 = \sum_{i=1}^{n} \frac{k_i}{x_i};$$

$$C_1 = \sum_{i=1}^{n} [x_i - (1/k_i)]; \qquad C_2 = \sum_{i=1}^{n} [(1/x_i) - k_i]$$

$$x_i = [f_1/f_2] \qquad \text{and} \qquad k_i = [F_1 \cdot f_2/F_2 \cdot f_1]$$

The root mean square error ($\Delta^2 r_i$) in the determination of r_1 and r_2 can be calculated as follows:

$$\Delta^2 r_1 = \Delta^2 A_2/(A_1A_2 - n^2)$$

$$\Delta^2 r_2 = \Delta^2 A_1/(A_1A_2 - n^2)$$

where Δ^2 = mean square error of experiment.

$$\Delta^2 = \sum_{i=1}^{n} \Delta_i^2/(n-2)$$

$$\Delta_i^2 = \left[r_1\sqrt{\frac{x_i}{k_i}} - r_2\sqrt{\frac{k_i}{x_i}} - \sqrt{k_i\ x_i} + \frac{1}{\sqrt{k_i \cdot x_i}}\right]^2$$

The values so evaluated are summarized in Table 2. These values show that the product of r_1 and r_2 remains less than unity indicating that all these copolymers are weakly ordered with a predominantly random distribution of the monomeric units in the polymer chain. In all these systems r_1 (alkylmethacrylate) is greater than r_2 (vinylic amide) indicating that the copolymers formed will be richer in alkylmethacrylates.

Solvent Effect

The experimental data (Table-2) clearly show a strong solvent influence on these copolymerizations. In particular, the copolymers obtained indioxane are always richer in acrylamide than the copolymers obtained in dimethyl formamide and dimethyl sulfoxide. For the acrylamide copolymerizations, it was assumed that the dielectric constant and polarity could be one of the possible reasons for the solvent dependence. The authors tried to correlate this influence with the enolization equilibrium of the amidic group. Such amide-enol equilibrium could be influenced by solvents of different polarity and dielectric constants. Other points which have to be considered for a complete evalution of this phenomenon can be different monomer solvations, different stabilities of the growing radicals and hydrogen bond formation in the different solvents. Monagle[6] *et al.* reported the copolymerization of methacrylamide with 1,2-dimethyl-5-vinyl pyridinium methylsulfate (DMVPMS) in solvents having different dielectric constants. The authors attributed the observed effect of the solvent on copolymerization reactivity to differences in the degree of ionization DMVPMS monomer as a result of differences in the dielectric constants of the solvent. In particular, the authors obtained copolymers richer in methacrylamide in solvents of low dielectric constants (such as acetic acid) than in solvents of high dielectric constant (such as water and dimethyl sulfoxide). On the basis of the results obtained in the present work,[7] it seems therefore reasonable to attribute the formation of acrylamide copolymers richer in acrylamide in solvents of low dielctric constants than in solvents of high dielectric constants. A similar behaviour was observed in the copolymerization of acrylamide and methacrylamide with methylmethacrylate[1,2] in dioxane and ethanol.

TABLE-2
REACTIVITY RATIOS OF ACRYLAMIDE COPOLYMERS CALCULATED BY YBR METHOD IN DIFFERENT SOLVENTS

Reactivity ratios	Solvent		
	dimethyl formamide (t = 36.7)	dimethyl sulfoxide (t = 46.7)	Dioxane (t = 2.2)
r_1 (MMA)	2.65 ± 0.03	3.16 ± 0.060	2.45 ± 0.33†
r_2 (AM)	0.14 ± 0.01	0.10 ± 0.002	2.55 ± 0.40
r_1^1 (EMA)	*2.57 ± 0.11	6.19 ± 0.810	1.19 ± 0.03
r_2^1 (AM)	0.11 ± 0.01	0.05 ± 0.010	0.30 ± 0.01

t = dielectric constant, * Reference 3, † Reference 1.

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