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# Synthesis, Characterization and Determination of Reactivity-Ratios of Acrylamide-Methacrylate Copolymers

P. RAGHUNATH RAO
*Department of Chemistry*
*Kakatiya University, Warangal-506 009, India*

Free radical copolymerisation of acrylamide (A) with five methacrylates, namely methacrylate (MM), ethyl methacrylate (EM), isopropyl methacrylate (IPM), butyl methacrylate (BM) and hexyl methacrylate (HM) were carried out in the presence of 2,2′-azobisisobutyronitrile (AIBN) in dimethylformamide (DMF) at 60°C. The percentage compositions of the copolymers were established by elemental analysis. The complymers were characterized by IR, $^1$H-NMR and $^{13}$C-NMR studies. The copolymerization reactivity ratios (r) were determined by both Finemann-Ross (FR) and Kelen-Tudos (KT) methods. The product of $r_1$ (methacrylate) and $r_2$ (A) 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. The order of reactivity of the alkyl methacrylates towards acrylamide radical is MM > EM > IPM > BM > HM.

## INTRODUCTION

Acrylic copolymers have acquired great importance for various industrial applications[1–3]. They serve as basic materials for the preparation of formulations used as base and top coats in leather industry. Saini *et al.*[4] have studied the free radical copolymerizations of acrylamide (A) with methyl methacrylate (MM) and styrene. Copolymerization of acrylamide (A) with styrene[5], n-butyl acrylate[6], acrylic acid[7], methyl vinyl ketone[8], acrylonitrile[9] and methacrylic acid[10] have also been studied. In our earlier work, we studied the copolymerization of methacrylamide (MA) with ethylmethacrylate (EM)[11] and butyl methacrylate (BM)[12]. In the present investigation, we report the synthesis, characterization and determination of reactivity ratios of acrylamide-methacrylate copolymers by thermal initiator like AIBN.

## EXPERIMENTAL

All the monomers were purified from inhibitor by washing with 5% aq NaOH, dried over $CaCl_2$ and distilled twice under reduced pressure. Acrylamide (A) was crystallized from chloroform. AIBN (Fluka) was crystallized from methanol. Dimethylformamide (DMF) was dried and distilled.

All copolymerizations were carried out in reaction tubes charged with the required amounts of monomers, solvent and initiator. The tubes were then sealed in a nitrogen atmosphere and maintained at 60 ± 0.1°C. Conversions were limited to 10%. The reactions were stopped by adding excess water as non-solvent. The copolymers were precipitated, washed thoroughly with ether and hexane to remove DMF and unreacted monomer. Reprecipitation was done from acetone solution. The total monomer concentration was kept at 1.6 ms/l. The initiator used was 0.6 gr/l.

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The acrylamide (A) contents of copolymer samples were determined from nitrogen analyses found by Carlo-Erba Model-1106 elemental analyser. The reactivity ratios were estimated by both Finemann-Ross (FR)[13] and Kelen-Tudos[14] methods.

## RESULTS AND DISCUSSION

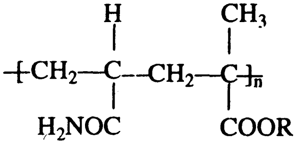
### Spectral Characterization

The infrared spectra of copolymers of acrylamide and alkyl methacrylates showed the characteristic strong absorption bands at 2980, 1740, 1680 and 1460 $cm^{-1}$ correspond to methylene CH stretching, >C═O strecthing in ester, >C═O stretching in amide and —$OCH_3$ stretching vibrations 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 copolymers.

$^1H$-NMR spectra of acrylamide and alkylmethacrylates showed methoxy protons of methyl methacrylate appear at $\delta$ 3.7, $\beta$-methylene protons that appear near $\delta$ 2.0 , $\alpha$-methyl protons appear at $\delta$ 1.0, and amide protons of acrylamide appear at $\delta$ 5.6–6.6. For AEM, AIPM, ABM and AHM copolymers, $\beta$-methylene and methine protons appear in the region of $\delta$ 1.2–2.3, $\alpha$-methyl protons and $CH_3$ group protons of alkyl part of ester appear in the region of $\delta$ 0.9–1.7, amide protons of acrylamide appear at $\delta$ 5.0–7.2, —$OCH_2$ protons of IPM appear at $\delta$ 4.5–5.0, —$OCH_2$ protons of BM appear at $\delta$ 3.6–4.0 and —$OCH_2$ protons of HM appear in the region of $\delta$ 3.8–4.2. In ABM and AHM copolymers methylene protons of alkyl part of ester appear at $\delta$ 1.8–2.9.

$^{13}C$–NMR spectra for few copolymers like AIPM, ABM and AHM were recorded. AIPM copolymer shows low field resonance at $\delta$ 177.4–178.8. Amide carbonyl peak may be assumed to be over lapping with the ester carbonyl peaks in this region. Signal at $\delta$ 69.4 is due to —$OCH_2$ carbon of isopropyl group. The resonance at $\delta$ 45.6–46.8 represent tertiary and quaternary carbons. The resonances at $\delta$ 22.0–23.8 are due to C—$CH_3$ and methyl groups of isopropyl ester. For ABM and AHM copolymers the resonances at $\delta$ 19.5–32.1 are due to methylene carbons of alkyl part of ester. The resonances at $\delta$ 16.9 and $\delta$ 14. 0 are due to $\alpha$-methyl and methyl carbons of butyl and hexyl groups of the ester.

Based on the above spectral evidence, the structure of acrylamide-alkyl methacrylate copolymer is given by:



$$-\!\!\left[CH_2-\underset{H_2NOC}{\overset{H}{C}}-CH_2-\underset{COOR}{\overset{CH_3}{C}}\right]_n$$

where R = —$CH_3$, —$C_2H_5$, —$CH(CH_3)_2$, —$C_4H_9$ and —$C_6H_{13}$.

feed compositions. The compositions of the copolymers formed from various feeds were determined from nitrogen contents (Table-1). These data were used for evaluation of reactivity ratios of the acrylamide-alkyl methacrylate systems by the Finemann-Ross and Kelen-Tudos methods.

TABLE-1
COPOLYMERIZATION OF ALKYLMETHACRYLATES (1) AND ACRYLAMIDE (2)

| Run | Feed composition of (A) in mole fraction [$M_2$] | N% in copolymer | Composition of copolymer in mole fraction (A) [$m_2$] |
|---|---|---|---|
| AMM$_1$ | 0.466 | 3.15 | 0.211 |
| AMM$_2$ | 0.532 | 3.89 | 0.261 |
| AMM$_3$ | 0.600 | 4.85 | 0.319 |
| AMM$_4$ | 0.666 | 5.40 | 0.351 |
| AMM$_5$ | 0.735 | 6.45 | 0.412 |
| AEM$_1$ | 0.372 | 2.26 | 0.172 |
| AEM$_2$ | 0.493 | 3.02 | 0.224 |
| AEM$_3$ | 0.538 | 3.32 | 0.245 |
| AEM$_4$ | 0.574 | 3.82 | 0.278 |
| AEM$_5$ | 0.649 | 5.12 | 0.361 |
| AIPM$_1$ | 0.423 | 2.87 | 0.235 |
| AIPM$_2$ | 0.523 | 3.72 | 0.295 |
| AIPM$_3$ | 0.624 | 4.77 | 0.366 |
| AIPM$_4$ | 0.655 | 5.25 | 0.396 |
| AIPM$_5$ | 0.677 | 6.49 | 0.469 |
| ABM$_1$ | 0.473 | 2.22 | 0.202 |
| ABM$_2$ | 0.523 | 2.68 | 0.239 |
| ABM$_3$ | 0.574 | 2.93 | 0.259 |
| ABM$_4$ | 0.624 | 3.60 | 0.309 |
| ABM$_5$ | 0.654 | 4.12 | 0.346 |
| AHM$_1$ | 0.466 | 1.95 | 0.208 |
| AHM$_2$ | 0.532 | 2.70 | 0.276 |
| AHM$_3$ | 0.598 | 3.63 | 0.352 |
| AHM$_4$ | 0.666 | 4.30 | 0.401 |
| AHM$_5$ | 0.785 | 5.48 | 0.481 |

## Finemann-Ross Method

Let us denote the molar concentration of the monomers in the feed ($M_1/M_2$) by F and the corresponding molar concentration ratio of the monomer components in the copolymer ($m_1/m_2$) by f. Then the copolymer equation is:

$$\frac{F(f-1)}{f} = r_1 \cdot \frac{F^2}{f} - r_2 \tag{1}$$

or

$$G = r_1 \cdot H - r_2$$

where $G = \frac{F(f-1)}{f}$ and $H = F^2/f$.

When G versus H is plotted, a straight line with $r_1$ as the slope and $-r_2$ as the intercept is obtained.

### Kelen-Tudos Method

The Kelen-Tudos equation can be given by

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{2}$$

where $\eta = \frac{G}{(\alpha + H)}$, $\xi = \frac{H}{(\alpha + H)}$, G and H are as defined earlier and $\alpha$ is an arbitrary constant obtained from minimum and maximum values of H using the relation $\alpha = \sqrt{H_{max}H_{min}}$. F = monomer feed ratio and f = copolymer composition. From the graph of $\eta$ vs. $\xi$, the intercept of $\xi = 1$ gives $r_1$ and the intercept at $\xi = 0$ gives $r_2/\alpha$.

In the present study, reactivity ratios of AMM, AEM, AIPM, ABM and AHM copolymers have been determined. The data given in Table-1 was used for the evaluation of reactivity ratios of acrylamide-alkyl metharcylate system by Finemann-Ross (F-R) and Kelen-Tudos (K-T) methods. The results are given in Table-2

TABLE-2
REACTIVITY RATIOS OF ACRYLAMIDE AND ALKYLMETHACRYLATES BY F–R AND K–T METHOD

| $M_1$ | $M_2$ | F-R | | K-T | |
|---|---|---|---|---|---|
| | | $r_1$ | $r_2$ | $r_1$ | $r_2$ |
| MM | Acrylamide | 2.43 | 0.11 | 2.52 | 0.10 |
| EM | ” | 2.70 | 0.12 | 2.74 | 0.12 |
| IPM | ” | 1.83 | 0.15 | 1.96 | 0.17 |
| BM | ” | 3.01 | 0.19 | 3.04 | 0.19 |
| HM | ” | 3.05 | 0.35 | 3.10 | 0.35 |

For all the systems the value of $r_1$ (alkyl methacrylate) is more than one, whereas $r_2$ (acrylamide) is less than one. The product of $r_1$ and $r_2$ remains less than unity indicating that the copolymers are weakly ordered with a predominantly random distribution of the monomer units in the polymer chain. The $r_1$ value which is more than one indicates that the propagation reaction types 11 and 21 will be preferred to type 12 and 22 and hence the probability of $M_1$ (methacrylate) entering into the copolymer chain is higher as compared to $M_2$ (amide). The copolymer formed will, therefore, be richer in $M_1$. Hence one can conclude that in all these systems $r_1$ (alkyl methacrylate) is greater than $r_2$ (vinylic amide) which indicates that the copolymers formed will be richer in alkyl methacrylates.

### Alkyl Effect

A perusal of the reactivity ratio data reveals that the rate of reaction increased with an increase in methacrylate concentration in the monomer feed.

The rate of polymerization depends on the nature of the alkyl group of the comonomer. This can best be understood from the $1/r_2$ values ($r_2 = (K_{22}/K_{21})$) that give a measure of the poly(acrylamide) radical, the higher the values of ($1/r_2$), the greater the chance that the methacrylate will add to the poly (acrylamide) radical. The order of reactivity of the alkyl methacrylates towards acrylamide radical is: MM > EM > IPM > BM > HM.

The relative reactivities of the methacrylates towards the acrylamide radical are governed by steric factors . It is shown that as the size of the alkyl group in alkyl methacrylates increased the tendency to react with acrylamide radical decreased. Surprisingly, the low $r_2$ values for AIPM compared with ABM and AHM suggest greater reactivity of IPM towards poly(acrylamide) radical despite the bulky isopropyl group. The poor reactivities of BM and HM compared with IPM may be attributed to the shielding effect arising from butyl and hexyl side groups of the corresponding radicals due to the flexibility and free movement associated with the side alkyl groups. This would hinder the approach of incoming monomer to react with the radicals. Similar observation has been made by Dhal *et al.* in the case of copolymers of glycidyl methacrylate with alkyl acrylates.[15]

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