

# Synthesis and Characterization of Methacrylic Acid–Ethyl Acrylate Copolymers

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## SYNOPSIS

Copolymerization of methacrylic acid (MAA) and ethyl acrylate (EA) was performed in aqueous medium in the presence of an emulsifier with MAA as the major component (53.7–82.3 mol %). Emulsion stability was studied as a function of concentration and the nature of the emulsifier (ionic or nonionic). Copolymers were characterized using IR and  $^1\text{H}$ -NMR spectroscopy.  $^{13}\text{C}$ -NMR spectra of MAA–EA copolymers have been discussed in terms of their triad monomer sequence distributions. Reactivity ratios of the MAA–EA pair were determined using a nonlinear least-square errors in variables method. Partition of the monomers in aqueous and organic phases was studied using a gas chromatographic technique. A two-loci polymerization mechanism was proposed on the basis of this partition behavior and the calculated composition of the oligomeric radicals formed in the initial stages of polymerization. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Copolymers of hydrophobic monomers like styrene, alkyl acrylates, acrylonitrile, and small amounts (1–10%) of polar unsaturated carboxylated monomers like acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA) are the products of commercial interest due to their applications in paints, adhesives, binders, thickeners, etc. Generally, the emulsion or the emulsifier free-emulsion polymerization technique is used for synthesizing the above-mentioned acrylic copolymers.

Investigations on the emulsion polymerization behavior of these systems by various authors<sup>1–12</sup> revealed that the reaction rate, reaction mechanism, latex stability, and properties of the final product are greatly affected by the concentration and the polarity of the acid monomers and partition of the acid monomers between the aqueous and organic phases. For such systems, the theory of homogeneous nucleation of particles first conceptualized by Jacobi<sup>13</sup> and Priest<sup>14</sup> and later developed by Fitch<sup>15</sup> is applicable. According to this theory, oligomeric

radicals are formed in the aqueous phase in the initial stages of polymerization, which precipitate after attaining the certain critical molecular weight and act as primary particles.

Guillaume et al.<sup>16</sup> proposed a two-loci polymerization mechanism for batch emulsifier-free emulsion polymerization of styrene and butyl acrylate (BA) in the presence of MAA. Studies on the polymerization of the AA–styrene system in emulsion revealed that the primary reaction locus shifts from the particles to the aqueous phase after the hydrophobic monomer styrene has been consumed.<sup>17</sup>

Investigations on the nucleation and particle growth of acrylate ester latexes containing various amounts of IA (up to 9% by wt) have shown that the major effect of IA is to decrease the number of particles formed in the earlier stages of emulsion polymerization. This is due to the incorporation of hydrophilic IA into acrylate oligomeric radicals formed in the aqueous phase, resulting into their increased water solubility and decreased probability of becoming precipitated to form primary radicals.<sup>18</sup>

Recently, Pan et al.<sup>19</sup> reported that in soapless polymerization of MMA and BA, introduction of MAA imparts heterogeneity in the copolymer composition, which is reflected by multiple glass transition temperatures ( $T_g$ ). From studies on the car-

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boxylated ethyl acrylate latexes (EA), Muroi<sup>20</sup> found that unsaturated acids are concentrated in the surface layers of particles in the course of emulsion polymerization, as expected from their chemical structure.

For studying the potential of new polymer systems for commercial applications, it is desirable to characterize them for chemical composition, tacticity, and sequence distribution of the monomer units in the polymer chains and correlate them with the physical and chemical properties of these copolymers.<sup>21,22</sup> Knowledge of the sequence distribution of the monomers in the polymer chains may supply information about the process of addition of monomers during radical copolymerization.<sup>23</sup> Such structural findings have become possible with the advent of <sup>13</sup>C-NMR spectroscopy.

Bovey<sup>24</sup> used high-resolution NMR spectroscopy for the determination of compositional and configurational sequences in polymers. Balard et al.<sup>25</sup> reported that <sup>13</sup>C-NMR spectra of nitrile carbons in polyacrylonitrile (PAN) can be interpreted in terms of steric triads and pentads. Pichot et al.<sup>26</sup> employed <sup>13</sup>C-NMR to elucidate the sequence distribution of poly(AN-co-MMA). Brar et al.<sup>27,30</sup> determined the reactivity ratios, number-average sequence length, and monomer sequence distribution using <sup>13</sup>C-NMR for a number of copolymer systems like AA-MMA, AN-EA, MMA-ethyl methacrylate, etc. Bajaj et al.<sup>31</sup> also demonstrated the potential of <sup>13</sup>C-NMR spectroscopy for measuring the AN units in PAN and AN-haloalkyl acrylate/methacrylate copolymers synthesized in various reaction media.

From the literature quoted above, it is evident that carboxylic acid monomers lead to several complexities in the emulsion polymerization. Since acrylic polymers containing MAA as the major comonomer are used as synthetic thickeners in textile printing,<sup>32–35</sup> in the present study, the polymerization of MAA-EA using the emulsion polymerization technique is reported. An attempt has been made to understand the mechanism of MAA-EA polymerization whether it is emulsion or emulsion and solution polymerization simultaneously. Copolymers obtained at high conversions were characterized using viscometry, infrared, and NMR spectroscopy to obtain insight into the structure.

## EXPERIMENTAL

### Materials

MAA (Fluka product) was distilled at 75°C/12 mmHg and EA (BDH Chemicals, India) was dis-

tilled at 50°C/80 mmHg before use. A combination of sodium lauryl sulfate (Glaxo Laboratories, India) and Hyoxide AAO, a nonyl phenyl ethylene oxide condensate (Hico Products) was used as an emulsifier. Potassium persulfate and sodium metabisulfite (BDH Chemicals, India) were used as redox initiators.

### Polymer Synthesis

MAA-EA copolymers of varying compositions (MAA 53.7–82.3 mol % and EA 17.6–46.3 mol %) were synthesized by using a semicontinuous emulsion polymerization technique. The recipe of a 20 g batch is given in Table I. A mixture of anionic sodium lauryl sulfate (2 wt % of monomers) and non-ionic Hyoxide AAO (3 wt % of monomers) was used as an emulsifier. Monomers were preemulsified using 60% of the total water (60 g), 60% of the total emulsifier, i.e., 0.24 g of sodium lauryl sulfate and 0.36 g of Hyoxide AAO, and 0.025 g of potassium persulfate. The remainder of the water, emulsifiers, and 0.050 g of sodium metabisulfite were charged into a 500 mL round-bottom flask, immersed in a constant temperature bath at 50°C, and equipped with a mechanical stirrer, a nitrogen inlet, a reflux condenser, and a dropping funnel. Monomer emulsion was then added to this polymerization flask slowly under constant agitation over a period of 25 min. A high degree of conversion (95–98%) could be obtained by carrying out the polymerization for 4 h. Emulsion was immediately broken with cold aqueous NaCl solution, filtered, and washed with slightly acidic water and subsequently with *n*-hexane. The white polymer obtained was dried in a vacuum oven for 24 h at 70°C.

For determination of reactivity ratios, another set of copolymers using the same recipe, but different

**Table I** Polymerization Recipe

Compound	Weight (g)
Methacrylic acid	10–16 (53.7–82.3 mol %)
Ethyl acrylate	4–10 (17.6–46.3 mol %)
Sodium lauryl sulfate	0.4 (2 wt % of monomer)
Hyoxide AAO	0.6 (3 wt % of monomer)
Potassium persulfate (KPS)	0.025 (0.125 wt % of monomer)
Sodium metabisulfite (bisulfite)	0.050 (0.25 wt % to monomer)
Distilled deionized water	100 (water : monomer = 5 : 1)

Time, 4 h; temperature, 50°C; atmosphere, nitrogen.

monomer feed ratios (MAA 10–85 mol %, and EA 15–90 mol %), were synthesized. Conversion was kept below 10% in these experiments.

### Reactivity Ratio Determination

Reactivity ratios of the MAA–EA pair were determined by a method based on the statistically valid error-in-variables model (EVM),<sup>36</sup> with the help of the RREVM computer program that takes into consideration the errors in determining the composition of comonomers in the copolymer and in the feed. The input parameters for this program are the composition of one monomer in the feed as well as in the copolymer and the initial estimate of reactivity ratios (obtained from the Kelen–Tudos method.<sup>37</sup> The copolymer composition was determined using <sup>1</sup>H-NMR.

### Concentration of Monomers in the Aqueous Phase

Monomer–water mixtures containing different proportions of two monomers (MAA 10–75 and EA 25–90 mol %) were prepared and stirred for 4 h. After equilibrating for 8 h, the aqueous and organic layers were separated and the aqueous layer was analyzed for MAA and EA content, using a gas chromatographic technique. A Nucon 5700 gas chromatograph with a 10% diethylene glycol succinate (DEGS) column was used for this purpose. The oven temperature was 200°C and the FID mode was used for detection.

### Polymer Characterization

#### Elemental Analysis

Elemental analysis of the copolymers was carried out using Carlo Erba 1106 elemental analyzer to determine the carbon and hydrogen contents of these copolymers.

#### Acidimetric Titrations

Concentration of MAA in these copolymers was determined by acidimetric titration of 0.5% polymer solution in methanol against the standard NaOH solution with phenolphthalein as an indicator.

#### Infrared Spectral Studies

IR spectra of MAA–EA copolymers were recorded in a KBr pellet using a Nicolet 5DX FTIR spectrometer.

### <sup>1</sup>H-NMR Studies

<sup>1</sup>H-NMR spectra of all the copolymers were recorded on a JEOL JNM FX 100 spectrometer operating at 99.55 MHz. Spectra were recorded at 90°C, using DMSO-*d*<sub>6</sub> as a solvent and tetramethylsilane as an internal standard.

### Proton Decoupled <sup>13</sup>C-NMR Studies

<sup>13</sup>C { <sup>1</sup>H }-NMR spectra were recorded on a Bruker 270 MHz spectrometer using DMSO + DMSO-*d*<sub>6</sub> as a solvent. All the spectra were recorded at 90°C and the chemical shifts are reported downfield to tetramethylsilane (TMS). Conditions of recording the spectra are as follows: frequency, 67.5 MHz; pulse repetition time, 2.0 s; and pulse width, 15 s. Calculations regarding the fractional peak area measurement were made, using a Lorentzian-shape curve-fitting computer program on an ICL-3960 computer system.

### Intrinsic Viscosity

Intrinsic viscosity of all the copolymers was measured using an Ubbelohde viscometer. A 0.5% solution of copolymers in methanol was used. Measurement was carried out in a thermostat at 30 ± 1°C.

## RESULTS AND DISCUSSION

As can be seen from the polymerization recipe (Table I), a very high amount of mixed emulsifier (5% on the wt of monomers) containing 0.6 parts Hyoxide AAO and 0.4 parts sodium lauryl sulfate had to be used for obtaining a stable emulsion. Preliminary investigations showed that sodium lauryl sulfate alone was insufficient to produce a stable emulsion, even when its concentration was increased from 0.4 to 2 wt % of the monomer.

The stability of emulsion is dependent on several factors like reaction temperature, chemical nature, and concentration of the monomers in the emulsion, concentration and chemical nature of the surfactants, and stirring speed during the polymerization.<sup>38</sup> Lock et al.<sup>18</sup> reported that flocculation of the particles can occur if preexisting particles attain a critical size at which they are no longer stable. This flocculation will not occur if there is sufficient adsorbed surfactant.

The HLB value (hydrophilic–lipophilic balance) of an emulsifier decides its suitability for different systems.<sup>39</sup> The HLB value of 8–15 has been found

to be suitable for an oil-in-water system.<sup>40</sup> On the basis of the HLB value, a nonionic emulsifier, Hyoxide AAO (a nonyl phenyl ethylene oxide condensate), having an HLB value of 12.8, was chosen (3% on the wt of monomers) for the present system, but no improvement in the stability of emulsion was observed. However, when a combination of anionic, sodium lauryl sulfate, and nonionic Hyoxide AAO was used, an emulsion, stable for more than 6 months, was obtained in all the cases except one formulation containing 82.3 mol % MAA (in the feed), which showed a tendency toward coagulation. A similar observation was made by Ugelstad et al.<sup>41</sup> during the emulsion polymerization of styrene, where significant differences were found in the stability of the emulsion obtained with the sodium lauryl sulfate-cetyl alcohol combination and sodium lauryl sulfate alone.

## Polymer Characterization

### Elemental Analysis

The C and H contents of the copolymers are given in Table II. These values are in close agreement with those calculated theoretically, on the basis of feed concentration, assuming 100% conversion.

### Acidimetric Titrations

When solution of these copolymers in methanol was titrated against the standard NaOH solution, the

MAA content was found to be much less than the amount of MAA taken in the feed (Table II), though the conversion in each case was 95–98%. A similar observation was made by Vijayendran<sup>1</sup> for the carboxylated polystyrene latexes. As neutralization time is quite rapid in the direct titration method, the acid groups present on the surface are readily available for neutralization, but the groups buried inside the particle core may not become neutralized, thereby leading to lower values of MAA obtained by acidimetric titrations. An indirect method of titration as suggested by Hen<sup>42</sup> also does not seem to be feasible for the copolymers containing vinyl acetate or acrylate esters, as these monomers may become hydrolyzed on keeping them in alkali for a long time, thereby resulting into a higher value of carboxylic acid than the actual acid content of the copolymer.

### Intrinsic Viscosity

The intrinsic viscosity of MAA–EA copolymers increases from 1.72 to 2.70 dL g<sup>−1</sup> as the EA content in the copolymer increases from 17.6 to 49.8 mol % (Table II). Intrinsic viscosity is a measure of molecular weight and hydrodynamic volume of the polymer. The hydrodynamic volume depends on the size, tacticity, and density of the polymer coils in solution.<sup>43</sup> The observed increase in the viscosity of EA-rich polymers may be due to increase in the molecular weight as well as increase in the size of the side substituent, i.e., ester group in EA as compared to carboxylic acid group of MAA. This would lead

**Table II** Polymer Characterization Data

Feed Concentration (Mol %)		Elemental Analysis		Copolymer Composition (mol %)				
				<sup>1</sup> H-NMR		Acidimetric Titrations MAA	[η] dL g <sup>-1</sup>	Yield (%)
MAA	EA	C% Exptl (Calcd)	H% Exptl (Calcd)	MAA	EA			
82.3	17.6	46.4 (51.3)	6.57 (6.63)	—	—	77.4	1.72	94.8
77.6	22.3	50.9 (51.7)	7.22 (6.69)	78.5	21.4	70.5	1.92	96.6
72.9	27.0	52.2 (52.0)	7.33 (6.73)	71.8	28.2	65.3	2.10	96.8
68.1	31.8	52.8 (52.4)	7.70 (6.78)	64.0	36.0	60.2	2.20	94.4
63.4	36.6	53.0 (52.8)	7.36 (6.83)	61.9	38.1	55.0	2.27	98.4
53.7	46.3	53.9 (53.6)	7.80 (6.93)	50.2	49.8	45.7	2.70	96.0

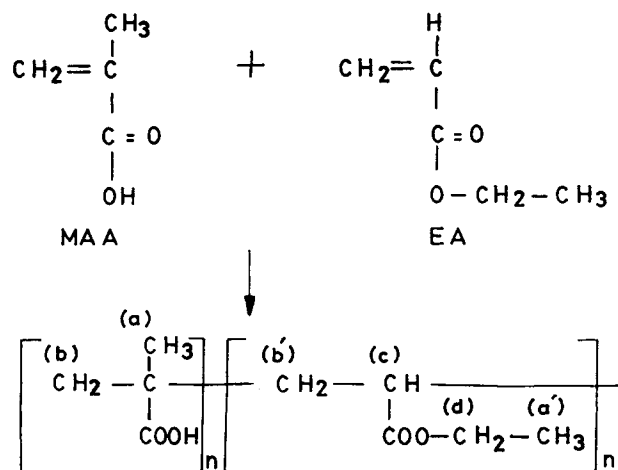
to increase in the overall dimensions of polymeric coils, resulting in a higher hydrodynamic volume.

### IR Studies

Various absorption bands in the IR spectra of copolymers have been assigned by comparison with the corresponding homopolymers, i.e., poly(ethyl acrylate) (PEA) and PMAA. In PMAA, a broad band extending from 3419 to 3512  $\text{cm}^{-1}$  due to the  $\text{—OH}$  stretching vibration and a strong band at 1700  $\text{cm}^{-1}$  due to the carbonyl stretching vibration of the carboxylic acid group of MAA was observed.  $\text{C—H}$  deformation (*sym*) of the methyl group at 1390  $\text{cm}^{-1}$  and splitting of the  $\text{C—O}$  stretching vibration into two components at 1270 and 1180  $\text{cm}^{-1}$  were observed that are characteristic of PMAA. In PEA, the carbonyl stretching vibration of the ester group was observed as a sharp band at 1740  $\text{cm}^{-1}$ . The rest of the absorption bands were the same as in PMAA, except one additional peak at 1040  $\text{cm}^{-1}$  due to  $\text{C—O—C}$  stretching of the ester group. The peak at 1390  $\text{cm}^{-1}$  was not present in PEA. All the peaks observed in the case of PMAA and PEA were also observed in the copolymers. The absorption due to the carbonyl stretching of the acid and ester units of the copolymer appeared as one, broad band in the range of 1700–1740  $\text{cm}^{-1}$ . They were not resolvable due to very close proximity. There is no shift in the position of absorption bands with a change in the copolymer composition; however, the intensity of the IR bands become affected by changing the composition of the copolymers.

### $^1\text{H-NMR}$ Studies

The main-chain carbon atoms of MAA and EA copolymers are represented by the following structural units:



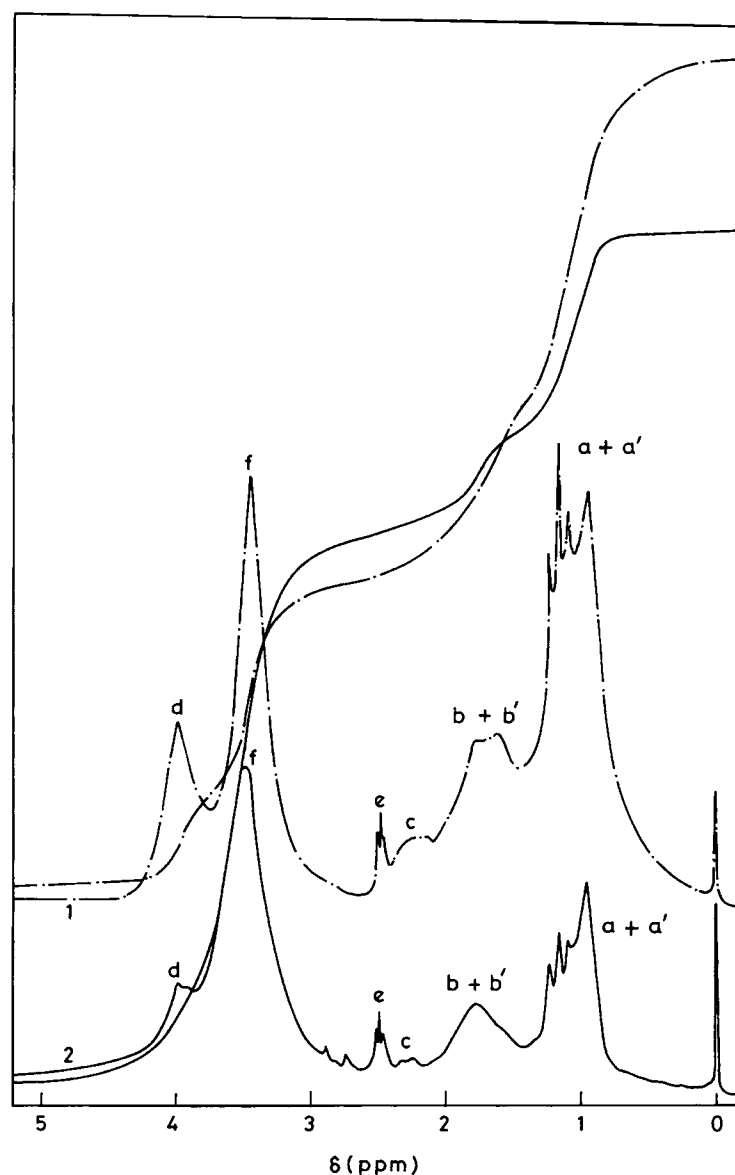
Assignment in the copolymers were made on the basis of comparison with the corresponding homopolymers. In PEA,  $\text{—CH}_3$ ,  $\text{CH}_2$ ,  $\text{—CH}$ , and  $\text{—OCH}_2$  protons appeared at 1.1–1.2, 1.5, 2.2, and 4.0  $\delta$ , respectively. In PMAA, methyl protons appeared as a singlet at 0.9  $\delta$ , and methylene protons, as a broad peak at 1.7–1.8  $\delta$ .  $^1\text{H-NMR}$  spectra of copolymers displayed an unresolvable multiplet ( $a + a'$ ) between 0.9 and 1.2  $\delta$  (Fig. 1). This multiplet is due to the methyl protons of MAA and methyl protons of the alkyl chain of EA. To resolve this multiplet, the triplet of methyl protons of EA was spin–spin decoupled. In the decoupled spectrum, the singlet at 0.9  $\delta$  is due to the methyl protons ( $a - a'$  decoupled) of the MAA unit (Fig. 2). The most up-field peak at  $\delta$  4.0 is due to  $\text{OCH}_2$  (d) protons of EA. A broad signal between 1.5 and 1.7  $\delta$  is assigned to methylene protons ( $b + b'$ ) of both EA and MAA. The signal at 2.7 (e) and  $\delta$  3.4 (f) are due to residual protons of  $\text{DMSO-}d_6$ . Methine protons (c) of the EA unit give a peak at  $\delta$  2.20.

The composition of the copolymers was calculated by measuring the intensity of peak due to  $\text{OCH}_2$  (d) protons at  $\delta$  4.0 of EA and then subtracting the contribution of EA from the multiplet of methyl protons of MAA and EA. Remaining is the contribution of MAA, and from this, the concentration of MAA in the copolymer was calculated. The results obtained were found to be much closer to the feed concentration than were the results obtained from acidimetric titrations (Table II).

### $^{13}\text{C}\{^1\text{H}\}$ -NMR Studies

In the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the copolymers, various resonance signals were assigned by comparison with the homopolymers. In case of PEA,  $\text{—CH}_3$ ,  $\text{—CH}_2$ , and  $\text{—CH}$  carbon signals appeared at  $\delta$  12.3–12.5, 35.0–36.0, and 41.3 ppm, respectively. The resonance signals around  $\delta$  58.5–58.7 and  $\delta$  172.5 ppm can be assigned, respectively, to  $\text{—OCH}_2$  and  $\text{>C=O}$  carbon in PEA. In PMAA,  $\text{—CH}_3$ ,  $\text{—CH}_2$ , and  $\text{—C—}$  quaternary carbon appeared at  $\delta$  15.5–19.0, 48.5–52.5, and 43.4–44.9 ppm, respectively. Carbonyl carbon appears as a multiplet from  $\delta$  176.6–178.2 ppm, demonstrating that the  $\text{>C=O}$  of PMMA is configurational-sensitive.

In MAA–EA copolymers, the signals around  $\delta$  12.3–12.5, 15.3–19.7, 43.1–45.8, 48.5–52.2, and 58.5–

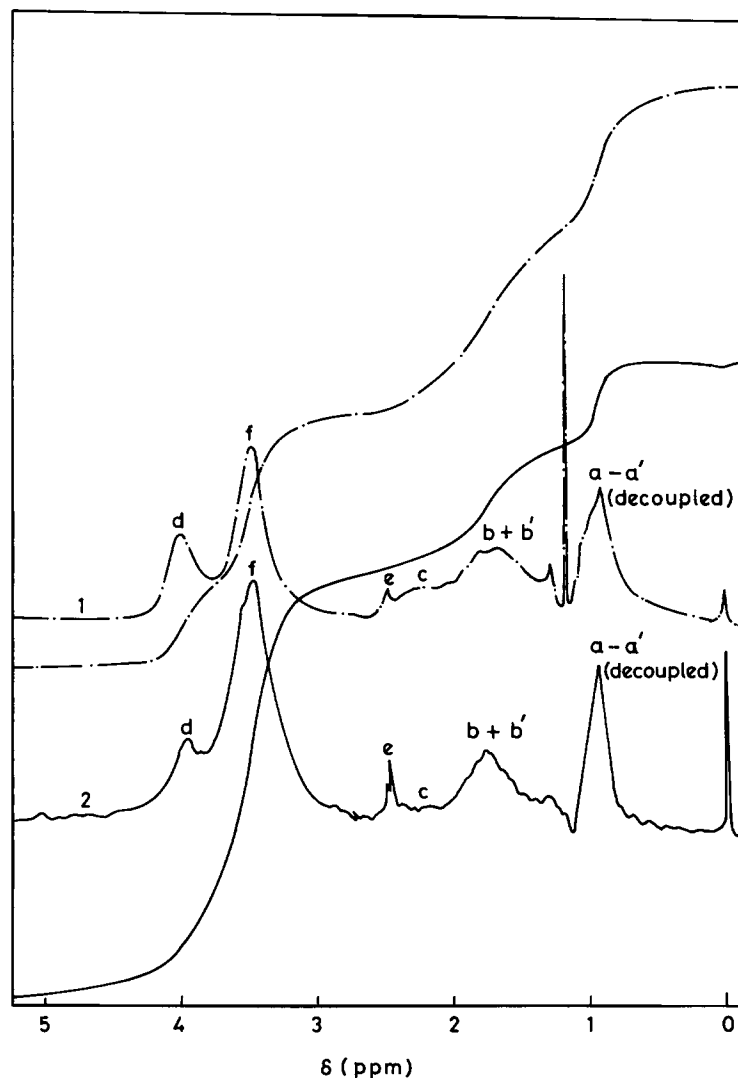


**Figure 1**  $^1\text{H}$ -NMR spectra of (1) 53.7:46.3 and (2) 72.9:27.0 MAA:EA copolymers.

58.7 ppm can be assigned to  $(-\text{CH}_3)_E$ ,  $(-\text{CH}_3)_M$ ,  $(-\text{C}-)_M$ ,  $(-\text{CH}_2)_M$ , and  $(-\text{OCH}_2)_E$ , respectively. These signals could not be used for the sequence analysis because of their poor resolution. The  $(-\text{CH}_2)_E$  and  $(-\text{CH})_E$  carbons of the EA unit overlapped with the  $\text{DMSO}-d_6$  signals; therefore, they could not be used for analysis of  $E$ -centered sequences. The carbonyl carbon of EA, which is configurational-insensitive, appeared as a well-resolved multiplet in the copolymer at  $\delta$  172.5–174.4 ppm, which indicates that the splitting is due to the sensitivity to compositional sequences. The carbonyl

carbon of MAA appeared in the range of  $\delta$  174.8–178.03 ppm, showing its sensitivity toward different monomer placements. In copolymers, there is a shift in the position of various functional groups of MAA and EA units as compared with the homopolymers. This effect is due to the change in the nature of adjacent monomeric units in the copolymer, which alters the chemical shifts of  $M$ - and  $E$ -centered triads.

The carbonyl carbon ( $\text{>C=O}$  of MAA and EA) expansions of three copolymers (containing MAA 82.3, 61.9, and 50.2 mol %, respectively) and PMAA are shown in Figure 3. As the concentration of MAA

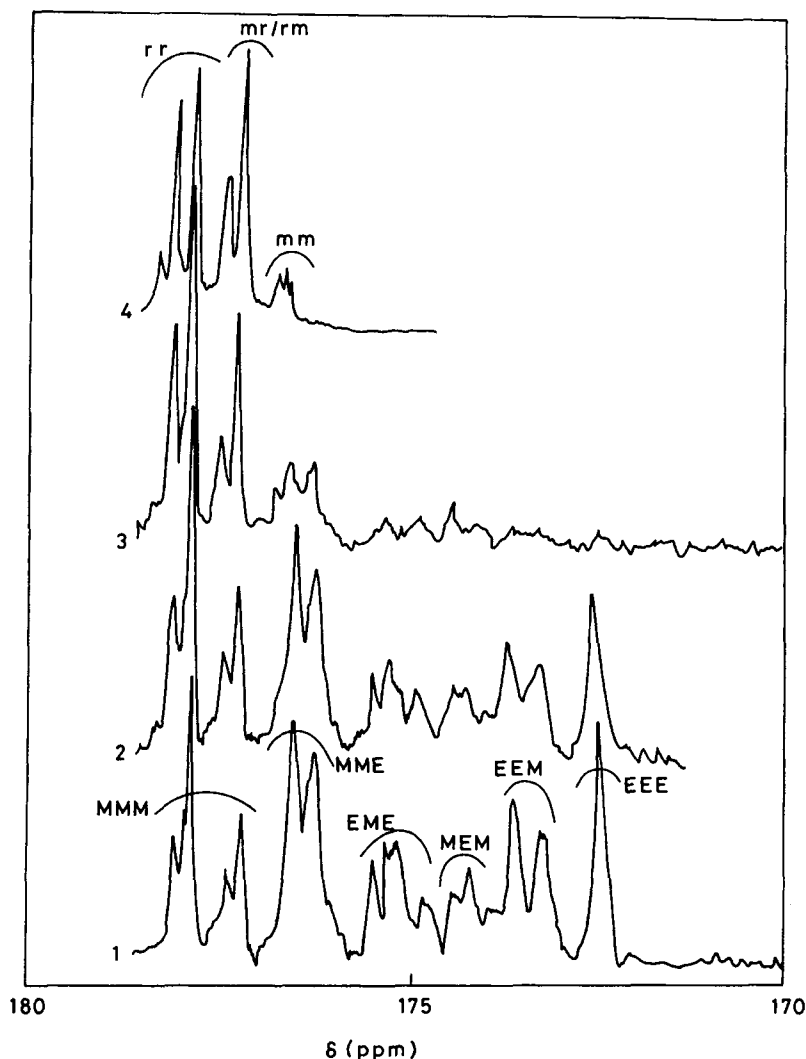


**Figure 2**  $^1\text{H}$ -NMR spectra (spin-spin decoupled) of (1) 53.7:46.3 and (2) 72.9:27.0 MAA:EA copolymers.

in the copolymer increases, the characteristic signal of PEA at  $\delta$  172.5 ppm decreases, whereas two new sets of signals centered at  $\delta$  173.5 and 173.8–174.4 ppm appeared. The three sets of signals with intensities changing with the copolymer composition can be assigned to the carbonyl carbon of the central *E* (EA) unit in *EEE*, *EEM/MEE*, and *MEM* triad sequences from high to low field. The assignment of signals was made on the basis of electronic interactions. Introduction of MAA to the *EEE* triad causes a downfield shift in the position of the *MEE* and *MEM* triads due to the deshielding effect of the carbonyl group of MAA. Concentration of various *E*-centered triads can be calculated from the relative areas of resonance signals in the  $^{13}\text{C}$   $\{^1\text{H}\}$ -NMR spectra of MAA-EA copolymers. These triad con-

centrations are the normalized areas of the respective resonance signals.

Similar information regarding the composition of *M* (MAA)-centered triads can be made using carbonyl carbon resonance region of MAA. Carbonyl carbon of MAA was found to be sensitive to configuration. In the homopolymer of MAA, this carbon appears as three sets of peaks at  $\delta$  177.79–178.24, 177.14–177.35, and 176.58–177.07 ppm. These peaks are assigned to *rr*, *rm/mr*, and *mm* triad sequences, respectively. This assignment has been done on the basis of assignments made by Klesper et al.<sup>44</sup> The concentration of these triads was calculated from the intensities of the corresponding resonance signals and the results are given in Table III. Pichot et al.<sup>3</sup> used  $-\text{CH}_3$  and  $-\text{C}-$  carbon resonance



**Figure 3** Carbonyl carbon expansions of  $^{13}\text{C}$   $\{^1\text{H}\}$ -NMR spectra of (1) 53.7:46.3, (2) 63.4:36.6, and (3) 82.3:17.6 MAA:EA copolymers and (4) PMAA.

signals to determine the concentration of these triads and their results are very close to the data presented in this study.

In the copolymer, the carbonyl carbon of MAA shows sensitivity toward the configuration as well as toward the composition. It appears at  $\delta$  174.8–178.03 ppm and shows splitting into three envelopes. The chemical-shift difference within the resonance signals and splitting pattern shows its sensitivity toward monomer sequences and cotacticity in the carbonyl carbon resonances of the MAA unit. An increase in the concentration of MAA units in the copolymer increases the intensity of the most downfield set of signals at  $\delta$  177.16–178.03 ppm, whereas that of the most upfield set of signals ( $\delta$  174.8–175.4 ppm) decreases. Because of this compositional variation in the intensities of *M*, the most downfield

resonance signal is assigned to the *MMM* triad and the most upfield to the *EME* triad. This effect is due to the increase in electron density at the carbonyl carbon of the central *M* unit, which may be due to the diamagnetic shielding from the anisotropy of immediate EA neighbors.

The concentration of various *M*-centered and *E*-centered triads, calculated from the relative areas of resonance signals, are given in Table III. As the concentration of MAA in the copolymer increased from 50.2 to 61.9 mol %, the concentration of the *MMM* triad increased from 0.36 to 0.45 mol % and that of the *EME* triad decreased from 0.25 to 0.24 mol %. In the case of *E* centered triads, the concentration of *MEM* triads increased and those of *EEE* triads decreased with an increase in the MAA concentration in the copolymer. In the copolymer con-



**Table III** *M*- and *E*-centered Triad Concentrations in MAA–EA Copolymers Determined by  $^{13}\text{C}$   $\{^1\text{H}\}$ -NMR Studies

Sample No.	MAA in Copolymer (Mol %)	Triads	Concn of Triads (Mol Fraction)
1	50.2	<i>MMM</i>	0.36
		<i>MME</i>	0.39
		<i>EME</i>	0.25
		<i>MEM</i>	0.19
		<i>EEM</i>	0.53
		<i>EEE</i>	0.28
2	61.9	<i>MMM</i>	0.46
		<i>MME</i>	0.34
		<i>EME</i>	0.19
		<i>MEM</i>	0.24
		<i>EEM</i>	0.48
		<i>EEE</i>	0.27
3	82.3	<i>MMM</i>	0.69
		<i>MME</i>	0.23
		<i>EME</i>	0.09
4	100	<i>rr</i>	0.10
		<i>rm/mr</i>	0.39
		<i>mm</i>	0.51

taining 82.3 mol % MAA, the concentration of *E*-centered triads was found to be negligible. As the polymerization was carried out up to 95–98% in all the cases, inhomogeneity in the monomer sequences in the polymer chains are likely to develop at such high conversions.

### Reactivity Ratios

The composition of the copolymers synthesized for the reactivity ratio determination (low conversion) was determined by  $^1\text{H}$ -NMR spectroscopy and subsequently used to determine the terminal model reactivity ratios (Table IV). The terminal model reactivity ratios were calculated using the EVM program, a nonlinear least-square errors in variables method. The initial estimate of reactivity ratios was made by the Kelen–Tudos method<sup>37</sup> and the  $r_1$  (MAA) and  $r_2$  (EA) values obtained were 2.9 and 0.162, respectively. These values are then fed in the computer program to calculate the exact values. The values obtained from the EVM program were  $r_1 = 2.58 \pm 0.13$  and  $r_2 = 0.157 \pm 0.08$ . The 95% posterior probability contour (PPC) for the MAA–EA system is shown in Figure 4.

In the present system, the value of  $r_1$  (2.58) is greater than unity, which means that the MAA radical would prefer to add to MAA than to EA. On the other hand, the value of  $r_2$  (0.157) suggests that EA radicals would prefer to add to MAA, and as the value is quite close to zero, EA seems to be almost incapable of undergoing homopolymerization. This is further substantiated by the  $^{13}\text{C}$   $\{^1\text{H}\}$ -NMR studies, where the concentration of *EEE* triads was found to be negligible in the copolymer containing 82.3 mol % MAA, due to the incapability of EA radicals toward homopolymerization.

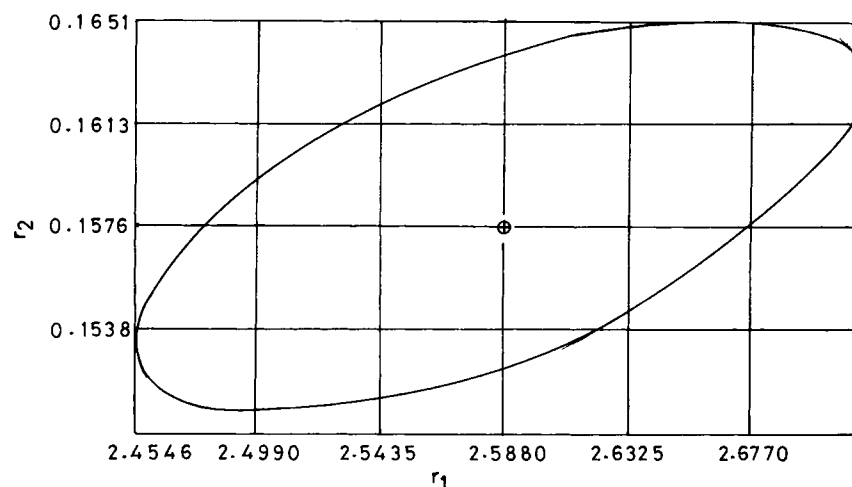
### Mechanism of Polymerization

The system under investigation contains MAA as the major comonomer (10–75 mol %), which, being

**Table IV** Composition of MAA–EA Copolymers

Sample No.	Feed Concn (Mol Fraction)		Copolymer Composition (Mol Fraction)		Conversion (%)	Reactivity Ratios	
	MAA	EA	MAA	EA		$r_1$ (MAA)	$r_2$ (EA)
1	0.1	0.9	0.34	0.66	10.6	2.9	0.162
2	0.25	0.75	0.57	0.43	8.5	(Kelen–Tudos method)	
3	0.40	0.60	0.71	0.28	8.0		
4	0.55	0.45	0.79	0.19	7.9		
5	0.70	0.30	0.81	0.18	7.0	(EVM program)	
6	0.85	0.15	0.88	0.11	6.5		

\* Copolymer composition calculated by  $^1\text{H}$ -NMR.



**Figure 4** Posterior probability contour (PPC) for MAA-EA pair. The + point represents the best estimate of  $r_1$  and  $r_2$ .

water-miscible, may lead to deviations from true emulsion polymerization. According to the literature,<sup>15</sup> the oligomeric radicals are generated in the aqueous phase of such systems, in the initial stages of polymerization, and they precipitate to form primary particles after attaining a critical molecular weight. Generation of such oligomeric radicals in the present system is also very likely. However, it is difficult to separate and analyze these radicals from the aqueous phase, but their composition can be predicted by statistical calculations. Therefore, for ascertaining the mechanism of MAA-EA polymerization, the concentration of both the monomers in the aqueous phase (prior to the polymerization) was determined. Four formulations containing 10–

75 mol % of MAA and 25–90 mol % of EA were investigated.

It is interesting to note (Table V) that the MAA, a water-soluble comonomer, preferred to remain in the organic phase (EA) when partitioned between water and EA. Only small amounts of MAA dissolved in water and its concentration in the aqueous phase increased with increase in MAA concentration in the feed. When MAA in the feed was increased from 4.86 to 6.43 mL, its concentration in the aqueous phase increased from 1.25 to 2.40 mL. Vijayendran<sup>1</sup> reported MMA to be the most hydrophobic among the three carboxylated monomers on the basis of partition coefficients of MMA (1.94), AA (0.175), and IA (0.012) in styrene and the water

**Table V** Monomer Concentration in the Aqueous Phase and Calculated Composition of Oligomeric Radicals in the Aqueous Phase

Sample No.	Monomer Concn in Feed (mL) (Mole Fraction)		Monomer Concn in Aqueous Phase (mL) (Mol)		Composition of Oligomeric Radical (Mol %)	
	MAA	EA	MAA	EA	MAA	EA
1	0.79 (0.1)	9.99 (0.9)	0.40 ( $4.55 \times 10^{-3}$ )	0.76 ( $8.22 \times 10^{-3}$ )	65.4	34.5
2	2.05 (0.25)	8.59 (0.75)	1.06 (0.012)	0.76 ( $8.22 \times 10^{-3}$ )	81.1	18.8
3	4.86 (0.55)	5.46 (0.45)	1.25 (0.014)	0.76 ( $8.22 \times 10^{-3}$ )	83.1	16.8
4	6.43 (0.75)	3.72 (0.25)	2.40 (0.028)	0.76 ( $8.22 \times 10^{-3}$ )	90.3	9.6

mixture. The results obtained in the present study are in conformity with their observations.

A small amount of EA ( $8.22 \times 10^{-3}$  mol) also miscibilized in water, but its concentration in the aqueous phase remained constant irrespective of the feed ratio. On the basis of the concentration of monomers in the aqueous phase and the reactivity ratios, the composition of oligomeric radicals in the aqueous phase was calculated using the following copolymer equations:<sup>45</sup>

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

and

$$F_2 = 1 - F_1$$

where  $r_1$  and  $r_2$  are the reactivity ratios;  $f_1$  and  $f_2$ , the concentration of monomers in the aqueous phase; and  $F_1$  and  $F_2$ , the monomer content in the oligomeric radical.

As the amount of MAA in the feed increases, its concentration in oligomeric radicals also increases (Table V), and they become more hydrophilic. Though the oligomeric radicals are constituted mainly of MMA (65–90 mol %), a small but significant amount of EA (9.6–34.5 mol %) has also been incorporated, as shown in Table V.

Fitch and Tsai<sup>46</sup> developed the following expression for the distance  $L$  traveled by an oligomeric radical before it precipitates from the aqueous phase:

$$L = \frac{2D_f DP_{\max}}{K_p[M]}$$

where  $D_f$  is the diffusion coefficient of the radical;  $DP_{\max}$ , the critical molecular weight at which oligomeric radical precipitates from the aqueous phase;  $K_p$ , the propagation rate constant for the oligomeric radical in water; and  $M$ , the molar concentration of the monomer.

If  $D_f$  or  $DP_{\max}$  increases,  $L$  is also increased. If the radical is more hydrophilic in nature, the  $DP_{\max}$  value will be higher. In the present MAA–EA system, the  $DP_{\max}$  of oligomeric radicals containing a higher amount of MAA is expected to be higher, leading to the water-soluble polymer formation by termination of these oligomeric radicals in the aqueous phase itself, thus more of aqueous-phase polymerization.

Information regarding the average sequence length of the two comonomers also helps in understanding the mechanism of MAA–EA polymeriza-

tion.<sup>18</sup> These calculations were made using the following equation given by Odian:<sup>45</sup>

$$(N_1)_x = (p_{11})^{x-1} \cdot p_{12}$$

$$(N_2)_x = (p_{22})^{x-1} \cdot p_{21}$$

where  $N_1$  and  $N_2$  are mol fractions of a given sequence length for MAA and EA, respectively, and  $p_{11}$  is the transition probability of forming the  $M_1M_1$  diad in the copolymer chain, and so on. From the transition probabilities, the average sequence length of the two monomers was calculated using following equations:

$$n_1 = \frac{1}{p_{12}} \quad \text{and} \quad n_2 = \frac{1}{p_{21}}$$

The average sequence length of MAA was found to increase with increase in the concentration of MAA in the aqueous phase. When MAA was 10 mol %, the average MAA sequence length was 2.42 and increased to 9.80 in the sample containing 75 mol % MAA. The average sequence length for all the four formulations can be presented as follows:

10 mol % MAA (– $M$ – $M$ – $E$ –) <sub>$n$</sub>

25 mol % MAA (– $M$ – $M$ – $M$ – $M$ – $E$ –) <sub>$n$</sub>

55 mol % MAA (– $M$ – $M$ – $M$ – $M$ – $M$ – $E$ –) <sub>$n$</sub>

75 mol % MAA (– $M$ – $M$ – $M$ – $M$ – $M$ – $M$ – $M$ – $M$ – $E$ –) <sub>$n$</sub> ,

where  $M$  and  $E$  represent MAA and EA units.

On the basis of these statistical calculations, it is demonstrated that the initial oligomeric radicals are composed mainly of MAA units, whereas EA units are interspersed between the blocks of various lengths of MAA. The block length of MAA decreases as the concentration of EA in feed increases. So, the oligomeric radicals containing more EA units will be able to precipitate out of the aqueous phase and form primary particles. Hydrophilic oligomeric radicals containing a greater amount of MAA will terminate in the aqueous phase, leading to water-soluble polymer formation.

On the basis of above discussion, the following mechanism can be postulated for the MAA–EA emulsion polymerization (Fig. 5):

- In the initial stages of polymerization, EA ( $8.22 \times 10^{-3}$  mol) and MAA ( $4.55 \times 10^{-3}$ – $0.028$  mol) miscibilized in water, become converted into oligomeric radicals.

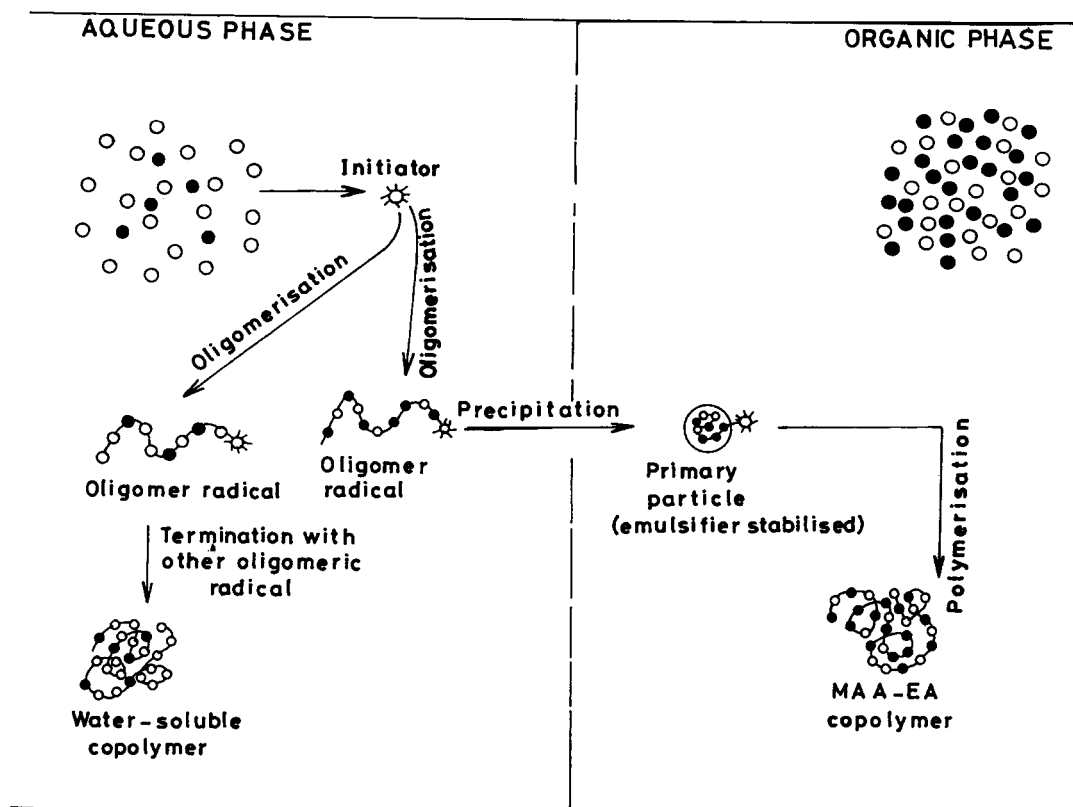


Figure 5 Schematic illustration of the mechanism of MAA-EA polymerization.

- The oligomeric radicals with very high MAA content remain in the aqueous phase, presumably become terminated, and form a water-soluble polymer. This water-soluble polymer, if present in significant amounts, may lead to increase in the viscosity of the latex, e.g., the latex having 82.3 mol % MAA in the feed showed an increase in the viscosity and, hence, a stable emulsion could not be obtained. In rest of the compositions, no such increase in the viscosity of the emulsion was observed.
- If the concentration of EA in the oligomeric radical is sufficient to provide enough hydrophobicity to it, the radical precipitates out of the aqueous phase and acts as a primary particle.

The authors are grateful to Dr. A. S. Brar of Chemistry Department of Indian Institute of Technology for the help provided in calculating the reactivity ratios and for useful discussions for  $^{13}\text{C}$ -NMR analysis. One of the authors (M. G.) wishes to thank the University Grants Commission, India, for the financial support provided in the form of a research fellowship.

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Received April 8, 1993

Accepted January 28, 1994