

Microemulsion Copolymerization of Methyl Methacrylate with Acrylonitrile

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ABSTRACT: The microemulsion (ME) and conventional emulsion (CE) copolymerizations of methyl methacrylate (MMA) with acrylonitrile (AN) are carried out at 70°C by employing *n*-butyl cellosolve as cosurfactant along with sodium lauryl sulfate as surfactant in the reaction medium and potassium persulfate as initiator. The copolymers are characterized by FTIR, NMR, TG/DTA, and GPC techniques. The reactivity ratios are evaluated by employing Fineman-Ross, Kellen-Tüdös (K-T), and Mayo-Lewis integration

methods. The K-T method yields reactivity ratios, r_{MMA} and r_{AN} , for the ME copolymerization of MMA and AN of 1.06 ± 0.01 and 0.14 ± 0.01 , and those for the CE copolymerization of MMA and AN are 2.19 ± 0.01 and 0.14 ± 0.01 , respectively. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 739–747, 2004

Key words: microemulsion copolymerization; conventional emulsion copolymerization; cosurfactant; reactivity ratios

INTRODUCTION

Studies on microemulsion (ME) polymerizations appear mostly after 1980.

A considerable number of homopolymerization studies by microemulsion polymerization methods have been performed.^{1–8} In contrast, little attention has been paid to the study of the copolymerization of microemulsions. Candau et al.^{9,10} investigated copolymerization of water-soluble monomers, acrylamide and sodium acrylate, by inverse, water-in-oil, microemulsion polymerization methods. The reactivity ratio values obtained by this method vary significantly from that of the copolymers prepared in solution or in an inverse emulsion, confirming a polymerization process by nucleation and interparticular collisions rather than by monomer diffusion through the continuous medium.

There are a few reports on copolymerizations in oil-in-water (O/W) microemulsions. Gan and co-workers^{11,12} studied the copolymerization of styrene (STY) with methyl methacrylate (MMA) and STY with acrylonitrile (AN) in ternary O/W microemulsions. The reactivity ratios obtained by these copolymerizations differ from the values reported for bulk copolymerization.^{13,14} These discrepancies were attributed to the fact that some of the MMA and AN was dissolved

in the aqueous phase, and it was suggested that the copolymerizations were carried out inside the microemulsion droplets. Microemulsion copolymerization¹⁵ of STY with methyl acrylate and *n*-butyl acrylate shows that the reactivity ratios differ from the values obtained by bulk and emulsion copolymerizations. These differences were ascribed to the differences in monomers partitioning in different phases of the reaction medium.

In the present study the ME and conventional emulsion (CE) copolymerizations of MMA with AN are carried out at 70°C by employing *n*-butyl cellosolve (BC) as cosurfactant along with sodium lauryl sulfate (SLS) as surfactant and with potassium persulfate (KPS) as initiator. The copolymers are characterized by FTIR, NMR, TG/DTA, and GPC techniques. The reactivity ratios are evaluated by different graphical procedures and the deviations from different copolymerization methods are discussed.

EXPERIMENTAL

Materials

The monomers, MMA (LR, Central Drug House (P) Ltd., Mumbai, India), and AN (LR, S.D. Fine Chem (P) Ltd., Boisar, India), were washed with 5% sodium hydroxide to remove inhibitor followed by distilled water. The washed monomers, MMA and AN, were dried over anhydrous sodium sulfate and anhydrous calcium chloride, respectively. The dried monomers were vacuum distilled and stored at -5°C in a refrigerator.

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TABLE I
Microemulsion Solution of Monomers

Total weight of the monomer mixture	5 g
<i>n</i> -Butyl cellosolve	1.8 g
Sodium lauryl sulfate	6.75 g
Water	75 ml

Acetone (AR, Fischer Inorganic and Aromatics Ltd., Chennai, India), methanol (AR, Fischer Inorganic and Aromatics Ltd.), dehydrated alcohol (ethanol) (Bengal Chemicals and Pharmaceuticals Ltd., Kolkata, India) and deuterated chloroform (CDCl₃) (Aldrich Chemicals Company, Inc.) were used as supplied without further purification. Tetrahydrofuran (THF) (AR, S.D. fine Chem (P) Ltd.) was purified by distillation over ferrous sulfate followed by dehydration over potassium hydroxide and the dehydrated THF was further purified by distillation.

KPS (LR, S.D. Fine Chem (P) Ltd.), SLS (commercial grade, HICO Products (P) Ltd., Mumbai, India), BC (AR, S.D. Fine Chem (P) Ltd.), and hydroquinone (AR, S.D. Fine Chem (P) Ltd.) were used as supplied without further purification.

Methods

Preparation of microemulsion solution of monomer mixtures

The monomer mixtures of MMA and AN along with *n*-butyl cellosolve in requisite quantities were solubilized in an aqueous solution of SLS with the use of a magnetic stirrer bar by stirring the solution for a period of 45–50 min or until the solution was uniform (Table I). This ME solution of the monomer mixtures was used for microemulsion and CE copolymerization experiments. Five compositions of the monomer mixtures, by keeping the total weight (5 g) of the monomers constant, were used in these recipes for ME and CE copolymerization experiments.

Microemulsion copolymerization

Microemulsion copolymerization of the comonomers, MMA and AN, was carried out by taking 30

mL of ME solution of the monomers (Table I) in a 50-mL reaction tube and this ME solution was purged with pure dry nitrogen to expel the dissolved oxygen and initiated with 9.1×10^{-4} M KPS solution at 70°C. The ME copolymerization reaction was arrested at low conversions by the addition of hydroquinone to the reaction mixture and the polymer from this ME copolymer solution was precipitated with acetone, washed, and dried in a vacuum oven at 60°C.

The ME copolymerization experiments were carried out with five different compositions of the monomer mixtures, MMA/AN, and the total weight of the monomers was kept approximately constant in all experiments (Table II).

Conventional emulsion copolymerization

The CE copolymerization of the monomer pair, MMA/AN, was carried out by purging the mixture of 20 mL of ME solution (Table I) and an excess of 2.5 g of monomers with nitrogen in a 50-mL reaction tube and by initiating this reaction mixture at 70°C with 9.1×10^{-4} M KPS solution. The composition of the monomer mixtures in the initial feed of CE copolymerization experiments was kept the same as in the ME solution experiments. The CE copolymerization reaction was arrested at low conversions by the addition of hydroquinone and the polymer formed in this CE copolymer solution was precipitated with acetone, washed, and dried at 60°C in a vacuum oven.

The CE copolymerization experiments were carried out with five different compositions of the monomer mixtures, MMA/AN, and the total weight of the monomers was kept approximately constant in all recipes (Table III).

Characterization of the copolymers

FTIR spectral analysis. FTIR spectra of the copolymers made by ME and CE copolymerizations in the present study were recorded on a Nicolet Impact 400 infrared spectrophotometer by casting thin films of the copol-

TABLE II
Microemulsion Copolymerization of MMA with AN

Sample no.	f_{MMA}	f_{AN}	F_{MMA}	F_{AN}	ΔH , KJ/mg	$\bar{M}_n \times 10^{-5}$	% Conversion
1	0.6845	0.3155	0.6590	0.3410	387.8	5.4320	23.07
2	0.4894	0.5106	0.6323	0.3677	353.0	1.9894	15.04
3	0.3421	0.6579	0.5132	0.4868	281.3	1.1473	10.80
4	0.2413	0.7587	0.4772	0.5228	217.1	0.9074	9.71
5	0.1587	0.8413	0.4119	0.5881	207.6	—	5.12

Note. f_{MMA} and f_{AN} are the molar fractions of monomers MMA and AN, respectively, in the initial feeds. F_{MMA} and F_{AN} are the molar fractions of the monomer units MMA and AN, respectively, in the copolymers, determined by H-NMR spectral analysis.

TABLE III
Conventional Emulsion Copolymerization of MMA and AN

Sample no.	f_{MMA}	f_{AN}	F_{MMA}	F_{AN}	$\bar{M}_n \times 10^{-5}$	% Conversion
1	0.6846	0.3154	0.7449	0.2551	8.2690	16.38
2	0.4893	0.5107	0.7305	0.2695	5.4748	4.20
3	0.3421	0.6579	0.6375	0.3625	2.3589	10.61
4	0.2413	0.7587	0.4489	0.5511	2.0624	8.50
5	0.1587	0.8413	0.4433	0.5567	—	3.66

Note. f_{MMA} and f_{AN} are the molar fractions of monomers MMA and AN, respectively, in the initial feeds. F_{MMA} and F_{AN} are the molar fractions of the monomer units MMA and AN, respectively, in the copolymers, determined by H-NMR spectral analysis.

ymers from acetone solutions between KBr windows of size 2.5×4 mm (Fig. 1).

NMR spectral analysis. The $^1\text{H-NMR}$ spectra of the copolymer samples made in the present study were recorded at ambient temperature (20°C) with the use of JEOL ECR 500-MHz high-resolution NMR spectrometer and chloroform-d (CDCl_3) as solvent under the following conditions: number of scans 16, receiver gain 66, spectral width 10 KHz, relaxation delay 4 s, and using 45° pulse width as $6.15 \mu\text{s}$ (Figs. 2 and 3).

TG/DTA analysis. The thermograms of the copolymers prepared by ME copolymerization in the present study were recorded with a Seiko TG/DTA 220 instrument in the temperature region 30 – 600°C at a heating rate of 20°C and with a nitrogen gas flow of 100 mL/min. α -Alumina was used as the reference in platinum pans (Fig. 4, Table II).

Gel permeation chromatography. The GPC analysis of the copolymers prepared with lower compositions of AN in the initial feeds were carried out by employing a Waters unit interfaced with a NEC (IBM AT Compatible) computer to evaluate their molecular weights (\bar{M}_n). A molecular weight calibration curve was obtained with polystyrene standards in the molecular weight range 2.3×10^3 to 3.1×10^6 (Polymer Laboratories, Church Stretton, Shropshire, UK). THF at a flow rate of 1 mL/min was used as the eluent (Fig. 5, Tables II and III).

RESULTS AND DISCUSSION

The FTIR spectra of the copolymers made by ME and CE copolymerization methods showed the asymmetric stretching vibrations due to the methyl group of the copolymers at 2953 – 2966 cm^{-1} . The asymmetric stretching vibrations due to the methylene group of the copolymer appear at 2927 – 2933 cm^{-1} and the symmetric stretching vibrations of the methyl group seem to overlap with the asymmetric stretching vibrations of the methylene group. The symmetric stretching vibrations of the methylene group appear at 2854 – 2861 cm^{-1} and the stretching vibrations of the methine group are observed in the region 2986 – 2999 cm^{-1} . The stretching vibrations due to the nitrile group appear at

2242 – 2249 cm^{-1} , and the stretching vibrations due to the carbonyl group appear near 1736 cm^{-1} and its overtone appears near 3450 cm^{-1} . The asymmetric bending vibrations due to the methyl and methylene groups are observed in the region 1446 – 1453 cm^{-1} . The stretching vibrations due to the $-\text{C-O-C}-$ group appear in the region 1196 – 1288 cm^{-1} . The asymmetric stretching vibrations of sulfate end-groups appear in the region 1387 – 1393 cm^{-1} , and symmetric stretching vibrations of the sulfate end groups appear near the region 1196 – 1229 cm^{-1} , which overlaps with the stretching vibrations due to the $-\text{C-O-C}-$ group. The symmetric bending vibrations due to the methyl group appear at 1367 cm^{-1} . The stretching vibrations due to unsaturated end groups appear at 1646 – 1670 cm^{-1} and the deformation vibrations due to unsaturated end groups are seen in the region 854 – 998 cm^{-1} . The rocking vibrations due to the methylene group appear at 755 – 768 cm^{-1} . The stretching vibrations due to $-\text{C-O-S}-$ groups appear at 814 – 821 cm^{-1} and the skeletal vibrations in the region 1123 – 1156 cm^{-1} (Fig. 1).

The proton NMR spectra of the copolymers prepared in the present study by ME and CE copolymerization methods show the chemical shifts due to methoxy protons in the region 3.452 – 3.767 ppm. The chemical shifts due to methine protons appear in the region 2.007 – 3.114 ppm, the resonance peaks due to methylene groups appear in the region 1.556 – 2.349 ppm, and the absorption bands due to methyl groups appear in the region 0.812 – 1.396 ppm. The area under the resonance peaks due to methoxy protons was taken as 3AMMA and the total areas under the resonance peaks due to methine, methylene, and methyl groups was taken as $(3\text{AAN} + 5\text{AMMA})$. The molar fraction (F_{MMA}) of the MMA units in the copolymer was obtained as $\text{AMMA}/(\text{AAN} + \text{AMMA})$ (Figs. 2 and 3, Tables II and III).

The TG/DTA analysis of the copolymers prepared by ME copolymerizations in the present study shows endothermic decompositions in the temperature region 330.3 – 445.7°C . There is no correlation observed between the onset of decomposition processes and the compositions of the copolymers. The energy values

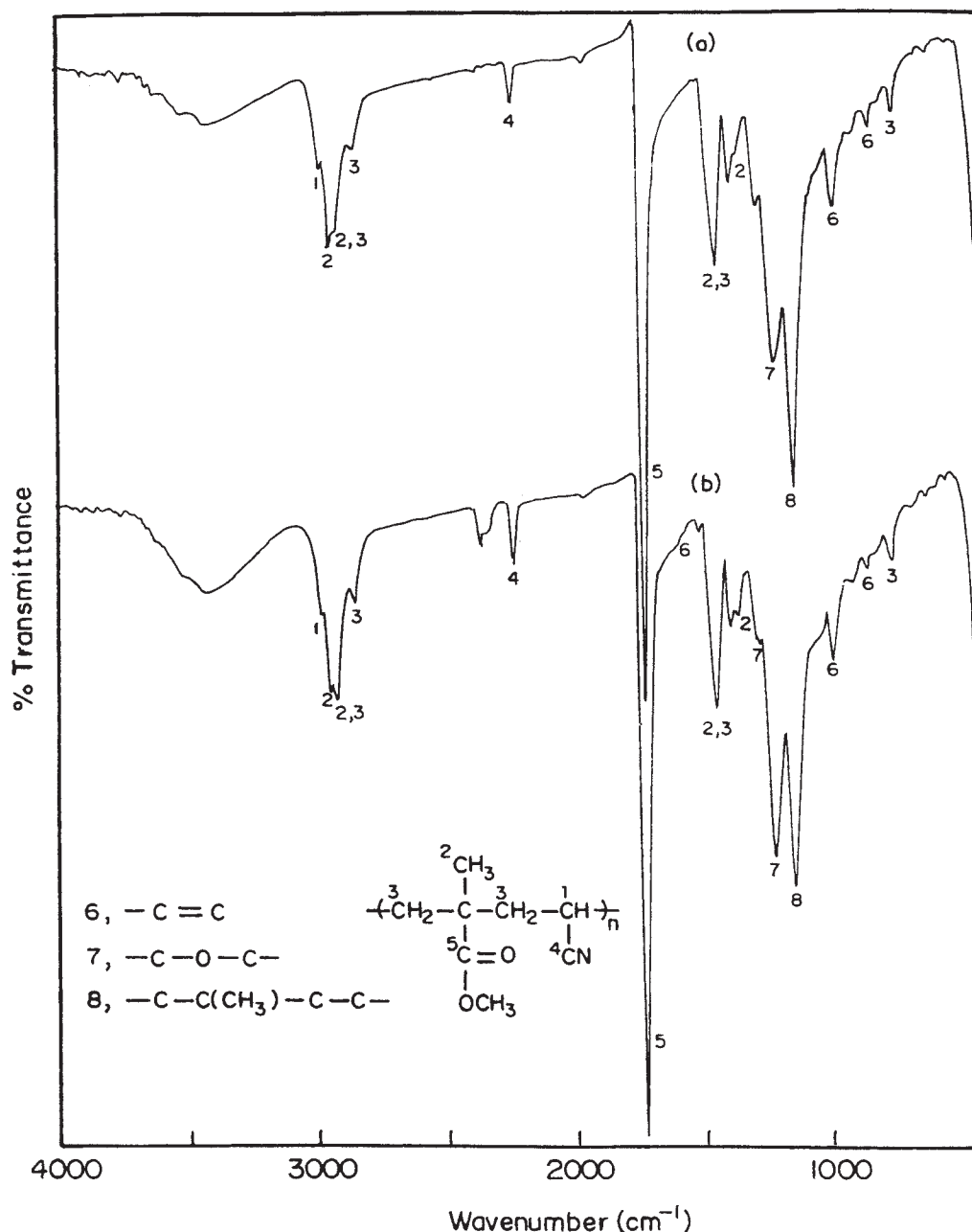


Figure 1 FTIR spectra of copolymer samples 4 and 5 prepared by (a) ME and (b) CE copolymerizations of MMA and AN, respectively (Tables II and III).

(ΔH) for the decomposition processes were evaluated from the areas of the endothermic curves and are reported in Table II (Fig. 4). The ΔH values show a decreasing trend with an increase of the AN content in the copolymers prepared by ME copolymerizations in the present study (Table II). The TG analysis shows that the percentage of weight loss under the present experimental conditions decreases slowly with an increase of the AN content in the copolymers but the first sample deviated from the regular order of decrease with the increase of AN content in the copolymers (Fig. 4).

There are also broad endothermic processes at low temperature regions starting at 40°C and continuing up to 265°C (Fig. 4). These endothermic processes may be due to evaporation of moisture or volatile solvent and low temperature transitions.

GPC analysis of the copolymer samples containing more than 44 mol % of MMA units in the copolymers was carried out by employing THF as the eluent (Fig. 5, Tables II and III). The molecular weights of copolymers obtained by ME copolymerization were lower than the values obtained by CE copolymerization methods. The GPC analysis of the

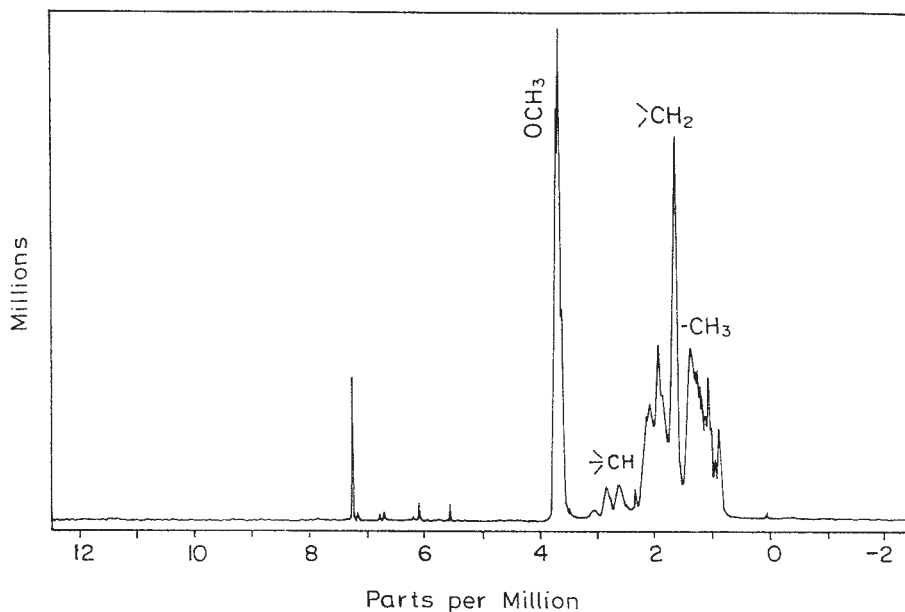


Figure 2 ¹H-NMR spectrum of copolymer sample 2 prepared by microemulsion copolymerization of MMA with AN (Table II).

copolymers containing higher proportions of AN units (>55.11 mol %) could not be carried out because these were insoluble in the THF solvent employed in these analyses.

Both the dilution factor and the chain transfer with the solvent influence the rate and degree of polymerization, and the degree of polymerization in the presence of a solvent is given by the expression¹⁶

$$\bar{P}_N = \bar{P}_{No} / (1 + x),$$

where \bar{P}_N and \bar{P}_{No} are the number average degrees of polymerization in the presence and in the absence of the solvent in the reaction medium and x for binary copolymerization in the presence of a solvent is given by the relation

$$x = \bar{P}_{No} \left\{ F_1 \frac{k_{1s}[S]}{k_{11}[M_1] + k_{12}[M_2]} + F_2 \frac{k_{2s}[S]}{k_{21}[M_1] + k_{22}[M_2]} \right\}.$$

Then the degree of polymerization can be expressed as

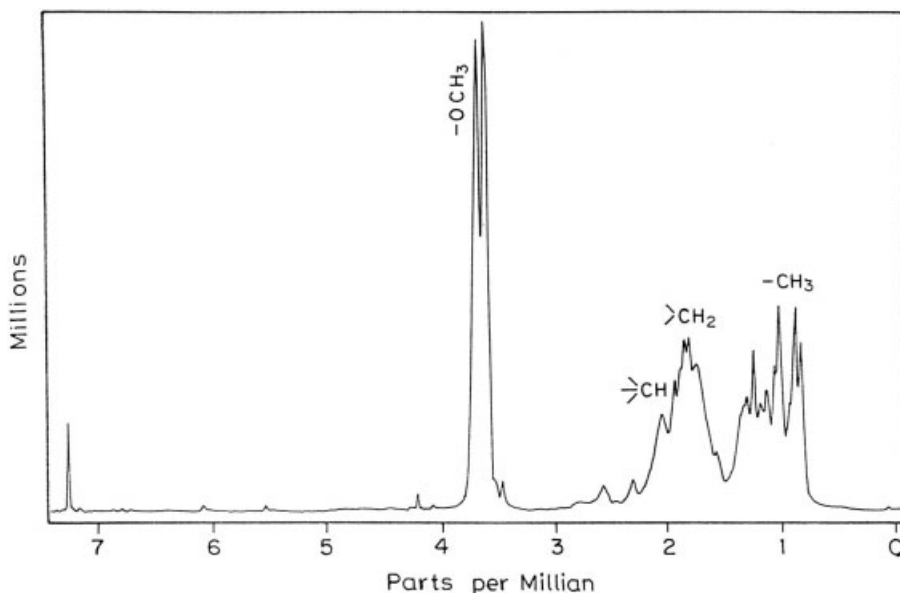


Figure 3 ¹H-NMR spectrum of copolymer sample 2 prepared by conventional emulsion copolymerization of MMA with AN (Table III).

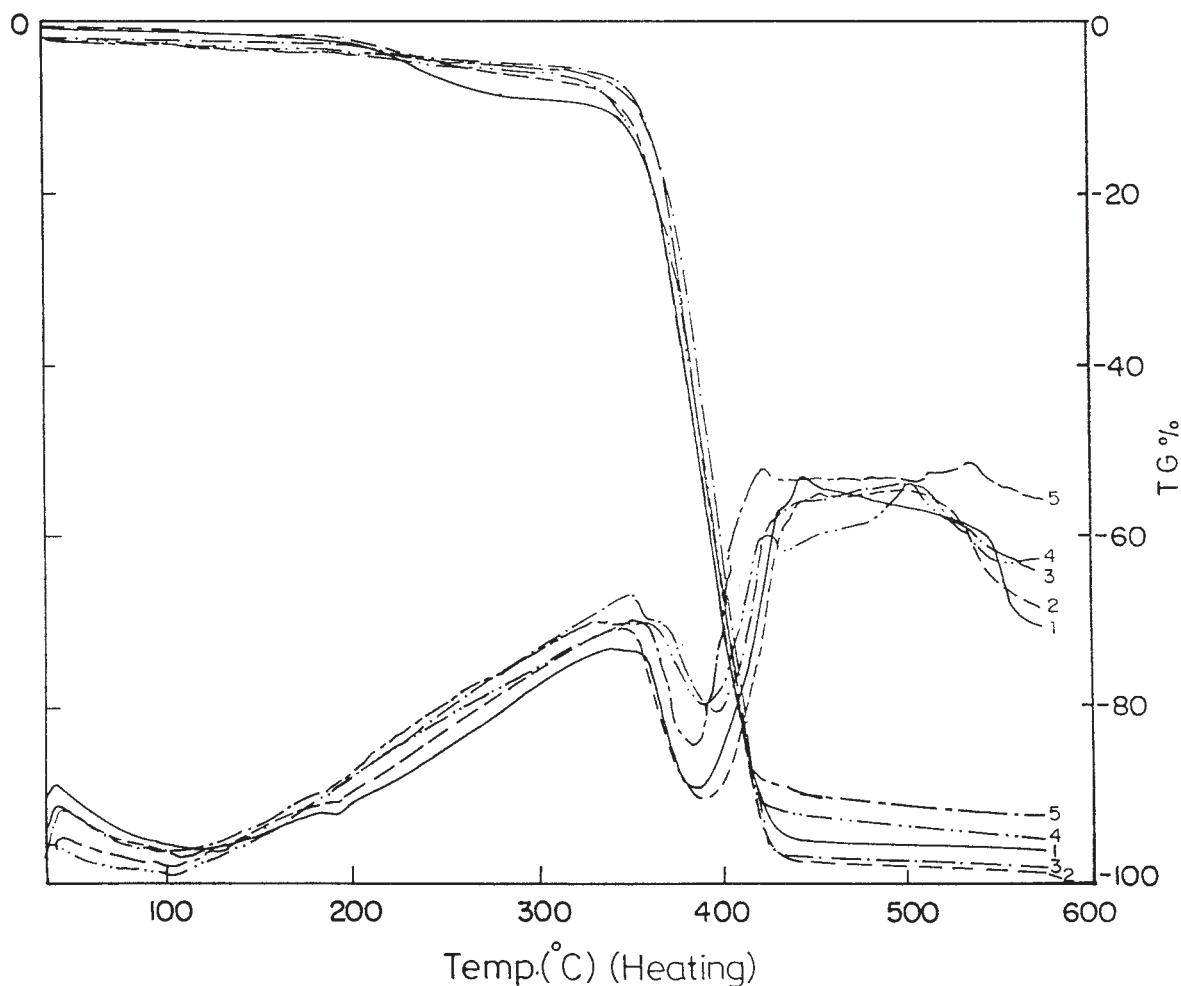


Figure 4 TG/DTA analysis of copolymer samples 1-5 prepared by microemulsion copolymerization of MMA with AN (Table II).

$$\frac{1}{\bar{P}_N} = \frac{1}{\bar{P}_{No}} + F_1 \left(\frac{k_{1s}}{k_{11}} \right) \frac{[S]}{[M_1] + (k_{12}/k_{11})[M_2]} + F_2 \left(\frac{k_{2s}}{k_{22}} \right) \frac{[S]}{(k_{21}/k_{22})[M_1] + [M_2]}$$

where $[S]$, $[M_1]$, and $[M_2]$ are the molar concentrations of solvent, monomer1, and monomer2; F_1 and F_2 are molar fractions of monomer1 and monomer2 in the copolymer; k_{11} , k_{12} , k_{21} , and k_{22} are normal propagation rate constants in the binary copolymerization; and k_{1s} and k_{2s} are rate constants for the reactions of solvent with monomer1 and monomer2, respectively.

It can be inferred from this relation that the degree of polymerization decreases with increases in the $[S]/[M]$ ratio, where $[M] = [M_1] + [M_2]$. In the present study the solvent, *n*-butyl cellosolve, which is used as the cosurfactant present in the ME globules along with the surfactant in the surface and with the monomers in the core. The ratio $[S]/[M]$ is higher in ME copolymer-

ization reaction medium compared to that of CE copolymerization systems where an excess of the monomers was added to the ME solutions and, hence, higher degrees of polymerizations in CE copolymerizations compared to ME copolymerizations are due to the presence of chain transfer reactions with the solvent in the reaction loci. Small amounts of chain transfer with the solvent will have a decided influence on the degree of polymerization.^{17,18}

Reactivity ratios of the monomer pair, MMA/AN

The reactivity ratios for the ME and CE copolymerizations of MMA and AN were evaluated by Fineman-Ross (F-R),¹⁹ Kelen-Tüdös (K-T),²⁰ and Mayo-Lewis integration (M-L-I)²¹ methods (Figs. 6-8). The reactivity ratios obtained by the ME copolymerization method for MMA (r_{MMA}) and AN (r_{AN}) in the present study are smaller than the values reported by bulk²² and solution²³ copolymerization methods (Table IV). The monomers, MMA and AN, are par-

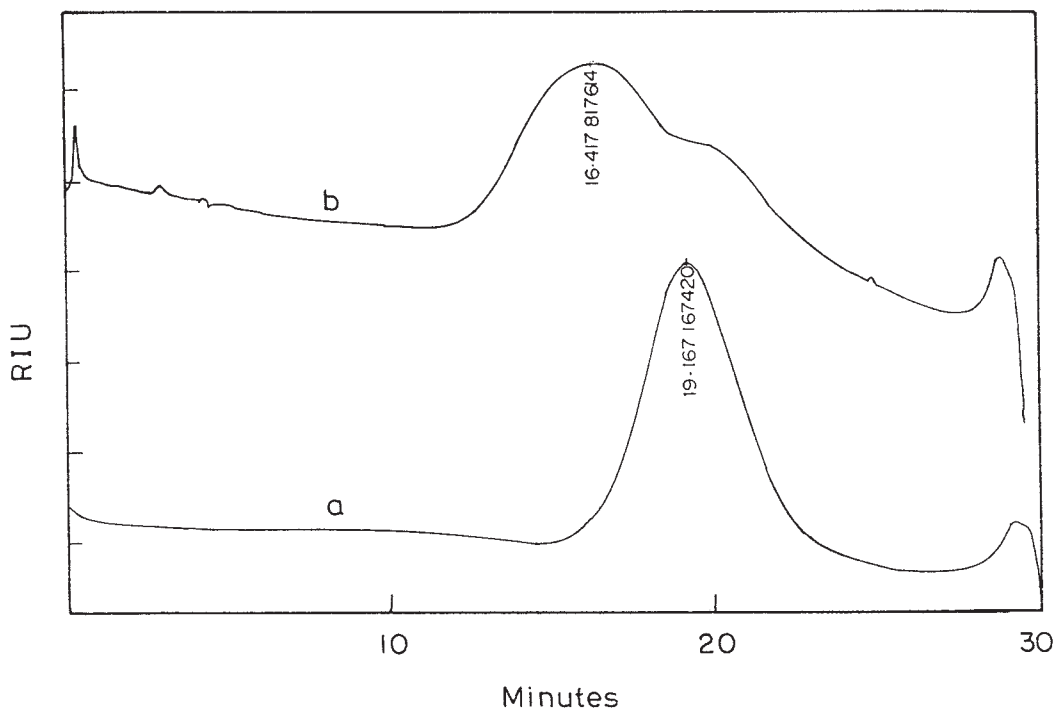


Figure 5 GPC analysis of the copolymer samples prepared by (a) microemulsion and (b) conventional emulsion copolymerization of MMA and AN with a molar ratio of 0.3421:0.6579 of the monomers in the initial feeds (Tables II and III).

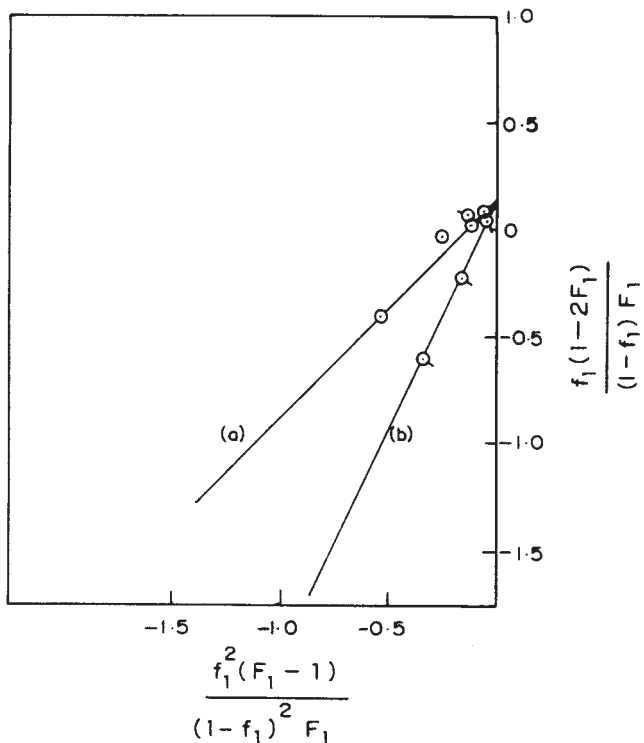


Figure 6 Fineman-Ross plots to evaluate the reactivity ratios for (a) ME and (b) CE copolymerizations of MMA with AN (Tables II, III, and IV).

tially soluble in water, and AN is more soluble than MMA. The cosurfactant *n*-butyl cellosolve employed in the present study is soluble in both monomers and is insoluble in water, and the monomers

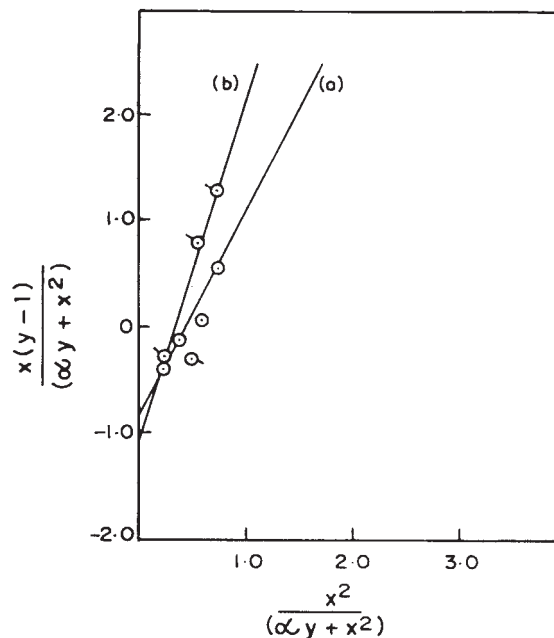


Figure 7 Kelen-Tüdös plots to evaluate the reactivity ratios for (a) ME and (b) CE copolymerizations of MMA with AN (Tables II, III, and IV).

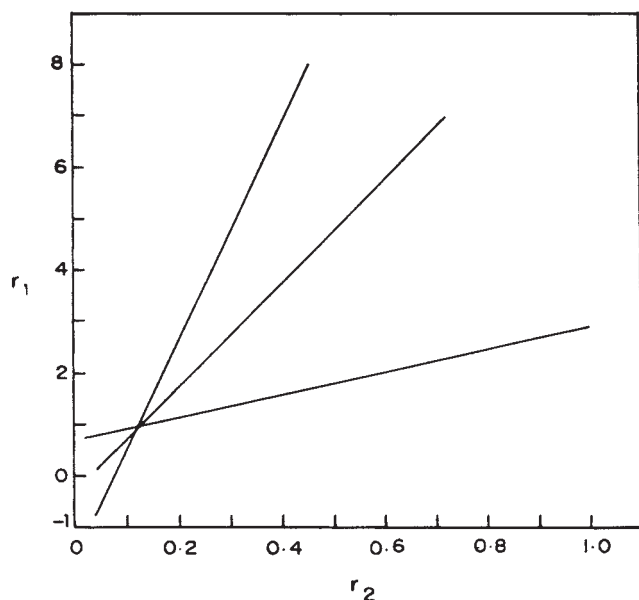


Figure 8 Mayo-Lewis integration method to evaluate the reactivity ratios for ME copolymerization of MMA with AN (Tables II and IV).

are mutually soluble in all proportions. The cosurfactant, BC, is present in the space of ME globules along with surfactant in the surface and with the monomers in the core. The presence of the cosurfactant may reduce the solubilities of the monomers in the aqueous medium due to thermodynamic considerations.²⁴ The presence of the solvent *n*-butyl cellosolve in the reaction loci can bring about changes in the reaction parameters.²⁵⁻³¹

The r_{MMA} and r_{AN} values obtained by the CE copolymerization method are different from the values obtained by the ME copolymerization method in the present study and also vary from the results of bulk²² and solution²³ copolymerization methods in the literature (Table IV). The cosurfactant exists in the emulsion globules and also with the monomer phases of the CE copolymerization systems. The monomers partitioning in the various phases^{11,12,15} (i.e., emulsion globules, aqueous, and monomer

phases) in the CE copolymerization reaction systems might influence these reaction parameters compared to ME (present study), bulk,²² and solution²³ copolymerization methods. The variation of r_{MMA} compared to r_{AN} obtained from the CE copolymerization method in the present study is more than the value from the ME copolymerization method compared to the literature results (Table IV). This difference in variation might be due to the higher solubility of AN compared to MMA in the aqueous medium,³²⁻³⁴ and the presence of solvent *n*-butyl cellosolve in the reaction loci might also bring about changes in these reaction parameters.²⁵⁻³¹

CONCLUSION

No correlation was observed between the compositions of the copolymers and the onset of the endothermic decompositions in the thermograms of the DTA analysis of the copolymers prepared by ME copolymerization. The TG curves show a slow decrease in percentage weight loss with the increase of AN content in the copolymers; only sample 1 deviates from the regular order of decrease. The presence of higher proportions of solvent *n*-butyl cellosolve in the ME reaction loci compared to CE copolymerization systems could cause a decrease in the degree of polymerization by the ME copolymerization method when chain transfer reactions due to solvent are present in the reaction loci. The reactivity ratios obtained by ME copolymerization are smaller than the values obtained by bulk and solution copolymerization in the literature, which is attributed to the presence of solvent in the reaction medium. The reactivity ratios obtained by the CE copolymerization method deviate from the values obtained by ME (present study), bulk, and solution copolymerizations. These deviations are considered to be due to the monomer partitioning in the various phases of the CE copolymerization reaction medium.

TABLE IV
Reactivity Ratios of the Monomer Pair, Methyl Methacrylate and Acrylonitrile

Polymerization method	Solvent in the reaction medium	Method of evaluation	Temperature (°C)	r_{MMA}	r_{AN}
Bulk ²²	—	—	60	1.35	0.18
Solution ²³	DMSO	—	60	1.44	0.16
Emulsion (present study)	<i>n</i> -Butyl cellosolve	F-R	70	2.10 ± 0.01	0.14 ± 0.01
	"	K-T	70	2.19 ± 0.01	0.14 ± 0.01
	"	M-L-I	70	2.32 ± 0.01	0.13 ± 0.01
Microemulsion (present study)	<i>n</i> -Butyl cellosolve	F-R	70	1.03 ± 0.01	0.14 ± 0.01
	"	K-T	70	1.06 ± 0.01	0.14 ± 0.01
	"	M-L-I	70	1.02 ± 0.01	0.13 ± 0.01

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