

Microemulsion and Conventional Emulsion Copolymerizations 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 sodium lauryl sulphate (SLS) and *n*-octanol (OA) as surfactant and cosurfactant, respectively, and potassium persulphate (KPS) as initiator. The copolymerization reactions are arrested at lower conversions, and the copolymers prepared are characterized by FTIR, NMR, TG/DTA, and GPC techniques. The reactivity ratios for microemulsion and conventional emulsion copolymerizations are evaluated by Fineman-Ross (F-R), Kelen-Tüdös (K-T), and Mayo-Lewis (M-L) graphical methods. The K-T method yields the reactivity ratios of MMA (r_{MMA}) and AN (r_{AN}) as 2.03 ± 0.02 and 0.10 ± 0.02 , and 1.97 ± 0.02 and 0.13 ± 0.02 , respectively, for ME and CE copolymerization methods. The results are compared with the literature. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1503–1510, 2002

Key words: copolymerization; FTIR; NMR; thermogravimetric analysis

INTRODUCTION

The homopolymerizations of microemulsions^{1–8} have been extensively investigated since 1980. In contrast, little attention has been paid to the study of the copolymerization of microemulsions. In water-in-oil (W/O) microemulsion copolymerizations, Candau et al.^{9,10} showed that the reactivity ratios for the copolymerization of both of the water-soluble monomers acrylamide (M_1) and sodium acrylate (M_2) in inverse microemulsions were close to unity. These values are significantly different from those reported in the literature ($r_1 \sim 0.95$; $r_2 \sim 0.30$) obtained from 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. When the copolymer of sodium 2-acrylamido-2-ethyl propane sulfonate (NaAMPS, M_1) and 2-methyl acryloyethyltrimethyl ammonium chloride (MADQUAT, M_2) was prepared through inverse microemulsion copolymerization,¹¹ $r_1 = 0.81$ and $r_2 = 1.97$.

There are also a few reports on copolymerizations in oil-in-water (O/W) microemulsions. Gan et al.^{12,13} studied the copolymerizations of styrene (STY) with methyl methacrylate (MMA) and STY with acrylonitrile (AN) in ternary O/W microemulsions. The reactivity ratios obtained by these copolymerizations are differing from the values reported for bulk copolymerizations.^{14,15} It was proposed that the difference was due to the fact that some of the MMA or AN was dissolved in the

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aqueous phase, and it was suggested that the copolymerizations were carried out inside the microemulsion droplets. Microemulsion copolymerizations¹⁶ of styrene (STY) with methyl acrylate (MA) and with *n*-butyl acrylate (BA) show that the reactivity ratios differ from the values obtained by bulk and emulsion copolymerizations. These differences were ascribed to be due to the differences in monomers partitioning in different phases of the reaction media.

In the present study the microemulsion and conventional emulsion copolymerizations are carried out at 70°C. The copolymers prepared are characterized by FTIR, NMR, TG/DTA, and GPC techniques. The reactivity ratios are evaluated by different graphical procedures, and the deviations in different copolymerization methods are discussed.

EXPERIMENTAL

Materials

Monomers, methyl methacrylate (MMA) (LR, Central Drug House (P) Ltd., Mumbai, India) and acrylonitrile (AN) [LR, s.d. fine chem (p) ltd., Boisar, India] are washed with 5% sodium hydroxide to remove inhibitor followed by distilled water. The washed monomers, MMA and AN, are dried over anhydrous sodium sulphate and anhydrous calcium chloride, respectively. The dried monomers are vacuum distilled and stored at -5°C in a refrigerator.

Acetone (AR, Fischer Inorganic & Aromatics Ltd., Chennai, India), methanol (AR, Fischer Inorganic & Aromatics Ltd., Chennai, India), dehydrated alcohol (ethanol) (Bengal Chemicals and Pharmaceuticals Ltd., Kolkata, India), and deuterated dimethyl sulphoxide (DMSO-d₆) (Aldrich Chemical Company, Inc., Milwaukee, WI) are used as supplied without further purification. Tetrahydrofuran (THF) (AR, s.d. fine chem (p) ltd., Boisar, India) is purified by distillation over ferrous sulphate.

Potassium persulphate (KPS) [LR, s.d. fine chem (p) ltd., Boisar, India], sodium lauryl sulphate (SLS) (LR, CHEMIX, Chennai, India), *n*-octanol (OA) (AR, Sisco-Chem Industries, Mumbai, India) and hydroquinone [AR, s.d. fine chem (p) ltd., Boisar, India] are used as supplied without further purification.

Table I

Total weight of the monomers mixture	5 g
<i>n</i> -Octanol	1.99 g
Sodium lauryl sulphate	6.75 g
Water	75 mL

METHODS

Preparation of Microemulsion Solutions of Monomers Mixtures

The monomers mixtures of MMA and AN along with *n*-octanol (OA) in requisite quantities are solubilized in the aqueous solution of sodium lauryl sulphate (SLS) with the use of a magnetic stirrer bar by stirring the solution for a period of 45–50 min or until the solution is uniform, and then the solution is allowed overnight for attaining equilibrium (Table I). This microemulsion solution of the monomers mixture is used for microemulsion (ME) and conventional emulsion (CE) copolymerization experiments. Seven compositions of the monomers mixtures by keeping the total weight of the monomers as constant are used in these recipes for microemulsion (ME) and conventional emulsion (CE) copolymerization experiments.

Microemulsion Copolymerization

Microemulsion copolymerization of these comonomers, MMA and AN, is carried out by taking 30 mL of ME solution of the monomers (Table I) in a 50-mL reaction tube, and this ME solution is purged with pure dry nitrogen to expel the dissolved oxygen, and by initiating it with 9.1×10^{-4} M KPS solution at 70°C. The ME copolymerization reaction is arrested at lower conversions by adding hydroquinone to the reaction mixture and the polymer from this ME solution is precipitated with methanol. The precipitated polymer is washed with ethanol and then with water to remove the impurities. The washed polymer is dried in a vacuum oven at 60°C.

The ME copolymerization experiments are carried out with seven different compositions of the monomers mixture, MMA/AN, and the total weight of the monomers is kept approximately constant in all these experiments (Tables I and II).

Conventional Emulsion Copolymerization

The CE copolymerization of the monomer pair, MMA/AN, is carried out by purging with nitrogen

Table II Microemulsion Copolymerization of Methyl Methacrylate with Acrylonitrile

S.No.	f_{MMA}	f_{AN}	F_{MMA}	F_{AN}	ΔH KJ/mg	$\bar{M}_n \times 10^{-5}$	% Conversion
1	0.6845	0.3155	0.8380	0.1620	332.97	10.1058	31.84
2	0.5669	0.4331	0.7749	0.2251	429.91	7.2214	28.08
3	0.4893	0.5107	0.7323	0.2677	545.82	5.9099	25.70
4	0.4171	0.5829	0.6869	0.3131	306.63	—	16.50
5	0.3506	0.6494	0.6333	0.3667	303.47	—	51.68
6	0.2460	0.7540	0.5604	0.4396	278.18	—	14.69
7	0.1713	0.8287	0.4945	0.5055	153.84	—	18.78

f_{MMA} and f_{AN} are mol fractions of MMA and AN in the initial feeds.

F_{MMA} and F_{AN} are mol fractions of MMA and AN in the copolymers determined from ^1H NMR spectral data.

the mixture of 20 mL of ME solution (Table I) and an excess of 2.5 g of total monomers 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 monomers mixture in the initial feed of CE copolymerization experiment is maintained the same as in the ME solution used in this experiment.) The CE copolymerization reaction is arrested at lower conversions with the addition of hydroquinone, and the polymer formed in this CE copolymerization solution is precipitated with methanol. The precipitated polymer is washed with ethanol and then with water, and the washed polymer is dried at 60°C in a vacuum oven.

The CE copolymerization experiments are carried out with seven different compositions of the monomers mixture, MMA/AN, and the total weight of the monomers is kept approximately constant in all these recipes (Table III).

Characterization of the Copolymers

FTIR Spectral Analysis

FTIR spectra of the copolymers made by ME and CE copolymerizations under the present study

are recorded on Nicolet Impact 400 Infrared Spectrophotometer by casting thin films of the copolymers from acetone solutions between KBr windows of size 2.5×4 mm (Fig. 1).

NMR Spectral Analysis

The NMR spectra of the copolymer samples made under present study are recorded with Bruker MSL 300P, 300 M Hz FT-NMR spectrometer, using deuterated dimethyl sulphoxide (DMSO- d_6) as solvent and tetramethyl silane as internal standard (Figs. 2–4).

TG/DTA Analysis

The thermograms of the copolymers made under present study are recorded with the use of Seiko TG/DTA 220 instrument in the temperature region of 30–600°C at a heating rate of 20°C and with a nitrogen gas flow at a rate of 100 mL/min. α -Alumina is used as the reference on platinum pans (Figs. 5 and 6, Tables II and III).

Gel Permeation Chromatography

The GPC analysis of the copolymers prepared with lower compositions of AN in the initial feeds

Table III Conventional Emulsion Copolymerization of Methyl Methacrylate with Acrylonitrile

S. No.	f_{MMA}	f_{AN}	F_{MMA}	F_{AN}	ΔH KJ/mg	$\bar{M}_n \times 10^{-5}$	% Conversion
1	0.6845	0.3155	0.8351	0.1649	423.59	18.1739	47.30
2	0.5669	0.4331	0.7612	0.2388	416.21	14.7090	49.80
3	0.4894	0.5106	0.7154	0.2846	385.65	7.5328	48.47
4	0.4171	0.5829	0.6696	0.3304	354.04	—	12.64
5	0.3507	0.6493	0.6177	0.3823	337.18	—	23.16
6	0.2461	0.7539	0.5582	0.4418	197.04	—	12.68
7	0.1713	0.8287	0.4641	0.5359	120.12	—	23.90

f_{MMA} and f_{AN} are mol fractions of MMA and AN in the initial feeds.

F_{MMA} and F_{AN} are mol fractions of MMA and AN in the copolymers determined from ^1H NMR spectral analysis.

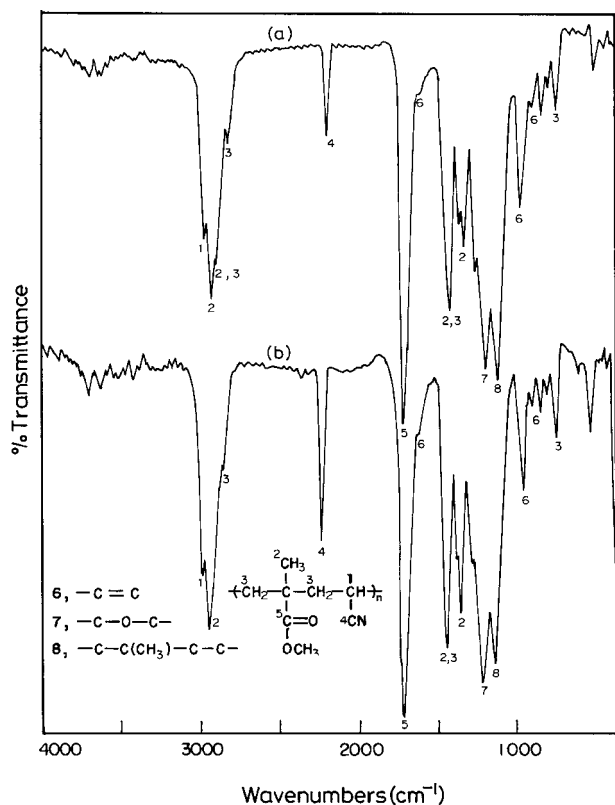


Figure 1 FTIR spectra of the MMA-AN copolymers made by (a) microemulsion copolymerization (sample 5) and (b) conventional emulsion copolymerization (sample 7).

are carried out by employing Waters unit interfaced with a NEC (IBM AT Compatible) computer to evaluate their molecular weights (\bar{M}_n). Molecular weight calibration curve is obtained with polystyrene standards in the molecular weight range 2.3×10^3 to 3.1×10^6 (Polymer Laboratories, Church Stretton, Shropshire, UK). Tetrahydrofuran (THF), at a flow rate of 1 mL/min, is used as an eluent (Fig. 7, Tables II and III).

RESULTS AND DISCUSSION

The FTIR spectra of the copolymers made by ME and CE copolymerization methods show the asymmetric stretching vibrations due to methyl group of the copolymers at $2951\text{--}2952\text{ cm}^{-1}$. The asymmetric stretching vibrations due to methylene group of the copolymer appear at 2928.4 cm^{-1} , and the symmetric stretching vibrations of methyl group seem to overlap with the asymmetric stretching vibrations of methylene group. The

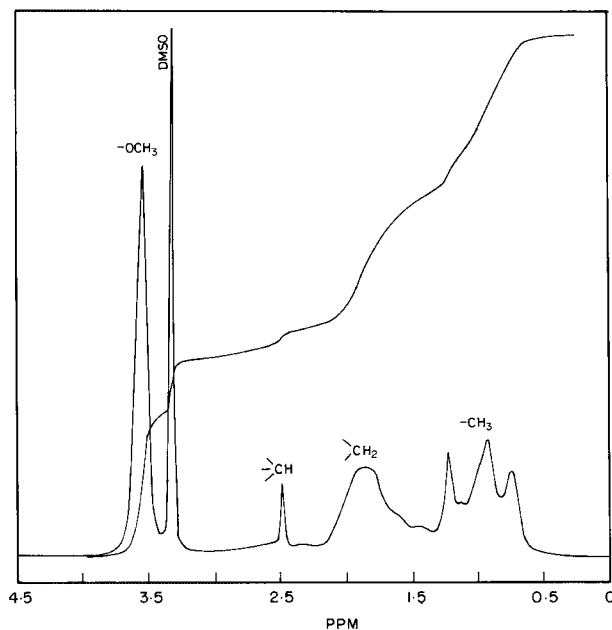


Figure 2 $^1\text{H-NMR}$ spectrum of the MMA-AN copolymer (sample 2) made by microemulsion copolymerization.

symmetric stretching vibrations of methylene group appear at $2851\text{--}2856\text{ cm}^{-1}$, and the stretching vibrations of methine group are ob-

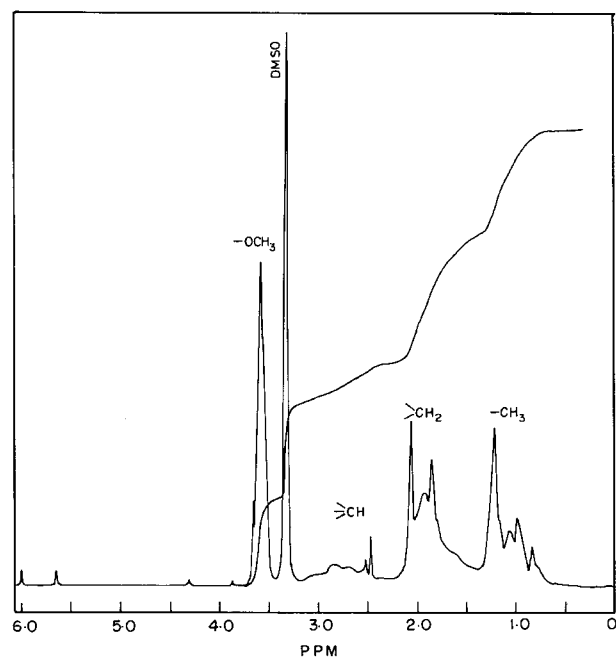


Figure 3 $^1\text{H-NMR}$ spectrum of the MMA-AN copolymer (sample 6) made by conventional emulsion copolymerization.

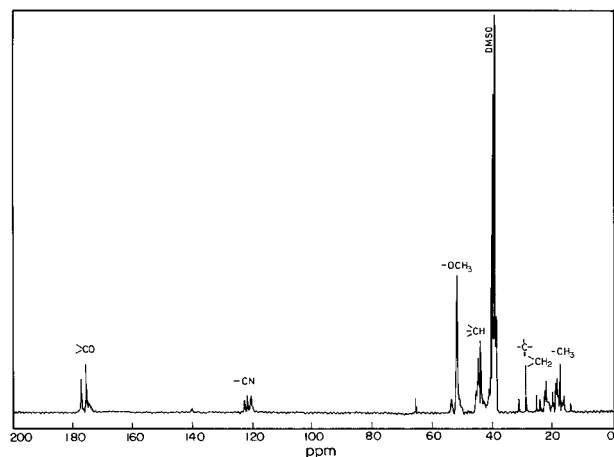


Figure 4 ^{13}C -NMR spectrum of the MMA-AN copolymer (sample 3) made by microemulsion copolymerization.

served in the region of $2987\text{--}2990\text{ cm}^{-1}$. The stretching vibrations due to nitrile group appear at $2240\text{--}2241\text{ cm}^{-1}$, and the stretching vibrations due to carbonyl group appear near $1727\text{--}1728\text{ cm}^{-1}$ and its overtone near 3450 cm^{-1} . The asymmetric bending vibrations due to methyl and methylene group are observed in the region of $1445\text{--}1448\text{ cm}^{-1}$, and the symmetric bending vibrations of methyl group appear at $1362\text{--}1389\text{ cm}^{-1}$. The stretching vibrations due to the —C—O—C— group appearing in the region of $1220\text{--}1283\text{ cm}^{-1}$. The skeletal vibrations due to the polymer backbone appear in the region of $1138\text{--}1146\text{ cm}^{-1}$. The stretching vibrations due to unsaturated end groups appear at 1635.7 cm^{-1}

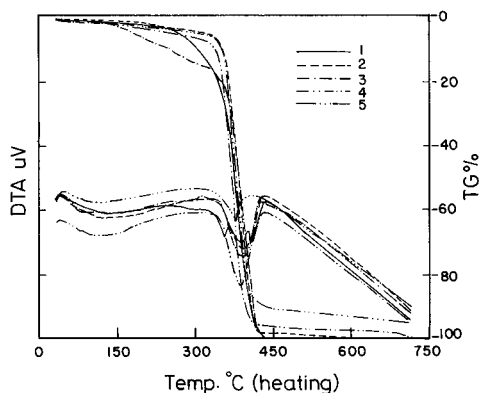


Figure 5 TG/DTA analysis of the MMA-AN copolymers made by microemulsion copolymerization: [MMA]/[AN] in the initial feeds: (1) 0.3986 : 0.1837, (2) 0.3578 : 0.2733, (3) 0.2808 : 0.3925, (4) 0.1887 : 0.5783, and (5) 0.1425 : 0.6896.

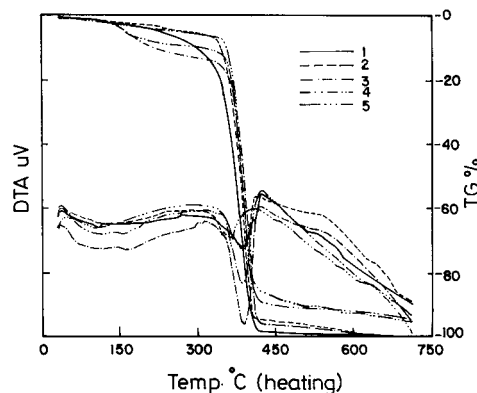


Figure 6 TG/DTA analysis of the MMA-AN copolymers made by conventional emulsion copolymerization. [MMA]/[AN] in the initial feeds: (1) 1.2454 : 0.5739, (2) 1.1240 : 0.8587, (3) 0.8858 : 1.2381, (4) 0.5920 : 1.8140, and (5) 0.4450 : 2.1529.

and the deformation vibrations due to unsaturated end groups are seen in the region of $748\text{--}986\text{ cm}^{-1}$. The rocking vibrations due to the methylene group overlap with the deformation vibrations of unsaturated end groups in the region of $749\text{--}764\text{ cm}^{-1}$. The absorption bands due to sulphate end groups (asymmetric stretching vibrations) overlap with absorption bands due to methyl and methylene groups in the region of $1362\text{--}1448\text{ cm}^{-1}$, and the symmetric stretching vibrations due to sulphate end groups overlap with the skeletal vibrations due to polymer backbone and with the stretching vibrations due to —C—O—C— groups in the region of $1138\text{--}1221\text{ cm}^{-1}$. And the stretching vibrations due to —C—O—S— groups appear at $811\text{--}816\text{ cm}^{-1}$ (Fig. 1).

The proton NMR spectra of the copolymers prepared under present study by ME and CE copolymerization methods show the chemical shifts

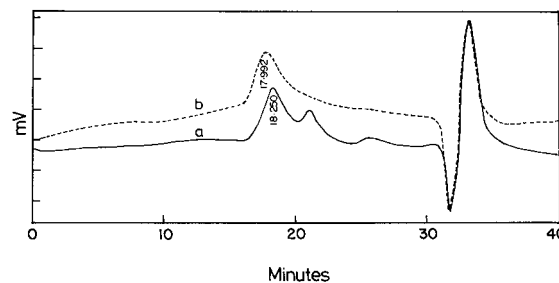


Figure 7 GPC analysis of MMA-AN copolymers made by (a) microemulsion (sample 2) and (b) conventional emulsion (sample 2) copolymerizations.

due to methoxy protons in the region of 3.545–3.670 ppm, and the solvent peak (DMSO- d_5) in the region of 3.302–3.377 ppm. The chemical shifts due to methine protons appear in the region of 2.385–3.054 ppm, and the methylene and methyl groups appear in the region of 0.727–2.073 ppm. The area under the resonance peaks due to methoxy protons is taken as 3AMMA and the total areas under the resonance peaks due to methine, methylene, and methyl groups is taken as $(3\text{AAN} + 5\text{AMMA})$. The mol fraction (F_{MMA}) of the MMA units in the copolymer is obtained as $\text{AMMA}/(\text{AAN} + \text{AMMA})$ (Figs. 2 and 3, and Tables II and III).

The ^{13}C -NMR spectra of the MMA-AN copolymers made under the present study show the chemical shifts due to carbonyl carbons in the region of 174.319–177.359 ppm, and the nitrile group appear in the region of 120.035–121.849 ppm. The resonance peaks due to methoxy carbons appear in the region of 50.121–53.634 ppm and the methine carbons at 42.750–45.503 ppm. The solvent peaks are observed at 38.657–40.441 ppm. The resonance peaks due to tertiary, methylene, and methyl carbons in the copolymers appear in the region of 13.943–37.399 ppm (Fig. 4).

The TG/DTA analysis of the copolymer samples made under present study by ME and CE copolymerizations show endothermic decompositions in the temperature region of 315.1–436.8°C. There is no any correlation observed between the compositions of the copolymers and the onset of decomposition processes. The energy values (ΔH) for the decomposition processes are evaluated from the areas of the endothermic curves, and are reported in Tables II and III (Figs. 5 and 6). The sample 1 containing higher proportions of MMA units, which is prepared by ME copolymerization method, yields three distinct endothermic processes at temperatures 354.6, 386.7, and 408.3°C (Fig. 5). Such observations were reported for the thermal decompositions of polymethyl methacrylate prepared by free radical polymerization.^{17,18} The ΔH value for the copolymers prepared by ME copolymerizations under present study increases initially with the increase of AN content and shows maximum for the third sample prepared with 65:35 (wt/wt) MMA/AN in the initial feed and then decreases slowly with the increase of AN content in the copolymers (Fig. 5 and Table II). There are no such observations noticed with the copolymers prepared by CE copolymerizations: there is only a slow decrease of ΔH values with the increase of AN content in the copolymers (Fig.

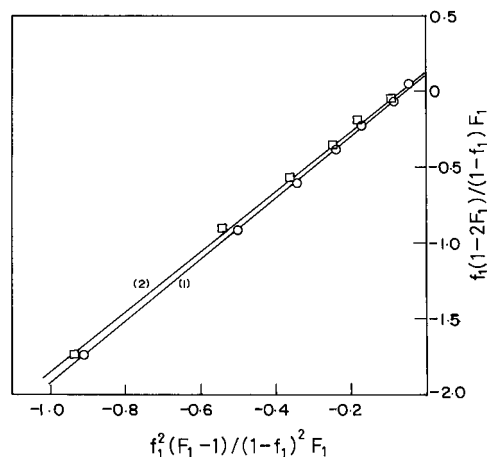


Figure 8 Fineman-Ross plots for the determination of reactivity ratios for (1) microemulsion and (2) conventional emulsion copolymerizations of MMA with AN.

6, Table III). The TG analysis shows that the percentage weight loss under present experimental conditions decreases slowly with the increase of AN content in the copolymers (Figs. 5 and 6).

There are also broad endothermic processes at low temperature regions starting already at 41°C and continuing upto 255°C (Figs. 5 and 6). These endothermic processes may be due to evaporation of moisture or volatile solvent, rupture of weak bonds, and low-temperature transitions.

GPC analysis of the polymer samples containing higher proportions of MMA units (>71 mol %) in the copolymers is carried out by employing THF as the eluent (Fig. 7 and Tables II and III). The copolymers prepared by CE copolymerizations yield higher molecular weights compared to the copolymers prepared by ME copolymerization experiments. These differences are considered to be due to the monomer starvation in ME copolymerization reaction media. The GPC analysis of the copolymers containing higher proportions of AN units could not be carried out as these are insoluble in THF solvent employed in these analysis.

Reactivity Ratios of the Monomer Pair, MMA/AN

The reactivity ratios for the ME and CE copolymerizations of MMA and AN are evaluated by Fineman-Ross (F-R),¹⁹ Kelen-Tüdös (K-T),²⁰ and Mayo-Lewis (M-L)²¹ methods (Figs. 8–10). The reactivity ratios obtained by ME and CE copolymerization methods for MMA (r_{MMA}) and AN

(r_{AN}) under the present study are differing from the values obtained by bulk²² and solution²³ polymerization methods in the literature (Table IV). These deviations may be due to the solubilities of the monomers in aqueous medium. Both the monomers are partially soluble in water, and the solubility of AN in water is more compared to MMA. The availabilities of these monomers at the reaction locii might not be the same as in bulk and solution polymerizations, which could cause the variations of the apparent reactivities of these monomers in ME and CE copolymerizations.²⁴⁻²⁶ The cosurfactant employed in the present study is soluble with both the monomers and is insoluble in water, and the monomers are mutually soluble by all proportions and also with the cosurfactant. The presence of solvent *n*-octanol in the reaction locii, which is used as cosurfactant, may bring about changes in these reaction parameters.²⁷⁻³³ The reactivity ratios obtained for the ME copolymerization method under the present study show small variations from the values obtained by the CE copolymerization method (Table IV). The cosurfactant *n*-octanol exists in the emulsion globules of the ME copolymerization systems along with the surfactant in the surface and in the core with the monomers. The cosurfactant OA exists in the emulsion globules and also with the monomer phases of the CE copolymerization systems. The solubilities of these monomers in aqueous media of these reaction systems are reduced com-

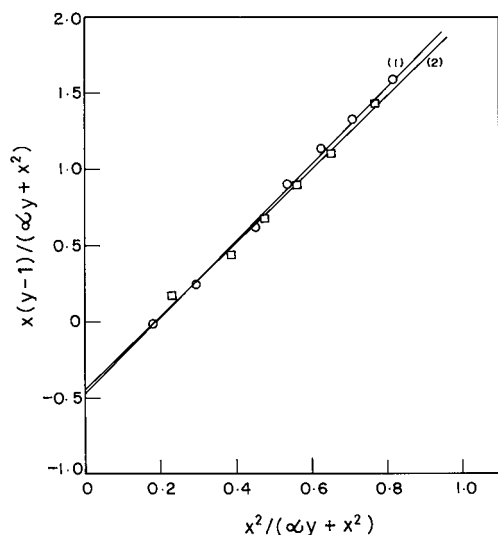


Figure 9 Kelen-Tüdös plots for the determination of reactivity ratios for the (1) microemulsion, and (2) conventional emulsion copolymerizations of MMA with AN.

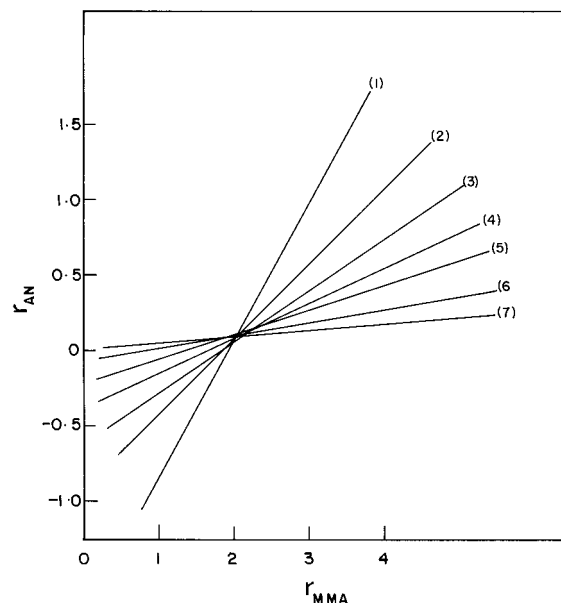


Figure 10 Mayo-Lewis line intersection method to evaluate the reactivity ratios for the microemulsion copolymerization of MMA with AN (Table II).

pared to their normal solubilities due to thermodynamic considerations.³⁴ The presence of cosurfactant in the emulsion globules of ME copolymerization systems, and in the emulsion globules and in the monomer phases of the CE copolymerization systems, might also influence these copolymerization parameters by bringing the changes in the monomer partitioning in various phases (i.e., emulsion globules and aqueous phase) of the reaction media.^{12,13,16}

CONCLUSIONS

There is no any correlation observed between the composition of the copolymers and the onset of the endothermic decompositions in the thermograms of the DTA analysis of the copolymers made by ME and CE copolymerization methods. The TG curves show a slow decrease of percent weight loss with the increase of AN content in the copolymers. The reactivity ratios for the ME and CE copolymerizations of MMA and AN differ from the values reported for bulk and solution copolymerizations of MMA with AN. These differences are attributed to be due to water solubilities of these monomers, and also due to the presence of the solvent *n*-octanol in the reaction locii. There is a small variation in the reactivity ratio values ob-

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> -Octanol	F-R	70	1.98 ± 0.02	0.13 ± 0.02
	<i>n</i> -Octanol	K-T	70	1.97 ± 0.02	0.13 ± 0.02
	<i>n</i> -Octanol	M-L	70	1.94 ± 0.02	0.14 ± 0.02
Microemulsion (present study)	<i>n</i> -Octanol	F-R	70	2.04 ± 0.02	0.10 ± 0.02
	<i>n</i> -Octanol	K-T	70	2.03 ± 0.02	0.10 ± 0.02
	<i>n</i> -Octanol	M-L	70	2.07 ± 0.02	0.11 ± 0.02

tained by ME and CE copolymerization methods, and this might be due to the variation of the monomer partitioning in different phases of the reaction media in these copolymerization systems.

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