

Microemulsion and Conventional Emulsion Copolymerizations of Styrene and *n*-Butyl Methacrylate, and Characterization of the Copolymers

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Received 9 September 1999; accepted 4 November 1999

ABSTRACT: Microemulsion (ME) and conventional emulsion (CE) copolymerizations of styrene (STY) with *n*-butyl methacrylate (BMA) were carried out at 70°C in an inert atmosphere by employing sodium lauryl sulfate as a surfactant, *n*-heptanol as a cosurfactant, and potassium persulfate as a free-radical initiator. Five different compositions of the monomer mixtures were employed in the initial reaction mixtures, and the copolymerization reactions were arrested at lower conversions. The copolymers made were characterized using FTIR, NMR, TG/DTA, GC, and GPC techniques. The compositions of the copolymers were evaluated from ¹HNMR spectral data. The reactivity ratios for the ME and CE copolymerizations of styrene with *n*-butyl methacrylate were evaluated by the Fineman–Ross (F–R), Kelen–Tüdös (K–T), and Mayo–Lewis (M–L) methods. The Fineman–Ross method yielded the reactivity ratios of styrene (r_{STY}) and *n*-butyl methacrylate (r_{BMA}) as 0.17 ± 0.02 and 0.60 ± 0.02 for ME copolymerization of styrene and *n*-butyl methacrylate, respectively. The r_{STY} and r_{BMA} for CE copolymerization of styrene and *n*-butyl methacrylate were obtained as 0.31 ± 0.02 and 0.55 ± 0.02 , respectively. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 398–408, 2000

Key words: microemulsion copolymerization; conventional emulsion copolymerization; reactivity ratios; characterization of polymers

INTRODUCTION

Copolymerization is the most general and powerful method of effecting systematic changes in polymer properties and is widely used in the production of commercial polymers and in fundamental investigations of structure–property relations. Reactivity ratios for copolymerizing monomers have become important in the prediction of the types of monomers that will combine to make polymers and in determining the regularity of

such polymeric materials. Several investigators^{1–4} have derived equations to evaluate the relative reactivity ratios of the monomers for binary copolymerization using the bulk copolymerization method.

The reactivity ratios should depend to some extent on conditions such as the reaction temperature, solvent environment, and emulsion polymerization. The effect of solvents with different dielectric constants, solubility parameters, and dipole moments have been studied in the literature.^{5–8} Other possible phenomena that can lead to the dependence of reaction velocity on the nature of the solvent are complex formation or solvation of one monomer by the solvent,^{9–11} and preferential solvation of the polymer coil by one of

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Journal of Applied Polymer Science, Vol. 77, 398–408 (2000)
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the monomers, causing heterogeneous repartition of the monomer mixture in solution (the bootstrap effect).^{12–15}

In general, copolymerizations in emulsion yield reactivity ratios in substantial agreement with those determined in mass, solution, or solvent–nonsolvent copolymerization.^{16,17} If one of the monomers is quite water soluble, its apparent reactivity is reduced.^{18–20} In emulsion copolymerization it is quite possible that monomers containing long alkyl groups will also exhibit reduced apparent reactivities due to their low rate of diffusion to the locus of polymerization.

Studies on copolymerization using the microemulsion polymerization method are rare in the literature. However, a few studies on the microemulsion copolymerizations of vinyl monomers have appeared in recent literature.^{21–23} The reactivity ratios of the monomer pairs determined by microemulsion copolymerization²² differ from that of bulk²⁴ and emulsion copolymerizations.²⁵ The different copolymerization behaviors by these methods of polymerizations are attributed to the different monomer ratios in the polymerization loci.^{22,23}

In the present study the microemulsion and conventional emulsion copolymerizations of styrene and *n*-butyl methacrylate were carried out at 70°C by employing sodium lauryl sulfate as a surfactant, *n*-heptanol as a cosurfactant, and potassium persulfate as a free-radical initiator. The copolymers prepared were characterized using FTIR, NMR, TG/DTA, GC, and GPC techniques. The relative reactivity ratios of these monomer pairs for the microemulsion and conventional emulsion copolymerizations were evaluated with the use of the graphical procedures from Fineman–Ross, Mayo–Lewis, and Kelen–Tüdös, and the results obtained by these methods of copolymerizations were compared with the results listed in the literature.

EXPERIMENTAL

Materials

Monomers, *n*-butyl methacrylate (BMA) (LR, BDH Chemicals Ltd., Poole, England), and styrene (STY) [commercial grade, Shin Ho Petrochemical (India) Ltd., Chennai, India] were washed with 5% sodium hydroxide, followed by distilled water. The washed monomers were dried over anhydrous sodium sulfate, and the dried

monomers were further purified by vacuum distillation in an inert atmosphere in an all-glass quick-fit set up and stored in a refrigerator at –5°C.

Potassium persulfate (KPS) (LR, s.d.fine chem pvt. Ltd., Boisar, India), sodium lauryl sulfate (SLS) (LR, Central Drug House Pvt. Ltd., Mumbai, India), *n*-heptanol (HA) (LR, s.d. fine chem pvt. Ltd., Boisar, India) and hydroquinone (AR, s.d.fine chem pvt. Ltd., Boisar, India) were used as supplied without further purification.

Acetone (AR, Fischer Inorganic & Aromatics Ltd., Chennai, India), methanol (AR, Fischer Inorganic & Aromatics Ltd., Chennai, India), methyl ethyl ketone (AR, s.d. fine chem pvt. Ltd., Boisar, India), and dehydrated alcohol (ethanol) (Bengal Chemicals & Pharmaceuticals Ltd., Calcutta, India) were purified using standard procedures.

Methods

Preparation of Microemulsion Solutions of Monomer Mixtures

The monomer mixtures of STY and BMA along with *n*-heptanol in requisite quantities were made soluble in an aqueous solution of sodium lauryl sulfate 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, and then the solution was allowed to sit overnight for to attain equilibrium (Table 1). This microemulsion solution of the monomers mixture was used for microemulsion and conventional emulsion copolymerization experiments. Five compositions of the monomer mixtures made while keeping the total weight of the monomers constant were used in these recipes for microemulsion (ME) and conventional emulsion (CE) copolymerization experiments.

Microemulsion Copolymerization

A 30-mL aliquot of the ME solution of the monomers mixture (Table I) was put into a 50-mL

Table I Microemulsion Solution of Styrene and *n*-Butyl Methacrylate

Water	75 mL
Sodium lauryl sulphate	6.75 gm
<i>n</i> -Heptanol	2.874 gm
Total weight of monomer mixture	3.9 gm

Table II Microemulsion Copolymerization of Styrene with *n*-Butyl Methacrylate

S. No.	f_1 (STY)	f_2 (BMA)	F_1 (STY)	F_2 (BMA)	% Δ of STY from GC	% Δ of BMA from GC	ΔH KJ/mg	\bar{M}_n $\times 10^{-5}$	% Conversion
1	0.2620	0.7380	0.2717	0.7283	74.85	25.14	367.39	0.588	18.8
2	0.4252	0.5748	0.3813	0.6187	71.96	28.04	462.57	0.422	10.4
3	0.5799	0.4201	0.4436	0.5564	77.65	22.35	678.58	0.342	12.0
4	0.7204	0.2796	0.5498	0.4502	84.91	15.09	513.15	0.348	9.0
5	0.8244	0.1756	0.6088	0.3912	86.39	13.61	598.50	0.472	9.0

f_1 and f_2 are mole fractions of STY and BMA in the initial feeds.

F_1 and F_2 are mole fractions of STY and BMA in the copolymers determined from $^1\text{HNMR}$ spectral data.

reaction tube, and the ME copolymerization of the monomers in this recipe was carried out in an inert atmosphere at 70°C by initiating with a $9.1 \times 10^{-4}\text{M}$ KPS solution. The ME copolymerization reaction was arrested at lower conversions with the addition of hydroquinone to the reaction mixture, and the copolymer was isolated by precipitation with methanol. The precipitated copolymer sample was washed with ethanol to remove unreacted monomer and surfactant from the copolymer, and then with water to remove water-soluble impurities. The washed copolymer was dried to a constant weight in a vacuum oven at 60°C .

The ME copolymerization experiments were carried out with five different compositions of the monomers, STY–BMA, while keeping the total weight of the monomers constant in all the ME recipes (Tables I and II).

Conventional Emulsion Copolymerization

The CE copolymerization of the monomer pair STY–BMA was carried out by putting 20 mL of the ME recipe (Table I) in a 50-mL reaction tube, supplying the excess monomers mixture with the

same composition in the reaction tube, and by initiating with a $9.1 \times 10^{-4}\text{M}$ KPS solution at 70°C in an inert atmosphere. The copolymerization in the reaction tube was arrested at lower conversions by the addition of hydroquinone to the reaction mixture, and the copolymer was isolated by precipitation in methanol. The precipitated copolymer was washed with ethanol and then with water, and the washed copolymer was dried to a constant weight in a vacuum oven at 60°C . The CE copolymerization experiments were carried out with five different compositions of the monomers STY–BMA, and the total weight of the monomers was maintained as constant for all five compositions in the reaction mixtures (Table III).

Characterization of the Copolymers

FTIR Spectral Analysis: The 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 copolymers from chloroform solutions between KBr windows sized 25×4 mm (Fig. 1).

Table III Conventional Emulsion Copolymerization of Styrene with *n*-Butyl Methacrylate

S. No.	f_1 (STY)	f_2 (BMA)	F_1 (STY)	F_2 (BMA)	% Δ of STY from GC	% Δ of BMA from GC	ΔH KJ/mg	\bar{M}_n $\times 10^{-5}$	% Conversion
1	0.2620	0.7380	0.3158	0.6842	76.67	23.33	577.43	1.993	6.5
2	0.4252	0.5748	0.4206	0.5794	78.58	21.42	530.01	15.682	60.0
3	0.5799	0.4201	0.4636	0.5364	76.54	23.46	657.51	9.387	26.2
4	0.7204	0.2796	0.6297	0.3703	80.24	19.76	715.46	0.847	7.4
5	0.8244	0.1756	0.6760	0.3240	84.90	15.10	729.16	4.661	14.6

f_1 and f_2 are mole fractions of STY and BMA in the initial feeds.

F_1 and F_2 are mole fractions of STY and BMA in the copolymers determined from $^1\text{HNMR}$ spectral data.

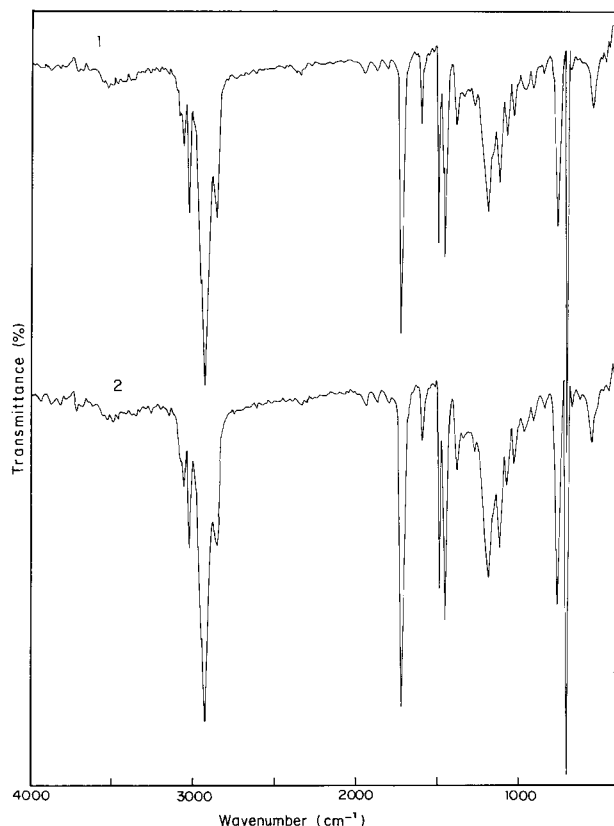


Figure 1 FTIR spectra of STY and BMA copolymers made by (1) microemulsion copolymerization (sample 5) and (2) conventional emulsion copolymerization (sample 5).

¹H and ¹³C NMR Spectral Analysis: High-resolution ¹H and ¹³C NMR spectra of the copolymer samples made by ME and CE copolymerization methods in the present study were recorded at ambient temperature with a Bruker MSL 300P, 300MHz FT-NMR spectrometer, using CDCl₃ as the solvent and tetramethylsilane as the internal standard (Figs. 2–4).

Pyrolysis Gas Chromatographic Analysis: The copolymer samples of STY–BMA made by ME and CE copolymerizations were analyzed using a Hewlett Packard 5840A gas chromatographic instrument attached with a HP pyroprobe 18580B unit (Tables II and III, Fig. 9).

y Program Operating Conditions

Pyroprobe

Interface temperature: 50°C

Ramp: 10°C/ms

Pyrolysis interval: 5 s

Final temperature: 500°C

Gas Chromatograph

Column: 6¹-10P OV17 Chrome WHP 100/200

Column temperature: 160°C

Nitrogen carrier: 10 mL/24 s

Injection port: 165°C

FID temperature: 290°C

TG/DTA Analysis: The copolymers of STY–BMA made by ME and CE copolymerizations in the present study were analyzed for their thermal behavior by using a Seiko TG/DTA 200 instrument in nitrogen atmosphere with a gas flow of 100 mL/min and at a heating rate of 20°C/min in the temperature region 30–600°C. Alumina was used as the reference on platinum pans (Tables II and III, Fig. 8).

Gel Permeation Chromatography: The molecular weights of copolymer samples prepared by ME and CE copolymerizations were evaluated by gel permeation chromatography (GPC) using a WATERS unit interfaced with an NEC (IBM AT compatible) computer and with tetrahydrofuran as the eluting solvent (Tables II and III, Fig. 10).

RESULTS AND DISCUSSION

Infrared spectroscopy is probably the method most extensively used for the investigation of polymer structure and analysis of the functional groups. The FTIR spectra of the copolymers made in the present study by ME and CE copolymerizations (Fig. 1) show the asymmetric stretching vibrations of —CH₃ groups in the region 2985–2994 cm⁻¹. The symmetric stretching vibrations of the —CH₃ group seem to overlap with the stretching vibrations of the —CH₂ group in the region 2952–2862 cm⁻¹. The IR absorption peaks for these copolymers in the region 2845–2852 cm⁻¹ may result from the symmetric stretching vibrations of the —CH₂ group. The absorption band in the 1730–1720 cm⁻¹ region is characteristic of —C=O stretching vibrations, and its overtone was observed near 3450 cm⁻¹. The absorption band in the region 1451–1443 cm⁻¹ results from the bending vibrations of —CH₃ group, and the bending vibrations of —CH₂ group was found in a slightly higher region in the IR absorption

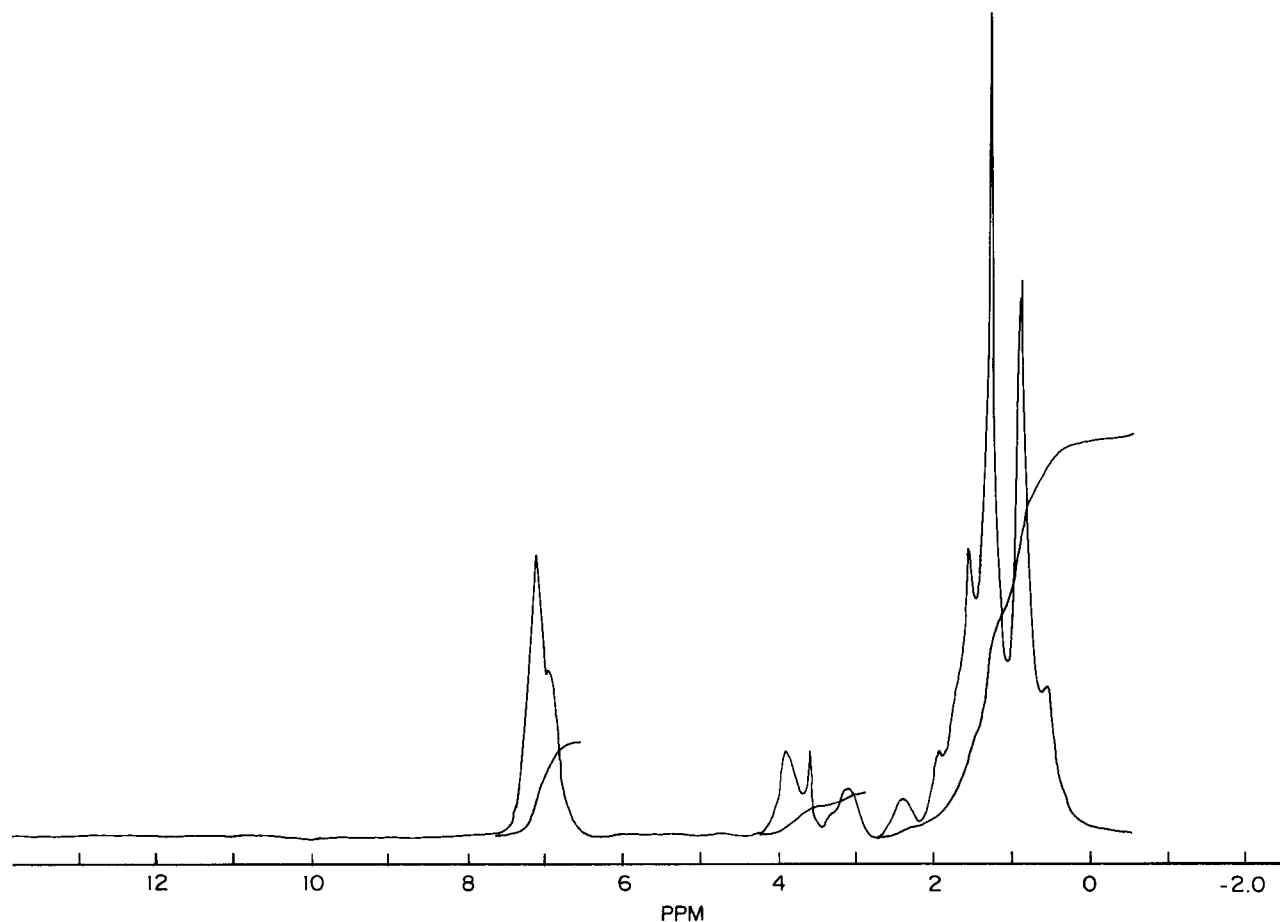


Figure 2 ^1H NMR spectrum of STY-BMA copolymer sample (2) made by microemulsion copolymerization.

spectra. The rocking vibrations of $-\text{CH}_2$ can be observed in the region $757\text{--}755\text{ cm}^{-1}$. The skeletal vibrations of polymer backbone, the $-\text{C}-\text{O}-\text{C}-$ stretching resonances, and the absorption due to sulfate end groups appear in the regions $1141\text{--}1148\text{ cm}^{-1}$, $1100\text{--}1280\text{ cm}^{-1}$, and $1367\text{--}1410\text{ cm}^{-1}$, respectively.

The IR spectra also show the characteristic absorption bands of a phenyl ring in the styrene. The $-\text{C}-\text{C}-$ stretching vibrations of a phenyl ring appear in the region $1591\text{--}1604\text{ cm}^{-1}$, and the $-\text{C}-\text{H}$ deformation vibrations of ring hydrogens are found in the region $730\text{--}770\text{ cm}^{-1}$. The $3000\text{--}3100\text{ cm}^{-1}$ band is assigned to $-\text{C}-\text{H}$ stretching vibrations of ring hydrogens, and the overtone and combination bands of $-\text{C}-\text{H}$ deformation vibrations are found in the region $1660\text{--}2000\text{ cm}^{-1}$.

Figures 2 and 3 are the typical ^1H NMR spectra of the copolymers STY-BMA, made by the ME and CE copolymerization methods, respectively.

The proton NMR spectra of the STY-BMA copolymers made under the present study show the chemical shifts from the phenyl protons in the region $6.92\text{--}7.24\text{ ppm}$, and the methyleneoxy ($-\text{OCH}_2-$) protons of the BMA units in the copolymer in the region $3.58\text{--}3.87\text{ ppm}$. The chemical shifts from the methine protons of the STY units in the copolymers are observed in the region $3.06\text{--}3.10\text{ ppm}$, and the chemical shifts resulting from the methylene groups in these copolymers are observed in the region $1.23\text{--}1.91\text{ ppm}$. The resonance peaks from the methyl groups in these copolymers appear in the $0.51\text{--}0.87\text{ ppm}$ region. The area of the resonance peaks due to phenyl protons of the STY units in the copolymers is taken as 5ASTY , and the total area of the resonance peaks resulting from the methine, methylene, and methyl groups in the copolymers is taken as $(3\text{ASTY} + 12\text{ABMA})$. By using the integral areas of the resonance peaks in the proton NMR spectra of STY-BMA copolymers, the mole frac-

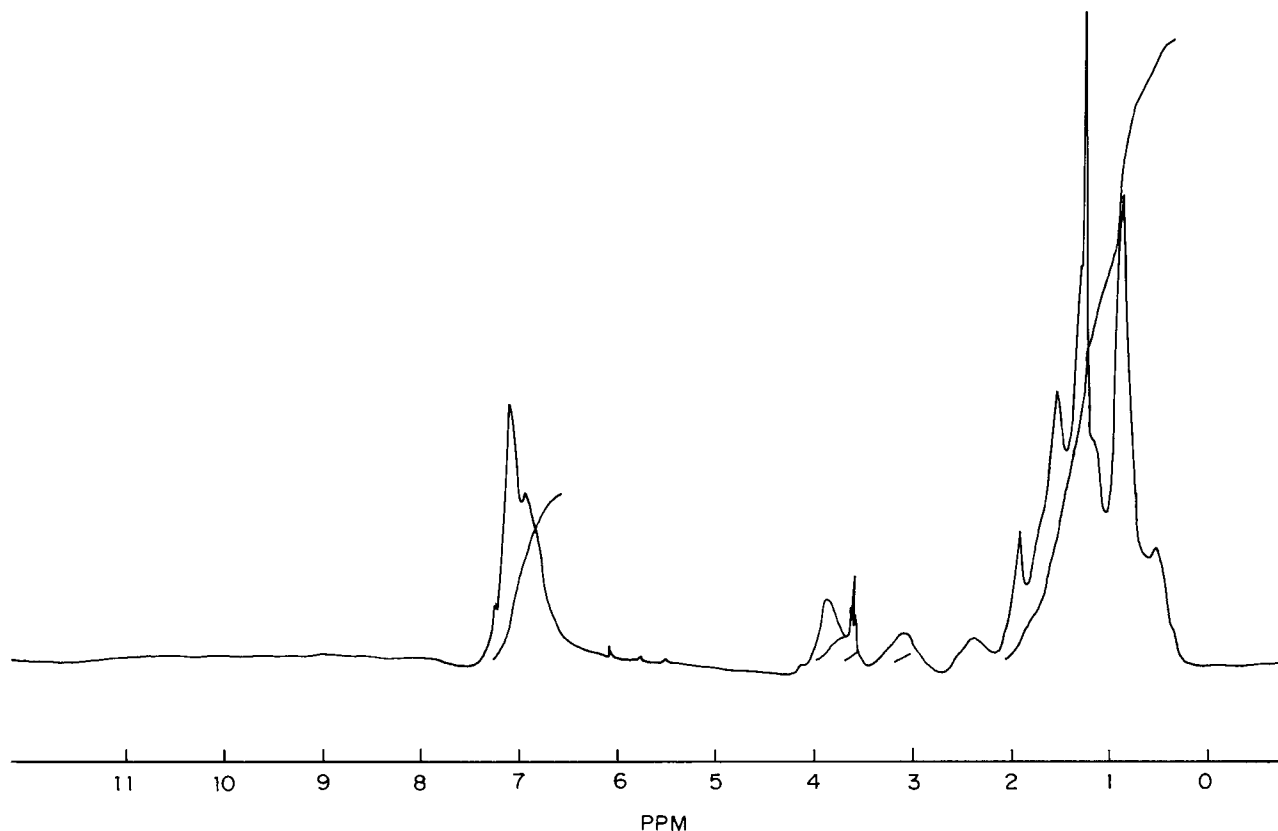


Figure 3 ^1H NMR spectrum of STY-BMA copolymer sample (2) made by conventional emulsion copolymerization.

tions of STY units (F_{STY}) in these copolymers are obtained as $\text{ASTY}/(\text{ABMA} + \text{ASTY})$ (Tables II and III, Figs. 2 and 3).

Figure 4 is the typical ^{13}C NMR spectrum of the copolymer STY-BMA, made by ME copolymerization. The ^{13}C NMR spectra of the STY-BMA copolymers made by ME and CE copolymerizations in the present study show the resonance peaks from carbonyl groups in the 176.15–177.07 ppm region, and the phenyl carbons of the STY units in the region of 125.70–145.65 ppm. The solvent (CDCl_3) peak appear in the region 76.54–77.44 ppm. The chemical shifts resulting from methyleneoxy carbons in ^{13}C NMR spectra of the copolymers appear in the region 62.86–64.42 ppm. The chemical shifts from methine and methylene groups, tertiary carbon atoms, and the methyl group of the STY-BMA copolymers appear in the region 13.64–52.29 ppm.

Pyrolysis gas chromatographic analysis of the STY-BMA copolymers made by ME and CE copolymerizations in the present study was carried out by pyrolyzing the copolymer samples at 500°C

and by passing the pyrolyzates with nitrogen carrier gas through the separating column (OV17) at a column temperature of 160°C, and the comonomer units were quantitatively detected with FID signal operating at 290°C (Tables II and III, Fig. 9). The values obtained for comonomer compositions by pyrolysis GC in the present study deviate from the results obtained from the ^1H NMR spectral data (Tables II and III). This might be a result of unreliable yields of STY and BMA units by unzipping of copolymer samples at pyrolysis temperature (500°C), employed in the present study, and of a lack of comparison of peak areas with calibration curves of copolymers with known compositions.^{26,27} Two copolymers of the same overall composition may differ widely in the way the two types of monomer units are distributed in the polymer molecule, and the pyrogram of a copolymer depends on the sequence-length distribution.²⁷

The TG/DTA analysis of STY-BMA copolymer samples made by ME copolymerizations was carried out under a nitrogen atmosphere in

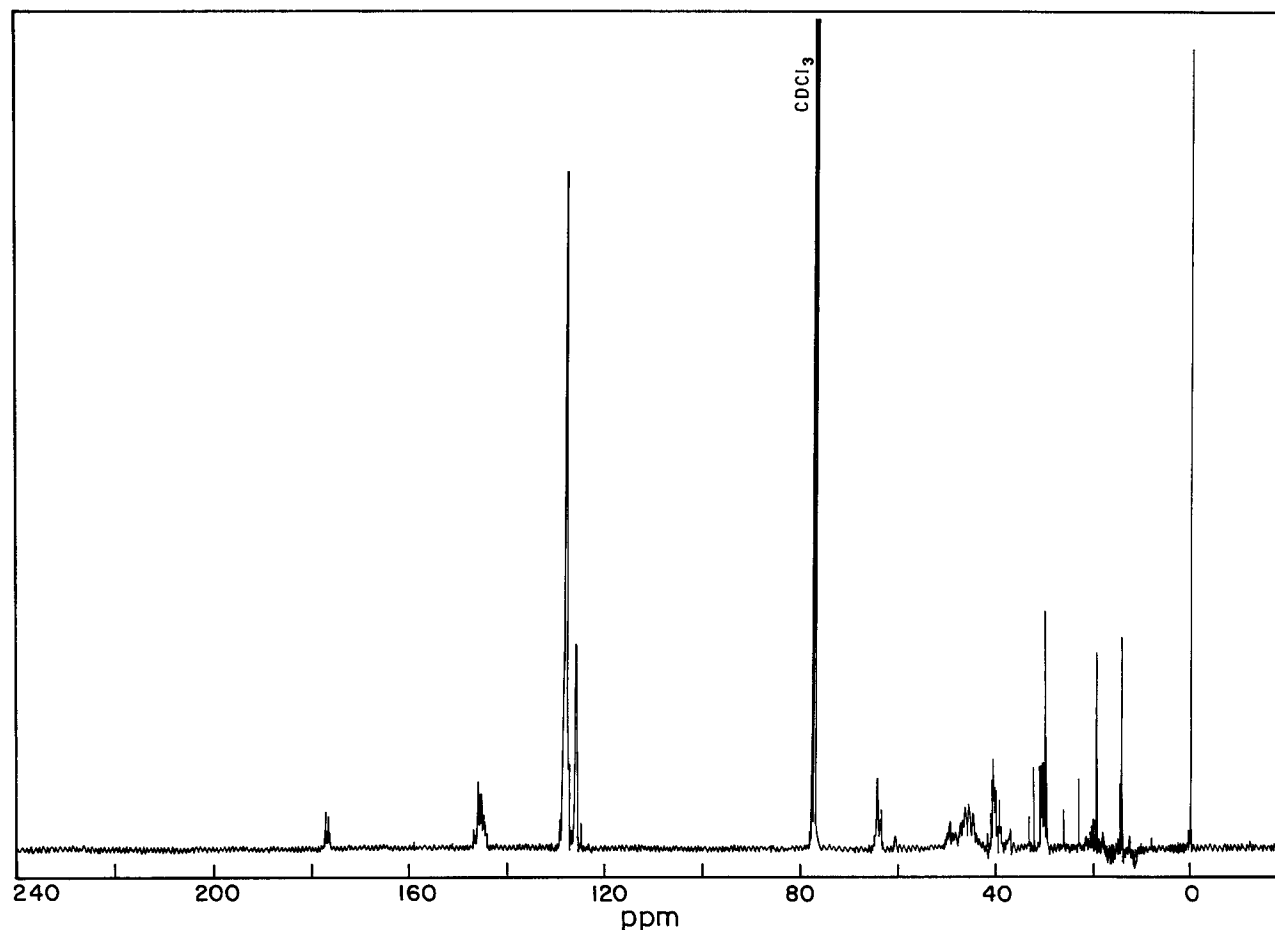


Figure 4 ^{13}C NMR spectrum of STY-BMA copolymer sample (5) made by microemulsion copolymerization.

the temperature region 30–600°C at a heating rate of 20°C/min (Fig. 8). The endothermic decompositions of these copolymer samples ap-

pear in the temperature region 300–457.5°C (Fig. 8). The energy values (ΔH) for these endothermic processes are evaluated and reported in

Table IV Reactivity Ratios of Monomers, Styrene, and *n*-Butyl Methacrylate

Polymerization Method	Solvent in the Reaction Medium	Method of Evaluation	Temperature (°C)	r_{STY}	r_{BMA}
Bulk ²⁸	—	F-R	60	0.56	0.40
Bulk ²⁹	—	—	50	0.63	0.64
Bulk ²⁹	—	—	70	0.54	0.64
Microemulsion (present study)	<i>n</i> -Heptanol	F-R	70	0.17 ± 0.02	0.60 ± 0.02
	"	M-L	"	0.18 ± 0.02	0.66 ± 0.02
	"	K-T	"	0.16 ± 0.02	0.64 ± 0.02
Emulsion (present study)	<i>n</i> -Heptanol	F-R	70	0.31 ± 0.02	0.55 ± 0.02
	"	M-L	"	0.31 ± 0.02	0.60 ± 0.02
	"	K-T	"	0.27 ± 0.02	0.56 ± 0.02

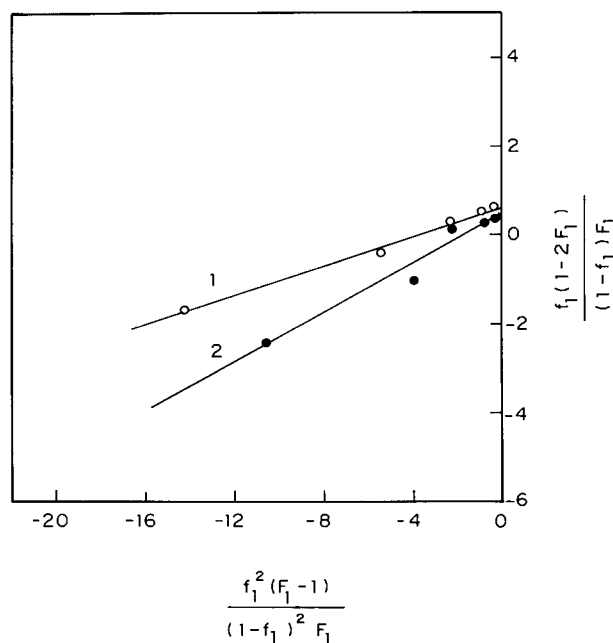


Figure 5 Fineman–Ross plots to evaluate the reactivity ratios of STY and BMA for (1) microemulsion and (2) conventional emulsion copolymerizations.

Table II. The endothermic decompositions shift to higher temperature regions with the increase of STY content in the copolymers. There are also slow endothermic processes at lower temperature regions (55.7–286.7°C). These endothermic processes at lower temperature regions may result from solvent evaporation, rupture of weak bonds, and low temperature transitions (Fig. 8).

TG/DTA analysis of STY–BMA copolymers made by CE copolymerizations was also carried out, and the thermograms are recorded in the temperature region 30–600°C. DTA analysis of the copolymers shows endothermic decompositions in the temperature region 307.5–448.6°C. The ΔH values for the endothermic effects are evaluated and reported in Table III. The endothermic decompositions shift to higher temperature regions with the increase of the STY content in these copolymers. There are also slow endothermic processes in the lower temperature region (50–287°C).

The STY–BMA copolymers prepared by ME and CE copolymerizations were analyzed for their molecular weights (\bar{M}_n) by gel permeation chromatography. The \bar{M}_n obtained for the copolymers prepared by CE copolymerizations are many fold (2.43–37.17) higher compared to the molecular

weights of the copolymers prepared by ME copolymerizations (Tables II and III, Fig. 10) in the present study. This may result from the monomer starvation in the ME copolymerization reaction media.

Reactivity Ratios of the Monomer Pair STY–BMA

The reactivity ratios for the ME and CE copolymerizations of STY and BMA were evaluated by employing the Fineman–Ross (F-R),³ Mayo–Lewis (M-L),² and Kelen–Tüdös (K-T)⁴ methods (Table IV, Figs. 5–7). In the present study, the Fineman–Ross method yielded the following results for the reactivity ratios r_{STY} and r_{BMA} : for the ME copolymerization of STY and BMA 0.17 for the former and 0.60 for the latter; and for CE copolymerization, the r_{STY} and r_{BMA} were 0.31 for the STY and 0.55 for the BMA. The r_{STY} and r_{BMA} for bulk copolymerization²⁹ of STY and BMA were reported as 0.54 and 0.64, respectively. In the present study the monomers and cosurfactant are miscible, and these are sparingly soluble in water.

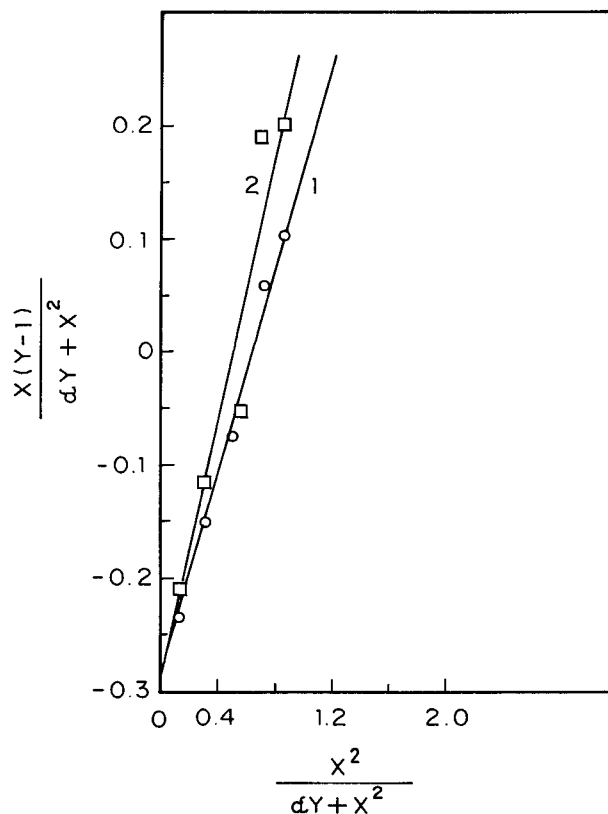


Figure 6 Kelen–Tüdös plots to evaluate the reactivity ratios of STY and BMA for (1) microemulsion and (2) conventional emulsion copolymerizations.

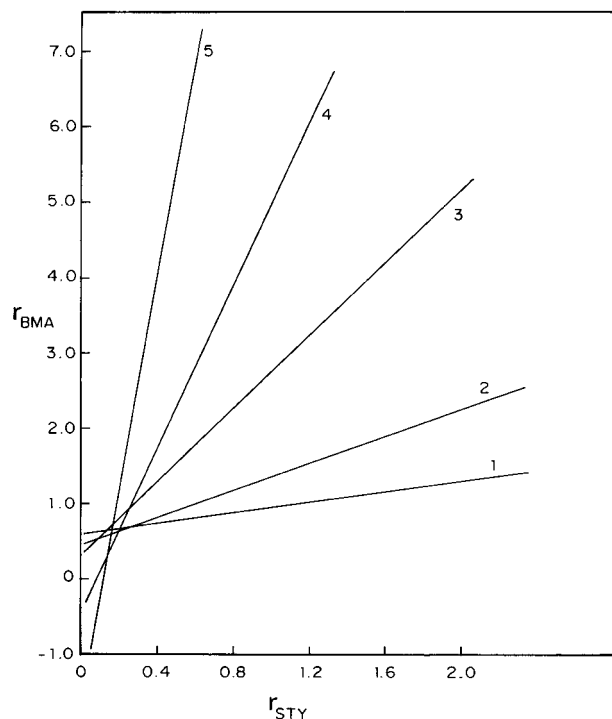


Figure 7 Mayo-Lewis method to evaluate the reactivity ratios for the microemulsion copolymerization of STY and BMA. The composition of STY and BMA in the copolymers: (1) 0.2717:0.7283, (2) 0.3813:0.6187, (3) 0.4436:0.5564, (4) 0.5498:0.4502, and (5) 0.6088:0.3912.

HA employed as cosurfactant is miscible with both the monomers, and because of thermodynamic considerations, the concentrations of the monomers and HA in the aqueous phase may be less than their normal solubilities.³⁰ HA exists in ME particles along with the surfactant in the surface and in the core with the monomers. HA is also exists in CE copolymerization systems in the present study. HA in these CE polymerization systems can partition in emulsion particles with surfactant and with monomers in the core, and it is also solubilized in the monomer particles as separate phase. The existence of HA in the reaction media may bring about the changes in the reactivity ratios compared to bulk copolymerization (Table IV).

The literature reports on many varied attempts to explain experimental results on solvent effects that invoke such diverse phenomena as solvent polarity, complex formation between solvent and chain end, and preferential solvation of the polymer coil by one of the two monomers ("bootstrap effect") or by the solvent, etc.¹¹

The difference in reactivity ratio values obtained by ME and CE copolymerizations of STY and BMA in the present study (Table IV) can be attributed to the difference of monomer partitioning in different phases (i.e., emulsion globules and aqueous phase) of ME and CE copolymerization systems.^{22,23}

CONCLUSIONS

The copolymers of STY-BMA made by ME and CE copolymerizations were analyzed with FTIR, ¹HNMR, ¹³CNMR, GC, TG/DTA and GPC techniques. The deviations of GC results from the values obtained by ¹HNMR for copolymer compositions might result from the unreliable yields of STY and BMA units caused by the unzipping of copolymers at pyrolysis temperature, 500°C. The TG/DTA analysis of the STY-BMA copolymer samples made by ME and CE copolymerizations in the present study shows shifts in the endothermic decomposition processes to a higher temperature region with the increase of STY content in the copolymers. The reactivity ratios of STY and BMA obtained through ME and CE copolymerizations in the present study differ from the bulk copolymerization values reported in the literature and are attributed to the presence of *n*-heptanol in the reaction media. The varied values obtained by ME and CE copolymerizations are considered as a result of the difference of monomer partition-

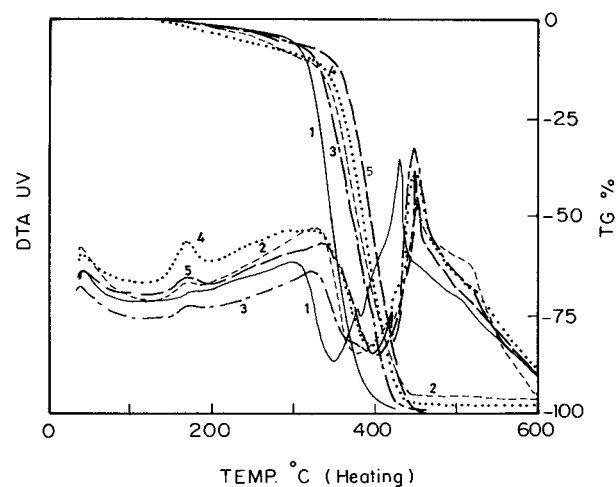


Figure 8 TG/DTA analysis of STY and BMA copolymers made by microemulsion copolymerizations (Table II).

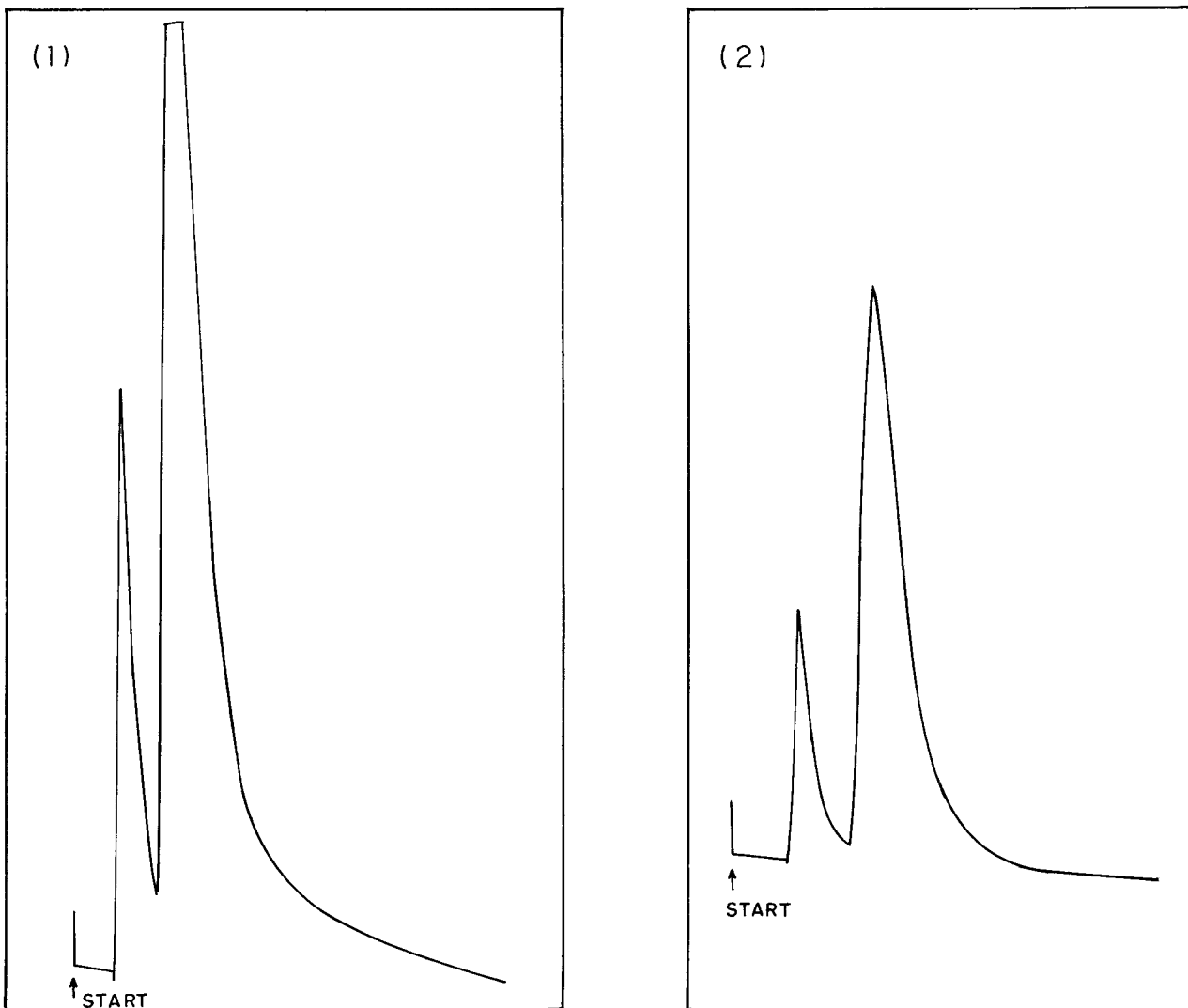


Figure 9 Pyrolysis gas chromatograms of STY-BMA copolymers made by (1) microemulsion (sample 3) and (2) conventional emulsion (sample 3) copolymerizations.

ing in different phases (i.e., emulsion globules and aqueous phase) of ME and CE copolymerization systems in the present study.

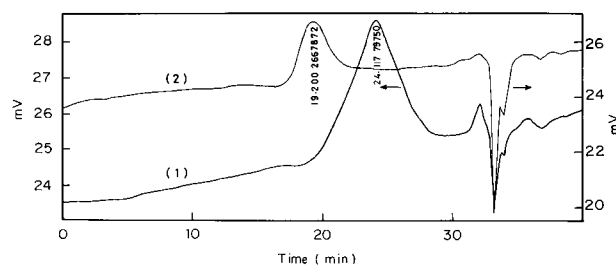


Figure 10 Gel permeation chromatograms of the copolymers made by (1) microemulsion (sample 2) and (2) conventional emulsion (sample 2) copolymerizations.

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