

Microemulsion and Conventional Emulsion Copolymerizations of Styrene with Methyl Methacrylate

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ABSTRACT: The microemulsion (M.E.) and conventional emulsion (C.E.) copolymerizations of styrene (STY) with methyl methacrylate (MMA) are carried out at 70°C by employing *n*-pentanol (PA) and *n*-octanol (OA), respectively, as cosurfactants along with sodium lauryl sulfate (SLS), as surfactant in the reaction media, and potassium persulphate (KPS) as initiator. The copolymers are characterized by FTIR, NMR, TG/DTA, and GPC techniques. The reactivity ratios are evaluated by employing Fineman-Ross (F-R), Kellen-Tüdös (K-T), and Mayo-Lewis integration (M-L-I) methods. The K-T method yields the apparent reactivity ratios, 0.73 (r_{STY}), 0.39

(r_{MMA}) and 0.55 (r_{STY}), 0.50 (r_{MMA}), respectively, for the M.E. and C.E. copolymerizations of STY and MMA with PA as the cosurfactant present in the reaction media. And the K-T method yields the apparent reactivity ratios, 0.56 (r_{STY}), 0.43 (r_{MMA}), and 0.42 (r_{STY}), 0.51 (r_{MMA}), respectively, for the M.E. and C.E. copolymerizations of STY and MMA with OA as the cosurfactant present in the reaction media. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3391–3401, 2007

Key words: emulsion polymerization; copolymerization; surfactants; FTIR; NMR

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 types of monomers, which will combine to give polymers and in determining the regularity of such polymeric materials. The reactivity ratios should depend to some extent upon the conditions of the reaction-temperature, solvent environment, emulsion polymerization, etc. The effect of solvents having different dielectric constants, solubility parameters, and dipole moments have been studied in the literature.^{1–4} Other possible phenomena that can lead to the dependence of reaction velocity upon the nature of the solvent are complex formation or solvation of one monomer by the solvent,^{5–7} and preferential solvation of the polymer coil by one of the monomers causing heterogeneous repartition of the monomer mixture in solution (bootstrap effect).^{8–11}

In general, copolymerizations in emulsion yield reactivity ratios in substantial agreement with those

determined in mass, solution, or solvent-nonsolvent copolymerization.^{12–14} If one of the monomers is quite water-soluble, its apparent reactivity is reduced.^{15–19} In emulsion copolymerization, it is quite possible that monomers containing long alkyl groups would also exhibit reduced apparent reactivities due to their low rate of diffusion to the locus of polymerization.

In contrast to emulsion copolymerizations, there are a few studies on copolymerizations of vinyl monomers by microemulsion (M.E.) polymerization methods in the literature.^{20–29} Candau et al.^{20,21} showed that the reactivity ratios of copolymerizations of both water-soluble monomers acrylamide (M_1) and sodium acrylate (M_2) in inverse M.E.s were close to unity. This is significantly different from the literature values ($r_1 \sim 0.95$, $r_2 \sim 0.30$) obtained from copolymers prepared in a solution or an inverse emulsion. Gan and coworkers^{22,23} studied the copolymerization of styrene (STY) with methyl methacrylate (MMA) and with acrylonitrile (AN) in ternary O/W M.E.s. The reactivity ratios obtained by these copolymerizations differ from the values reported for bulk copolymerizations, and these differences arose due to the partitioning of the monomers, MMA and AN, in M.E. droplets and in the aqueous phases of the M.E. copolymerization systems, due to their higher water solubilities compared with STY monomer. M.E. copolymerizations²⁴ of STY with methyl acrylate and with *n*-butyl acrylate show that the reactivity ratios differ from the values obtained by

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TABLE I
Microemulsion Solution of Monomers

Total weight of the monomer mixture	5 g
<i>n</i> -Pentanol/ <i>n</i> -octanol	1.62 g/1.66 g
Sodium lauryl sulphate	6.75 g
Water	75 mL

bulk and emulsion copolymerizations. These differences were predicted to be due to the occurrence of copolymerizations in the intersides of emulsifier layers and not in the center of microdroplets.

In this study, the microemulsion (M.E.) and conventional emulsion (C.E.) copolymerizations of STY with MMA are carried out at 70°C by employing *n*-pentanol (PA) and *n*-octanol (OA) as cosurfactants, respectively, along with sodium lauryl sulfate (SLS) as surfactant and potassium persulphate (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

Monomers, styrene (STY) (LR, Ottokemi, Mumbai, India) and methyl methacrylate (MMA) (LR, Central Drug House (P), Mumbai, India) are washed with 5% sodium hydroxide to remove inhibitor followed by washing with distilled water. The washed monomers, MMA and STY, are dried over anhydrous sodium sulfate. The dried monomers are vacuum distilled under inert atmosphere and stored at -5°C in a refrigerator.

Acetone (SQ, Qualigens Fine Chemicals, Mumbai, India), methanol (AR, Fischer Inorganic and Aromatics, Chennai, India), dehydrated alcohol (ethanol) (Bengal Chemicals and Pharmaceuticals, Kolkata, India), and deuterated chloroform (CDCl₃) (Aldrich, Milwaukee, WI) are used as supplied without further

purification. Tetrahydrofuran (THF) (AR, s.d.fine chem (p), Boisar, India) is purified by distillation over ferrous sulfate followed by dehydration over potassium hydroxide and the dehydrated THF is further purified by distillation.

Potassium persulphate (KPS) (LR, s.d.fine chem (p), Boisar, India), sodium lauryl sulfate (SLS) (commercial grade, HICO products (P), Mumbai, India), *n*-pentanol (PA) (AR, Riedel - De Haen, Seelze, Germany), *n*-octanol (OA) (SISCO Chem Industries, Mumbai, India), and hydroquinone (AR, s.d.fine chem (p), Boisar, India) are used as supplied without further purification.

Methods

Preparation of microemulsion solution of monomers mixture

The monomers mixture of STY and MMA along with the cosurfactant in requisite quantities is solubilized in the aqueous solution of SLS with the use of a magnetic stirrer bar by stirring the mixture for a period of 45–50 min or until the solution is uniform (Table I). Complete solubility of the oil phase in micellar solution is observed in microemulsion (M.E.) solution of the monomers. This M.E. solution of the monomers mixture is used for M.E. and conventional emulsion (C.E.) copolymerization experiments. Seven different compositions of the monomers mixtures by keeping the total weight (5.0 g) of the monomers constant in these M.E. solutions are used in the recipes for M.E. and C.E. copolymerization experiments.

n-Pentanol (PA) and *n*-octanol (OA), respectively, are used as cosurfactants in two separate batches of these copolymerization experiments under present study.

Microemulsion copolymerization

Microemulsion (M.E.) copolymerization of the comonomers, STY and MMA, is carried out by initiating

TABLE II
Microemulsion Copolymerization of STY with MMA by Employing *n*-Pentanol as Cosurfactant in the Reaction Medium

Sample no.	f_{STY}	f_{MMA}	F_{STY}	F_{MMA}	ΔH (kJ/mg)	$\bar{M}_n \times 10^{-4}$	% Conversion
1	0.8024	0.1976	0.7827	0.2173	757.18	16.337	54.30
2	0.6867	0.3133	0.6850	0.3150	421.35	8.542	32.94
3	0.5920	0.4080	0.6147	0.3853	412.05	0.849	15.06
4	0.4986	0.5014	0.5828	0.4172	329.34	9.595	45.15
5	0.3882	0.6118	0.4957	0.5043	343.97	7.322	23.46
6	0.2853	0.7147	0.3979	0.6021	221.47	5.504	18.21
7	0.1947	0.8053	0.3110	0.6890	303.87	6.742	23.33

f_{STY} and f_{MMA} are the mole fractions of monomers STY and MMA, respectively, in the initial feeds. F_{STY} and F_{MMA} are the mole fractions of the monomer units STY and MMA, respectively, in the copolymers, determined by ¹H NMR spectral analysis.

TABLE III
Conventional Emulsion Copolymerization of STY and MMA by Employing *n*-Pentanol as Cosurfactant in the Reaction Medium

Sample no.	f_{STY}	f_{MMA}	F_{STY}	F_{MMA}	ΔH (kJ/mg)	$\overline{M}_n \times 10^{-4}$	% Conversion
1	0.8024	0.1976	0.7600	0.2400	396.18	27.696	16.85
2	0.6867	0.3133	0.6427	0.3573	389.77	12.451	11.91
3	0.5919	0.4081	0.5813	0.4187	370.10	17.057	13.72
4	0.4985	0.5015	0.5133	0.4867	441.22	20.924	14.34
5	0.3882	0.6118	0.4342	0.5658	383.96	16.678	9.5
6	0.2853	0.7147	0.4093	0.5907	399.07	20.701	19.73
7	0.1947	0.8053	0.3052	0.6948	215.66	23.598	29.68

f_{STY} and f_{MMA} are the mole fractions of monomers STY and MMA, respectively, in the initial feeds. F_{STY} and F_{MMA} are the mole fractions of the monomer units STY and MMA, respectively, in the copolymers, determined by ^1H NMR spectral analysis.

30 mL of M.E. solution of the monomers (Table I) in a 50 mL reaction tube under inert atmosphere at 70°C with a 9.1×10^{-4} M KPS solution. The M.E. copolymerization reaction is arrested at lower conversions by the addition of hydroquinone to the reaction mixture and the polymer formed in this M.E. copolymer solution is precipitated with acetone. The precipitated polymer is washed with ethanol-water mixture and dried in a vacuum oven at 60°C.

The M.E. copolymerization experiments are carried out with seven different compositions of monomer mixtures of STY and MMA, and the total weight of the monomers is kept approximately constant (~ 4.96 wt %) in all these experiments (Tables II and IV).

Conventional emulsion copolymerization

The conventional emulsion (C.E.) copolymerization of the comonomers, STY and MMA, is carried out under inert atmosphere at 70°C by initiating the mixture of 20 mL of M.E. solution (Table I) and an excess of 2.5 g of monomers in a 50 mL reaction tube with 9.1×10^{-4} M KPS solution. The composition of the monomers mixture in the initial feed of C.E. copolymerization experiment is kept the same as in the M.E. solution. The extra monomers mixture

added to the M.E. solution initially exists as separate phase and disappears when copolymerization reaction reaches 7–10% conversions. The C.E. copolymerization reaction is arrested at lower conversions with the addition of hydroquinone and the polymer formed in this C.E. copolymer solution is precipitated with acetone. The precipitated polymer is washed with ethanol-water mixture and dried at 60°C in a vacuum oven.

The C.E. copolymerization experiments are carried out with seven different compositions of the monomer mixtures of STY and MMA, and the total weight of the monomers is kept approximately constant (~ 15.58 wt %) in all these recipes (Tables III and IV).

Characterization of the copolymers

FTIR spectral analysis

FTIR spectra of the copolymers made by M.E. and C.E. copolymerizations with PA as cosurfactant in the reaction media are recorded on Nicolet Impact 400 Infrared Spectrophotometer by casting thin films of the copolymers from chloroform solutions between KBr windows of size 2.5×4 mm² and by keeping these films in the beam of infrared radiation with variable wave lengths (Fig. 1).

TABLE IV
Microemulsion and Conventional Emulsion Copolymerizations of STY with MMA by Employing *n*-Octanol as Cosurfactant in the Reaction Medium

Sample no.	M.E. copolymerization					C.E. copolymerization				
	f_{STY}	f_{MMA}	F_{STY}	F_{MMA}	% Conversion	f_{STY}	f_{MMA}	F_{STY}	F_{MMA}	% Conversion
1	0.8024	0.1976	0.7703	0.2297	17.77	0.8024	0.1976	0.7076	0.2924	20.07
2	0.6867	0.3133	0.6396	0.3604	9.34	0.6867	0.3133	0.5965	0.4035	13.92
3	0.5919	0.4081	0.6037	0.3963	12.78	0.5919	0.4081	0.5485	0.4397	10.48
4	0.4986	0.5014	0.5211	0.4789	12.92	0.4985	0.5015	0.5485	0.4515	18.65
5	0.3882	0.6118	0.4401	0.5599	7.83	0.3882	0.6118	0.4306	0.5694	8.45
6	0.2853	0.7147	0.3667	0.6333	14.06	0.2853	0.7147	0.3338	0.6662	16.91
7	0.1947	0.8053	0.3027	0.6973	15.10	0.1947	0.8053	0.2549	0.7451	10.61

f_{STY} and f_{MMA} are the mole fractions of monomers STY and MMA, respectively, in the initial feeds. F_{STY} and F_{MMA} are the mole fractions of the monomer units STY and MMA, respectively, in the copolymers, determined by ^1H NMR spectral analysis.

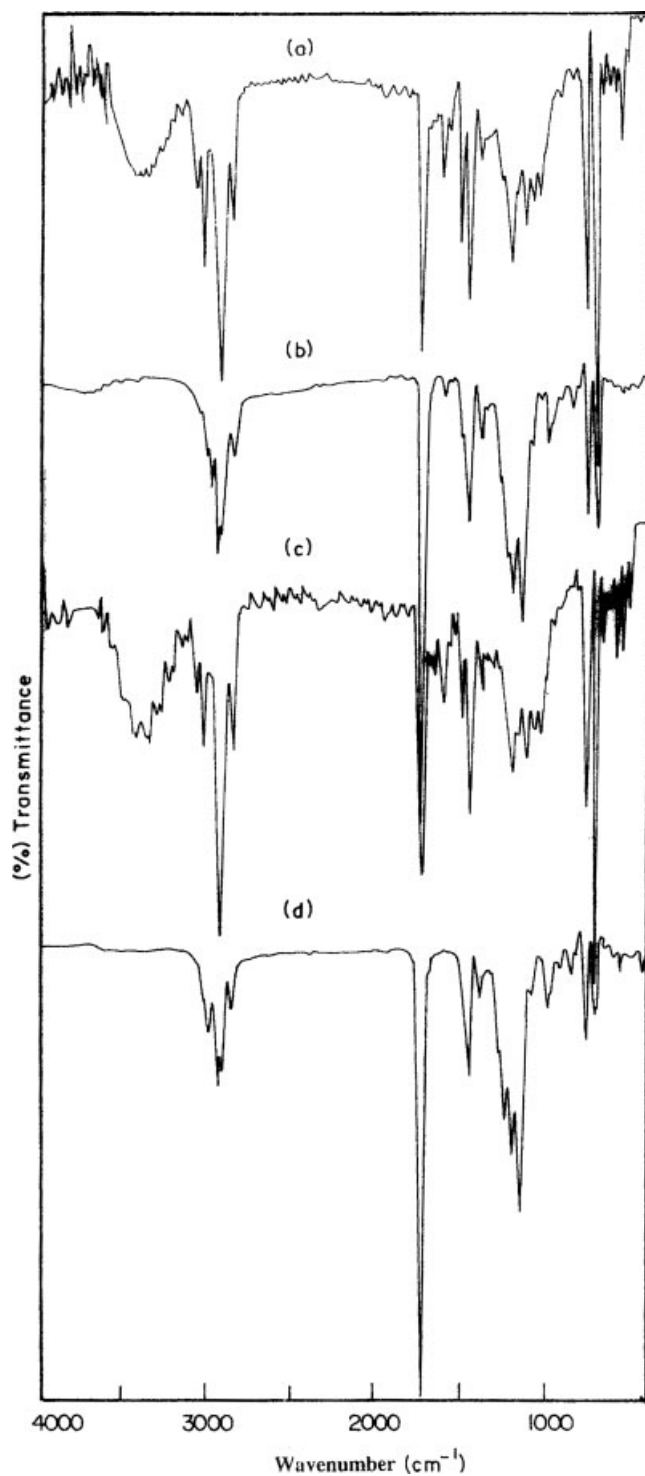


Figure 1 FTIR spectra of copolymer samples made by (a and b) M.E. (c and d) C.E. copolymerizations. Compositions of the comonomer units, STY/MMA, in the copolymers: (a) 0.7827/0.2173, (b) 0.3110/0.6890, (c) 0.7600/0.2400 and (d) 0.3052/0.6948.

NMR spectral analysis

The NMR spectra of the copolymer samples made under present study are recorded with JEOL ECR

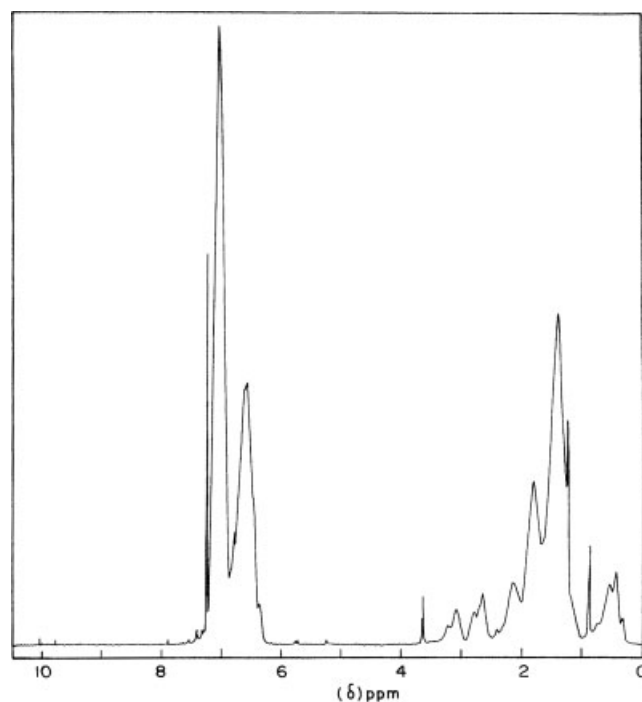


Figure 2 ^1H NMR spectrum of the copolymer sample (1) prepared by M.E copolymerization with *n*-octanol as cosurfactant (Table 4).

500 MHz high resolution NMR spectrometer (Japan) and by using deuterated chloroform (chloroform- d) as solvent (Figs. 2 and 3; Tables II-IV).

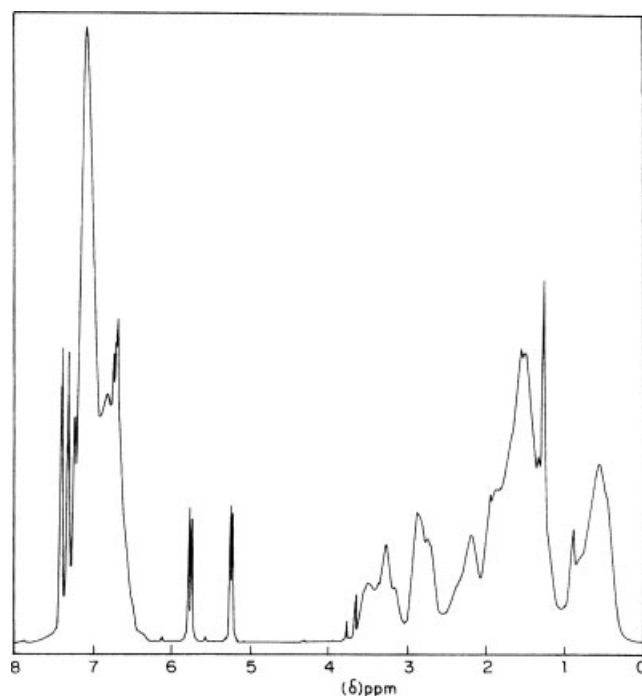


Figure 3 ^1H NMR spectrum of the copolymer sample (3) prepared by C.E. copolymerization with *n*-pentanol as cosurfactant (Table 3).

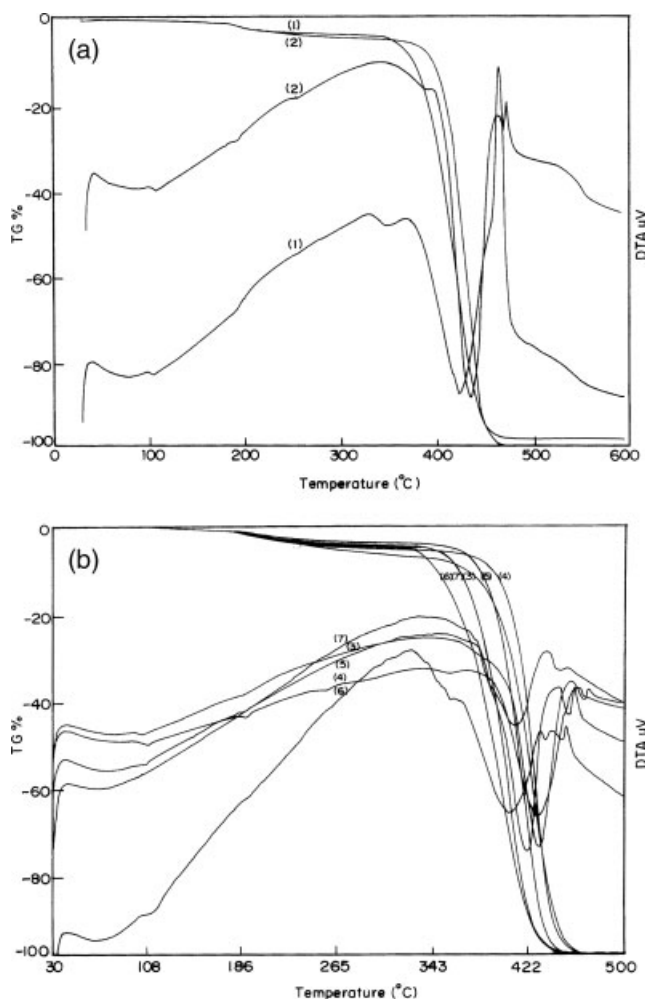


Figure 4 (a) TG/DTA analysis of the copolymer samples prepared by M.E. copolymerizations (Table 2). (b) TG/DTA analysis of the copolymer samples prepared by C.E. copolymerizations (Table 2).

TG/DTA analysis

The thermograms of the copolymers prepared by M.E. and C. E. copolymerizations with PA as cosurfactant in the reaction media are recorded with the use of 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 is used as the reference on platinum pans [Figs. 4(a,b) and 5; Tables II and III].

Gel permeation chromatography

The GPC analysis of the copolymers prepared by M.E. and C.E. copolymerizations with PA as cosurfactant in the reaction media 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 molec-

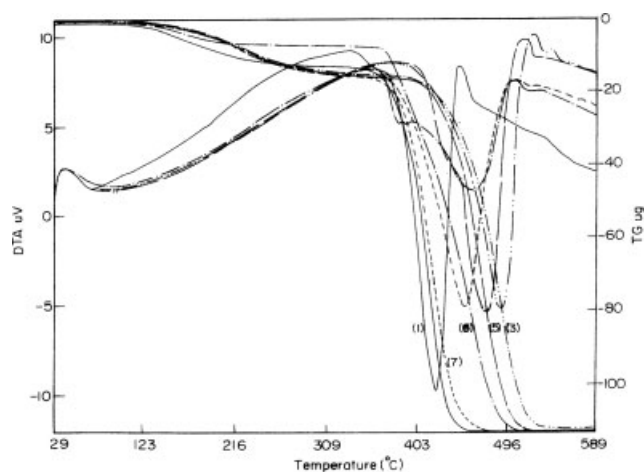


Figure 5 TG/DTA analysis of the copolymers prepared by C.E. copolymerizations with *n*-pentanol as cosurfactant (Table 3).

ular 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. 6; Tables II and III).

RESULTS AND DISCUSSION

The M.E. and C.E. copolymerization reactions are arrested at lower conversions. The C.E. copolymer solutions are more turbid compared with M.E. copolymer solutions. This implies that the emulsion particles swell while polymerization proceeds considerably in C.E. copolymerizations and to a lesser extent in M.E. copolymerizations.

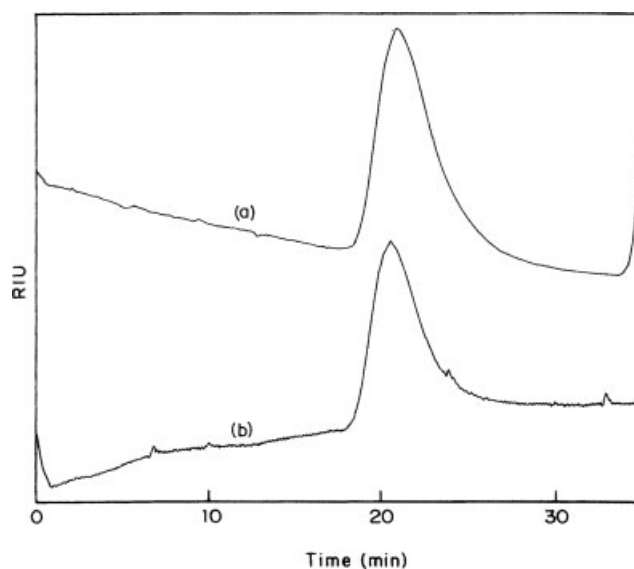


Figure 6 Determination of molecular weights by GPC analysis. (a) Copolymer sample (2) prepared by M.E. copolymerization and (b) copolymer sample (2) prepared by C.E. copolymerization (Tables 2 and 3).

Infrared spectroscopy is probably the most extensively used method for the investigation of polymer structure and the analysis of the functional groups. The FTIR spectra of the copolymers made by M.E. and C.E. copolymerization methods with PA as the cosurfactant in the reaction media show the asymmetric stretching vibrations due to methyl group of the copolymers at 2986–2999 cm^{-1} . The asymmetric stretching vibrations due to methylene group of the copolymer appear at 2921–2954 cm^{-1} and the symmetric stretching vibrations of methyl group seem to overlap with the asymmetric stretching vibrations of methylene group. The symmetric stretching vibrations of methylene group appear at 2848–2861 cm^{-1} . The absorption bands at 1730–1736 cm^{-1} are the characteristic stretching vibrations due to carbonyl groups of copolymers and its overtone appear near 3450 cm^{-1} . The asymmetric bending vibrations due to methyl and methylene groups are observed in the regions, 1446–1472 cm^{-1} and 1486–1499 cm^{-1} , respectively. The absorption bands in the region 1381–1394 cm^{-1} are due to the symmetric stretching vibrations of CH_3 and the weak band at 1321 cm^{-1} may be due to the wagging vibrations of CH_2 groups in the copolymers. The stretching vibrations due to C—O—C group appear in the region 1070–1281 cm^{-1} . The IR absorption spectra in the region 1124–1150 cm^{-1} are due to the skeletal vibrations of the polymer backbone, overlapping with the stretching vibrations of C—O—C groups in the copolymer. The rocking vibrations of $(\text{CH}_2)_2$ groups of the copolymers appear near 757–769 cm^{-1} (Fig. 1).

The IR absorption spectra also show characteristic absorption bands of a phenyl ring in the STY. The stretching vibrations of ring hydrogens appear in the region 3026–3085 cm^{-1} . The overtone and combination bands of CH deformation vibrations of phenyl groups appear in the region 1660–2000 cm^{-1} . The absorption bands at 1598–1611 cm^{-1} may be due to C—C stretching vibrations of phenyl ring. The IR bands at 1486–1578 cm^{-1} may also be due to stretching vibrations of C—C linkages of phenyl ring overlapping with asymmetric bending vibrations of CH_3 and CH_2 groups. The absorption bands at 757–769 cm^{-1} are deformation vibrations of ring hydrogens overlapping with rocking vibrations of $(\text{CH}_2)_2$ groups in the polymer. The absorption bands at 702–709 cm^{-1} are due to ring deformation vibrations (Fig. 1).

The ^1H NMR spectra of the copolymers prepared under present study by M.E. and C.E. copolymerization methods show the chemical shifts due to methyl protons in the region 0.2956–1.1751 ppm, methylene protons in the region 1.2438–2.0149 ppm, and the methine protons in the region 2.1324–2.6462 ppm. The resonance peaks due to methoxy protons appear in the region 2.6558–3.8674 ppm and the phenyl pro-

tons appear in the region 6.3557–7.1796 ppm. There are minor resonance peaks due to unsaturated groups in these copolymers in the region 5.2232–5.7642 ppm. The area under the resonance peaks due to phenyl protons is taken as 5ASTY, methoxy protons is taken as 3AMMA, and the total areas under the resonance peaks due to methine, methylene and methyl groups is taken as (3ASTY + 5AMMA). The mole fraction (F_{STY}) of the STY units in the copolymer is obtained as $\text{ASTY}/(\text{ASTY}+\text{AMMA})$ (Figs. 2 and 3; Tables II–IV).

DTA directly measures the heat-energy change occurring in a substance, it is theoretically possible to detect and measure any physical transition and chemical reaction that is accompanied by a heat-energy change. The TG/DTA analyses of the STY-MMA copolymers prepared by M.E. copolymerizations with PA as cosurfactant in the reaction media show small endothermic processes in the temperature region 322.3–348.6°C and major endothermic processes of decompositions appearing in the region 364.6–396.6°C. The initial endothermic processes may be due to the scission at unsaturated end groups and the second major endothermic processes are due to random chain scissions.^{30,31} No endothermic curves are recorded due to the scission of head-to-head linkages in most of these DTA thermograms in lower temperature region.^{30,31} For the major endothermic processes the peak temperature decreases with the increase of MMA units in the copolymers. The energy values (ΔH) for these decomposition processes are evaluated from the areas of the endothermic curves and are reported in Table II [Figs. 4(a,b)]. The ΔH values show decreasing trend with the increase of MMA content in the copolymers (Table II). The TG analyses show the maximum decomposition and weight loss in the range 95.7–99.6% and no correlation is found with the composition of the copolymers. There are also broad endothermic processes at low temperature regions starting from 45°C and continuing up to 260°C [Figs. 4(a,b)]. These endothermic processes may be due to evaporation of moisture or volatile solvent, rupture of weak bonds, and low temperature transitions.

TG/DTA analyses of STY-MMA copolymers made by C.E. copolymerizations with PA as cosurfactant in the reaction medium are also carried out (Fig. 5). These show small endothermic processes in temperature region 311.4–339.2 °C and the major endothermic decomposition processes at 339.2–382.5°C. The initial endothermic processes may be due to the scission at unsaturated end groups and the second major endothermic processes are due to the random chain scission.^{30,31} No endothermic curves are recorded due to the scission of head-to-head linkages in most of these thermograms in the lower temperature regions,^{30,31} only the copolymer containing max-

imum MMA units shows distinct endotherms at 168°C, 249.9°C, and 280.9°C in the lower temperature region where scission of head-to-head linkages appears.^{30,31} For the major endothermic processes the peak temperature decreases with the increase of MMA units in the copolymers. The energy values (ΔH) for these decomposition processes are evaluated from the areas of the endothermic curves and are reported in Table III. The ΔH values do not show any correlation with the compositions of the copolymers (Table III). The TG analyses show the maximum decomposition and weight loss in the range 95.1–99.4%. There are also broad endothermic processes at low temperature regions starting from 45°C and continuing up to 260°C. These endothermic processes may be due to evaporation of moisture or volatile solvent, rupture of weak bonds, and low temperature transitions.

GPC analyses of the copolymer samples prepared by M.E. and C.E. copolymerizations with PA as cosurfactant in the reaction media are carried out with THF as eluent (Fig. 6; Tables II and III). The molecular weights of copolymers obtained by M.E. copolymerizations are lower than the values obtained by C.E. copolymerization methods.

Both dilution factor and 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 an expression:³²

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

where \bar{P}_N and \bar{P}_{No} are the number average degrees of polymerizations 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:

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

$[S]$, $[M_1]$, and $[M_2]$ are the molar concentrations of solvent, monomer 1 and monomer 2; F_1 and F_2 are mole fractions of the monomer 1 and monomer 2 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 monomer 1 and monomer 2, respectively.

It can be inferred from this relation that the degree of polymerization decreases in consequence of increases in $[S]/[M]$ ratio, where $[M] = [M_1] + [M_2]$. In the present study the solvent, PA, which is used as cosurfactant is present in the M.E. globules along with the surfactant in the surface and with the monomers in the core. The ratio $[S]/[M]$ is higher in M.E. copolymerization reaction media compared with that of C.E. copolymerization systems where excess of monomers are added to the M.E. solutions of the monomers and hence, higher degrees of polymerizations in C.E. copolymerizations compared with M.E. copolymerizations 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 degree of polymerization.^{12,13,33}

Reactivity ratios of the monomer pair, STY/MMA

The apparent reactivity ratios for the M.E. and C.E. copolymerizations of STY and MMA are evaluated by Fineman-Ross (F-R),³⁴ Kelen-Tüdös (K-T),³⁵ and Mayo-Lewis integration (M-L-I)³⁶ methods (Figs. 7–10; Tables II–V). The values obtained by the K-T method for both the copolymerizations are compared with the literature results (Table V). The appa-

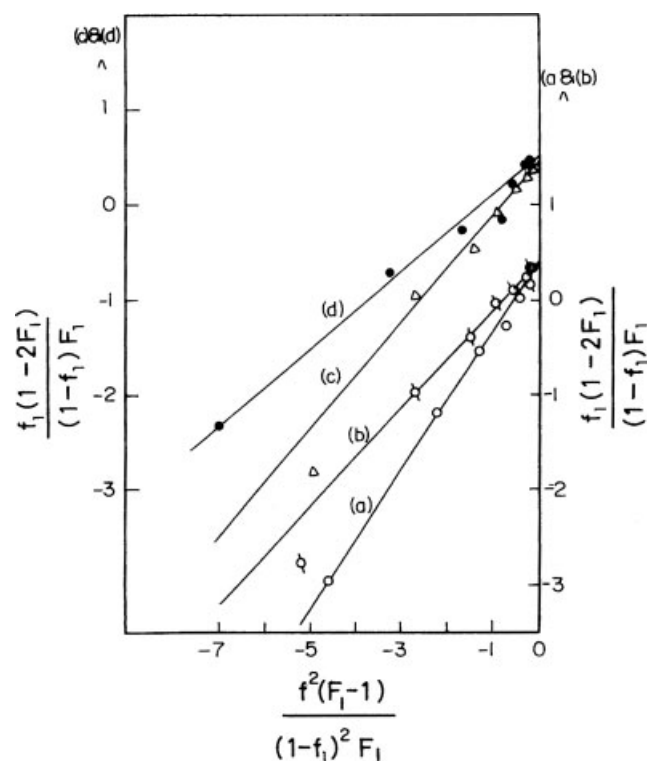


Figure 7 Fineman-Ross method to determine the reactivity ratios for the M.E. (a & c) and C.E. (b & d) copolymerizations of STY with MMA. (a & b) *n*-pentanol as cosurfactant and (c & d) *n*-octanol as cosurfactant in the reaction media, respectively (Table 2, 3 & 4).

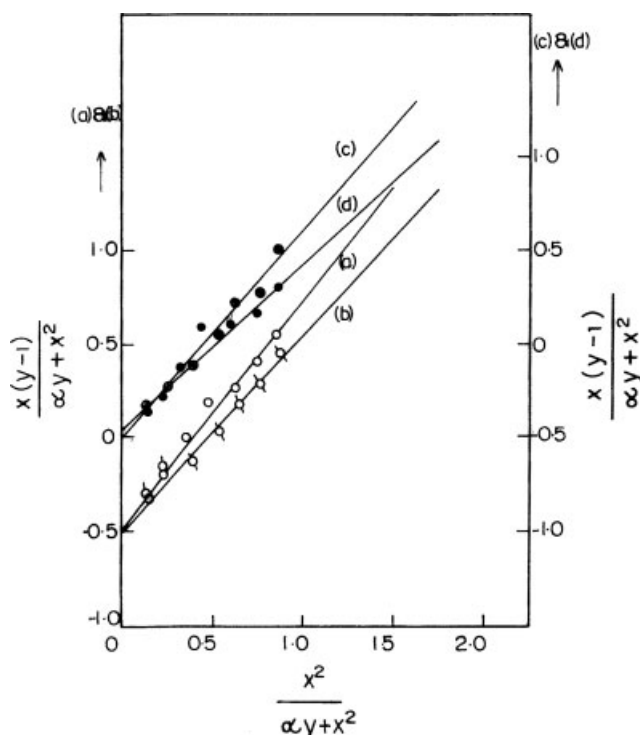


Figure 8 Kelen-Tüdös method to determine the reactivity ratios for the M.E. (a & c) and C.E. (b & d) copolymerizations of STY with MMA (a & b) *n*-pentanol as cosurfactant and (c & d) *n*-octanol as cosurfactant in the reaction media, respectively (Tables 2, 3 and 4).

rent reactivity ratios, r_{STY} and r_{MMA} , obtained by M.E. copolymerization method with PA as the cosurfactant in the reaction medium in the present study

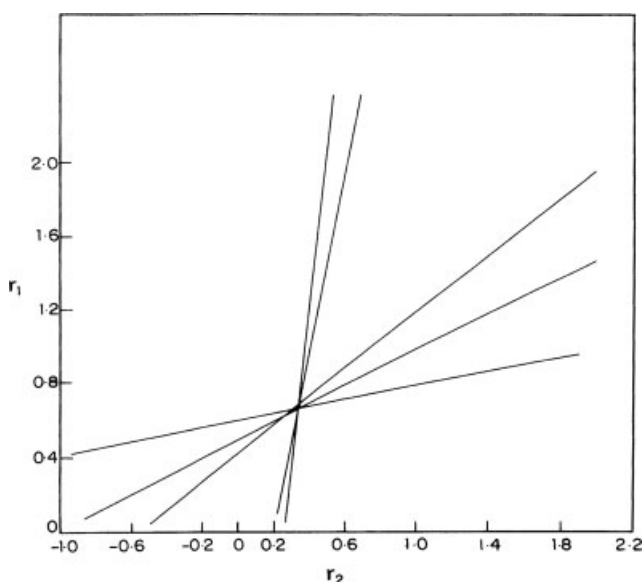


Figure 9 Mayo-Lewis integration method to determine the reactivity ratios for the M.E. copolymerization of STY with MMA by employing *n*-pentanol as cosurfactant in the reaction medium (Table 2).

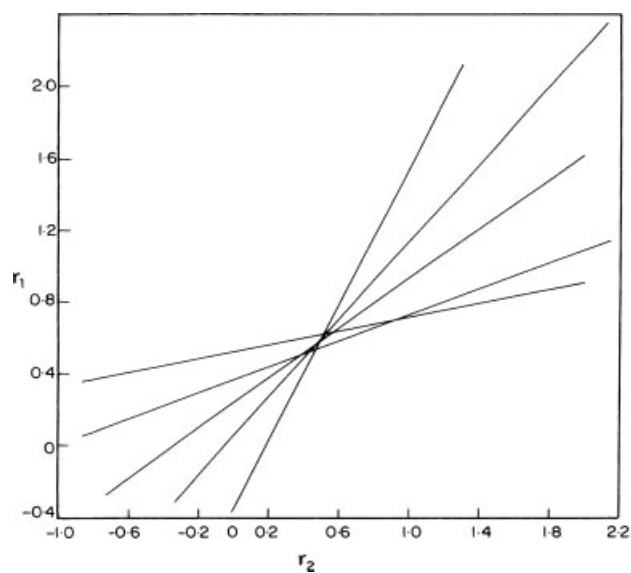


Figure 10 Mayo-Lewis integration method to determine the reactivity ratios for the C.E. copolymerization of STY with MMA by employing *n*-pentanol as cosurfactant in the reaction medium (Table 3).

are differing from the values reported by bulk,³⁷ solution^{1,38-40} and emulsion⁴¹ copolymerization methods, and are similar to the values reported by M.E.²² copolymerization method in the literature (Table V). These deviations under present experimental conditions compared with literature values obtained by other copolymerization methods can be discussed in terms of various factors:

1. The variation of propagation rate constants with temperature¹⁴ that can bring changes in these reaction parameters with temperature.
2. The monomer 1 is sparingly soluble in water and the monomer 2 is having the solubility to the extent of 2 wt % in water. Therefore, the availability of these monomers at the reaction loci may not be the same as in bulk and solution polymerizations, which can cause the variation of apparent reactivities of these monomers in this reaction system.¹⁵⁻¹⁹
3. The cosurfactant, PA, is insoluble in water and soluble in all proportions with both the monomers. The cosurfactant present in the emulsion globules along with the surfactant in the surface and with the monomers in the core. The presence of solvent, PA, in the reaction loci which is used as cosurfactant may bring about changes in these reaction parameters.¹⁻¹¹
4. The emulsion globules are surrounded by thick emulsifier layer, with the monomers in the core. The composition of the monomers inside the emulsifier layers may be different from the center of the emulsion particles; this can also affect

TABLE V
Reactivity Ratios of the Monomer Pair, Styrene and Methyl methacrylate

Polymerization method	Solvent in the reaction medium	Method of evaluation	Temperature (°C)	r_{STY}	r_{MMA}	
Bulk ³⁷	–	F-R	60	0.47	0.45	
Solution ³⁸	Benzene	EVM	60	0.51	0.44	
Solution ³⁸	Benzonitrile	EVM	60	0.47	0.65	
Solution ³⁸	Chlorobenzene	EVM	60	0.43	0.47	
Solution ³⁹	Benzyl alcohol	EVM	60	0.45	0.42	
Solution ⁴⁰	Methyl cyanoacetate	EVM	75	0.26	0.59	
Solution ⁴⁰	Methyl cyanoacetate/benzene	EVM	75	0.55	0.95	
Emulsion ⁴¹	–	EVM	44	0.44	0.46	
Emulsion (present study)	<i>n</i> -Pentanol	F-R	70	0.50 ± 0.01	0.40 ± 0.01	
		K-T	70	0.55 ± 0.01	0.42 ± 0.01	
		M-L-I	70	0.58 ± 0.01	0.51 ± 0.01	
	<i>n</i> -Octanol	F-R	70	0.40 ± 0.01	0.50 ± 0.01	
		K-T	70	0.42 ± 0.01	0.51 ± 0.01	
		M-L-I	70	0.45 ± 0.01	0.48 ± 0.01	
	Microemulsion ²²	–	K-T	60	0.74 ± 0.09	0.38 ± 0.04
			F-R	60	0.73	0.38
	Microemulsion ²⁹	–	EVM	60	0.60	0.37
Microemulsion (present study)	<i>n</i> -Pentanol	F-R	70	0.73 ± 0.01	0.40 ± 0.01	
		K-T	70	0.73 ± 0.01	0.39 ± 0.01	
		M-L-I	70	0.66 ± 0.01	0.32 ± 0.01	
	<i>n</i> -Octanol	F-R	70	0.57 ± 0.01	0.45 ± 0.01	
		K-T	70	0.56 ± 0.01	0.43 ± 0.01	
		M-L-I	70	0.60 ± 0.01	0.45 ± 0.01	

EVM, error in variable method.⁴²

the composition of the monomers in the reaction loci. Such a discrepancy was explained by the monomer partitioning in different phases (intersides of the emulsifier layer and center of the emulsion globules) of the reaction medium.²⁴

The values obtained by M.E. copolymerization method are differing from the values obtained by C.E. copolymerization method with PA as cosurfactant in the reaction media under present study. PA employed as cosurfactant is miscible with both the monomers, and because of thermodynamic considerations, the concentrations of the monomers and PA in the aqueous phase may be less than their normal solubilities.⁴³ PA exists in M.E. particles along with the surfactant in the surface and in the core with the monomers. PA also exists in C.E. copolymerization systems in the present study. PA in the C.E. polymerization systems partitions in emulsion particles with surfactant in the surface and with the monomer in the core, and it is also solubilized in the monomer particles as separate phase. There can be more dilution of monomers at the reaction loci in M.E. copolymerization reaction systems compared to C.E. copolymerization systems. The differences in apparent reactivity ratio values obtained by M.E. and C.E. copolymerizations of STY and MMA in the present study (Table V) can be attributed to the differences of monomers partitioning in different

phases (i.e., emulsion globules, aqueous and monomer phases) of these reaction systems.^{22–24}

The apparent reactivity ratio values obtained by using OA as cosurfactant in the reaction media for M.E. and C.E. copolymerizations of STY and MMA show variations from the literature results (Table V). And also the values obtained from the M.E. copolymerization method deviates from the values obtained by C.E. copolymerization method with OA as cosurfactant under the present study (Table V). The differences of the results obtained by M.E. and C.E. copolymerizations with OA as the cosurfactant in these reaction media, and also deviations from the literature results (Table V) may be due to reasons, such as temperature variation of the reaction medium,¹⁴ differences in the solubilities of monomers in aqueous phase,^{19–23} presence of the solvent OA in the reaction loci,^{1–11} and differences of the monomer partitioning in different phases of the reaction media.^{22–24}

The apparent reactivity ratios obtained with PA as cosurfactant in the reaction medium are differing from the values obtained with OA as cosurfactant under present study. The reactivity ratio of STY decreases whereas the reactivity ratio of the *n*-butyl acrylate increases while the polarity of the solvent in the reaction medium increases.⁴⁴ A similar behavior was observed in STY/MMA copolymerization system when the copolymerization was performed in benzene, chlorobenzene, and benzonitrile; that is, the apparent reactivity ratio of STY diminished and the

MMA reactivity ratio increased with the increase of solvent polarity.⁴⁵ This behavior apparently indicated that the solvent polarity had an important effect on the reactivities of the two radicals. The solvent polarity first was considered by Ito and Otsu,³⁹ who stated that the observed variation of the reactivity ratios in the STY/MMA copolymerization were due to the polarized structure of MMA in the transition state when the solvent polarity increased. Besides the polarity effect, other mechanisms also have been proposed to describe the effect of solvents. Monomer–monomer, monomer–solvent, or radical–solvent (which may be not only a solvent but also one or both comonomers) complexes and the so-called boot-strap model also could explain the apparent variations of the copolymerization parameters in the different solvents. To date, there is experimental evidence^{38,46–49} that the bootstrap model is the most appealing as a general model. The dipole moments, 1.7 D and 1.68 D, respectively, of PA and OA are nearer values, and the dielectric constants (ϵ), 13.9 (at 25°C) and 10.34 (at 20°C), respectively, of PA and OA are not much different values to show variations in apparent reactivity ratios of STY and MMA in the present study. Harwood suggested⁹ that solvent effects in copolymerization are not manifested in the chain end reactivity but rather in a solvent partitioning. Thereby, an equilibrium may exist in which monomers are distributed between the solvent and the domains of growing polymer radicals. However, bootstrap effects may arise when the effective free-monomer concentration, radical concentration, or both differ from those calculated through the monomer-feed ratios, leading to discrepancies between predicted and actual propagation rates.⁴⁷ In this way, when radical–solvent or monomer–solvent complexes do not propagate, the effect of complexation is to alter the radical or monomer concentration, causing a bootstrap effect.⁴⁷

CONCLUSIONS

The TG/DTA analyses show that the peak temperatures for the major endothermic processes decrease with the increase of MMA content in the copolymers for both the copolymers obtained by M.E. and C.E. copolymerizations with PA as cosurfactant in the reaction media. The presence of higher proportions of solvent PA in the M.E. reaction loci compared with C.E. copolymerization systems could cause the decrease of degree of polymerization by M.E. copolymerization method, where dilution and chain transfer with the solvent influence the degree of polymerization. The variation of the reactivity ratios obtained in the present study by different methods and from those of literature values are explained

due to the factors such as temperature variation, solvent environment, differences of the solubilities of the monomers in the aqueous medium and differences in the partitioning of monomers in various phases of the reaction media.

References

- Price, C. C.; Walsh, J. G. *J Polym Sci* 1951, 6, 239.
- Sideridou-Karayannidou, I.; Seretoudi, G. *Polymer* 1997, 38, 4223.
- Ryttel, A. *J Appl Polym Sci* 1992, 45, 1911.
- Ryttel, A. *J Appl Polym Sci* 1998, 67, 715.
- Cais, R. E.; Farmer, R. G.; Hill, D. J. T.; O'Donnell, J. H. *Macromolecules* 1979, 12, 835.
- Barton, J.; Borsig, E. *Complexes in Free Radical Chemistry*; Elsevier: Amsterdam, 1988.
- O'Driscoll, K. F.; Monteiro, M. J.; Klumperman, B. *J Polym Sci Part A: Polym Chem Ed* 1997, 35, 515.
- Pichot, C.; Guyot, A.; Strazielle, C. *J Polym Sci Part A: Polym Chem Ed* 1979, 17, 2269.
- Harwood, H. *J Macromol Chem Macromol Symp* 1987, 10/11, 331.
- Hill, D. J. T.; Lang, A. P.; Munro, P. D.; O'Donnell, J. H. *Eur Polym J* 1992, 28, 391.
- Kaim, A. *J Macromol Sci Pure Appl Chem* 1996, 33, 1711.
- Smith, W. V. *J Am Chem Soc* 1946, 68, 2069.
- Smith, W. V. *J Am Chem Soc*, 1948, 70, 2177, 3695.
- Lewis, F. M.; Walling, C.; Cummings, W.; Briggs, E.; Mayo, F. R. *J Am Chem Soc* 1948, 70, 1519.
- Fordyce, R. G.; Chapin, E. C. *J Am Chem Soc* 1947, 69, 581.
- Fordyce, R. G.; Chapin, E. C. *J Am Chem Soc* 1948, 70, 2489.
- Fordyce, R. G.; Ham, G. E. *J Am Chem Soc* 1947, 69, 695.
- Fordyce, R. G.; Ham, G. E. *J Polym Sci* 1948, 3, 891.
- Bataille, P.; Bourassa, H. *J Polym Sci Part A: Polym Chem Ed* 1989, 27, 357.
- Candau, F.; Zekhnini, Z.; Heatley, F. *Macromolecules* 1986, 19, 1895.
- Candau, F.; Zekhnini, Z.; Heatley, F.; Franta, E. *Colloid Polym Sci* 1986, 264, 676.
- Gan, L. M.; Lee, K. C.; Chew, C. H.; Ng, S. C.; Gan, L. H.; *Macromolecules* 1994, 27, 6335.
- Lee, K. C.; Gan, L. M.; Chew, C. H.; Ng, S. C. *Polymer* 1995, 36, 3719.
- Xu, X.; Ge, X.; Zhang, Z.; Zhang, M. *Polymer* 1998, 39, 5321.
- Mendizabal, E.; Rodriguez, R. R.; Robelero, V.; Puig, J. E.; Velazquez, R.; Castano, V. *Int J Polym Mater* 1995, 30, 167.
- Zhang, Z.; Zeng, Z.; Chen, Y.; Wu, C.; Gao, J. *J Appl Polym Sci* 1997, 66, 2543.
- Váisková, V.; Juraničová, V.; Bartoîn, J. *J Makromol Chem* 1991, 192, 1339.
- Capek, I.; Juraničová, V.; Bartoîn, J. *Eur Polym J* 1999, 35, 691.
- Klumperman, B.; Aerdt, A. M. *Macromolecules* 1996, 29, 6679.
- Kashiwagi, T.; Inaba, A.; Brown, J. E. *Macromolecules* 1986, 19, 2160.
- Popovič, I. J.; Katsikas, L.; Weller, H.; Schrötter, S.; Velíčko-vič, J. S. *J Appl Polym Sci* 1993, 50, 1475.
- Mayo, F. R.; Lewis, F. M.; Walling, C. *Disc Faraday Soc* 1947, 2, 285.
- Alfrey, T.; Hardy, V. *J Polym Sci* 1948, 3, 500.
- Fineman, M.; Ross, S. D. *J Polym Sci* 1950, 5, 259.
- Kelen, T.; Tüdös, F. *J Macromol Sci Chem* 1975, 9, 1.
- Mayo, F. R.; Lewis, F. M. *J Am Chem Soc* 1944, 66, 1594.
- Kale, L. T.; O'Driscoll, K. F.; Dinan, F. J.; Uebel, J. J. *J Polym Sci Part A: Polym Chem Ed* 1986, 24, 3145.

38. Klumperman, B.; O'Driscoll, K. F. *Polymer* 1993, 34, 1032.
39. Ito, T.; Otsu, T. *J Macromol Sci Chem* 1969, 3, 197.
40. Talpur, M. M.; Kaim, A. *J Macromol Sci Pure Appl Chem* 1994, 31, 535.
41. Goldwasser, J. M.; Rudin, A. *J Polym Sci Part A: Polym Chem Ed* 1982, 20, 1993.
42. Dube, M.; Amin Sanayei, R.; Penlidis, A.; O'Driscoll, K. F.; Reilly, P. M. *J Polym Sci Part A: Polym Chem Ed* 1991, 29, 703.
43. Guo, J. S.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part A: Polym Chem Ed* 1989, 27, 691.
44. Fernández-García, M.; Fernández-Sanz, M.; Madruga, E. L.; Cuervo-Rodríguez, R.; Hernández-Gordo, V.; Fernández-Monreal, M. C. *J Polym Sci Part A: Polym Chem Ed* 2000, 38, 60.
45. Madruga, E. L.; San Roman, J.; del Puerto, M. A. *J Macromol Sci Macromol Sci Chem* 1979, 13, 1105.
46. Davis, T. P. *Polym Commun* 1990, 31, 442.
47. Coote, M. L.; Davis, T.; Klumperman, B.; Monteiro, M. *J Macromol Sci Rev Macromol Chem Phys* 1998, 38, 567.
48. Klumperman, B.; Kraeger, I. R. *Macromolecules* 1994, 27, 1529.
49. Madruga, E. L. *Makromol Chem Rapid Commun* 1993, 14, 581.