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High solids content semicontinuous microemulsion copolymerization of methylmethacrylate and butylacrylate

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The possibility of obtaining high-solids-content microlatexes was investigated. It was found that, for the semicontinuous copolymerization of methylmethacrylate and butylacrylate coagulum-free 45.20% solid content latexes can be obtained through microemulsion polymerization using Dowfax 2A-1 surfactant. The effect of the amount of surfactant, type of cosurfactant, type and concentration of initiator and temperature on solid content was studied. The chemical, freeze–thaw, storage and mechanical stabilities of the latexes were determined. © 1997 Elsevier Science Ltd.

(Keywords: microemulsion; copolymerization; high solids content)

INTRODUCTION

Emulsion polymerization has been an important and widely used process in the production of a large number of polymers. Among its many advantages, it attains both high molecular weights and high reaction rates. However, in recent years miniemulsion has started replacing emulsion polymerization. In the coming years microemulsion polymerization will acquire far greater importance than at present. In contrast to the opaque and milky conventional emulsions and miniemulsions, microemulsions are isotropic, optically transparent or translucent and thermodynamically stable. The dispersed phase consists of very small droplets of 10–50 nm diameter, which results in the characteristic transparency or translucency of microemulsions. Polymerization in o/w, w/o or lamellar microemulsions results in latexes, porous materials and gels of specific properties.

The kinetics and mechanism of conventional polymerization have been studied extensively and the principal locii for initiation of latex particles are proposed to be monomer swollen micelles[1,2] and aqueous phase[3,4]. Monomer droplets are usually considered not to play a significant role in conventional emulsion polymerization other than as a reservoir of monomer, due to their small surface area as compared to monomer-swollen micelles. However, polymerization in the monomer droplets may become much more significant when the size of the emulsified droplets is decreased.

Miniemulsions are produced by dispersing monomer in water by means of vigorous mechanical agitation or homogenization. Ugelstad *et al.*[5] showed experimentally that, by dispersing the monomer into submicron-level monomer droplets, the area available for radical capture increases drastically and the monomer droplets become the main locus for particle formation. Chamberlain *et al.*[6] and Choi *et al.*[7] found that the particle formation stage of miniemulsion polymerization was much larger than for conventional emulsion polymerization. This was attributed to the low free-radical adsorption efficiency of the monomer droplets. In addition, these authors, as well as Tang *et al.*[8], found that not all monomer droplets become polymer particles.

In microemulsion polymerization, the principal locus of particle nucleation is the emulsified monomer droplets (or the monomer swollen micelles). Atik and Thomas[9] investigated the microemulsion polymerization of styrene initiated by AIBN and γ-radiation in which the system contained more than 95% water. Jayakrishnan and Shah[10] investigated styrene and methyl methacrylate (MMA) microemulsion polymerization. Polymerization in the classical emulsion was faster than in the microemulsion. Feng and Ng[11] investigated the kinetics of styrene and MMA in SDS-pentanol/water microemulsion systems. Peroxodisulfate initiated systems result in a higher initial rate, whereas oil-soluble initiator systems show higher conversion. Gan *et al.*[12–14] have carried out extensive work on microemulsion polymerizations of MMA and other acrylate monomers, using various types of surfactant. On polymerizing a system of MMA/CTAB/water with KPS, it was found[12] that turbid emulsions can be changed progressively to transparent microemulsions merely by increasing the surfactant concentration. Capek and Potisk[15] studied oil-in-water microemulsion and emulsion polymerizations of butylacrylate (BA) initiated by ammonium peroxodisulfate and dibenzoyl peroxide with SDS. Emulsion polymerization was faster than microemulsion. The overall activation energy (E_0) for BA radical polymerization was found to decrease in the following order: bulk or solution

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(120 kJ mol^{-1}) > microemulsion (60 kJ mol^{-1}) > emulsion polymerization (15 kJ mol^{-1})[15]. Kinetics and mechanisms of direct and inverse microemulsion polymerization are given in detail in a recent thorough review[16]. However, microemulsion polymerization latexes contain a low percentage of solid with a high percentage of surfactant/cosurfactant. In this work we are thoroughly investigating the effect of a somewhat virgin surfactant. Dowfax 2A-1, on the overall polymerization features and properties of the latexes.

EXPERIMENTAL

Materials

AR-grade methylmethacrylate (MMA) (Sisco Chem India) and butylacrylate (BA) (BDH, India) were purified by treating with 5% sodium hydroxide solution followed by washings with deionized water to remove inhibitor. They were further dried over fused calcium chloride before vacuum distillation under nitrogen atmosphere. Potassium persulfate (KPS) (Sisco Chem India), ammonium persulfate (Sisco Chem India), azo *bis* iso butyronitrile (AIBN) (Sisco Chem India) and benzoyl peroxide (Bz_2O_2) (Fluka) of extra pure grade were used without further purification. Dowfax 2A-1 (Dow, USA) surfactant was used as received.

Synthesis

Polymerization was carried out in a 500 ml reactor with a reflex condenser, Teflon stirrer, nitrogen inlet and feed inlet. Semi-continuous copolymerization was carried out using the recipes given in *Table 1*. The micellar solution, containing ~90% Dowfax 2A-1 with respect to the total surfactant in the recipe, was charged into the reactor and heated to 80°C. The solution was purged with nitrogen. The initiator, dissolved in a minimum quantity of water, was added just before the feed flow was started. The feed, containing ~10% of the surfactant with respect to the total surfactant in the recipe and the whole of the monomer MMA–BA (1 : 1) and 25% of water with respect to the total water in the recipe, was added over 3 h. The polymerization was continued thereafter in batch for about 1.5 h. The reaction was arrested by adding 20 ppm of hydroquinone.

Characterization

The average particle size of the polymerized microemulsion was determined using a JEOL-JEM 100 SX transmission electron microscope and uranyl acetate as the staining reagent. A drop of polymerized latex was added to 2 ml of 2% uranyl acetate solution. One drop of this diluted latex was put on a copper grid which had been coated with a thin layer of Formvar. Average particle size was calculated by considering 100 particles per 25 cm^2. Particle size distribution was determined by using a Brookhaven B 90 (USA) particle size analyser.

Water, GPC 150C, was used to determine the number-average and weight-average molecular weights and polydispersity, using tetrahydrofuran solvent.

High resolution ^{1}H-n.m.r. of the polymers was recorded in $CDCl_3$ on a 500 MHz Bruker n.m.r. spectrometer.

Thermal analysis was carried out in pure nitrogen atmosphere at 10°C min^{-1} heating rate.

Viscosity measurements of dilute solutions containing 0.3 to 1.0 g dl^{-1} of the polymer in acetone were carried out using an Ubbelohde dilution viscometer in a thermostatted bath with ±0.05°C temperature control.

Viscosity, mechanical stability, chemical stability, freeze–thaw stability and storage stability of the final latexes were studied. The viscosity of the final latex was determined with a Brookfield viscometer model LVTD using spindle no. 1 at 60 rpm at 25°C.

Mechanical stabilities were determined at room temperature with a high speed (14 000 rpm) stirrer (Dispermat F 105). The latex taken from the reactor at the end of the polymerization was subjected to high shear for 10 min. The sample was then filtered through a nylon cloth (63 mesh) and the retained solid was washed with water. The dry weight of the coagulum material was taken as a measure of mechanical stability.

Electrolytic stability was determined by titrating 100 g of the latex with 5% $Al_2(SO_4)_3$. The amount of $Al_2(SO_4)_3$ required to coagulate the latex was used as the measure of electrolytic stability.

To determine freeze–thaw stability, the latexes were subjected to a number of cycles where the sample was frozen at −10°C for 12 h and then allowed to thaw at room temperature for 12 h. Both the amount of coagulum formed and the increase of the particle size were taken as a measure of freeze–thaw stability.

RESULTS AND DISCUSSION

Recipes used in the semicontinuous polymerization of methylmethacrylate (MMA) and butylacrylate (BA) are given in *Table 1*. In the 'S' series of reactions, to optimize the surfactant concentration, surfactant concentration was varied between 1.5 and 6.0% with the monomer concentration kept at ~30% w/w. Very little difference was observed in percent conversion and percent solid with variation in surfactant concentration around 3.0%. At lower and higher concentrations of surfactant, coagulum formation was observed, and hence 2.0–3.0% of surfactant for ~30% monomer is recommended. This results in a monomer/(surfactant + cosurfactant) ratio between 10 and 12. At this condition, latex particles were observed to be of ~40 nm size. At low concentrations of the anionic surfactant Dowfax 2A-1, coagulum formation takes place as a result of promotion of electrostatic instability of the latex particles. A decrease in the double layer thickness with decreased surfactant concentration results in decreased stability of the latex particles. At higher surfactant concentration, the stability of the latex may be reduced because of an increase in ionic concentration of the continuous phase.

To improve the percentage of solid in the latex, monomer concentration was varied from 30% to 50%, keeping the MMA : BA ratio at 1 : 1 and the monomer/(surfactant + cosurfactant) ratio ~10. At higher concentrations of monomers, above 45%, coagulum formation was observed because of reduced stability of the latex with increase in ionic concentration of the continuous phase. Solid percent was improved from 33.2 to 53.6. At 36.95% solid the viscosity was 0.15 poise, whereas at 45.2% it was 4.04 poise. At 53/6% solid the viscosity increased considerably.

Under identical conditions, latexes produced from polymerization of MMA and BA show 33% solid and no coagulum. However, the particle size in the latex (*Table 2*) was observed to be 22 and 60 nm for PMMA and PBA respectively. On polymerizing MMA–BA (1 : 1) under identical conditions, the latex showed particles with almost the average particle size of PMMA and PBA latexes (*Table 2*). Interestingly, with the surfactant sodium dodecyl sulfate, methylmethacrylate gave a larger particle size than butylacrylate. This indicates that the nature of Dowfax 2A-1 is playing a critical role, resulting in a lower particle size microlatex for MMA than for BA.

In reactions 'D' no cosurfactant was used, whereas in 'DP' pentanol and in 'DA' acrylamide was used as shown in the recipe. The average particle size was observed to be smaller for DA (with acrylamide) than for D (no cosurfactant). However, when pentanol was used as a

Table 1 Recipes used in the series of experiments

	Monomer %	Water %	Dowfax 2A-1	Cosurfactant %	Initiator %	% conversion	% solid	% coagulum
				Acrylamide	APS			
MMA	31.08	65.60	2.85	0.32	0.15	98.52	32.48	–
BA	31.08	65.60	2.85	0.32	0.15	98.93	32.62	–
MMA–BA	31.08	65.60	2.85	0.32	0.15	99.10	32.67	–
Variation of surfactant concentration								
S-1	31.44	66.37	1.71	0.33	0.15	99.78	32.70	4.5
S-2	31.40	65.88	2.25	0.32	0.15	100.0	33.00	–
S-3	31.08	65.60	2.85	0.32	0.15	99.10	32.67	–
S-4	31.00	64.84	3.69	0.32	0.15	90.62	30.19	3.0
S-5	30.39	63.31	5.85	0.31	0.14	90.25	30.47	5.0
Variation in monomer concentration, keeping monomer: (surfactant + cosurfactant) ratio constant								
M-1	31.08	65.60	2.85	0.32	0.15	99.10	32.67	–
M-2	35.53	60.75	3.20	0.38	0.14	98.15	39.95	–
M-3	40.39	55.37	3.72	0.40	0.12	98.61	42.18	–
M-4	42.56	52.64	4.24	0.45	0.11	99.91	45.20	–
M-5	48.86	45.55	4.99	0.50	0.10	100.00	51.96	8.0
Variation in initiator type								
					KPS			
I-1	40.39	55.36	3.72	0.40	0.13	91.30	39.05	2
					APS			
I-2	40.39	55.37	3.72	0.40	0.12	98.61	42.18	–
					AIBN			
I-3	40.39	55.40	3.72	0.40	0.08	96.52	40.25	3
					BPO			
I-4	40.39	55.38	3.72	0.40	0.11	–	33.48	14
Effect of cosurfactant								
				Pentanol	APS			
DP	40.39	55.37	3.72	0.40	0.12	90.03	37.61	3
				Acrylamide				
DA	40.39	55.37	3.72	0.40	0.12	98.61	42.18	–
D	40.45	55.70	3.73	–	0.12	96.15	40.8	–
Variation in temperature								
				Acrylamide				
MBA-70	40.39	55.37	3.72	0.40	0.12	97.87	41.86	–
MBA-80	40.39	55.37	3.72	0.40	0.12	98.61	42.18	–
MBA-90	40.39	55.37	3.72	0.40	0.12	83.26	35.61	6.3
MB-70	40.45	55.70	3.73	–	0.12	89.64	38.04	–
MB-80	40.45	55.70	3.73	–	0.12	96.15	40.80	–
MB-90	40.45	55.70	3.73	–	0.12	93.92	39.86	8.2
Variation of ammonium persulfate concentration (based on water)								
MBA I 21	40.39	55.37	3.72	0.40	0.10 M(0.12%)	98.61	42.18	–
MBA I 22					0.02 M	100.00	42.84	–
MBA I 23					0.03 M	100.00	42.84	–
MBA I 24					0.05 M	100.00	42.84	–
MB I 21	40.45	55.70	3.73	–	0.01 M(0.12%)	96.15	40.80	–
MB I 22					0.02 M	100.00	41.48	–
MB I 23					0.03 M	100.00	41.48	–
MB I 24					0.05 M	100.00	41.48	–

Table 2 Average particle size D_n (nm) and $|\eta|(\mathrm{dl\,g^{-1}})$ for synthesized latexes and polymers

	Solid %	Av. particle size (nm)	$|\eta|(\mathrm{dl\,g^{-1}})$
MMA	32.48	22.0	1.22
BA	32.62	60.0	
MMA–BA	32.67	40.5	1.39
S-2	33.00	42.5	1.37
S-3	32.67	40.5	1.39
M-1	32.67	40.5	
M-3	42.18	35.4	1.41
M-4	45.20		1.68
D	40.80	39.4	1.73
DP	37.60	49.7	1.06
DA	42.18	35.4	1.41
I-1	39.05	45.3	1.15
I-2	42.18	35.4	1.41
I-3	40.25	37.5	1.50
MBA-70	41.86		1.55
MBA-80	42.18	35.4	1.41
MB-70	38.04		1.33
MB-80	40.80	39.3	1.73
MBA-I-21	42.18	35.4	1.41
MBA-I-22	42.84		1.45
MBA-I-23	42.84		1.38
MB-I-21	40.80	39.3	1.73
MB-I-22	41.50		1.53
MB-I-23	41.50		1.30
MB-I-24	41.50		1.06

cosurfactant, percent solid was decreased with coagulum formation and latex particles also showed ~25% increase in size. This may be because of non-solvent action of pentanol.

A TEM micrograph of the system D shows a bimodal distribution of particle size, one with a particle size of 28 nm and the other with 50.8 nm. This is shown in *Figures 1a* and *b*.

In series 'I', various initiators—water-soluble potassium persulfate, ammonium persulfate, oil-soluble azo *bis* iso butyronitrile and benzoyl peroxide—have been used. Among them, ammonium persulfate gives the highest percent solid without coagulum formation and with the smallest latex particles and higher intrinsic viscosity. With ammonium persulfate, latexes with particle size 35.4 nm and $|\eta| = 1.413\,\mathrm{dl\,g^{-1}}$ were obtained; with KPS, average particle size was 45.31 nm and $|\eta| = 1.152\,\mathrm{dl\,g^{-1}}$. With AIBN, the system at 40.2% solid showed gelling whereas, with Bz_2O_2, an emulsion with a large amount of coagulum was formed.

In the study of effect of temperature on copolymerization using ~40% concentration of MMA–BA, it was observed that at high temperature the percent solid and percent conversion are lower and coagulum formation takes place. Hence an 80°C temperature was maintained throughout the work. This effect was observed in the presence (MBA 70, 80 and 90) as well as the absence of cosurfactant acrylamide (MB 70, 80 and 90) (*Table 1*).

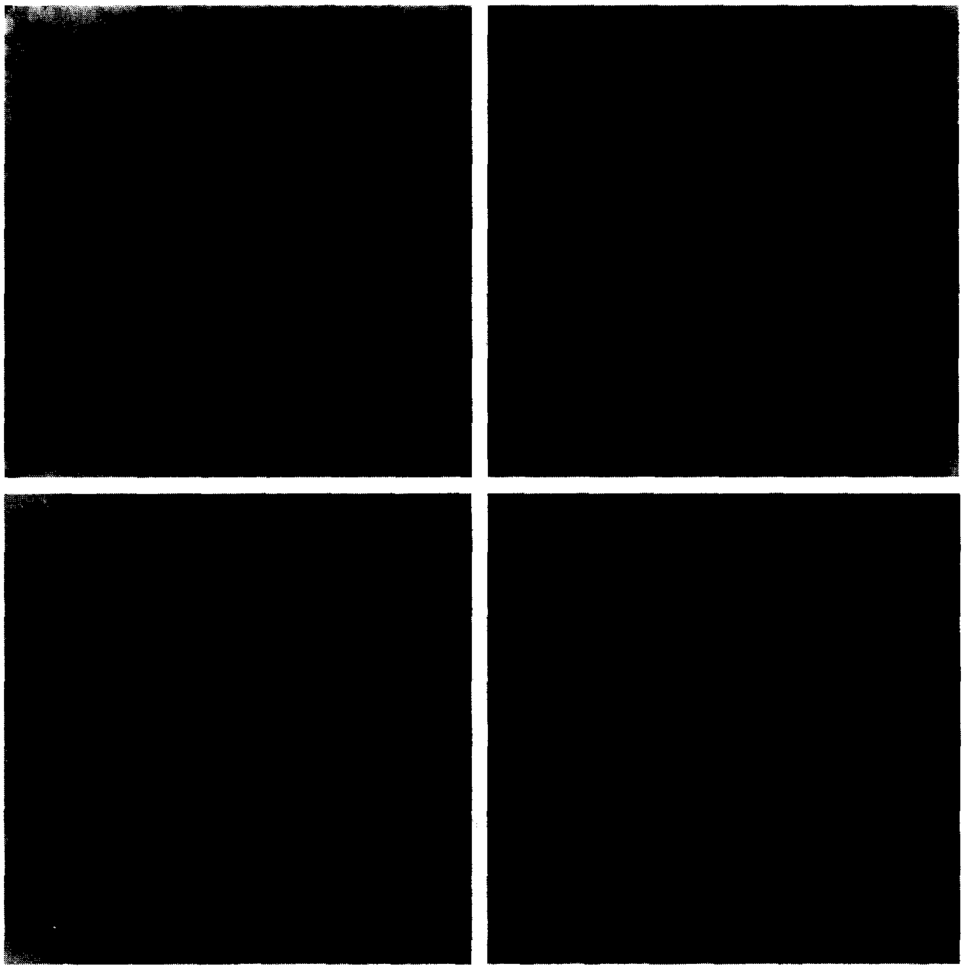

Figure 1 (a) Transmission electron micrograph (TEM) of the latex from recipe D, × 50 000; (b) TEM of the latex from recipe D, × 100 000; (c) TEM of latex particles from recipe MMA, × 50 000; (d) TEM of the latex particles from recipe M-1, × 50 000

The effect of concentration of ammonium persulfate was studied at 80°C for systems with and without acrylamide. The concentration studied was 0.01 M to 0.5 M (based on water). At higher concentrations intrinsic viscosity decreases, as shown in *Table 2*.

In our work latexes with high solid percentage (45.2%) and low particle size (30 nm) were achieved, whereas Shah *et al.*[17] have reported latexes with maximum 41% solid. Most of the surfactants reported for microemulsion polymerization have only one ionic charge per molecule, whereas Dowfax 2A-1 has two. The structural formula shows that each molecule of Dowfax surfactant consists of a pair of sulfonate groups on a diphenyloxide backbone. The hydrophile may be a linear or branched alkyl group composed of 6–16 carbons. Two charged groups in close proximity yield an overlapping zone of enhanced negative charge. This higher local charge density results in greater intermolecular attraction and therefore an increased probability of solvating and coupling action. The ether linkage between the two benzene rings of each molecule of Dowfax 2A-1 surfactant is flexible. This flexibility allows the benzene rings to rotate around the oxygen. It follows that the distance between the sulfonates is variable, allowing the molecule to interact readily with structures as compact as individual ions or as bulky as long chain hydrocarbons.

N.m.r. study

Figure 2 shows the signals obtained in high resolution ^{1}H-n.m.r. for methylmethacrylate–butylacrylate copolymer. It is reported[18] that, in the case of poly(butylacrylate) (PBA), the $-OCH_2$ proton appears around δ4.0 ppm and α–CH, β–CH$_2$ and $^4CH_3-$ protons appear at δ2.2–2.4 ppm, δ1.8–2.0 ppm and δ0.91–0.96 ppm respectively. In case of poly(methylmethacrylate)[19], an $-OCH_3$ resonance signal appears around δ3.5 ppm, β–CH$_2$– protons around δ2.0 ppm and α–CH$_3$ protons between δ1.5 and δ1.0 ppm. *Figure 2* shows the signal between δ3.62 and δ3.98 ppm due to $-O^1CH_2$ protons, and at δ2.09 ppm due to α–CH, at δ1.58 ppm due to $-^2CH_2-$, at δ1.36 ppm due to $-^3CH_2$ and at δ0.93 ppm due to $-^4CH_3$ of butylacrylate. The signals obtained at δ3.58 ppm may be assigned to $-OCH_3$ and at δ1.10 ppm and δ1.25 ppm to α–CH$_3$ of methylmethacrylate. The β–CH$_2$ signal appears at δ2.07 ppm and δ1.81 ppm. These values coincide with the values reported for PBA[18] and PMMA[19]. The positions of signals and their intensities show that a copolymer of methylmethacrylate and butylacrylate has formed in equimolar proportion.

G.p.c. analysis

Table 3 shows the weight-average and number-average molecular weights and polydispersity of representative samples. M-2 and M-4 are the systems with ~30% surfactant and 36.7 and 45% solid content and D is a system without acrylamide and with ~41% solid content. System D shows a bimodal distribution with overall molecular data $\bar{M}_n = 4.18 \times 10^5$, $\bar{M}_w = 11.96 \times 10^5$ and polydispersity 2.86. When data quantitation was carried out for both the peaks, the values were for peak (1): $\bar{M}_n = 24.28 \times 10^5$, $\bar{M}_w = 26.89 \times 10^5$ and polydispersity 1.11, and for peak (2): $\bar{M}_n = 3.08 \times 10^5$, $\bar{M}_w = 5.51 \times 10^5$ with polydispersity 1.79. This unequivocally indicates the operation of more than one route of polymerization, i.e. simultaneously, with nucleation in monomer swollen micelles, or in monomer droplets and homogeneous nucleation in the aqueous phase. Bimodal molecular weight distribution has been reported by other research workers[11,20,21] also. Johnson and Gulari[20] reported two populations with average molecular weights of 3×10^5 and 3×10^6 by g.p.c. and quasielastic light scattering. The polydispersity of samples M-2 and M-4 is 5.56 and 5.14, respectively (*Table 3*). The high polydispersity is also indicative of more than one route of polymerization, in monomer droplets and in monomer swollen micelles or homogeneous nucleation, or in all three operating simultaneously.

Particle size distribution

Figures 3 and *4* show the particle size distribution of

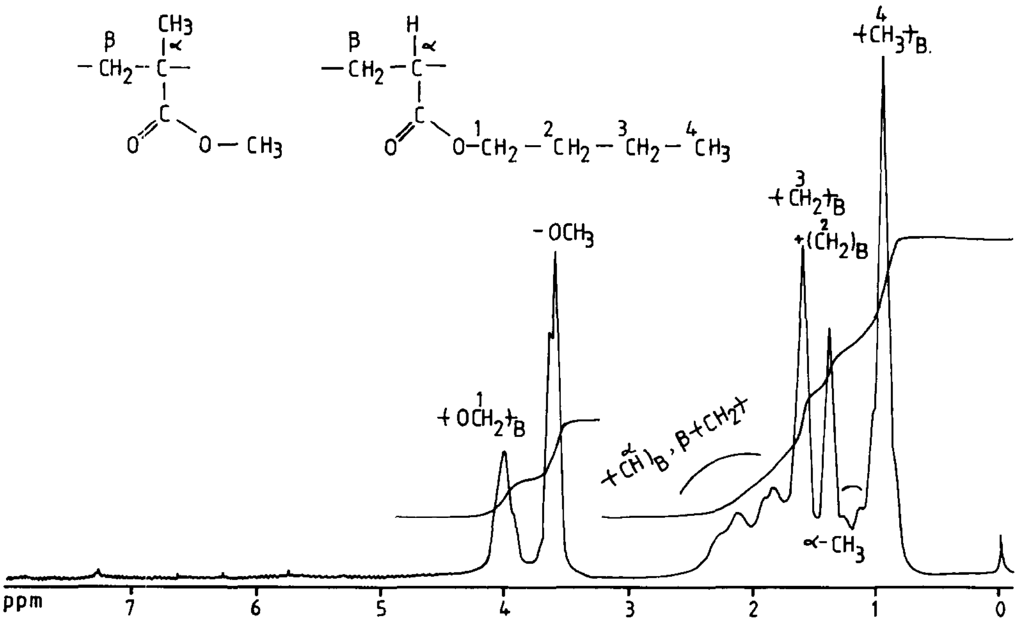

Figure 2 ^{1}H-n.m.r. spectrum from P(MMA–BA)

Table 3 Weight-average, number-average molecular weights and polydispersity results of the studied samples synthesized using Dowfax 2A-1 at 80°C with ammonium persulfate (0.3% with respect to monomer)

Sample[a]	$\bar{M}_w(\times 10^5)$	$\bar{M}_n(\times 10^5)$	Polydispersity
M-2	7.12	1.28	5.56
M-4	11.7	2.27	5.14
D[b]	11.96	4.18	2.86
	(i) 26.89	(i) 24.28	(i) 1.11
	(ii) 5.59	(ii) 3.08	(ii) 1.78

[a] M-2, M-4, D compositions as given in *Table 1*
[b] D shows bimodal distribution

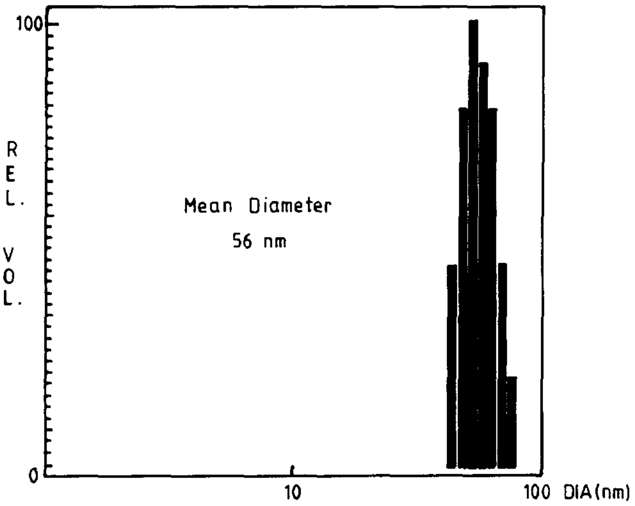

Figure 3 Particle size distribution of the latex from recipe DA

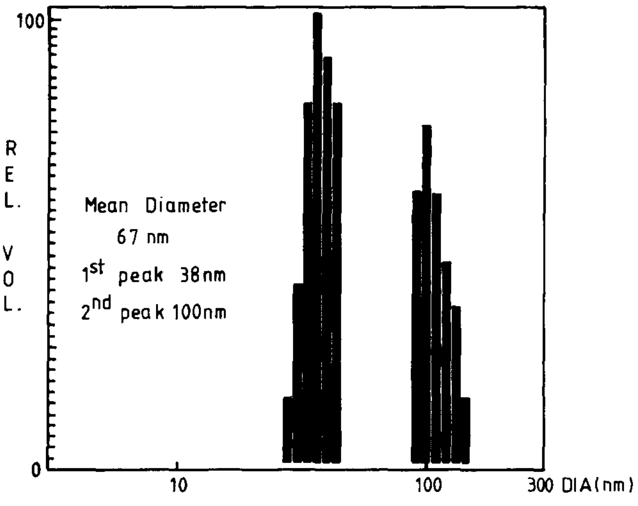

Figure 4 Particle size distribution of the latex from recipe D

the latex from recipes DA and D. The mean diameter of the latex from DA is 56 nm, with 25% of the particles below 37 nm and 50% below 46 nm. For latex from recipe D, a bimodal distribution was observed with the first peak at 38 nm and the second at 101 nm. The mean diameter was 67 nm, with 25% of the particles below 36 nm. This bimodal distribution is indicative of nucleation of polymerization taking place by more than one route.

Thermal analysis

Table 4 shows the thermal analysis results of representative samples. *Figure 5* shows the t.g.a., d.t.g. and d.t.a. curves of polymers synthesized using recipe D (*Table 1*). Samples of D and DP show single-step degradation. Sample DA shows two-step degradation, the first step involving 6% weight loss. This indicates the incorporation of acrylamide in the polymeric chain. The data of sample DA (*Table 1*) are of the second step. The degradation starts around 220°C, though for D it is at 260°C, and 30% degradation is observed at 420°C. This is a typical degradation pattern of acrylate polymers. The d.t.g. curve shows the highest rate, 19.2% min^{-1} at 402.4°C, for sample D. T_m and T_d are melting and decomposition temperatures of the samples. From t.g. curves, activation energy was calculated using Broido's equation. The activation energy of sample D, without any cosurfactant, and that of DP, with pentanol as cosurfactant, shows considerable difference: 14.83 kcal mol^{-1} and 10.90 kcal mol^{-1} respectively, indicating some difference in the internal structure of the products.

Mechanical stability

The microemulsion latexes from recipes M-2 and M-4 were tested for mechanical stability at 14000 rpm for 10 min. Both latexes showed good mechanical stability with no coagulum. No increase in particle size was observed.

Electrolytic stability

The microemulsion latexes from recipes M-2 and M-4 were tested for electrolytic stability using 5% aluminium sulfate. 100 g of M-2 microemulsion latex required 20 ml of $Al_2(SO_4)_3$, whereas M-4 required 18 ml of the same for complete coagulation. Dowfax 2A-1 is an anionic emulsifier which promotes electrostatic stabilization of the latex particles. On adding $Al_2(SO_4)_3$ electrolyte, decrease of the double layer thickness takes place. This results in decrease in the stability of the latex particles.

Freeze–thaw stability

Latex can freeze during storage of transportation and therefore resistance to freeze–thaw cycles is very important for commercialization. The latexes from recipes M-2 and M-4 were tested for freeze-thaw stability by being subjected to cycles where the sample was frozen at −10°C for 12 h and then allowed to thaw at room temperature for 12 h. Both M-2 and M-4 showed excellent stability to three cycles. When freezing occurs, ice crystals separate from the unfrozen latex, reducing the volume of the continuous phase and increasing the ionic concentration of this phase. Therefore, the stability of the latex is reduced and the latex, which is subjected to high pressure, coagulates. On the other hand, non-ionic surfactants with long ethoxy chains can reduce coagulation during the freeze–thaw process[22]. The diphenyl oxide backbone of Dowfax 2A-1 surfactant may be playing the role of ethoxy chains, reducing coagulation during the freeze–thaw process and increasing the stability.

CONCLUSIONS

The effect of the type and amount of surfactant, diphenyl oxide disulphonate, on the overall polymerization features and final product properties for the semicontinuous

Table 4 Thermal analysis[a]

	D.t.a.		T.g.a.				D.t.g.	
	T_m (°C)	T_d (°C)	T_1 (°C)	T_{50} (°C)	T_{90} (°C)	E (kcal mol^{-1})	Rate (% min^{-1})	Temp. (°C)
D	330	393	261.0	388.75	415.0	14.83	19.2	402.4
DP			223.9	370.77	396.2	10.90	16.1	375.4
DA	296	395	217.5	386.88	412.5	10.38	15.4	400.1

[a] T_1, T_{50} and T_{90} are the decomposition temperatures for 1%, 50% and 90% weight loss; E is activation energy of degradation

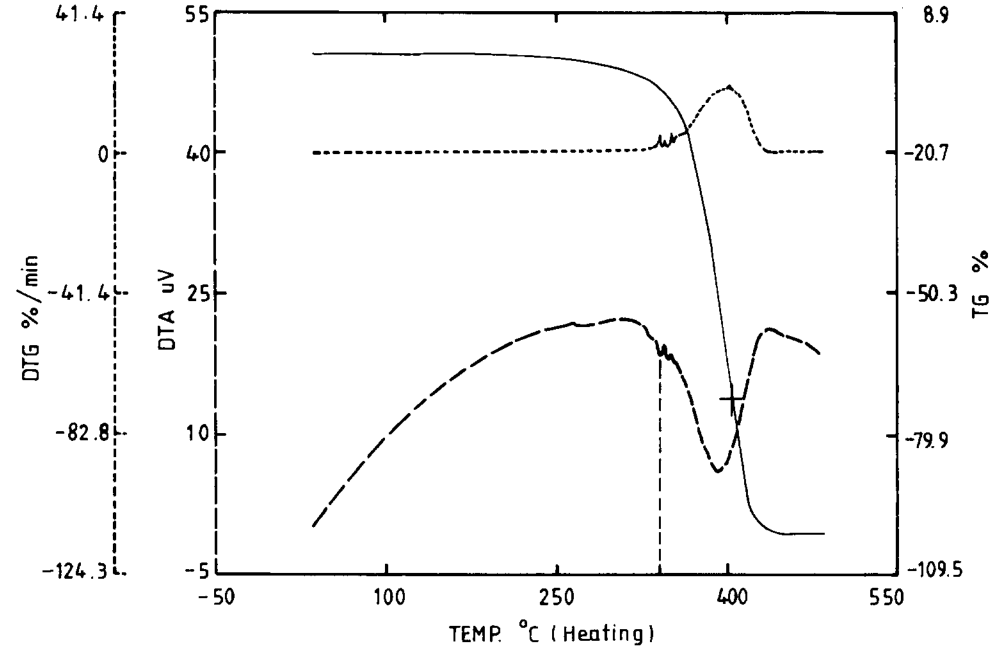

Figure 5 T.g.a., d.t.a. and d.t.g curves for sample D

microemulsion copolymerization of methylmethacrylate and butylacrylate was investigated. A microemulsion latex of 45.2% solid with 30 nm particle size was achieved. The weight-average molecular weight of the polymers was 1.22×10^6. Bimodal distribution of molecular weights and particle size distribution was observed in one particular case, indicating more than one route of nucleation: micellar nucleation and nucleation in monomer droplets or homogeneous nucleation. The high polydispersity is also indicative of more than one route of nucleation. The tested latex showed mechanical, electrolytic and freeze–thaw stability.

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