Methacrylate-Based Nanoparticles Produced by Microemulsion Polymerization

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ABSTRACT: Nanoparticles of methacrylate comonomers were obtained by microemulsion polymerization by using cetyltrimethylammonium bromide as the stabilizer. Stable and bluish transparent latexes were produced from these polymerizations in which potassium persulphate was used as the initiator. The viscosity average molecular weights were in between 6×10^5 and 1.25×10^6. The average diameters of the latex particles were in the range of 20–40 nm, which was obtained by scanning tunneling microscopy. The average particle diameter increased both with an increase in the relative amount of the comonomers and their type. The glass transition temperatures of these polymers obtained by DSC were in the range of 30–103°C, and decreased with the increase in the comonomer ratio. The comonomer ratios in the final copolymers were obtained from ^{1}H-NMR spectra, which were smaller than those ratios used in the original recipes. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 569–575, 2000

Key words: nanoparticles; methacrylate comonomers, microemulsion polymerization

INTRODUCTION

The concept of polymerization in microemulsions appeared only in the early 1980s.[1–3] Polymerization in microemulsions allows the synthesis of ultrafine latex particles within the size range of 10–100 nm and with narrow size distributions.[4–9] In contrast to the opaque and milky conventional emulsions and miniemulsions, microemulsions are isotropic, optically transparent or translucent, and thermodynamically stable.

These microemulsions are very simple to create: monomer is dispersed in water using dodecyl sulfate sodium or cetyltrimethylammonium bromide as surfactants; the subsequent polymerization by means of water-soluble (e.g., potassium persulphate) or oil-soluble (e.g., azo-bis isobuty-ronitrile) initiators produces a stable latex in high yield. In most cases, cosurfactants (e.g., 1-pentanol) are required. The droplet size is thermodynamically controlled by the amount and character of the surfactant. Functionalization of the latexes is conveniently performed by the addition of functional comonomers.

It is less complicated to study microemulsion polymerization in a ternary system without a cosurfactant. Polymerization in three-component microemulsions is easier to model and to understand because, among other factors, partitioning of components between the microemulsion domains is simpler to measure or to estimate, and no extraneous chain transfer agent or modifiers (such as alcohol cosurfactants or electrolytes) are present. Styrene and methyl methacrylate are typical monomers have been polymerized in ternary oil-in-water microemulsions.[10–22]

Microemulsion polymerization has been studied by several groups. Some examples areas follows: Gan and coworkers produced PMMA in ternary microemulsions using the cationic surfac-

Table I   The Abbreviations for the Homo- and Copolymers Synthesized

Abbreviation	Homo or Copolymers
Homopolymers	
PMMA	Polymethylmethacrylate
PEMA	Polyethylmethacrylate
PBMA	Polybutylmethacrylate
Copolymers	
P(MMA/EMA) 75/25[a]	Poly(methyl and ethylmethacrylate)
P(MMA/EMA) 50/50[a]	Poly(methyl and ethylmethacrylate)
P(MMA/EMA) 25/75[a]	Poly(methyl and ethylmethacrylate)
P(MMA/BMA) 75/25[a]	Poly(methyl and butylmethacrylate)
P(MMA/BMA) 50/50[a]	Poly(methyl and butylmethacrylate)
P(MMA/BMA) 25/75[a]	Poly(methyl and butylmethacrylate)

[a] These numbers shows the weight ratio of the comonomers used in the initial mixture.

tants stearyl trimethylammonium chloride (STAC), cetyl trimethylammonium bromide (CTAB), and dodecyl trimethylammonium bromide (DTAB) with either a water-soluble or an oil-soluble initiator and found that the longer the hydrophobic chain length of the surfactant, the smaller the latex particles.[23] Kaler and coworkers also have produced small latexes from styrene and from several different methacrylic esters using cationic surfactants.[12,19,24–26] Larpent and Tadros found optimum mixtures of nonionic surfactants [Triton N-150 and Triton N-57, nonylphenoxy poly(ethylene glycols) having averages of 15 and 5 ethylene oxide units, respectively], to form microemulsions of MMA and of styrene in water, and produced small latex particles at varied surfactant-to-monomer ratios using ascorbic acid/hydrogen peroxide as a redox initiator.[27]

In this study we attempted to microemulsion polymerization of methyl, ethyl, and butyl methacrylates in ternary systems. Production and characterization of these microemulsions are presented in this communication.

EXPERIMENTAL

Materials

The methacrylate monomers, i.e., methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BMA) (Fluka, USA) were treated with an aqueous solution of NaOH (10% by weight) to remove the inhibitor. The surfactant, cetyltrimethylammonium bromide (CTAB) (Fluka) and the initiator, potassium persulphate (KPS) (Aldrich, Milwaukee, WI) were used as re-

ceived. Distilled/deionized water was used in all experiments.

Microemulsion Polymerization

Microemulsion polymerizations were carried out in ternary oil-in-water (o/w) system. The mixture containing proper amounts of the comonomers (MMA, EMA, or BMA), were added to the aqueous solution of CTAB into a 100-mL glass reactor that was agitated at room temperature by means of a magnetic stirrer for about 10 min. It was then stored at 4°C for about 24 h to reach equilibrium. Prior to polymerization, initiator was added to the solution, and nitrogen gas was flowed through the medium for about 1–2 min to remove dissolved oxygen. The reactor was then placed in a shaker in a temperature control bath, and polymerization was realized at constant temperature of 60°C for 24 h. Note that, prior the polymerization, the medium was a transparent liquid, while after polymerization the latex obtained was bluish and clear. Washing the latex particles with methanol and water several times cleaned the latex (to remove the surfactant). The total amount of monomers, and the initial concentrations of the surfactant and initiator were 6.33, 9.3% (by weight) and 2.5 mM (based on water) in the experiment. In this study, we changed only the type and relative amount of methacrylate comonomers in the polymerization recipes. Either each monomer or comonomers with three different weight ratios, namely, 25, 50, or 75% were polymerized. The abbreviations for the homo and copolymers, which are used in the rest of this article, are given in Table I.

Table II Viscosity Average Molecular Weights of the Homo/Copolymers, and Monomer Conversions

Homo or Copolymers	MW_v ($\times 10^6$)	Conversion (%)
Homopolymers		
PMMA	1.42	70
PEMA	1.12	55
PBMA	1.03	77
Copolymers		
P(MMA/EMA) 75/25	0.98	67
P(MMA/EMA) 50/50	0.63	80
P(MMA/EMA) 25/75	1.04	85
P(MMA/BMA) 75/25	1.75	73
P(MMA/BMA) 50/50	1.14	72
P(MMA/BMA) 25/75	0.83	73

The polymerization yield was obtained by extraction of copolymer from the latex particles by chloroform, and by weighting the solid phase after complete removal of the unconverted monomers by a controlled drying.

Viscosity measurements were used to obtain average molecular weights of the polymers produced in this study. Viscosities of the polymer solutions with different concentrations (0.1–2.0 g/100 mL) measured with a capillary viscometer (i.e., Ubbelhode viscometer) in a constant temperature water bath at 25.0 ± 0.1°C. The polymer was dissolved in chloroform and the "flow times" for the solvent (t_0) and the polymer solution (t) were measured. The relative viscosity (η_r) was then found from t_0/t values. Specific viscosity (η_{sp}), which is equal to ln ηr was plotted against polymer concentration (c). From the intercept at Y-axis after extrapolation, the intrinsic viscosity, i.e., [η] was obtained. The follwing Mark-Houwink equations were used to calculate viscosity average molecular weights:[28]

$$[\eta] = K \cdot MW_v^a$$

Note that the K values for PMMA, PEMA, and PBMA are 5.5×10^{-5}, 5.2×10^{-5} and 4.9×10^{-5}, and a values for PMMA, PEMA, and PBMA are 0.79, 0.78, and 0.78, respectively. For copolymers, average values were used.

The particle size of the nanoparticles were measured by a novel technique, i.e., scanning tunneling microscopy (STM). Details of these measurements are given elsewhere.[29] For STM imag-

ing of the latex particles, the latex samples (5 μL containing 0.1 mg particles per mL) were deposited onto freshly cleaved highly oriented pyrolitic graphite (HOPG), and dried at room temperature. Then, the STM images were taken, 2 V sample bias, and a tunneling current of a 20 pA. Etched tips of Pt/Ir (80 : 20) wires (0.5 mm in diameter, Digital Instruments, Santa Barbara, CA) were used. Prior to use the tips were washed in acetone.

Thermal transitions to obtain glass transition temperatures (Tg) were recorded by a differential scanning calorimeter (DSC) (Shimadzu, Model DSC-50, Japan). Nitrogen was used as the sweeping gas. Samples (5–10 mg) were heated at a scan rate of 10°C/min from 25 to 300°C followed by rapid cooling.

Polymer samples were dissolved in CDCl$_3$, and ^{1}H-MR spectra were recorded in a NMR spectrometer (Brucker AC 250, USA) working at 500 MHz at room temperature. The sample concentration in CDCl$_3$ was 1% (w/v). The internal standard was tetramethylsilane, and chemical shifts were expressed in ppm.

RESULTS AND DISCUSSION

In this study we attempted to polymerize methacrylate monomers (namely, methyl methacrylate,
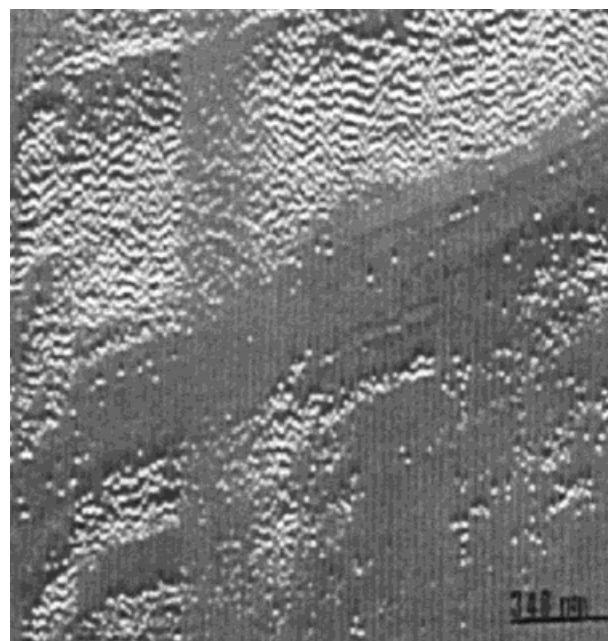
Figure 1 A representative STM micrograph of PMMA nanoparticles.

Table III   The Average Particle Size of the Homo or Copolymers

Homo or Copolymers	Average Particle Diameter (nm)
Homopolymers	
PMMA	28.7
PEMA	36.5
PBMA	44.8
Copolymers	
P(MMA/EMA) 75/25	29.3
P(MMA/EMA) 50/50	30.7
P(MMA/EMA) 25/75	33.9
P(MMA/BMA) 75/25	30.3
P(MMA/BMA) 50/50	33.3
P(MMA/BMA) 25/75	36.5

[a] The standard deviations were smaller than ± 2.5 in all cases.

ethyl methacrylate, and butyl methacrylate) to produce homo and/or copolymeric nanoparticles in microemulsions using CTAB as the surfactant. Note that prior to polymerization the microemulsions of the monomer droplets were transparent at the reaction temperature, which is 60°C, and as polymerization proceeded, the mixtures developed a bluish tint, indicating the presence of the forming polymeric nanoparticles. Visible changes in the appearance of the polymeric latices were followed, but no signs of coagulation were observed for up to 6 months.

Average Molecular Weights/Conversion

Table II shows the viscosity average molecular weights and conversions of the homo and copolymers produced in this study. Notice that the highest molecular weights were observed for the PMMA homopolymer, which is MW_v: 1.72×10^5. The average molecular weights for PEMA and PBMA homopolymers and other copolymers are somewhat lower (but not very significantly) than these values. In emulsion and microemulsion polymerization, the average molar masses and the average mass distributions are controlled by chain transfer reaction to monomer.[30] Calculation using the chain transfer to monomers shows that the average-number molar masses for emulsion-made and microemulsion-made polymethacrylates should be in the range of 106 g/mol. In fact, several investigators have reported values of MW_w larger than 106 g/mol for polymethylmethacrylate,[14,19] butylmethacrylate,[21] and hexylmethacrylate.[31]

The monomer conversions, which were in the range of 55–85%, are presented in the last column of Table II. Other authors have also reported conversions smaller than 70% after 2 h of reaction, for the unbuffered polymerization of styrene, methylmethacrylate, and buthylmethacrylate in microemulsions stabilized with DTAB and initiated with KPS.[6,13,14,21] Morgan et al. have studied polymerization of hexyl methacrylate in cationic microemulsions stabilized with cationic surfactants (DTAB, CTAB, etc.) do not reach high conversions with KPS, unless the pH of the reaction medium is controlled to neutral or slightly basic pH.[31] This is because the persulphate ions, besides dissociating to give free radicals, are hydrolyzed to produce bisulphate ions, which cause the drop in pH. This drop in pH in unbuffered polymerization result low reaction rates and conversions.
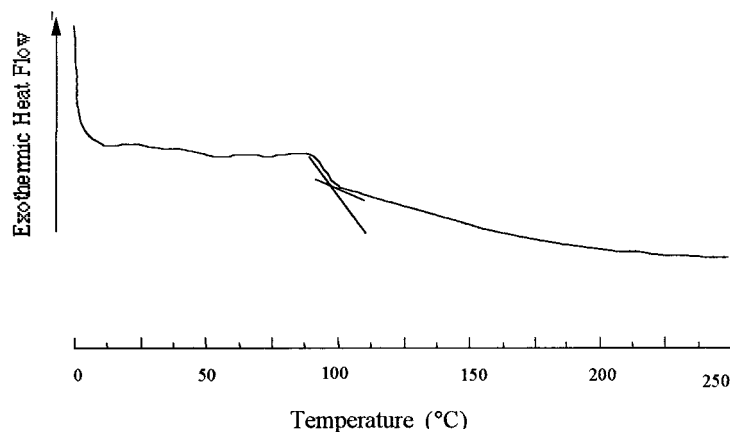
Figure 2   A representative DSC thermogram of PMMA microemulsion particles.

Table IV   The Glass Transition Temperatures of the Homo or Copolymers

| Homo or Copolymers	Glass Transition Temperature (°C)
Homopolymers	
PMMA	103
PEMA	71
PBMA	30
Copolymers	
P(MMA/EMA) 75/25	100
P(MMA/EMA) 50/50	85
P(MMA/EMA) 25/75	81
P(MMA/BMA) 75/25	60
P(MMA/BMA) 50/50	50
P(MMA/BMA) 25/75	45

To obtain the average particle size, a novel technique, i.e., scanning tunnelling microscopy (STM) was used. Details of these STM studies were given elsewhere.[29] A typical micrograph taken is shown in Figure 1, which indicates that the polymeric particles are quite spherical and almost uniform in size, and there are no aggregates. Note that average diameter was calculated by evaluating these micrograph containing approximately 500–1000 microspheres. The average particle sizes of the nanoparticles produced are given in Table III.

Notice that the largest and smallest particles were obtained with PBMA and PMMA homopolymers, which were about 44.8 and 28.7 nm, respectively. This may be due to the hydrophobic chain length, which was the longest in the case of of butylmethacrylate and the shortest in methylmethacrylate. The PMMA particle size increased by addition of more hydrophobic comonomer (EMA or BMA) at higher relative ratios. Most probably increasing the alkyl chain length of metcrylate monomer, the cosurfactant effect of the monomer reduced. The buthylmetacrylate (or ethylmethacrylate) monomer is located more in the hydrophobic core of the droplets than MMA, which may be partially at the w/o interface, thus accounting for the observed increased in size.

Thermal Transitions

Thermal transitions were analyzed by DSC. A typical DSC thermogram, which was for the PMMA microemulsion particles, is given in Figure 2. Notice that all of the polymers (or copolymers) produced were exhibited only glass transitions (T_g) (no melting temperature), which means that they were all amorphous. Table IV gives the glass transition temperatures for both homo and copolymers. Note that the highest T_g value (103°C) was obtained for PMMA particles, which was about the same values reported in literature, which were in the range of 100–115°C.[31,32] The T_g values for PEMA and PBMA were 61 and 30°C, respectively, which were lower than those we obtained.[33] Notice that T_g values were in the range of 30 and 103°C, which were dependent on both the type and relative ratio of the comonomers used, as expected.

(A)

ppm

(B)

ppm
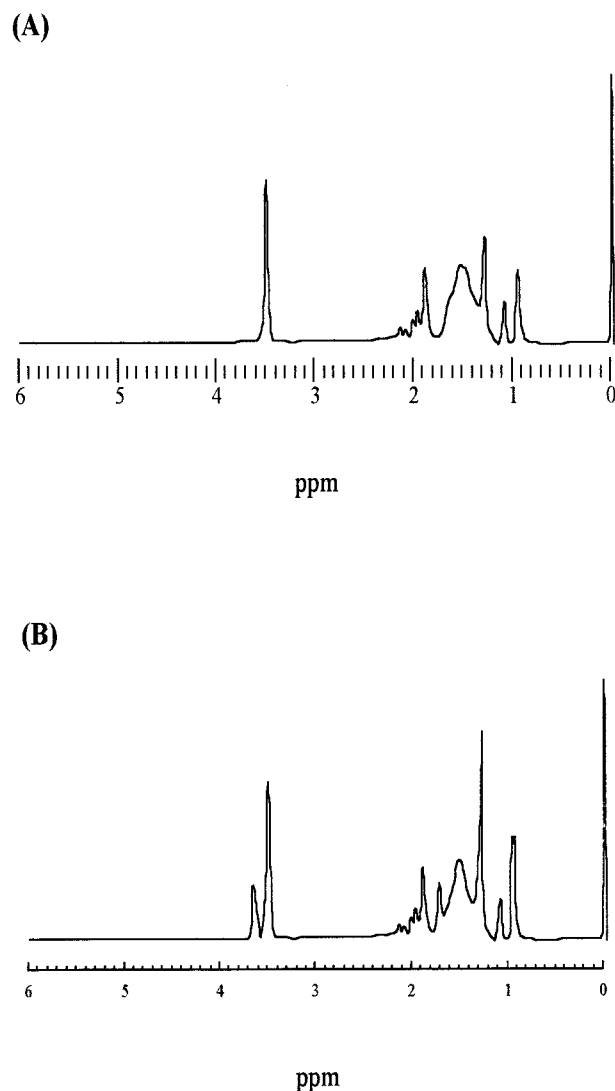
Figure 3   Representative ^{1}H-NMR spectra: (A) for the PMMA homopolymer; (B) for the P(MMA/EMA) 50/50 copolymer.

Table V   The Comonomer Ratios in the Final Copolymers Produced

Copolymers	Comonomer Ratio[a] (MMA/EMA or MMA/BMA)	Comonomer Ratio[b] (MMA/EMA or MMA/BMA)
P(MMA/EMA) 75/25	74.5/25.5	72.5/27.5
P(MMA/EMA) 50/50	60/40	49/51
P(MMA/EMA) 25/75	49/51	26/74
P(MMA/BMA) 75/25	65/35	60/40
P(MMA/BMA) 50/50	51/49	33/67
P(MMA/BMA) 25/75	36/64	14/86

[a] Estimated from the NMR spectra.
[b] Estimated from the reactivity ratios.[35]

Structural Analysis by NMR

Two represantative high resolution ^{1}H-NMR spectra, one for the PMMA homopolymer and the other for the P(MMA/EMA) 50/50 copolymer, are illustrated in Figure 3(A) and (B), respectively. The NMR signals for ester methyl resonance appear around 3.5 ppm, β-methylene protons appear around 2.0 ppm, and α-methyl protons appear between 1.0 and 1.5 ppm. For a syndiotactic polymer, the methylene resonance is expected to give singlets, as both the methylene protons will have similar environments in their immediate vicinity.[22] However, an observed singlet shows broadening due to residual isotactic resonances, which complicates the spectrum with fine structures. For homopolymer PMMA-synthesized microemulsion polymerization, we have observed five peaks between 1.87 and 2.15 ppm, indicating the dominant isotacticity.

For the ester methyl resonance of the PMMA homopolymer, we observed a single peak at 3.64 ppm. On the other hand, for the copolymers, there were two peaks at 3.42 and 3.52 ppm, corresponding to the copolymer ester methyl and ethyl resonances. Therefore, in this study, the comonomer ratios in the final copolymers we compared the peak areas at 3.42 and 3.52 ppm. Note that this was 0.0777/0.0793 for the P(MMA/EMA) 50/50 (estimated from the spectra given in Fig. 3). It should be remembered that the initial comonomer ratio was 50/50 for this copolymerization. Small difference reflects the differences in the reactivity ratios of the comonomers. Similar procedure was followed to obtain the comonomer ratios for other copolymers. As summarized in Table V, the final comonomer ratios (the ratio of MMA to EMA or

BMA) are lower than the initial comonomer ratios, in all cases, due to the lower reactivity of MMA comparing to the other two comonomers, EMA and BMA.

For comparison, theoretical compositions of the copolymers were also calculated from the reactivitiy ratios (r_1) of these monomers, which were 0.52 and 0.81 for MMA/BMA and MMA/EMA, respectively.[28] These theoretical values were also tabulated in Table V.[35] As seen here, the relative amount of MMA in the final copolymers were smaller than those calculated from the NMR spectra.

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