Nanoparticles Carrying Hydroxyl Groups Produced by Microemulsion

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ABSTRACT: Methylmethacrylate and 2-hydroxyethylmethacrylate were polymerized in oil-in-water microemulsions that were stabilized by cetyltrimetylammonium bromide (CTAB). Microemulsions that prepared changed continuously from transparent microemulsions to turbid emulsions by increasing the HEMA weight percentage as a comonomer. Polymerization was initiated with an oil-soluble initiator, azobisizobutyronitrile (AIBN). Stable P(MMA-HEMA) latexes were obtained about 40 nm in diameter. Molecular weights of the copolymers were in the range of $1.89–2.03 \times 10^6$. The glass transition temperatures of these copolymers, which were obtained by differential scanning calorimeter, were in the range of 95–99°C. The comonomer ratio in the final copolymers were obtained from the nuclear magnetic resonance spectra, which were smaller than the comonomer ratios used in the original recipes. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 237–242, 2001

Key words: microemulsion polymerization; nanoparticles; methylmethacrylate; hydroxyethylmethacrylate

INTRODUCTION

The concept of polymerization in microemulsions appeared only in the early 1980s.[1–3] Polymerization in microemulsions allows the synthesis of ultra fine 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.

Several groups have studied microemulsion polymerization. Styrene and methylmethacrylate are typical monomers that have been polymerized in ternary oil-in-water microemulsions.[10–27] Gan and coworkers produced PMMA in ternary micro-

emulsions using the cationic surfactants 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, 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 our previous study, we have polymerized methyl, ethyl, and butylmethacrylates in ternary microemulsion systems, and investigated their film forming abilities.[28–30] Here, we attempted to

introduce hydroxyl groups on the surface of the nanoparticles in the sizes range from 10 to 100 nm, aiming to create active surface groups that may be further treated to obtain carrier matrices for several biological molecules (oligopeptites, oligonucleotids, etc.). We selected 2-hydroxyethyl-methacrylate (HEMA) as the hydroxyl carrying comonomer, and methylmethacrylate (MMA) as the main component, and copolymerized these two comonomers in microemulsions. This communication gives production and characterization of these nanoparticles.

EXPERIMENTAL

Materials

The monomer, methylmethacrylate (Fluka, USA) was commercial grade, and was treated with an aqueous solution of NaOH (10%) to remove the inhibitor. 2-Hydroxyethylmethacrylate was commercial grade (Fluka) and was used as purchased. The surfactant, cetyltrimetylammonium bromide (CTAB) (Fluka) and the initiator, azobisizobutyronitrile (AIBN) (Aldrich, Milwaukee, WI) were used as received. Distilled/deionized water was used in all experiments.

Microemulsion Polymerization

Microemulsion polymerizations were all carried out in ternary oil-in-water (o/w) system, which consisted of the surfactant (CTAB), comonomers (MMA and HEMA), and distilled water in well-shaken glass vessels in a temperature control bath at constant temperature. We polymerized both MMA and MMA/HEMA mixtures (containing a 95/5 or 90/10 MMA/HEMA, weight ratio). We used the following abbreviations for these polymers in the later part of the text: PMMA, P(MMA/HEMA)-95/5, and P(MMA/HEMA)-90/10, respectively. Note that we were note able to increase the HEMA content in the initial mixtures more than 10% by weight, because these latexes were very unstable and agglomerations were observed.

A typical ternary microemulsion procedure for MMA-HEMA that we have applied was as follows: the mixture containing proper amounts of the comonomers were added to the aqueous solution of CTAB into a 100-mL glass vessel, which 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 vessel 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).[28,29]

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 following Mark-Houwink equation was used to calculate the viscosity average molecular weights:[28]

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

Assuming that the HEMA content of the nanoparticles are quite small comparing to MMA, we used the "K" and "a" values of PMMA, which are 5.5 × 10^{-5} and 0.79, respectively.[32]

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.[29,31] For STM imaging 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 on a 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 were obtained by using a differential scanning calorimeter (DSC) (Shi-

350 nm
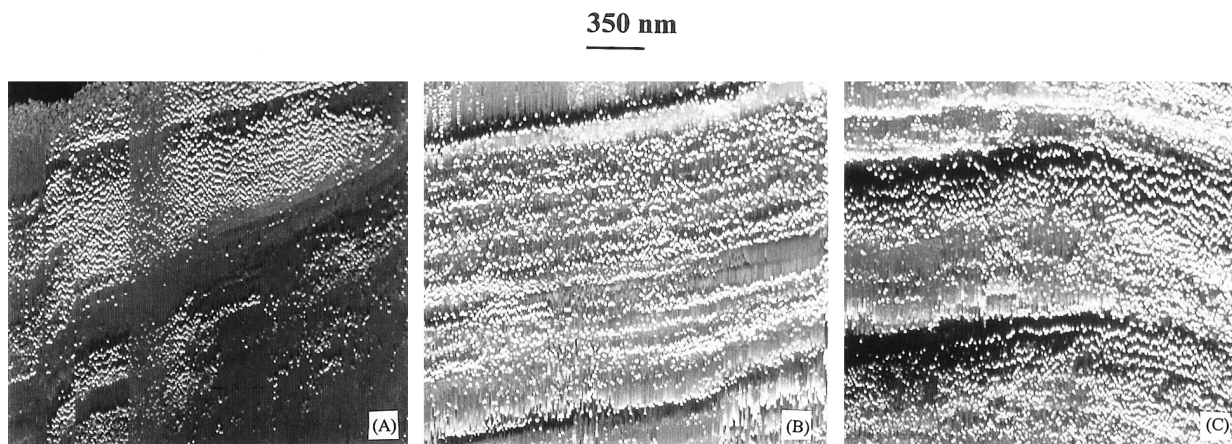
Figure 1 Typical STM micrographs of nanoparticles produced: (A) PMMA; (B) P(MMA/HEMA)-95/5; (C) P(MMA/HEMA)-90/10.

madzu, 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.

FTIR spectra of the nanoparticles were obtained by using an FTIR spectrophotometer (Schmadzu, Model: FTIR-8000 series, Japan) with KBr (IR grade)-nanoparticle mixtures in powder form.

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 copolymerize methyl methacrylate and 2-hydroxyethyl methacrylate in microemulsions. Prior to polymerization, the samples were transparent at the reaction temperature, and as polymerization proceeded, the mixtures developed a bluish tint or became translucent indicating the presence of slightly larger collodial particles.

To obtain the average particle size, STM was used. Typical micrographs taken are shown in Figure 1. In STM it was possible to focus on each particle by increasing the magnification and measured the diameter accurately. We have measured diameters of about 200 nanoparticles (randomly selected) on each graph. The average values and standard deviations were then calculated. Table I gives the average particle size of the homo- and copolymers, which was about 28 nm for the PMMA homopolymer, while including HEMA as comonomer in the formulations caused a notable increase (up to 42.2 nm) in the average particle size.

Note that we also attempted to increase the HEMA content of the nanoparticles. Addition of HEMA in the initial mixture more than 10% caused a significant change in the size distribution and formation of very large particles and even agglomeration in the medium. Therefore, we have not used more than 10% in the initial comonomer mixtures. We believe that it would be enough to create a surface layer carrying OH groups because HEMA is hydrophilic and therefore should stay at the particle surface (which is water–oil interface).

Two characteristic parameters of the microemulsion products that we have determined are the viscosity average molecular weights and conversions, which are given in Table II.

Table I The Average Particle Size of the Homo- and Copolymers

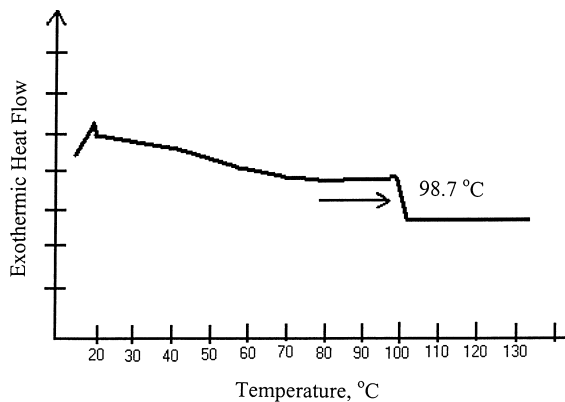| Homo- or Copolymers	Average Particle[a] Diameter (nm)
PMMA	28.0
P(MMA/HEMA)-95/5	40.0
P(MMA/HEMA)-90/10	42.2

[a] The standard deviations were smaller than ±3.2 in all cases.

Table II   Viscosity Average Molecular Weights of Polymers and Monomer Conversions

Homo- or Copolymers	MW_v ($\times 10^6$)	Conversion (%)
PMMA	4.04	98
P(MMA/HEMA)-95/5	2.03	92
P(MMA/HEMA)-90/10	1.89	90

Table III   The Glass Transition Temperatures of the Homo and Copolymers

| Homo- or Copolymers	Glass Transition Temperatures (°C)
PMMA	103.0
P(MMA/HEMA) 95/5	98.7
P(MMA/HEMA) 90/10	94.7

Monomer conversions were determined from the total amount of monomer (comonomer) used and the amount of polymer obtained. As seen here, conversions are over 90%, and are quite comparable with the literature data.[10,14,21,24] Note that much lower conversions are reported in the related literature including our previous study, in which water-soluble initiators have been used.[6,13,14,21,28,34] Because oil-soluble initiator AIBN were used in this study, the electrostatic cage effect did not seem, so high conversions were achieved.

Notice that the highest molecular weights were observed for the PMMA homopolymer, which is MW_v: 4.04×10^6. The average molecular weights for P(MMA/HEMA)95/5 and P(MMA/HEMA) 90/10 copolymers are somewhat lower (but not very significantly) than those for the PMMA homopolymer. In emulsion and microemulsion polymerization, the average molar masses and the average mass distributions are controlled by chain transfer reaction to monomer.[33] In the related literature, average-number molar masses for microemulsion-made polymethacrylates were reported around 10^6 g/mol or even larger.[14–19,21] In our previous study, we have copolymerized

MMA, EMA, and BMA, in which a water-soluble initiator (KPS) with 2.5 mM concentration was used; the viscosity average molecular masses were in the range of $0.63–1.75 \times 10^{-6}$.[28] In this study, we used an oil-soluble initiator (AIBN) with the concentration of 0.5 mM with respect to water, which is much lower than those water-soluble initiator (KPS) that we have used in the previous study. It is commonly known that decreasing the initiator concentration results in pro-

Figure 2   A represantative DSC thermogram of the P(MMA/HEMA) 90/10 nanoparticles.
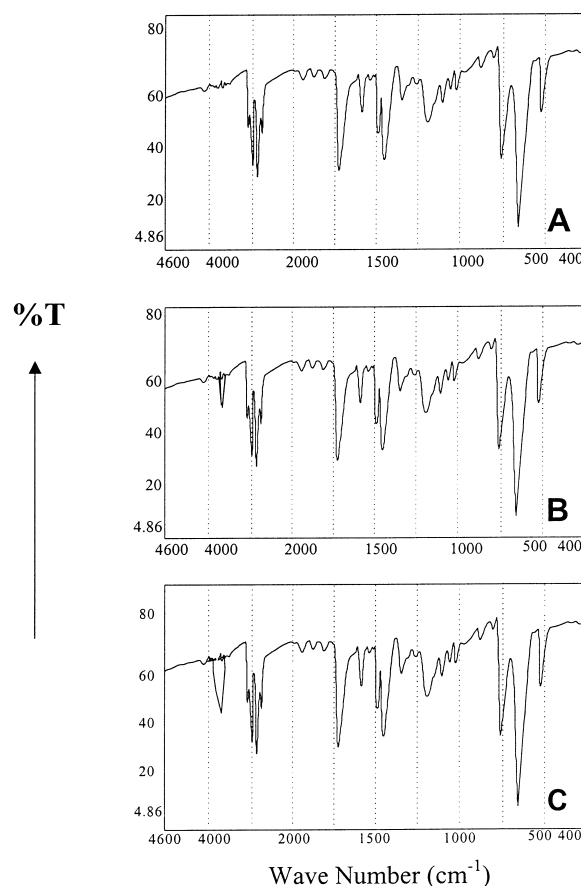
Figure 3   Represantative FTIR spectra of nanoparticles: (A) PMMA; (B) P(MMA/HEMA)-95/5; (C) P(MMA/HEMA)-90/10.

duction of polymers with higher molecular weights.[15] Therefore, one expects higher molecular weights with AIBN with lower concentrations. However, AIBN is less efficient than KPS in producing an effective free radical concentration for polymerization because of the high rate of mutual termination of primary radicals generated in the small volume of a microemulsion droplets.[15,21] Therefore, the difference between the molecular weights of PMMA produced with AIBN or KPS were obtained as 4.04×10^6 or 1.42×10^6, respectively.

Thermal transitions were analyzed by DSC. A typical thermogram of the PMMA/HEMA-90/10 copolymer is given in Figure 2. Note that all of the copolymers produced showed only glass transition temperatures (T_g) (no melting points), which means that they were all amorphous. Table III gives the glass transition temperatures of the polymers produced in this study. The T_g of the PMMA homopolymer is 103°C, while the T_gs of

Table IV   The Comonomer Ratios in the Final Copolymers Produced

Copolymers	Comonomer Ratio (MMA/HEMA)
P(MMA/HEMA)-95/5	96.2/3.8
P(MMA/HEMA)-90/10	93.0/7.0

the P(MMA/HEMA) copolymers were in the range of 95–99°C. Note that the T_g value of PHEMA homopolymer is about 56°C.[32] However, because the HEMA portion in the copolymers was low, the T_gs of the copolymers were somewhat lower than those for the PMMA homopolymer, but not very significantly.

Three represantative FTIR spectra, for PMMA homopolymer and the P(MMA/HEMA)- 95/5 and P(MMA/HEMA)-90/10 copolymers are given in Figure 3. The C—H stretching vibrations at about $2800–2900 \text{ cm}^{-1}$, the C—O absorption peak at about $1000–1100 \text{ cm}^{-1}$, and the C—H in plane bending at about 1500 cm^{-1} are similar for the homo- and copolymers. The only difference on the spectra of the copolymers is the wide and intense band centered at 3550 cm^{-1}, which indicates the (O—H) stretching vibration. By increasing the comonomer ratio, the intensity of this band was also increased.

Three represantative high resolution ^{1}H-NMR spectra for PMMA homopolymer and the P(MMA/ HEMA)- 95/5 and P(MMA/HEMA)-90/10 copolymers are illustrated in Figure 4(A)–(C), 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 the ester methyl resonance of the PMMA homopolymer [Fig. 3(A)], we observed a single peak at 3.64 ppm. On the other hand, for the copolymers, we could identify a signal at 4.1–4.2 ppm different from the PMMA spectra, which belongs to the ester hydroxyethyl methacrylate protons. By comparing these two characteristic peak areas, comonomer ratios were calculated and given in Table IV. Note that, the final comonomer ratios are lower than the initial comonomer ratios due to the different reactivity ratios of MMA and 2-HEMA.[32]
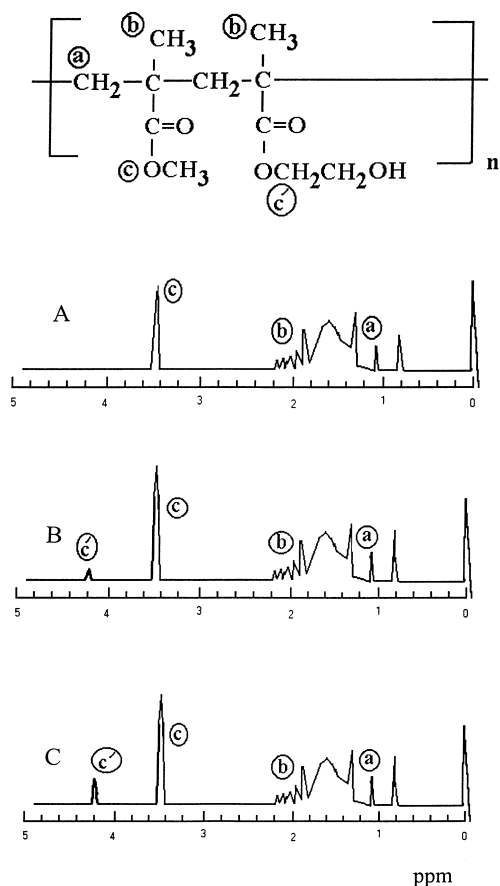
Figure 4 Represantative ^{1}H-NMR spectra of nanoparticles: (A) PMMA; (B) P(MMA/HEMA)-95/5; (C) P(MMA/HEMA)-90/10.

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