Synthesis and Structure of the Poly(methyl methacrylate) Microlatex

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ABSTRACT: Microemulsion polymerization is a new approach for preparing nanosize polymer materials. In this article, a nanosize poly(methyl methacrylate) (PMMA) was prepared by a novel microemulsion polymerization. The kinetics of the polymerization and the effects of the temperature, the monomer, and emulsifier/water ratio on the polymerization were investigated by means of the conversion, the transmittance, and the refractive index measurements. The structure of the obtained PMMA microlatex was studied through transmission electron microscopy (TEM), nuclear magnetic resonance (^{1}H-NMR), and differential scanning calorimetry (DSC). The results show that the polymerization exhibits typical kinetic characteristics of a microemulsion polymerization, i.e., there only exists two rate stages: a stage of increasing rate, and a stage of decreasing rate, and no constant rate stage is observed during the polymerization. The obtained PMMA microparticles are very uniform, regular, and small, being about 17–33 nm in the number-average diameter. The polymer has higher molecular weight (1.71 $\times 10^6$ viscosity average molecular weight), higher tacticity (51% syndiotacticity), and higher glass transition temperature (127°C), much different from the commercial PMMA. Experimentally, a stable and transparent PMMA microlatex with higher polymer content (30–40 wt %), lower weight ratio of emulsifier to water (E/W $\leq$ 0.03) and emulsifier to monomer (E/M $\leq$ 0.05) as well as smaller particle size (d_p < 40 nm), has been prepared, which is very important for the industrialization of the microemulsion polymerization technique. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2839–2844, 2002

Key words: synthesis; structure; emulsion polymerization

INTRODUCTION

Microemulsion polymerization is a new and effective approach for preparing nanosize polymer materials. Since Stoffer and Bone first reported microemulsion polymerization of methyl methacrylate (MMA) and methyl acrylate (MA) in 1980,[1,2]

the technique has attracted much more attention.[3–9] Most researchers have focused on styrene (ST)—a typical and nonpolar monomer mostly used in study of emulsion polymerization, with only limited work with MMA—a polar monomer that can be polymerized to poly(methyl methacrylate) (PMMA)—also an important polymer material. Gan et al.[7] studied kinetics of MMA polymerization in ternary microemulsions and used a long alkyl-chain cationic surfactant to stabilize the system. Pilcher and Ford[8] also used the cationic surfactant as emulsifier and investigated structure and properties of the PMMA microla-

tex. Zhao et al.[9] used the microemulsion polymerization technique to prepare irreversible nearly transparent physical polymeric hydrogels and obtain a PMMA microlatex with 10–30 wt % solidcontent and about 20 nm in particle diameter. Compared to the early research, these studies really develop the topics of microemulsion polymerization, including further understanding of the kinetics of the microemulsion polymerization and preparation of a stable microlatex. Nevertheless, there still exist many problems in the field, such as a higher ratio of emulsifier to water (usually higher than 0.1) and emulsifier to monomer (usually higher than 1), lower polymer content (usually lower than 10–30 wt %), and higher price of the used cationic emulsifier as well as usage of a coemulsifier. Furthermore, the structure of PMMA prepared by microemulsion polymerization of MMA is not as clear. These problems greatly restrict industrialization of the microemulsion polymerization technique, and hence, restrict the application of the technique. Thus, it is very important to reduce the emulsifier content and increase the monomer content in the feed, and hence, increase the polymer content in the obtained latex. In this article, we try to prepare a PMMA microlatex with lower emulsifier/water ratio ($\leq$0.03), lower emulsifier/monomer weight ratio ($\leq$0.05) and higher polymer content (30–40 wt %) without a cationic emulsifier and coemulsifier via a new microemulsion polymerization technique, to study the polymerization kinetics and structure of the PMMA microlatex, and hence to provide a new approach for preparing nanosize polymer materials.

EXPERIMENTAL

Materials

Methyl methylacrylate (MMA) was obtained from the Chengdu Rong Feng Chemical Factory (China), and was purified by rectification. Potassium persulfate (KPS) and sodium dodecyl sulfate (SDS) were products of the Beijing Chemical Factory (China) and the Wu Han Chemical Factory (China), respectively, and both chemicals were of analytical purity. Deionized water was used for all experiments.

Synthesis of the Poly(methyl methacrylate) Microlatex

The poly(methyl methacrylate) (PMMA) microlatex was synthesized through microemulsion polymerization by a semicontinuous feeding using KPS as the initiator and SDS as the emulsifier in a three-neck 250-mL round-bottom flask equipped with a reflux condenser, a mechanical stirrer, and a thermometer. The reaction temperature was 70–90°C, and the reaction time was 3–5 h. The pure PMAA was obtained by precipitating the microlatex using 5 wt % CaCl$_2$ aqueous solution, washing the precipitates by deionized water, and then heating the clear precipitate at 40°C in a vacuum.

Characteristics

Conversion, Transmittance, and Refractive Index

The conversion x% of the polymerization was determined by weight method and calculated as follows:

$$x\% = (W_1/W_2) \times (1/W) \times 100\% \qquad (1)$$

where the W_1 and W_2 were weights of the dry polymer and the polymer latex, respectively. The W was weight percent of the monomer in the feed.

The transmittance of the polymer latex was measured using a 721A type spectrophotometer at 500 nm and ambient temperature, and the refractive index of the polymer latex was detected by an Abbe refractometer at ambient temperature.

Particle Size

The particle size of the PMMA latex was determined by transmission electron micrograph. The procedure was as follows.

The polymer latex was first diluted to about 4 wt % concentration with deionized water and then placed on a Cu grid for about 1 min. The excess latex was removed by touching a piece of filter paper to the drop. After that, a drop of 1% phosphorus wolfram acid solution was placed on the grid for another minute to stain the sample. The transmission electron microscopy was performed on a H-600 type instrument. Diameters of at least 300 randomly chosen particles were measured directly from the micrograph and the number average diameter d_p was finally calculated using eq. (2), where d_i was the diameter of a particle and n_i is the number of the particles with d_i diameter.
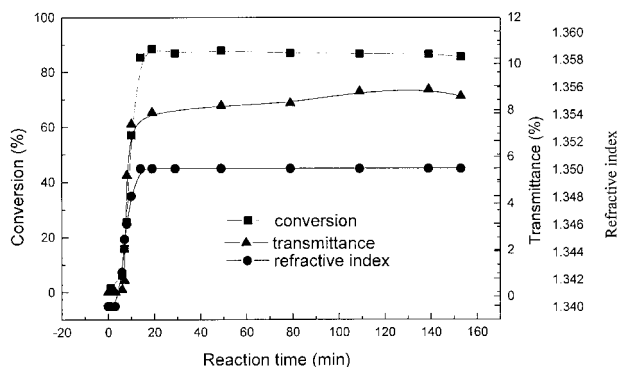
$$d_p = \sum d_i/n_i \qquad (2)$$

Figure 1 Effects of the reaction time on the conversion, the transmittance, and the refractive index of the polymer microlatex.

Molecular Weight

The molecular weight of the obtained PMMA was measured by viscometry according to the literature[10] and determined as follows:

$$[\eta] = KM^a \tag{3}$$

where M is the viscosity average molecular weight of the PMMA, K and α are 7.7×10^3 (mL/g) and 0.7,[11] respectively, for PMMA in acetone at 30°C. $[\eta]$ is the intrinsic viscosity that was measured via viscometry with an Ubbelohde viscometer.

Glass Transition Temperature

The glass transition temperature (T_g) of the PMMA was measured through a 2910 type differential scanning calorimeter (DSC) (America TA. Co.) in nitrogen atmosphere. The scan rate of the temperature was 10°C/min, and the temperature range was from 295 to 500 K.

Tacticity

The tacticity of the PMMA was measured by the AVANCE 300 type DIGITAL NMR instrument (Switz BRUKER Co.) at 400 MHz and ambient temperature using $CDCl_3$ as solvent. The tacticities of the samples were calculated from the integrated ratios of the syndiotactic (rr), isotactic (mm), and heterotactic (mr) triad signals.[7,12,13]

RESULTS AND DISCUSSIONS

Figure 1 shows variation of the conversion, the transmittance, and the refractive index of the polymer latex with the reaction time. It can be seen that these three variables have the same change trends with the reaction time. As polymerization proceeds, the three values increase in a very short time, i.e., in about 6 min. With a further increase of the reaction time, the values change only slightly, typically characteristic of a microemulsion polymerization. In other words, there exist two rate stages in the MMA's microemulsion polymerization, i.e., increasing rate stage and decreasing rate stage, and there is no constant rate stage observed, which is much different from the conventional emulsion polymerization. In a conventional emulsion polymerization, the size of a monomer droplet is much larger than that of a micelle. The polymerization hence occurs mainly in the micelle while the monomer droplet, here, mainly plays the role of providing the monomer to the reactive micelle particles until the monomer is consumed, behaving as a constant rate region during the reaction.[14] In a microemulsion polymerization, however, both micelles and monomer droplets are nucleation sites for the polymer particle formation due to their near and very small size, and hence, their nearly equal capacity to capture radicals. With the polymerization, both the micelles and the monomer droplets consume the monomer, the monomer concentration in the system decreases rapidly, resulting in a rapid reduction in the reaction rate, leading to nearly constant conversion, transmittance, and refractive index of the latex after a very short reaction time. From Figure 1, a very interesting result is obtained IN that, with the polymerization, the transmittance of the latex increases, rather than decreases, indicating a phase transition of the system and a unique kinetics characteristics of the microemulsion polymerization.

Figure 2 shows that the higher temperature (80°C) is more helpful to increase the conversion than the lower temperature (70°C), but the temperature does not affect the trend of the conversion with the reaction time, indicating the same kinetics of the microemulsion polymerization of MMA at these two temperatures.

Figure 3 shows that, within 4 hours, increase of the monomer MMA content in feed causes a decrease in the transmittance and an increase in both of the conversion and the refractive index of the latex. With increase of the monomer content in feed from 10 to 40 wt %, the weight ratio of the emulsifier to the monomer decreases from 0.26 to 0.04 as the emulsifier/water weight ratio is 0.03,
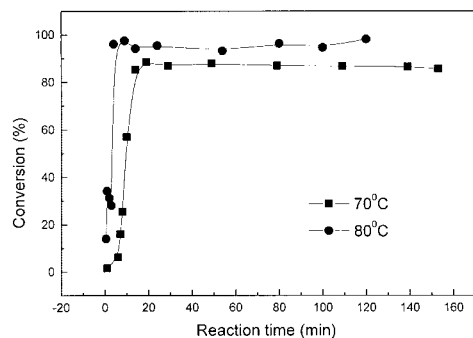
Figure 2 Effect of the reaction time on the conversion of the polymer latex at different temperatures.

(a)

(b)

Figure 4 Transmission electron micrographs of the obtained PMMA microlatex with (a) 30 wt % and (b) 40 wt % monomer contents.

and the encounter rate of intermonomer molecules in the micelles increases greatly, resulting in an increase in the conversion. At the same time, increase of the MMA content in the feed leads to an increase in polymer content in the latex and an increase in polymer particle size due to the decrease of the emulsifier/monomer ratio. The higher polymer content would result in an increase in refractive index of the latex because the refractive index of both monomer and water are lower than that of the corresponding polymer. The decrease of the latex transmittance resulted from the increase of particle size with decrease of emulsifier/monomer ratio (see Fig. 4) From Figure 4 it is obvious that, when the monomer content in feed is 30 and 40 wt %, the number-average diameters of the obtained polymer particles are 17 and 42 nm, respectively.

Figure 5 shows transmission electron micrographs of the obtained PMMA microlatex at different emulsifier/water weight ratios while Table I gives the corresponding number-average diam-
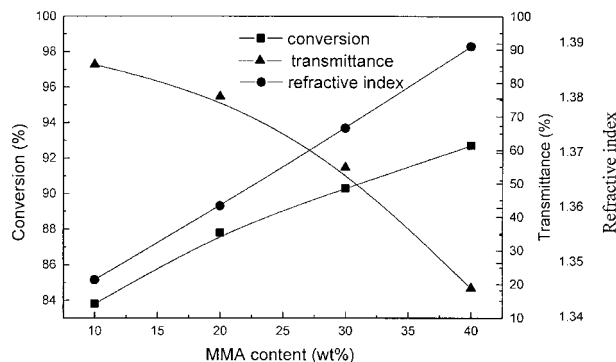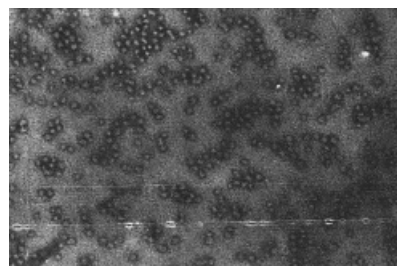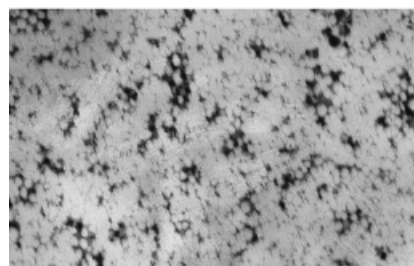

Figure 3 Effects of the MMA content in feed on the conversion, the transmittance, and the refractive index of the polymer microlatex.

eters of the polymer particles. From Figure 5, it can be seen that the polymer particles are very uniform and are nearly spherical. The data of Table I, calculated by statistical measurements of the particles in the micrographs, indicate that the particle sizes are very small. Even when the emulsifier/water weight ratio is only 0.01, the particle size is only 33 nm in diameter. With an increase of the emulsifier/water weight ratio, the particle shape remains nearly unchanged while the particle size decreases, indicating that the particle size can be controlled by adjusting the emulsifier/water ratio. Combing the results of Figures 4 and 5, very important information is obtained, namely that the nanosize PMMA particles can be obtained conveniently by the new microemulsion polymerization using higher monomer content in feed and lower emulsifier/water ratio. This result is very important and practical, and useful for industrialization of the microemulsion polymerization technique.

The ^{1}H-NMR spectrum (Fig. 6) of the obtained PMMA shows three peaks appearing at the highest field, which represent methacrylate methyl groups of varying tacticity.[13] The band at about 0.90 ppm represents syndiotactic (rr) methyl, the band at about 1.06 ppm arises from atactic (mr) methyl groups and the weak band at about 1.25 ppm represents the resonance of the isotactic
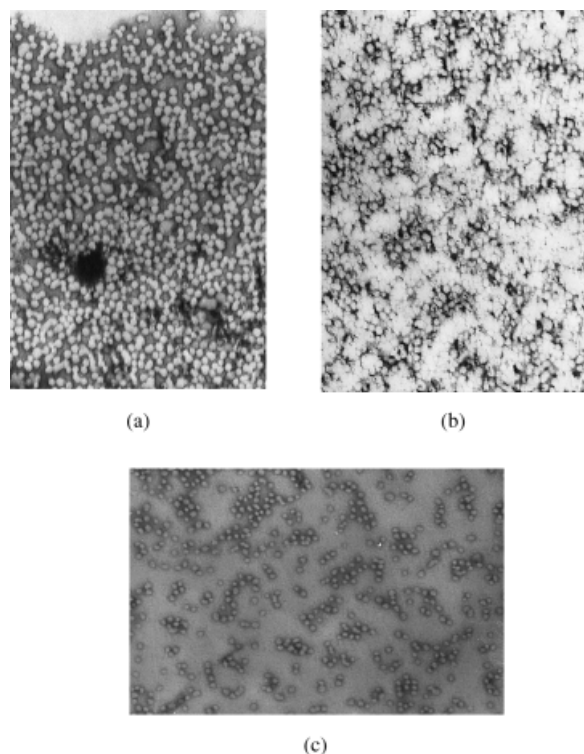
Figure 5 Transmission electron micrographs of the obtained PMMA microlatex with (a) 0.01, (b) 0.02, and (c) 0.03 emulsifier/water weight ratios.

Figure 6 ^{1}H-NMR spectrum of the obtained PMMA.

(mm) methyl groups.[13] The corresponding isotactic, atactic, and syndiotactic methylene groups absorb in the chemical shift range from 1.4 to 2.4 ppm[13] and the methyl ester protons resonate at the lowest near 3.6 ppm.[13] From Figure 6 the tacticity of the sample was calculated by the integrated ratios of the rr, mm, and mr, which, together with the molecular weight, are shown in Table II.

From Table II, it is obvious that the PMMA prepared by the new microemulsion polymerization has higher molecular weight and a relatively regular molecular structure which will certainly result in higher glass transition temperature (T_g) (see Fig. 7)

From Figure 7 it can be seen that the glass transition temperature of the obtained PMMA is about 127°C, much higher than that of the commercial PMMA (T_g = 105°C),[7] and there is an exothermic peak appearing at the curve. It has been known that the T_g of PMMA depends greatly on the tacticity of the polymer. Tacticity of the PMMA prepared by the new microemulsion polymerization is 51% rr, larger than that of the commercial PMMA (43% rr).[7] The higher ratio of the syndiotacticity (rr) produces a special and regular structure, and hence, leads to an increase in the T_g. This also can be explained by the "pauci-chain theory."[15] In a microparticle formed via microemulsion polymerization, there only exist a very few, sometimes even only one, polymer chains, which make the polymer chain orient regularly. The regular structure of polymer in a particle

Table I Number Average Diameters of the PMMA Particles with Different Emulsifier/Water Weight Ratios

Emulsifier/water weight ratio	0.01	0.02	0.03
Number average diameter d_p (nm)	33	25	17

Monomer content in feed is 30 wt %.

Table II Viscosity Average Molecular Weight and Tacticity of the PMMA Obtained by the Semicontinues Microemulsion Polymerization

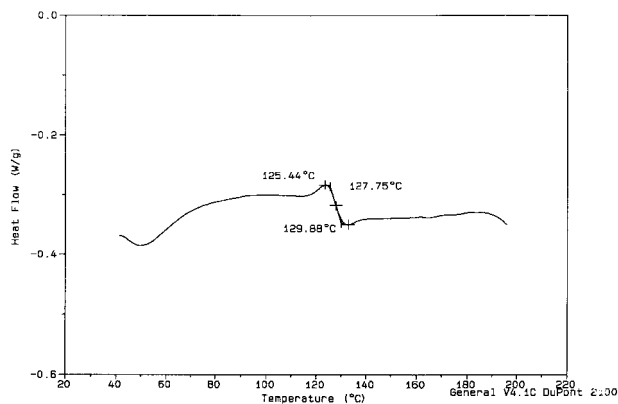|	Tacticity		
M_η	rr (%)	mm (%)	mr (%)
1.71×10^6	51.0	9.50	39.50

Figure 7 DSC curve of the obtained PMMA.

results in an increase in the T_g. The appearance of the exothermic peak can be attributed to entanglement between segments.[15] According to the "pauci-chain theory," conformation of the pauci-chain is controlled by the kinetics of the polymerization. When the temperature comes near to T_g, the segments have sufficient capacity for motion due to fewer entanglements in a pauci-chain, resulting in entanglement between segments that lead to a decrease and, hence, a release of energy; thus, there appears an exothermic peak in the DSC curve.

CONCLUSIONS

Microemulsion polymerization of MMA via semicontinuous feeding could prepare a stable and transparent PMMA microlatex with higher polymer content (30–40 wt %), lower weight ratio of emulsifier to water (E/W $\leq$ 0.03), and emulsifier to monomer (E/M $\leq$ 0.05) as well as smaller particle diameter ($\underline{dp}$ < 40 nm). The prepared PMMA has special microstructure compared with commercial PMMA, including higher molecular weight, higher syndiotacticity, and hence, higher T_g, which give this PMMA special properties. Microemulsion polymerization provides a new approach for preparing nanosize polymer materials.

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