3454 *Macromolecules* **1998,** *31,* 3454−3460

Structures and Properties of Poly(methyl methacrylate) Latexes Formed in Microemulsions

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Received November 24, 1997; Revised Manuscript Received March 23, 1998

ABSTRACT: Polymerizations of methyl methacrylate (MMA) in ternary oil-in-water microemulsions using the cationic surfactants stearyltrimethylammonium chloride (STAC), cetyltrimethylammonium bromide (CTAB), or a mixture of nonionic nonylphenoxy poly(ethylene glycol) surfactants produce latex particles having weight average diameters of 17−41 nm. The small particle sizes and high molecular weights ($M_w = (2.5-6.5) \times 10^6$) indicate that most samples consist mainly of particles containing one polymer chain. The particle size varies little when the surfactant to monomer weight ratio is ≥1. Polymerizations using STAC at 35 °C produce smaller particles than at 60 °C. Radical polymerization of MMA in microemulsions produces predominantly syndiotactic PMMA containing 58−61% *rr* triads at 60 °C and 63−65% *rr* triads at 35 °C. The high molecular weight PMMA samples have T_g = 125−126 °C.

Introduction

Polymerization of nonpolar monomers in oil-in-water microemulsions produces latex particles <50 nm in diameter, compared with those >100 nm from conventional emulsion polymerizations.[1−4] The initial microemulsion is a thermodynamically stable mixture of monomer, surfactant, and water in which the amount of surfactant often exceeds the amount of monomer, and the monomer is swollen into surfactant micelles. The first polymerizations in microemulsions employed an aliphatic alcohol as a cosurfactant.[5−10] Recently attention has been focused on kinetics and mechanisms of polymerizations in three-component microemulsions,[11−24] but little attention has been paid to the structures and the properties of the polymers. Here we report the tacticities and the glass transition temperatures of poly(methyl methacrylate) (PMMA) formed in ternary microemulsions.

Polymerizations in one dimension by confinement of vinyl monomers in the narrow channels of clathrate crystals of urea, thiourea, cyclotriphosphazines, and deoxycholic acid give more highly isotactic or more highly syndiotactic polymers than polymerizations in solution or in bulk.[25−31] Polymerization reactions confined to two dimensions in lipid bilayers and in monolayer films have also been studied,[32−34] but the only report of tacticity of which we are aware is predominantly syndiotactic poly(methacrylic acid) from polymerization of vesicles of dioctadecyldimethylammonium methacrylate.[35,36] We wondered if confinement of the monomer in the small volume of a microemulsion might influence the microstructure of the polymer formed therein. Unlike polymers formed in one- and two-dimensional confined spaces, the polymers formed in these small spheres might be produced in quantities large enough for commerce.

Some of the smaller latexes formed in microemulsions contain an average of little more than one macromolecule per particle. For restricted volume to affect the tacticity of the polymer, the relative free energies of activation of the propagation steps leading to the various stereochemical sequences of repeating units must differ from those of solution and bulk polymerization. In the small volume of a latex particle formed in a microemulsion, the polymer chain must have more gauche conformations than in its unperturbed state, especially near the surface of the particle, so that the path of its random walk turns back into the particle, as illustrated in Figure 1. For example, one molecule of PMMA having a molecular weight of 1×10^6 and a density of 1.20 g/cm^3 occupies a sphere of diameter 13.8 nm. In a Θ solvent or in the bulk amorphous phase, the unperturbed root-mean-square end-to-end distance of that PMMA molecule is 55 nm,[37] and the sphere that would enclose all of its chain segments in most conformations is even larger. Therefore, the polymer formed in a microemulsion is conformationally restricted. If the propagating chain end is also restricted during polymerization, the tacticity of the polymer may be altered.

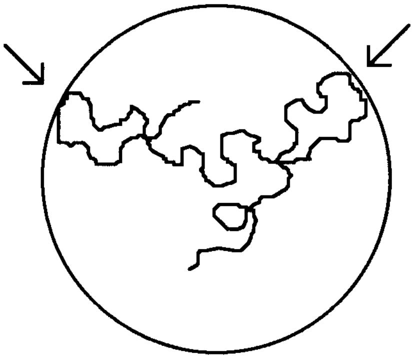

Figure 1. Polymer chains at the inner surface of the sphere must have gauche conformations to turn them back into the sphere.

We report here the particle sizes, molecular weights, tacticities, and glass transition temperatures of PMMA formed in microemulsions. MMA was chosen as the monomer because changes in tacticity are easily determined by NMR spectroscopy,[38,39] and the tacticity of PMMA is known to depend strongly on the temperature of radical polymerization.[40−46]

Experimental Section

Materials. Stearyltrimethylammonium chloride (STAC, >97%), cetyltrimethylammonium bromide (CTAB, >98%), and dodecyltrimethylammonium bromide (DTAB, >99%) from TCI,

S0024-9297(97)01722-1 CCC: $15.00

Table 1. Compositions of Microemulsions Based on Literature Procedures[12,22]

surfactant	amount, g	H_2O, mL	MMA, g	initiator	amount, mg
STAC	2.8	30	2.5	ascorbic acid 30% H_2O_2	30 370
Triton N-150	4.64	28	2.73	ascorbic acid	28
Triton N-57	0.54			30% H_2O_2	400
DBS	0.012				
STAC	2.8	30	2.54	KPS	2
CTAC	2.5	26	2.14	KPS	1.5
CTAB	3.2	31	3.2	AIBN	1.5

Table 2. Particle Sizes and Molecular Weights of PMMA Produced at Varied Temperatures and Surfactant to Monomer Weight Ratios[a]

sample description	D_n, nm[e]	D_w, nm	DLS, nm	$M_w \times 10^{-6}$	M_w/M_n	n_p[f]
STAC−Redox[b,c]	15	17	21	0.156	2.2	6.5
Triton−Redox[b,c]	27	30	36	3.0	2.0	2.4
STAC−KPS[b,d]	26	32	49	4.4	1.8	2.2
CTAC−KPS[b,d]	26	34	49	2.9	2.2	4.1
CTAB−AIBN[b,d]	28	37	44	1.4	2.2	11
STAC−KPS[d]						
$S = 0.01$	70	80	98	5.5	1.5	32
$S = 0.1$	24	31	44	7.0	2.1	1.3
$S = 0.5$	25	28	39	6.5	1.4	1.0
$S = 1$	26	27	41	4.4	1.2	1.3
$S = 2$	22	26	38	5.0	1.6	1.0
$S = 3$	21	26	42	5.8	1.7	1.0
STAC-AIBN[d]						
$S = 0.1$	39	62	69	5.0	3.9	16
$S = 0.5$	35	41	56	5.9	1.6	3.7
$S = 1$	24	28	42	5.4	1.6	1.2
$S = 2$	22	26	40	4.5	1.5	1.1
$S = 3$	27	31	45	5.4	1.6	1.6
CTAB−KPS[d]						
$S = 0.1$	55	63	51	4.9	1.5	17
$S = 0.5$	21	28	45	6.5	2.5	1.0
$S = 1$	20	25	38	4.2	2.0	1.0
$S = 2$	19	23	38	2.7	1.7	1.2
$S = 3$	18	21	38	2.5	1.4	1.0
Triton N-150/Triton N-57/DBS[c]						
$S = 1$	37	45	64	4.0	1.9	7.3
$S = 2$	34	41	58	2.7	1.8	8.1
$S = 3$	29	33	52	3.0	1.4	3.6
STAC−Redox[c]						
$S = 0.01$	44	63	72	0.075	2.8	1100
$S = 0.1$	36	44	54	0.090	1.8	300
$S = 0.5$	22	28	38	0.035	2.0	180
$S = 1$	19	24	32	0.041	2.1	92
$S = 2$	11	18	29	0.036	4.1	39

[a] Microemulsions contained 30 mL of water, 1.5 g of MMA, and 1 wt % of KPS, 0.5 wt % of AIBN, or 0.03 g ascorbic acid and 0.4 g 30% hydrogen peroxide. [b] See Table 1. [c] 35 °C. [d] 60 °C. [e] Standard deviations ranged from 4 to 12 nm. [f] Average number of polymer chains per latex particle calculated from D_w, M_w, and PMMA density of 1.18 g cm^{-3}.

sodium dodecylbenzenesulfonate (DBS) from Polysciences Inc., Triton N-150 from Union Carbide, and Triton N-57 from Aldrich were used as received. Methyl methacrylate (MMA) from Aldrich was vacuum distilled. Potassium persulfate (KPS) from Sigma, ascorbic acid from Aldrich, and a 30% hydrogen peroxide solution from Fisher were used as received. 2,2′-Azobisisobutyronitrile (AIBN) from Aldrich was recrystallized from ethanol. Water was deionized and distilled, and had resistivity >1 MΩ cm^{-1} after exposure to air.

Polymerizations. Typical compositions of microemulsions that have been polymerized are given in Table 1. The general procedure is illustrated by the example in Table 2 using STAC at a surfactant to monomer weight ratio (S) of $S = 2$ with KPS as the initiator.

To 3.0 g of STAC in a three-neck 50 mL round-bottom flask equipped with a condenser, a mechanical stirrer, and a nitrogen inlet was added 29.0 mL of deionized water. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until polymerization was finished. The flask was placed in a 60 °C oil bath, and the mixture was stirred for 1 h until it became homogeneous. MMA, 1.50 g, was added, and the solution was stirred for 30 min to form a transparent microemulsion. A solution of 15.0 mg of KPS (1 wt % relative to monomer) in 1.0 mL of deionized water was added, and the solution was stirred for 4 h in an oil bath at 60 °C to produce a transparent solution with a bluish tint. The sample had no odor, indicating that no monomer remained.

The polymerizations using the Triton surfactants and a trace of DBS at differing surfactant-to-monomer ratios were performed by first mixing the surfactants and water. MMA was added and stirred for 30 min. For redox initiation the ascorbic acid was dissolved in 1 mL of deionized water, and the hydrogen peroxide was added to this solution immediately before addition to the microemulsion.

Particle Size Measurements. An aliquot of the latex was diluted 15:1 with deionized water and sonicated for 1 h. A drop of this sample was placed on a Formvar-coated Cu grid for 1 min, the excess latex was removed by touching a piece of filter paper to the drop, and the grid was dried in air for 1 min. A drop of 1% uranyl acetate solution was placed on the grid for 1 min to stain the sample, the excess solution was removed with filter paper, and the grid was dried in air. Transmission electron microscopy was performed using a JEOL 100-CS2 instrument with 100 μA filament current, 80 kV accelerating voltage, and the electron beam normal to the sample plane. Diameters of at least 50 randomly chosen particles were measured directly from the micrograph negatives using an optical microscope with a calibrated stage. No size standards were used, and reported sizes were calculated from the nominal instrument magnification. The number and weight average diameters were calculated using eqs 1 and 2 where D_i is the diameter of a particle and n is the number of particles measured.

$$D_n = \sum D_i/n \tag{1}$$

$$D_w = \sum D_i^4/\sum D_i^3 \tag{2}$$

Particle sizes were also measured by dynamic light scattering (DLS). The signal from the scattered light of an argon ion laser (Spectra-Physics 2020−05) was collected from latex samples diluted 20:1 at a scattering angle of 90° and analyzed using an ALV-5000 digital correlator.

Precipitation of Polymer Samples. To 5 mL of latex dispersion in a 30 mL beaker was added 20 mL of methanol and mixed, and the mixture was allowed to stand overnight. The precipitated polymer was vacuum filtered, washed successively with methanol and water, and dried in a vacuum desiccator for 24 h at 60 °C. No surfactant peaks were detected in the ^1H NMR spectra of $CDCl_3$ solutions of the polymers.

Molecular Weight Analyses. Molecular weights were measured by size exclusion chromatography (SEC) using a series of 10^6 Å, 10^5 Å, and 10^4 Å 10 μm PLgel columns from Polymer Laboratories at a flow rate of 1.0 mL/min at 40 °C using a Hewlett-Packard (HP) series 1100 chromatograph. The sample size injected was 20 μL of a 1.0 mg/mL solution in THF. The measurements were calibrated with polystyrene standards having molecular weights of 6 000 000, 900 000, and 233 000 in one solution and 1 800 000, 390 000, and 100 000 in a second solution. Molecular weights were calculated using the HP Chemstation software and a GPC Macro supplied by HP. Values were not corrected to PMMA standards by universal calibration because there were already large uncertainties in the measurements from possible shear degradation. Such corrections would increase the reported molecular weights.

Glass Transition Temperatures. T_g values were measured using a Perkin-Elmer Model DSC-2 differential scanning calorimeter and 10 mg samples at a scan rate of 10 deg/min from 300 to 450 K followed by rapid cooling. The instrument was calibrated with naphthalene (mp = 353.4 K) and indium (mp = 429.8 K). Since the T_g from the first measurement of each sample often was higher than that from subsequent measurements, T_g is reported as the average of measurements 2−4 using the midpoint method. The T_g values of the standards were reproducible to better than 0.2 K. The T_g of independent samples from one polymerization was reproducible to ±1 K.

Tacticity Measurements. ^{1}H NMR analyses were performed at 400 MHz using $CDCl_3$ solutions at room temperature. The tacticities of the samples were measured from the integrated ratios of the syndiotactic (*rr*), isotactic (*mm*), and heterotactic (*mr*) triad signals.[39] NMR analyses of a few samples were performed at 110 °C in deuterated *o*-dichlorobenzene to improve the resolution of the spectra. The tacticities measured at 110 °C were identical with those measured at room temperature. Only results from room-temperature spectra are reported. The tacticity analyses of the PMMA produced using STAC and redox initiation were perfomed at 300 MHz.

Results

Procedures for polymerization of methyl methacrylate (MMA) in microemulsions were modified from ones already known to produce small latex particles. Typical compositions are in Table 1. Gan and co-workers[22] produced PMMA in ternary microemulsions using the cationic surfactants stearyltrimethylammonium chloride (STAC), cetyltrimethylammonium bromide (CTAB), and dodecyltrimethylammonium 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 and more stable the latex particles. The results in Table 2 show smaller particles produced using CTAB (C_{16}) than STAC (C_{18}) cationic surfactants. Kaler and co-workers also have produced small latexes from styrene and from several different methacrylic esters using cationic surfactants.[15,16,19,20,23,24] Larpent and Tadros[12] found optimum mixtures of nonionic surfactants (Triton N-150 and Triton N-57, nonylphenoxy poly(ethylene glycols) having averages of 15 and five 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.

All microemulsion compositions in Tables 1 and 2 having a surfactant to monomer weight ratio $S \geq 1$ lie within the single phase regions of previously published phase diagrams for the ternary surfactant/MMA/water mixtures.[12,16,22] Polymerizations were performed with both water-soluble and oil-soluble thermal initiators at 60 °C and with a redox initiation mixture of hydrogen peroxide and ascorbic acid at 35 °C. The sizes and molecular weights of the PMMA latexes formed were similar to those previously reported. Prior to polymerization the samples containing surfactant to monomer weight ratios of $S \geq 1$ were transparent at the reaction temperature, and as polymerization proceeded, the mixtures became turbid or developed a bluish tint, indicating the presence of colloidal particles. In contrast, samples containing cationic surfactants at $S \leq 0.1$ were turbid initially and remained so during polymerization. In one case, using STAC/monomer = 0.1 and potassium persulfate as initiator, the mixture started turbid and cleared somewhat to give a dispersion with a bluish tint after polymerization.

Stability of Latexes. Of the cationic surfactants, STAC produced the most stable latexes. PMMA particles from DTAB microemulsions (not reported in the tables) precipitated immediately after polymerization was complete. Although Full and co-workers[23] obtained stable polystyrene latexes in microemulsions prepared with salt solutions and mixtures of dodecyltrimethylammonium bromide and didocedyldimethylammonium bromide, we did not obtain stable microemulsions using only dodecyltrimethylammonium bromide and the same amount of MMA as with the longer chain cationic surfactants. The latexes produced using CTAB aggregated slightly after standing for about one month. The latexes produced using STAC at $S \geq 1$ showed no visible signs of coagulation for up to 6 months. Slight coagulation was observed in samples from STAC−KPS at $S = 0.1$ and $S = 0.5$ after 1 week.

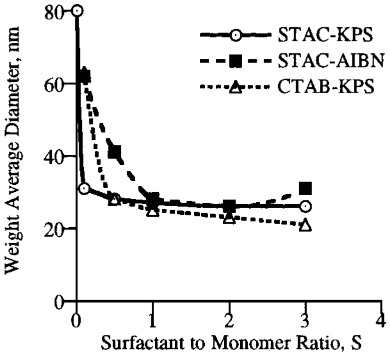

Figure 2. Particle sizes decrease with increasing surfactant to monomer weight ratio.

Polymerizations using a mixture of nonionic surfactants were carried out at 35 °C with ascorbic acid/hydrogen peroxide as initiator. The mixtures of MMA and Triton surfactants did not form stable microemulsions at 60 °C. The latexes obtained with the nonionic surfactants at 35 °C and $S \geq 1$ showed no sign of coagulation over six months, but the particles obtained at $S = 0.1$ and 0.5 precipitated shortly after polymerization. One sample prepared with the Triton surfactant mixture (Table 1) showed no coagulation after 2 years.

Particle Sizes. The sizes measured by transmission electron microscopy (TEM) and by dynamic light scattering (DLS) generally agreed well. Sizes from DLS were slightly larger than the sizes from TEM as expected, since DLS measures a diffusion coefficient due to the particle and the hydrated counterions in the electrical double layer. The diffusion coefficient is used to calculate a *z*-average diameter from the Stokes−Einstein equation, whereas the number average and weight average diameters are reported from the TEM measurements. Although we excluded obvious aggregates of the particles from the measurements of the electron micrograph negatives, some aggregates may have been counted. Aggregates are counted in the DLS measurements. Consequently the diameters reported in Table 2 are upper limits, and there is not always good agreement between the TEM and the DLS results.

The dependence of particle sizes on surfactant to monomer weight ratios is reported in Table 2 and Figure 2. At $S = 0.01$, a ratio typical of normal emulsion polymerizations, the particles were larger than those formed with more surfactant, but quite small for an emulsion polymerization due to the small amount of monomer (5 wt %) and perhaps to the C_{18} surfactant. TEM images of the $S = 0.1$ and $S = 3$ samples made with CTAB are in Figures 3 and 4. Because the average size of the particles obtained with STAC−KPS and $S = 0.1$ did not correlate with results from other S ratios,

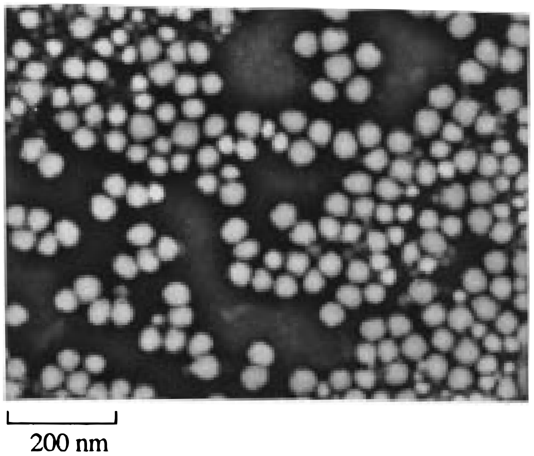

Figure 3. Transmission electron micrograph of the sample CTAB−KPS, $S = 0.1$.

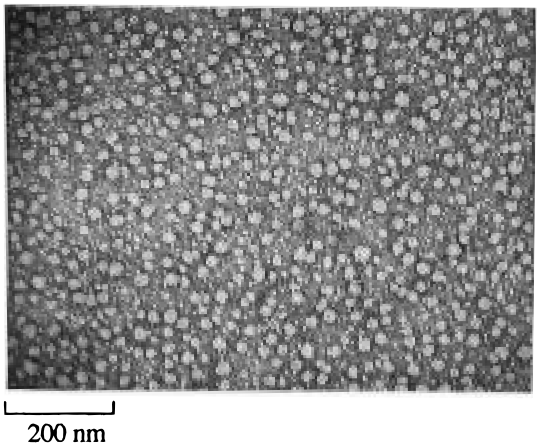

Figure 4. Transmission electron micrograph of the sample CTAB−KPS, $S = 3.0$.

the experiment was duplicated with the same results.

Sizes of the PMMA particles produced in microemulsions using STAC and the oil-soluble initiator, AIBN, are reported in Table 2 and Figure 2. Again at $S < 1$ particle sizes decreased with increasing S, and at $S \geq 1$ the particle sizes did not vary significantly.

The sizes of the latex particles prepared using the nonionic surfactants decreased with increasing surfactant to monomer weight ratios at $S \geq 1$, but the particles were larger than those produced using cationic surfactants, even though the polymerizations were performed at 35 °C. Using STAC, the particles produced at 35 °C were smaller than those produced at 60 °C.

Molecular Weights. The PMMA samples prepared in microemulsions have $M_w = (2.5-6.5) \times 10^6$ using cationic surfactants and thermal initiators, or using nonionic surfactants and a redox initiator. These M_w values are typical of PMMA and polystyrene prepared in microemulsions.[22,24] Some of the molecular weight distributions in Table 2 were difficult to measure because of tailing of the chromatographic peak, which would affect M_n more than M_w. It is also possible that shear degradation of the PMMA broadened some of the molecular weight distributions. A M_w/M_n value of 1.4 was obtained from a polystyrene standard of $M_w = 6 \times 10^6$ reported by the supplier to have $M_w/M_n = 1.2$. Much lower molecular weights were obtained using STAC with hydrogen peroxide/ascorbic as redox initiator, which we attribute to chain transfer to Cl_2 produced from chloride ion and hydrogen peroxide.[47]

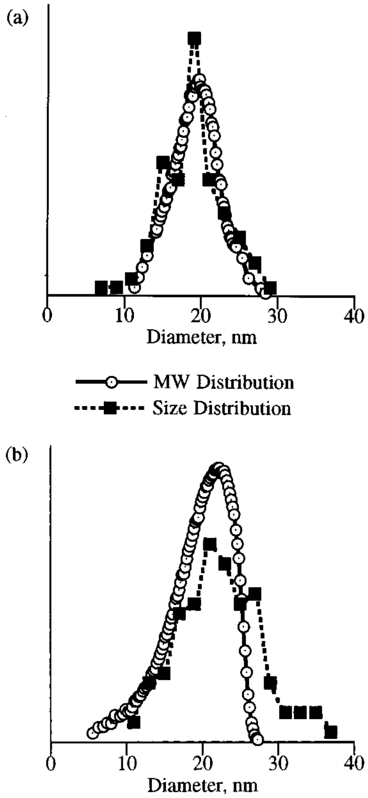

Figure 5. Particle size distributions as weight fraction vs particle diameter from TEM measurements (closed symbols) and from SEC molecular weights (open symbols) converted to particle diameter assuming $d = 1.20$ g cm^{-3} for (a) sample STAC−KPS, $S = 3$, $n_p = 1.0$, and (b) CTAB−KPS, $S = 3$, $n_p = 1.0$. Each graph is normalized so that the two distributions have equal areas.

Number of Polymer Chains per Latex Particle. The number of polymer chains per particle, n_p, was calculated for each PMMA sample from the weight average mass of a particle according to eq 3, where M_p

$$n_p = M_p N_A / M_w \qquad (3)$$

$$M_p = V_p d \qquad (4)$$

= mass of a particle, $N_A = 6.02 \times 10^{23}$ mol^{-1}, M_w = weight average molecular weight, V_p = volume occupied by a particle corrected for a volume of surfactant assumed to be a monolayer, d = density of particle = 1.18 g cm^{-3} (measured by pycnometry), and 100% conversion of monomer to polymer was assumed. Full and co-workers[23] used the number-average radius and weight-average molecular weights in their similar calculations, and in some cases, they obtained $n_p < 1$, which is physically impossible. Gan and co-workers[22] used the hydrodynamic radius from dynamic light scattering and M_w for their calculations of n_p. The results reported in Table 2 show $n_p < 2$ for most of the latexes produced using cationic surfactants and $S \geq 1$. Lesser S ratios gave larger particles and $n_p > 2$, and the combination of STAC with hydrogen peroxide/ascorbic acid gave much larger n_p values due to lower molecular weights.

The particle sizes and molecular weight distributions of two samples having n_p values of 1.0 are superposed in Figure 5. In the limit of exactly one macromolecule per particle, the size distributions measured by TEM

Table 3. Tacticities and Glass Transition Temperatures[a]

sample[b]	*rr*	*mr*	*mm*	T_g, °C
Plexiglas	0.43	0.40	0.17	105
STAC−Redox	0.58	0.30	0.12	114
Tritons-Redox	0.66	0.31	0.03	123
STAC−KPS				
$S = 0.01$	0.60	0.35	0.05	122
$S = 0.1$	0.60	0.35	0.05	126
$S = 0.5$	0.59	0.34	0.07	
$S = 1$	0.59	0.35	0.06	125
$S = 2$	0.59	0.35	0.06	
$S = 3$	0.59	0.35	0.06	126
STAC-AIBN				
$S = 0.1$	0.61	0.32	0.07	
$S = 0.5$	0.61	0.35	0.04	126
$S = 1$	0.60	0.35	0.05	126
$S = 2$	0.58	0.34	0.08	
$S = 3$	0.60	0.35	0.05	125
CTAB−KPS				
$S = 0.1$	0.61	0.33	0.06	
$S = 0.5$	0.61	0.34	0.05	125
$S = 1$	0.61	0.34	0.05	125
$S = 2$	0.60	0.35	0.05	
$S = 3$	0.59	0.35	0.06	126
STAC−Redox				
$S = 0.01$	0.65	0.32	0.03	125
$S = 0.1$	0.66	0.31	0.03	124
$S = 0.5$	0.64	0.32	0.04	122
$S = 1$	0.64	0.32	0.04	122
$S = 2$	0.63	0.32	0.05	121
Triton-Redox				
$S = 1$	0.64	0.32	0.04	125
$S = 2$	0.64	0.32	0.04	126
$S = 3$	0.63	0.32	0.05	126

[a] Error limits are ±0.02 for tacticities[50] and ±1 °C for T_g. [b] See Tables 1 and 2.

and the molecular weight distributions should be identical, as they are to a first approximation for these samples.

Tacticity of PMMA. The tacticities of the PMMA samples were analyzed to the triad level from ^{1}H NMR spectra of $CDCl_3$ solutions by measuring the integrated areas of the syndiotactic (*rr*), isotactic (*mm*), and heterotactic (*mr*) triads.[38,39] The samples prepared in microemulsions (Table 3) are more highly syndiotactic (58−65% *rr*) than commercial PMMA (∼43% *rr*). The tacticity did not vary with the surfactant-to-monomer ratio from $S = 0.01$ to $S = 3$ and did not vary with surfactant at a fixed temperature. Thus the tacticities of PMMA produced in microemulsions were the same as those of the PMMA produced in normal emulsions. The percent syndiotactic triads increased with decreasing polymerization temperature, from 58 to 61% *rr* at 60 °C to 63−65% *rr* at 35 °C.

Glass Transition Temperatures. Table 3 reports the T_g values. Samples prepared in microemulsions at either 60 or 35 °C have $T_g = 125{-}126$ °C. The lower molecular weight samples obtained using STAC and hydrogen peroxide/ascorbic acid had slightly lower T_g (∼122 °C), but none are close to the $T_g = 105$ °C of the commercial PMMA, which was 43% *rr*.

Discussion

Mechanism of Particle Formation. The present understanding of the mechanisms of polymerization in microemulsions has developed due to contributions from several research groups,[10,21,24] and has been elaborated in the greatest detail by Morgan, Lusvardi, and Kaler[24] to explain polymerizations in pseudo-ternary mixtures of hexyl methacrylate, dodecyltrimethylammonium bromide/didodecyldimethylammonium bromide, and water. Their discussion is particularly relevant to our results, because it explains formation of particles containing only one polymer chain as follows.

(1) Initial Conditions. The starting microemulsions containing $S \geq 1$ consist of monomer-swollen surfactant micelles, which are about 6 nm in diameter according to SANS (small angle neutron scattering) measurements of ternary microemulsions of styrene, cationic surfactant, and water.[20,23] The number of micelles increases with increasing surfactant concentration, and the size of the micelles may decrease slightly with increasing *S* because of a decreasing amount of monomer per micelle.

(2) Initiation. Both water-soluble KPS and oil-soluble AIBN initiate polymerization. The final particle sizes and molecular weights of the PMMA do not depend significantly on the initiator, as shown in Table 2. Radicals generated in the aqueous phase from KPS initiate polymerization of MMA in the water. Oligomeric PMMA radicals are captured by monomer-swollen micelles, where polymerization continues to high molecular weight. Because of the small volume of the polymerizing particle, two radicals in one particle would result in fast termination. AIBN forms a pair of 2-cyano-2-propyl radicals in the organic phase. There is rapid termination, and no polymer is formed unless one of the radicals escapes the micelle, leaving behind one radical for polymer chain growth. Because of intraparticle termination the efficiency of initiation by AIBN is lower than that of KPS for polymerization of styrene in microemulsions.[48]

(3) Particle Size and Molecular Weight. The product particles are 20−30 nm in diameter, much larger than the 6 nm diameter of starting micelles, yet many of them contain only one macromolecule. Growth of more than one polymer molecule in a particle is uncommon because at all times the number of uninitiated monomer-swollen micelles greatly exceeds the number of polymer particles, and consequently, there is a high probability that a new polymer chain will start in a micelle rather than in a polymer particle. The particle size and molecular weight are independent of the surfactant-to-monomer ratio at $S \geq 1$ and are controlled by chain transfer to monomer or to surfactant. A 6 nm diameter micelle containing 50 wt % of MMA accounts for 30 000 amu of MMA, whereas the final molecular weight is often $M_w = 4\ 500\ 000$. Therefore, a large amount of monomer must be transported into the particle from uninitiated micelles during growth of a single polymer chain. The time required for growth of PMMA chains of molecular weights $(1{-}10) \times 10^6$, calculated from the propagation rate constant and local concentration of monomer in the growing particle, is on the order of 10−100 s. The molecular weight and particle size are controlled by chain transfer to monomer or surfactant, and the monomer or surfactant radical escapes from the particle into the aqueous phase. Escape is expected because a small radical diffuses a mean distance of >100 nm during the time of one propagation step of MMA polymerization. This diffusion distance is much larger than the diameter of the particle. The high probability of escape of small radicals from micelles also explains why the oil-soluble initiator AIBN leads to polymers having the same particle size and molecular weight as the polymers from a water-soluble initiator. In the aqueous phase a small radical, regardless of origin, either terminates by reaction with another radical or enters a micelle and initiates a new chain polymerization.

(4) Termination of the Chain Reaction. If a growing polymer radical traps a small radical from the aqueous phase, or if AIBN produces new radicals in an already growing particle, diffusion-controlled termination results. Although termination of PMMA occurs by both combination and disproportionation, both types of termination reactions of a polymer radical and a small radical produce one macromolecule. Most termination of kinetic chains must occur in the aqueous phase. The probability of termination in a polymer particle is low because the probability of a radical from the aqueous phase entering a growing particle rather than an uninitiated micelle is low.

(5) Product Mixture. After polymerization is finished, the mixture consists of 20−30 nm diameter surfactant-coated PMMA particles and a larger number of much smaller surfactant micelles, as observed using SANS[20,23] for polymerization of styrene in a dodecyltrimethylammonium bromide/water microemulsion.

Tacticity of PMMA. One goal of this investigation was to determine how polymerization in the confined three-dimensional space of a microemulsion affects the tacticity of the polymer chain. We chose to study PMMA because its tacticity is known to vary greatly with the temperature of radical polymerization.[40−46] The microstructure of the polymer chain depends on the free energies of activation of the propagation steps for conversion of the radical end of a PMMA chain to a new stereocenter. The penpenultimate as well as the penultimate stereocenter of a growing PMMA chain in solution influences the configuration of the new stereocenter.[49] The tacticities of radical PMMA deviate slightly from Bernoullian statistics.[45,50] In a microemulsion the growing chain end could be located in a monomer/polymer mixture in the core of the particle or at the surface in contact with surfactant and perhaps water as well as monomer. Since the solvent can also influence the stereochemistry of propagation,[45] one might expect altered tacticity from polymerization in a microemulsion because the surfactant environment at the surface of a particle is considerably different from the usual bulk monomer/polymer mixture. We also note that the conformation of a polymer chain in a microemulsion is more compact than its usual random coil conformation. A random coil of PMMA of molecular weight 1×10^6 has an unperturbed root-mean-square end-to-end distance of 55 nm in bulk,[37] compared with a diameter of 13.8 nm of a compact particle of one polymer chain, assuming that the density of the single macromolecule is the same as that of bulk glassy PMMA. The compact size requires more gauche conformations in the polymer chain. More gauche conformations near the end of a growing polymer chain may influence the probability of formation of *meso* and *racemic* diads. Thus there are several reasons why the tacticity of PMMA formed in a microemulsion might differ from that formed in bulk.

The experimental results, however, show that the tacticity of the PMMA at the triad level does not depend on the type or hydrophobic chain length of the surfactant or on the surfactant-to-monomer ratio over a range of compositions from conventional latexes formed when $S = 0.01$ to microemulsion latexes formed when $S \geq 1$. Possible reasons for this lack of variation of tacticity with the composition of the polymerizing mixture are (1) that the primary locus of propagation is in the bulk of the particle and (2) that the tacticity of the chain is not affected by the environment of the particle surface.

Temperature, however, does affect the tacticity of PMMA formed by radical polymerization. The % *rr* values from this work for samples polymerized at 35 and 60 °C are higher than most but not out of the normal range of experimental variations.[40−46]

Glass Transition Temperatures. The PMMA samples prepared in emulsions and microemulsions at either 35 or 60 °C consistently had $T_g = 125{-}126$ °C, which is much higher than the values of 105−107 °C commonly cited in textbooks and in ref 51. These differences cannot be due to the high molecular weight of our samples, because there should be little effect of molecular weight on T_g when $M > 10^5$.[52] A more careful selection of recent reports of the T_g of PMMA indicate that the usual value for materials from bulk polymerization is about 115 °C.[53] However, the T_g of PMMA is known to depend greatly on tacticity. Comparison of our results with the literature in which both T_g and tacticity are reported and the molecular weights are high enough for T_g to be its upper limit shows the T_g values of our PMMA samples to be the highest for 59−65% *rr* samples, but not by more than experimental uncertainties.

One possible reason for our high T_g values is that a single precipitation into methanol removed low molecular weight components that would depress T_g. Attempts to purify PMMA from microemulsions by dialysis failed to remove all of the surfactant. We cannot evaluate whether the literature samples were fractionated.

A more interesting possibility is that the more compact conformations required by confinement of PMMA in a single particle increase T_g. It is known that single chain polystyrene differs spectroscopically and thermally from ordinary polysytrene.[56] Precipitation of the glassy particles of the PMMA microemulsion into methanol at room temperature should not mix the polymer chains appreciably. Our T_g values are from the second, third, and fourth DSC scans from 25 to 175 °C at 10 deg min^{-1}. If the isolated chains of PMMA have higher T_g, the chains must not mix during the T_g measurements. Consequently, we tried to anneal a sample at 175 °C in the DSC. The T_g was still 125 °C after 14 h and decreased only to 124 °C after 72 h. Reprecipitations of two samples which had $T_g = 126$ °C (CTAB, $S = 3$ and STAC/KPS, $S = 2$) from chloroform into hexane (a method that should produce highly entangled chains) gave PMMA with $T_g = 122$ and 123 °C, respectively. Thus the samples first isolated from microemulsions have a T_g value 3−4 °C higher than they do after reprecipitation. We also prepared a PMMA sample in bulk by photoinitiation at 35 °C and found $T_g = 117$ °C before and $T_g = 121$ °C after reprecipitation of the polymer into hexane. This verifies that methanol removes low M components that depress T_g. Thus the evidence points to higher T_g of the single chain particles, but not beyond a reasonable doubt.

Commercial samples of PMMA such as a cell cast sheet typically have a T_g of about 105 °C. The highest T_g of a commercial PMMA is about 115 °C.[56] An economical process for polymerization to PMMA having T_g around 125 °C, like the PMMA produced in the microemulsions or emulsions, would be important commercially. The major economic problems with PMMA from emulsions are the need to isolate the polymer and the need to remove the surfactant.

Conclusions

Polymerizations of MMA in ternary microemulsions containing alkyltrimethylammonium halide surfactants produce 20–30 nm diameter latex particles consisting of one polymer chain when the surfactant to MMA weight ratio is at least one. The water-soluble potassium persulfate and the oil-soluble AIBN initiators gave the same results, which are consistent with a model in which the molecular weight and size of the single chain particle are controlled by radical chain transfer to monomer and escape of the monomer radical from the particle. The triad tacticities of the PMMA formed in the microemulsions are 58–61% *rr* at 60 °C and 63–65% *rr* at 35 °C and do not depend on surfactant structure, surfactant to monomer weight ratio, or water-soluble vs oil-soluble initiator. The T_g values of the PMMA formed in both the emulsions and the microemulsions are 125 °C, higher than those of PMMA of the same tacticity produced by bulk or solution polymerizations.

Acknowledgment. This research was supported by National Science Foundation Grant DMR9502636. Funds for the 400 MHz NMR spectrometer of the Oklahoma Statewide Shared NMR Facility were provided by the National Science Foundation (BIR-9512269), the Oklahoma State Regents for Higher Education, the W. M. Keck Foundation, and Conoco, Inc. We thank S. Jones, U. Nobbmann, and B. J. Ackerson for the particle size measurements by dynamic light scattering and M. Cholod of Rohm & Haas Co. for discussion of T_g's of PMMA.

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MA971722M