Synthesis of nanosize poly(methyl methacrylate) microlatexes with high polymer content by a modified microemulsion polymerization

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Summary   Nanosize poly(methyl methacrylate) (PMMA) microlatexes with high PMMA/surfactant ratio have been successfully prepared by a modified microemulsion polymerization, i.e., continuous and slow addition of monomer (MMA) to the polymerizing MMA microemulsion with mild stirring. Number-average diameters of 33-46 nm with narrow polydispersity ($D_v/D_n = 1.1$) and polymer content of 6-24 wt% were achieved using low levels of surfactant (dodecyltrimethylammonium bromide, DTAB) — less than 1 wt% of the reaction mixture. Particle diameter depended on polymerization temperature, MMA content, and concentrations of initiator and surfactant. Larger particles were formed when temperature was too high, initiator concentration was too high, or surfactant concentration was too low.

Introduction

Microemulsion polymerization has been widely studied since the first studies by Stoffer,[1,2] Atik,[3] etc. in the early 1980's. A microemulsion may be defined as thermodynamically stable and optically transparent dispersion composed by water, oil and surfactant; in many cases a cosurfactant is required. Microemulsion polymerization is polymerization of monomers while they are in a microemulsion. The process can yeild stable polymer latexes with particle size of about 10 to 100 nm. Macromolecules in the particles often possess high molecular weights. Potential applications for the polymer nanoparticles include drug delivery, microencapsulation, and oil recovery. Since 1980, a number of papers (for example, see refs. 4-23) have described microemulsion polymerization of water-insoluble[4-16] and water-soluble monomers,[17-19] among which some describe four- or five-component microemulsions,[4-10] and others describe ternary microemulsions.[11-15]

However, all the above microemulsion polymerization processes, except those used to prepare bicontinuous systems,[20,21] require high (up to 20 wt% of the total reactor charge) surfactant concentration to form stable polymer latexes with polymer content of less than 10 wt%. Thus, polymer/surfactant ratios in the resultant latexes are usually smaller than 1, which is an obvious drawback in comparison with those latexes from conventional emulsion polymerization. High surfactant levels and low polymer contents limit the application of microemulsion latexes in industry. Hence, to make microemulsion polymerization more practical it is desirable to minimize the surfactant amount and maximize polymer content. Recently, Gan et al.[24,25] reported the polymerization of styrene

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and MMA in ternary Winsor I-like systems with the solids content of up to 15 wt% and particle diameter in the range of 30 -100 nm. Puig et al.[26] showed the preparation of polystyrene latexes with as high as 40 wt% solids content by semicontinuous addition of monomer, but the surfactant amount was still very high, i.e., 14.1 wt%. MMA and butylacrylate were copolymerized in microemulsion through semicontinuous addition of a monomer emulsion to obtain high solids content by Devi et al.,[27] but a water-soluble comonomer such as acrylamide was used, which was undesirable in some applications. We previously described a broadly applicable method (so called "modified microemulsion polymerization procedure") to prepare polymer nanoparticles (< 20 nm) with polymer contents of up to 30 wt% and 1-1.5 wt% surfactant, using a redox initiator system capable of initiating at ambient temperature.[28]

The goal of our present study is to prepare nanosize PMMA microlatexes with high polymer content and a high polymer/surfactant ratio using a thermal initiator. We used a modified microemulsion polymerization process, in which an MMA microemulsion with low MMA concentration was initiated and then MMA was continuously and slowly added into the polymerizing system with mild stirring to avoid disturbing the stability of the microemulsion. The resulting PMMA microlatexes had high polymer contents as well as nanosize particles with narrow size polydispersity.

Experimental

Materials.   MMA from Aldrich was distilled under reduced pressure before polymerization. Dodecyltrimethylammonium bromide (DTAB) with the purity of 99% from Aldrich was used as received. Potassium persulfate (KPS) from Aldrich was purified by recrystallization from water. Deionized water was used for all experiments.

Modified microemulsion polymerization process.   Detailed polymerization conditions and characterization of the products are summarized in Table 1.

A typical polymerization procedure was: In a 200-mL 3-neck flask equipped with a reflux condenser, a thermometer, an addition funnel, a small-sized stir bar (e.g., 8x13 mm) driven by a magnetic stirrer and N_2 inlet and outlet, was loaded with transparent ternary microemulsion composed of 2 g of MMA, 1 g of DTAB, and 92 g of water. A solution of 81 mg of KPS (3 mmol/L, based on initial microemulsion) in 5 g of water was added and N_2 was bubbled through the microemulsion for 5 minutes. The flask was heated to 60°C and kept for 10 minutes. Then 9 g of MMA in the addition funnel was continuously and slowly added into the polymerizing microemulsion during 2-3 hrs with mild stirring (ca. 200 rpm). After the addition was complete, the flask was kept at 60°C for another 2 hrs.

Unless otherwise stated, the initial microemulsion was composed of 2 g of MMA, 1 g of DTAB and 97 g of water, the added MMA from addition funnel was 9 g, KPS concentration was 3 mmol/L (based on initial microemulsion), and the reaction temperature was 60 °C.

In order to keep track of the change of particle size of PMMA microlatexes during the microemulsion polymerization, microlatex samples (ca. 0.3 mL) for particle size measurements were withdrawn every 15-20 minutes using a 1-mL syringe, quenched with 2 wt% hydroquinone aqueous solution, and put into an ice/salt bath to further inhibit the polymerization. Then, the particle size was analyzed.

Particle size determination   Particle size and particle size distribution (PS & PSD) were determined by dynamic light scattering on L&N Microtrac Particle Analyzer 9200 series

from Leeds & Northrup Co. Microlatexe samples were diluted with deionized water to the concentration with about 0.1 wt% of PMMA. The number- (D_n), volume- (D_v), and area-(D_a) average diameters were calculated by the instrument. The polydispersity is expressed as D_v/D_n (D_v equals to weight-average diameter, D_w, when polymer particles are assumed to have the identical density regardless of their particle sizes),[29] and the specific surface area (SSA) was calculated from D_a, i.e., *SSA = 6 / D_a* (SSA is in m²/g and D_a in microns). The particle size was checked with a Hatichi H-500H Transmission Electron Microscope. One drop of a latex was thoroughly mixed with 1 mL of 0.1 wt% phosphotungsic acid (PTA) water solution. A drop of the mixture was then placed on a copper grid coated with a thin layer of Formvar. The diameters measured by two methods were in agreement, and only light scattering results are presented here.

Molecular weight determination   Molecular weight and molecular weight distribution (MW & MWD) were measured by Gel Permeation Chromatography (GPC) apparatus equipped with Hewlett Parkard (HP) Series 1050 Quad Pump and HP 1047A Differential Refractometer. Tetrahydrofuran (THF) was used as eluent at a flow rate of 0.9 mL/min., and polystyrene standards were used for calibration.

Table 1. Polymerization conditions and characterization results of PMMA microlatexes.

	Polymerization conditions [a]		D_n	D_v/D_n	SSA	M_w	M_w/M_n
	Fixed conditions	Variables	(nm)		(m²/g)	(×10⁵)	
	DTAB: 1 g	4	33.3	1.12	167.0	--	--
	[KPS]: 3 mmol/L	9	38.7	1.10	145.4	11.0	2.6
I	React. Temp: 60 °C	14	40.4	1.16	133.9	--	--
	Variables: added MMA	19	42.8	1.11	131.3	13.6	3.1
	(g)	24	44.6	1.14	124.6	--	--
		29	46.5	1.11	121.1	17.9	2.4
	DTAB: 1 g	0.5	31.4	1.19	170.1	--	--
	Added MMA: 9 g	1.0	32.3	1.15	169.4	19.3	2.4
II	React. Temp: 60 °C	2.0	36.8	1.10	153.9	--	--
	Variables: [KPS]	3.0	38.7	1.10	145.4	11.0	2.6
	(mmol/L)	5.0	68.9	1.45	69.6	--	--
	Added MMA: 9 g	0.5	92.1	1.11	61.0	--	--
III	[KPS]: 3 mmol/L	1.0	38.7	1.10	145.4	11.0	2.6
	React. Temp: 60 °C	2.0	35.6	1.08	160.1	--	--
	Variables: [DTAB] (g)	3.0	32.6	1.18	165.1	12.3	3.0
	Added MMA: 9 g	50	38.0	1.23	137.3	--	--
IV	[KPS]: 3 mmol/L	60	38.7	1.10	145.4	11.0	2.6
	DTAB: 1 g	70	46.1	1.07	124.2	2.9	2.1
	Variables: T (°C)	80	65.9	1.11	85.3	--	--

[a] MMA in initial microemulsion (totally 100 g) was always maintained at 2 g, and KPS concentration (in mmol/L) was based on the initial microemulsion.

Results and discussion
Modified microemulsion polymerization procedure.   The transparent o/w microemulsion region is very narrow and near the water-rich corner in MMA/DTAB/H_2O phase diagram.[11] In this corner, a stable MMA microemulsion requires a quite large quantity of
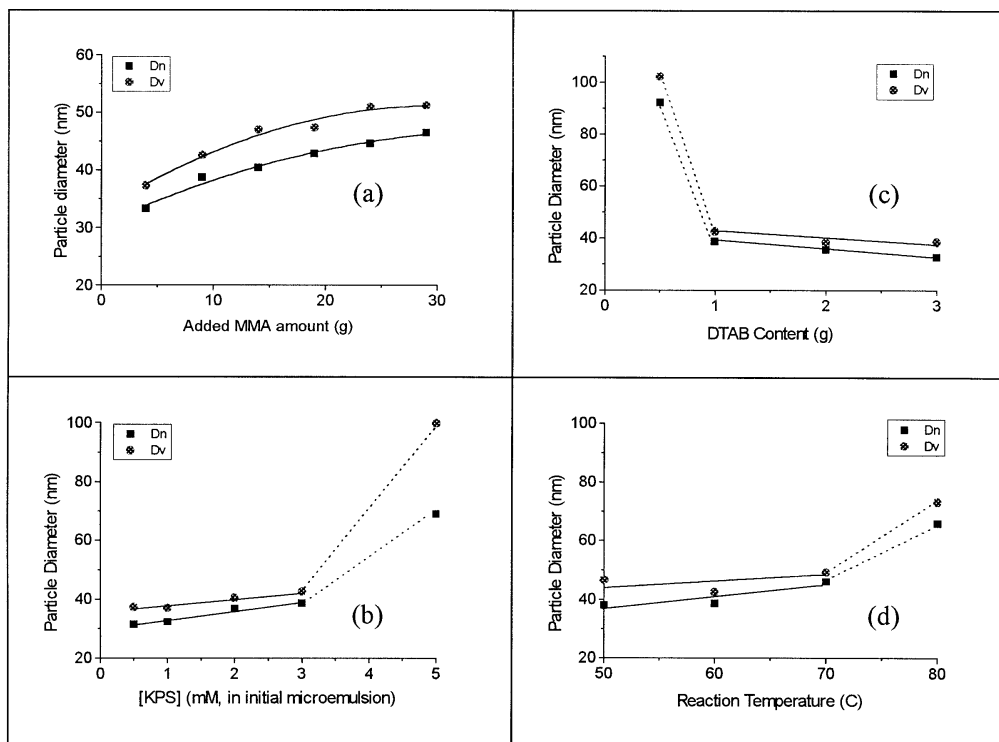
Figure 1. Dependence of particle size of PMMA microlatexes on polymerization conditions: (a) added MMA amount; (b) KPS concentration in initial microemulsion; (c) DTAB content; and (d) reaction temperature.
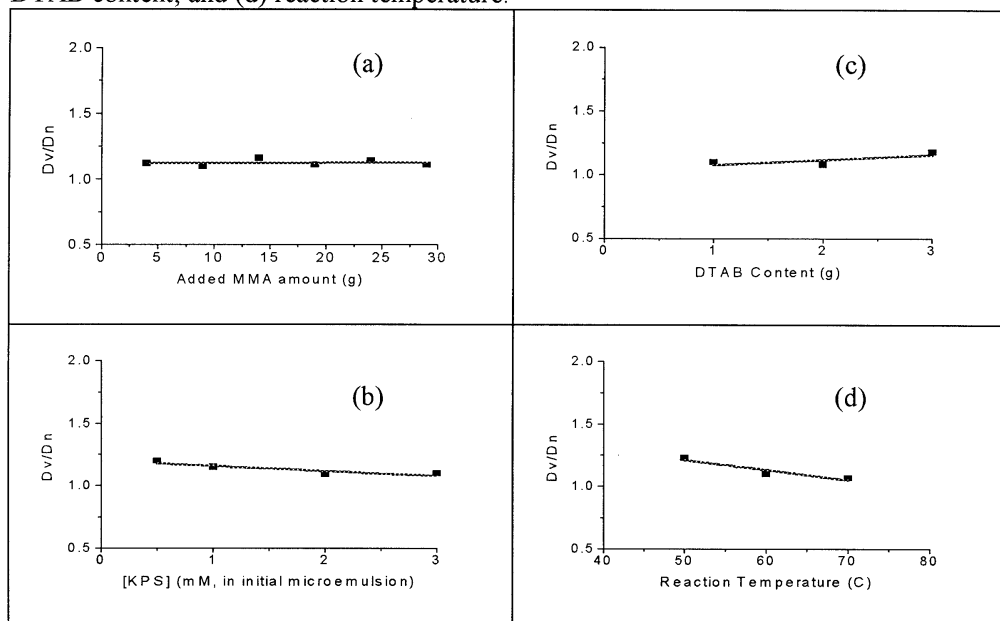

Figure 2. Dependence of particle size polydispersity of PMMA microlatexes on polymerization conditions: (a) added MMA amount; (b) KPS concentration; (c) DTAB content; and (d) reaction temperature.

DTAB (ca. equal amount of DTAB with MMA is needed if MMA concentration is higher than about 5 wt%), otherwise, only turbid conventional emulsions or two-phase systems can be obtained. In our procedure, the initial MMA microemulsion was composed of 2 g of MMA, 1 g of DTAB, and 97 g of H_2O so that only a small percentage of MMA is in the microemulsion. The solubility of MMA in water is about 1.5 wt% at 25 °C.[30] If MMA concentration was higher than 3 g, transparent microemulsion could not be obtained with 1 g DTAB. After the microemulsion was initiated by KPS, most of the MMA was slowly and continuously added into the reacting microemulsion with mild stirring. Unreacted MMA formed a very thin layer on the top of the microemulsion and MMA could diffuse into the microemulsion to maintain an equilibrium among all components as MMA was gradually consumed. By this procedure, translucent or semi-translucent PMMA microlatexes with nanosize particles and high PMMA content were prepared. These PMMA microlatexes were stable for more than one year. It should be noted here that the addition speed of MMA must be slow (ca. 0.5 mL/10min.), otherwise bulk PMMA will form above the microemulsion, especially along the flask wall. The mild stirring helps the reacting microemulsion form homogeneously, however, the size of stir bar and stirring speed should be moderate. If the stir bar is too big and/or the stirring speed is too fast, the stable microemulsion will be disturbed by incorporating too much MMA from the upper layer.

Effect of MMA content on particle size of PMMA microlatexes. Figure 1(a) shows D_n and D_v of PMMA microlatexes increased with the increasing MMA amount added by addition funnel. D_n ranged from 33 to 46 nm as the added MMA changed from 4 to 29 g, meanwhile the polydispersity for all latexes was always around 1.1 [Figure 2(a)], which was relatively more monodisperse than common o/w microemulsion polymerized latexes. The conversions of MMA in all polymerizations were between 89 and 93 wt% as determined by the solids content of produced microlatexes. It is interesting that high-polymer-content (ca. 24 wt%) PMMA microlatexes with so small particles (D_n: 46.5 nm and D_v: 51.5 nm) can be produced using only 1 wt% DTAB in initial microemulsion. As a comparison, a conventional emulsion of 7 g of MMA, 1 g of DTAB and 92 g of water was polymerized at 60 °C using KPS (3 mmol/L) as initiator, and D_n and D_v of the produced latex were 49.4 and 53.6 nm, respectively. These partilces were larger than those of the microlatex with 10 wt% PMMA (D_n: 38.7 nm and D_v: 42.6 nm) and even larger than those of the microlatex with 24 wt% PMMA prepared using the modified microemulsion polymerization process.

Effect of initiator concentration on particle size of PMMA microlatexes. In these experiments, the polymerization recipes were the same as shown in experimental section except that KPS concentration in the initial microemulsion was varied from 0.5 to 5 mmol/L. As shown in Figures 1(b) and 2(b), particle size of PMMA microlatexes increased gradually and polydispersity decreased slightly as [KPS] changed from 0.5 to 3 mmol/L. However, at [KPS] of 5 mmol/L, the particle size was relatively large, and the product was rather turbid in comparison with others. This result may be due to the occurrence of inter-particle aggregation, i.e., at high initiator concentration, the nucleation was very fast and thus the number of small polymer-containing particle was also very large, increasing surface area above the level that could be stablized by only 1 wt% DTAB and resulting in aggregation.

Effect of DTAB amount on particle size of PMMA microlatexes. In this study, DTAB content was varied from 0.5 to 3 g, while MMA content was fixed at 2 g and the remainder was made up with water to 100 g in initial microemulsion. As shown in Figure 1(c), as DTAB content decreased from 3 to 1 g, the particle size increased slightly. Unexpectedly, polydispersity narrowed with decreasing DTAB concentration [Figure 2(c)]. But if DTAB content was too low, e.g., 0.5 g, large particles were produced again, suggesting that 0.5 g of DTAB was insufficient to protect PMMA-containing particles from aggregation to form large particles under these experimental conditions. On the other hand, 1 g of DTAB was sufficient.

Effect of reaction temperature on particle size of PMMA microlatexes. The reaction temperatures were changed from 50 to 80 °C, while keeping other experimental conditions unchanged. The dependence of particle size on reaction temperature is illustrated in Figure 1(d); D_v/D_n decreased as temperature increased from 50 to 70 °C [Figure 2(d)]. When polymerized at 80 °C, PMMA latex with large particle size was produced. A possible explanation is that the concentration of small particles being initiated at 80 °C is too large for the available surfactant to stablize as individual particle, analogous to the situation with high initiator levels.

Molecular weights of PMMA nanoparticles. It can be seen from Table 1 that the produced PMMA microparticles generally had the weight-average molecular weights (M_w) of about $1 - 2 \times 10^6$, except the one polymerized at 70 °C which had the M_w of 2.9×10^5. The molecular weight polydispersities (M_w/M_n) were from 2 to 3. With the increasing of MMA amount and the decreasing of KPS concentration, the M_w of PMMA nanoparticles increased, meanwhile, DTAB concentration had only little influence on the molecular weight.

Change of particle size of PMMA microlatex during polymerization. It can be seen from Figure 3 (a) that both D_n and D_v increased during the addition of MMA, and the PMMA-containing particles continued to grow until 35 min. after MMA addition was complete. Then the particle size leveled off. The PMMA particles formed at early stage of polymerization in microemulsion can be regarded as the seeds for further growth of polymer-containing particles. The upper thin layer MMA here had the function of monomer reservoir in conventional emulsion polymerization, which could continuously provide monomer to the microemulsion so that the growth of polymer particles could continue. This is much different with what we have observed previously[28] in the system of NMA/SDS/1-pentanol/H_2O initiated by a redox initiator at ambient temperature, in which both D_n and D_v remained almost constant throughout the reaction [Figure 3(b)].

In the system of MMA/SDS/1-pentanol/H_2O initiated by a redox initiator at ambient temperature,[28] D_n does not change throughout the entire reaction period possibly because the free radicals, either newly formed or transferred from polymeric radicals, are likely to enter the uninitiated monomer-containing micelles, where they would start growth of a new polymeric particle, instead of staying within the particles where they were formed, thus increasing the particle sizes. Because the continuous nucleation was almost along the whole polymerization period, the particle size distribution was much broader (D_v/D_n 1.2-1.6).[28] The main factor giving rise to this phenomenon may be the low polymerization temperature, besides the solubility of monomer and initiator. However, in the process studied here, at high reaction temperature, MMA could more easily enter and
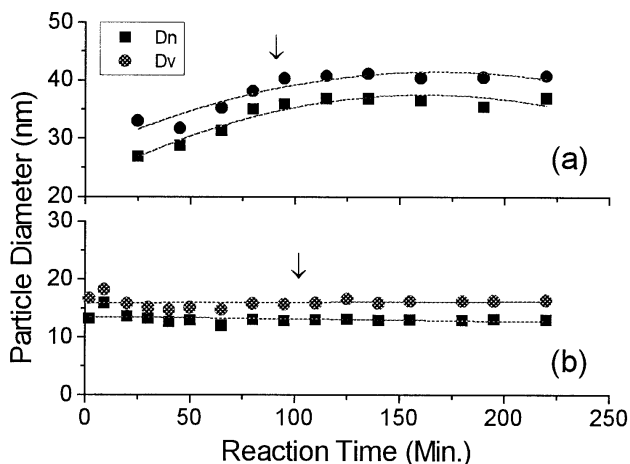
Figure 3. Comparison of particle size change during two microemulsion polymerization processes. (a) The process described in this paper, composition (g): MMA 2, DTAB 1, and water 97, added MMA 9, [KPS] 3 mmol/L (based on initial microemulsion), and reaction temperature 60 °C; (b) A process described previously,[28] composition (wt%): MMA 14.0 (2.0 in initial microemulsion), SDS 1.4, 1-pentanol 0.2, water 84.4, APS/TMEDA 2 mmol/L, and reaction temperature 40 °C. The arrow indicates the end of monomer addition. The lines represent the polynomial regression fittings done by MicroCal Origin.

diffuse into polymer-containing particles. At the same time, the possibility for polymeric particles to collide and then to aggregate to form larger particles would be increased even if the homogeneous nucleation might be still dominant. They both resulted in the particle size increase during polymerization. Due to the fact found by Guo et al[6,7] that in o/w microemulsion polymerization polymerizing particles can absorb much more monomer than unpolymerized particles, the final PMMA microlatexes should have uniform particle size, which has been demonstrated by the above results (D_v/D_n around 11).

Acknowledgements

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