Emulsifier-Free Miniemulsion Polymerization of Styrene and the Investigation of Encapsulation of Nanoparticles with Polystyrene via This Procedure Using an Anionic Initiator

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ABSTRACT: Emulsifier-free miniemulsion polymerization of styrene was investigated in the presence of potassium persulfate (KPS) as an anionic initiator and cetyl alcohol as a costabilizer using ultrasonic irradiation and comparison of this procedure with conventional emulsifier-free emulsion polymerization showed that this method has a remarkably higher polymerization rate (R_p), smaller size of particles, and narrower molecular weight distribution via gravimetric measurement, transmission electron microscopy (TEM), and gel permeation chromatography techniques, respectively. Then, the encapsulation of magnetite (Fe_3O_4) and titanium dioxide (TiO_2) nanoparticles with polystyrene was investigated using this procedure. Attempt to encapsulate magnetite nanoparticles failed; however, the encapsulation of titanium dioxide nanoparticles was successfully carried out via this procedure using KPS in both cases. TEM proved the presence of TiO_2 nanoparticles in polymer particles, and thermogravimetric analysis was used to determine the percentage of TiO_2 in the products. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1244–1250, 2007

Key words: styrene; potassium persulfate (KPS); emulsifier-free miniemulsion; nanoparticles; encapsulation

INTRODUCTION

Miniemulsions are classically defined as aqueous dispersions of relatively stable oil droplets within a size range of 50–500 nm.[1,2] In comparison with conventional emulsion polymerization, miniemulsion polymerization has a wider range of applications and advantages. In this method, various inorganic–organic hybrid nanocomposites containing nanomaterials such as carbon nanotubes[3] and nanoparticles, such as Fe_3O_4,[4,5] TiO_2,[6] SiO_2,[7] etc., that have recently been receiving growing attention can be produced. These inorganic nanoparticles can possess functions such as magnetic susceptibility, electrical conductivity, catalytic activity, or electroactivity, and so they may possibly form functional composites (or nanocomposites).[8,9] It has been well known that organic–inorganic hybrid materials and polymeric nanocomposites present the properties of both the inorganic nanoparticles and the polymer by combining thermal stability, mechanical strength, or electronical and optical properties with flexibility and the ability to form films.[10,11] Miniemulsion polymerization can also produce polymeric hybrids,[12] polymer nanoparticles,[13] nanocapsule compounds,[14] high-solid content lattices,[15,16] etc.

In miniemulsion polymerization very small droplets called nanoreactors[17] are prepared by high shearing a system containing monomer, water, surfactant, costabilizer, and initiator. Surfactant concentration is maintained below the critical micelle concentration to avoid micellar nucleation.[18] A hydrophobic costabilizer (such as hexadecane, cetyl alcohol, oil-soluble initiator, and dye, etc.[17,19,20]) retards the degradation of the miniemulsion droplets via Ostwald ripening[21] and the subsequent propagation reaction occurs primarily in submicrometer monomer droplets. Each of these droplets can be regarded as an individual nanophase reactor. It has been known that in miniemulsion polymerization, particle nucleation mechanisms are based on droplet nucleation and homogeneous nucleation. The droplet nucleation mechanism suggests that the droplets formed during the emulsification step are polymerized directly via a radical that enters these monomer droplets and reacts with the monomer present there. The homogeneous nucleation is a second possible mechanism for miniemulsion polymerization and its importance is for the so-called surfactant-free emulsion polymerization. In this case, the latex seeds are created from oligomers in the water phase, and the monomer is brought to the nucleation site by diffusion.[22] Because

of these two mechanisms, one of the advantages of the miniemulsion (or inverse miniemulsion) polymerization technique is in the encapsulation of nanoparticles that can be carried out via directly dispersing the hydrophobic inorganic particles in the monomer phase and nucleating all the droplets containing inorganic particles in miniemulsions.[4,6,23,24] Likewise, it was shown that it is possible to make continuous and very smooth inorganic films of some functional inorganic materials from the liquid state, based on appropriately composed inverse miniemulsions.[9]

Emulsion polymerizations in the absence of initially added emulsifier or surfactant can be considered to produce monodisperse and "clean" latexes which can be used in a wide variety of industries such as coatings, adhesives, biomedicine, and biotechnology.[25–27] In such systems the water-soluble initiator such as 2, 2' azobis (2-amidinopropane) dihydrochloride (V-50) polymerizes the slightly water-soluble monomers, such as styrene, in aqueous phase to form oligomeric radicals with sulfate end groups, which are surface active and form droplets or micelles.[25,26]

We have recently reported the combination of the two aforementioned techniques, miniemulsion polymerization and emulsifier-free emulsion polymerization, in the term emulsifier-free miniemulsion polymerization, to obtain the advantage of encapsulation of magnetite nanoparticles with polystyrene via this procedure using ultrasonic irradiation over the conventional emulsifier-free emulsion polymerization using a cationic initiator, 2,2'-azobis(2-amidinopropane)dihydrochloride (V-50) in both cases.[26] We have also shown that emulsifier-free miniemulsion polymerization has a higher polymerization rate and narrower molecular weight distribution than conventional emulsifier-free emulsion polymerization.[27]

In this work, emulsifier-free miniemulsion polymerization took place in the presence of KPS (as an anionic initiator) and the effect of ultrasonic duration was studied and the products were analyzed by transmission electron microscopy (TEM) and gel permeation chromatography (GPC) analyses. The rate of polymerization (R_p) of emulsifier-free miniemulsion polymerization was also studied. Then, the encapsulation of magnetite and titanium dioxide nanoparticles with polystyrene was investigated using this procedure and the products were analyzed by TEM and thermogravimetric analysis (TGA). The procedure was compared with conventional emulsifier-free emulsion polymerization using KPS as initiator in both cases.

EXPERIMENTAL

Materials

The used styrene, potassium persulfate (KPS), cetyl alcohol, tetrahydrofuran, THF (HPLC and for synthesis

TABLE I
The Used Sonication Times and Percentage of Added Nanoparticles, and Obtained Number Averages (d_n) and Inversed Dispersion Indexes (DI^{-1}) in Experiments

Exp. no.	Fe_3O_4 (wt %)	TiO_2 (wt %)	Sonication time (min)	d_n (nm)	DI^{-1}
1	–	–	13	383	1.4377
2		–	18	229	1.0087
3	–	–	20	224	1.0081
4	–	–	–	762	1.0151
5	10	–	20	–	–
6	–	10	20	217	1.1492
7	–	10	–	732	1.1245

grades) $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, ammonium hydroxide (25%), and oleic acid were purchased from Merck Chemical (Whitehouse Station, NJ). The styrene was purified by distillation under vacuum and was stored in a dark bottle at $-20°C$ until required. The initiator (KPS) was used without purification. Oleic acid-coated magnetite nanoparticles with an average diameter of about 10 nm and containing 21.79 wt % of oleic acid were produced in our lab[26] via coprecipitation of Fe^{3+} and Fe^{2+} ions in the presence of ammonium hydroxide and oleic acid and stored to use. Hydrophobic fumed titanium dioxide with 21 nm in average particle size treated with octylsilane (about 4 wt %) was obtained from Degussa (Frankfurt am Main, Germany) as AEROXIDE® T 805 and used. Double distilled water and technical grade methanol were used.

Miniemulsion polymerization

The procedure for emulsifier-free miniemulsion polymerization was carried out in a two-stage process: (1) for preparation of miniemulsion, first, 0.10 g of cetyl alcohol as costabilizer was dissolved in 4.0 g styrene monomer. The mixture was added to 100 mL of water containing 0.20 KPS as an initiator. Second, these mixtures were sonicated with LABSONIC®P (400 W, B. Braun, Göttingen, Germany) at power output of 90% for the given times (Exp. Nos. 1–3 in Table I) under inert gas of N_2 while being stirred. During sonication, the temperature of mixtures increased depending on ultrasonification duration and to prevent evaporation of mixture the container of sonication was equipped with a condenser. And (2) for polymerization of miniemulsion, the aforementioned miniemulsions were polymerized at 70°C under mechanical stirring with half-moon shaped Teflon stirrer at 320 rpm under inert gas of N_2 in a container equipped with a condenser.

Encapsulation of nanoparticles

Magnetite (0.40 g) or TiO_2 (0.40 g) nanoparticles (Exp. Nos. 5–7 in Table I) were dispersed in 6.0 g of

styrene monomer having 0.10 g of cetyl alcohol and these mixtures were sonicated for 30 s to obtain homogenous dispersion. The resultant stable oil-based dispersion was added to 100 mL of water containing 0.20 g of KPS. Then, these mixtures were sonicated for given time and polymerized like the process described for emulsifier-free miniemulsion polymerization. The recipe used to encapsulate the nanoparticles is also given in Table I.

The procedures for conventional emulsifier-free emulsion polymerization and encapsulation of nanoparticles in this system were similar to the one described for emulsifier-free miniemulsion polymerization and the encapsulation of nanoparticles except that they do not have sonication (Exp. Nos. 4 and 7 in Table I). To better compare these two systems (emulsion and miniemulsion), cetyl alcohol was added to both.

Characterization

All products obtained in aforementioned experiments were centrifuged at 2000 rpm for 5 min and then analyzed.

Conversions of styrene monomer in polymerizations were gravimetrically measured after the samples were dried at about 60°C under vacuum to constant weight.

A CEM 902A ZEISS TEM with an accelerating voltage of 80 kV was used to obtain information about the morphology and size of polymer particles. Samples were prepared by placing a droplet (1 μL) of polymer dispersion, along with a droplet of water, on a copper grid covered by formvar foil (200 mesh), dried, and analyzed. To measure size and size distribution, a number of about 100 latex particles (from the TEM micrographs) were counted to calculate the d_n as number average ($\Sigma n_i d_i / \Sigma n_i$), the d_w as weight average ($\Sigma n_i d_i^4 / \Sigma n_i d_i^3$) and the DI^{-1} as inversed dispersion index (d_w/d_n) showing polydispersity of particle size, where d_i is diameter of latex particles and n_i is the number of polymer particle with d_i in diameter (see Ref. 1, Chap. 12, and Ref. 27).

GPC analyses were performed by using Agilent 1100 series (Böblingen, Germany) GPC system. For GPC analyses, the obtained latexes were dried at 60°C under vacuum, dissolved in tetrahyrofuran (THF) precipitated in large amounts of methanol, and dried again. The products were dissolved in THF and injected. The mobile phase was THF with flow rate of 1 mL/min. GPC data were recorded at 30°C on a mixed organic column equipped with RI detector.

TGA was carried out using a Model TGAQ50 (TA Instruments, New Castle, De USA) at 20°C/min for heating rate under inert gas of Ar for dried samples latexes.

RESULTS AND DISCUSSION

Miniemulsion polymerization

To obtain miniemulsion polystyrene latex particles in the absence of any added emulsifier using KPS as an anionic water soluble initiator under ultrasonic irradiation, some experiments were carried out. Considering our previous works,[26,27] constant amounts of monomer and initiator were used and the sonication time was investigated to obtain a good product containing monodisperse miniemulsion latex particles. These sonication times are given in Table I. In Exp. No. 1, the mixture of styrene containing cetyl alcohol and water containing KPS was sonicated for 13 min and the temperature of the mixture (monomer in water containing initiator) increased up to about 78°C. After sonication, a product with two phases was obtained: one phase was an organic transparent layer over the other opaque aqueous phase containing dispersed organic emulsion. Then, this miniemulsion was polymerized at 70°C and the organic transparent layer gradually disappeared during polymerization for several hours. After polymerization, a white latex and little polystyrene aggregates were obtained. TEM analysis, Figure 1, for this experiment showed that there was a wide range of particle sizes for latex below and above 500 nm (200 nm–1 μm) in diameter of which the number average (d_n) and the inversed dispersion index (DI^{-1}) as polydispersity of particle size are also shown in Table I. This is a result of two mechanisms due to
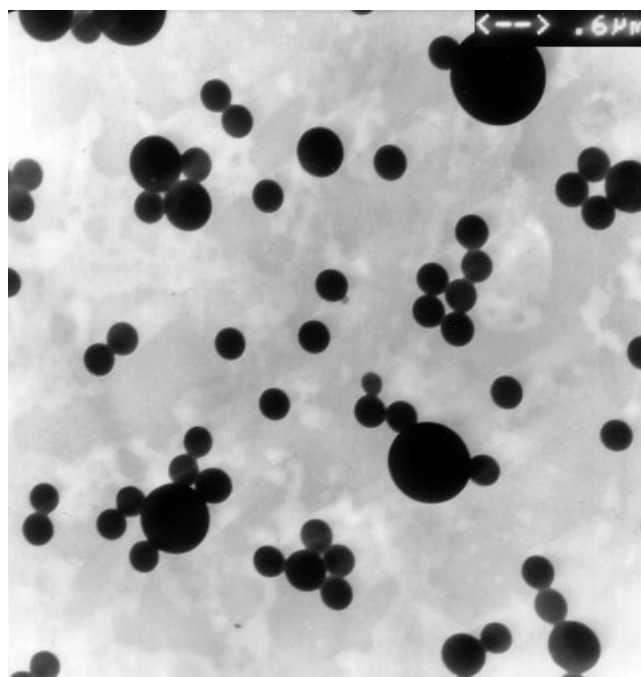

Figure 1 TEM micrograph of the latex particles obtained from Exp. No. 1 with 13 min for sonication time.
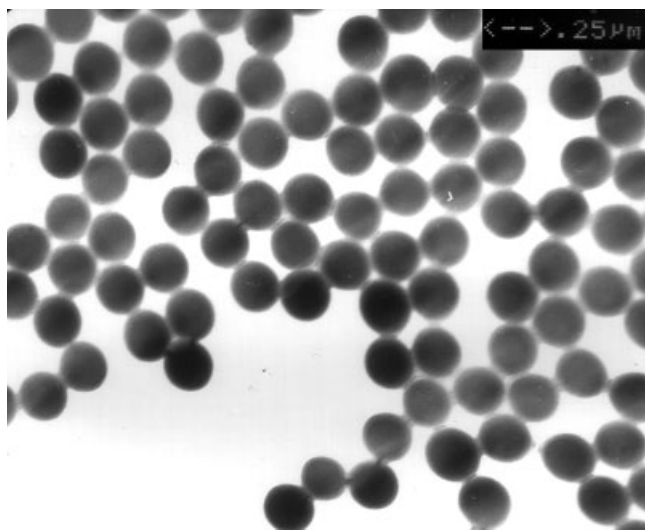
Figure 2 TEM micrograph of the latex particles obtained from Exp. No. 2 with 18 min for sonication time.

inadequate amount of concentration of the oligomeric radicals with surface activity that act as surfactant in this experiment due to inadequate duration of sonication.[26,27] The first mechanism was conventional emulsifier-free emulsion polymerization that acts for organic layer obtained after sonication and produces polymer particles above 500 nm (up to 1 μm) in diameter. The second mechanism was for emulsifier-free miniemulsion that produces polymer particles between 200 and 500 nm in diameter and acts for aqueous phase obtained after sonication.[26,27] So, we increased the duration of sonication to raise the efficiency of initiator as the source of the oligomeric radicals with surface activity in the beginning of the polymerization process (i.e., after miniemulsification stage). In Exp. No. 2, the mixture of styrene containing cetyl alcohol and water containing KPS was sonicated for 18 min and the temperature of the mixture increased up to about 85°C. After sonication for 18 min, we obtained one aqueous phase without organic layer. Subsequent polymerization of this miniemulsion at 70°C gave monodisperse polystyrene latex particles below 500 nm (at about 200–250 nm) in diameter of which the d_n and DI^{-1} are also shown in Table I. Figure 2 is TEM micrograph for latex obtained in Exp. No. 2 that had monodisperse polymer particles with number average (d_n) of 229 nm and the inversed dispersion index (DI^{-1}) of 1.0087 and did not have latex particles above 500 nm in diameter (formed by conventional emulsion mechanism) due to increasing the amount of concentration of the oligomeric radicals with surface activity and increasing dispersed organic phase in aqueous phase. Comparison of the amount of DI^{-1} of Exp. No. 2 (1.0087) with the amount of DI^{-1} of Exp. No. 2 (1.4377) shows that the distribution of particles

(DI^{-1}) in Exp. No. 2 is close to unit and also is narrower than that in Exp. No. 1 due to the increasing amount of concentration of the oligomeric radicals with surface activity that makes miniemulsion better due to increasing sonication time. The effect of further lengthening of sonication time up to 20 min in Exp. No. 3 was not significant on size of latex particles. The d_n and DI^{-1} of latex particles in this experiment are also given in Table I. Comparison of miniemulsion polymerization using V-50[27] with miniemulsion polymerization using KPS as initiators in the absence of emulsifier shows that a system using KPS needs longer sonication in the miniemulsion stage than a system using V-50 (18 versus 12 min).

Comparison of miniemulsion and emulsion polymerization

We attempted to compare the results of TEM and GPC analyses and monomer conversions of emulsifier-free miniemulsion polymerization with those of conventional emulsifier-free emulsion polymerization method using KPS as initiator in both cases. The conventional emulsion polymerization did not have sonication as shown in Table I (Exp. No. 4). Figure 3 is TEM micrograph for latex produced in Exp. No. 4. As this figure shows, the size of the latex particles was about 800 nm in diameter that was significantly larger than that in emulsifier-free miniemulsion polymerization (Fig. 2). The d_n and DI^{-1} of latex particles in Exp. No. 4 are also given in Table I.
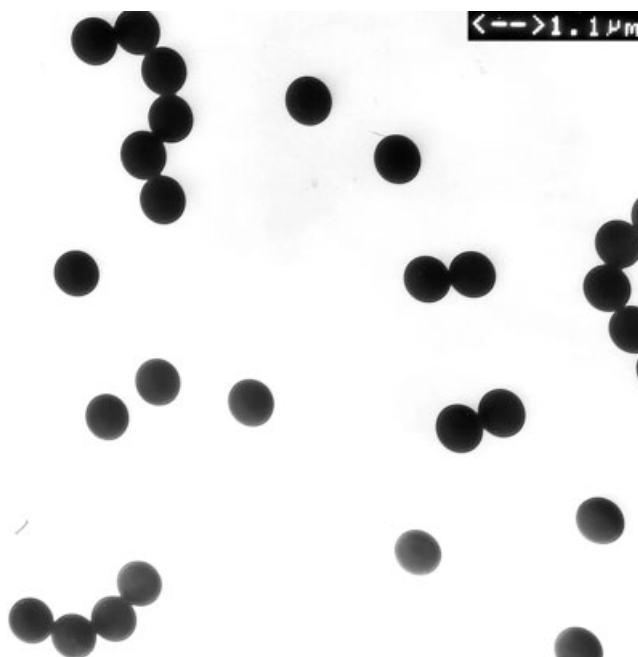

Figure 3 TEM micrograph of the latex particles obtained from Exp. No. 4, emulsifier-free conventional emulsion polymerization.
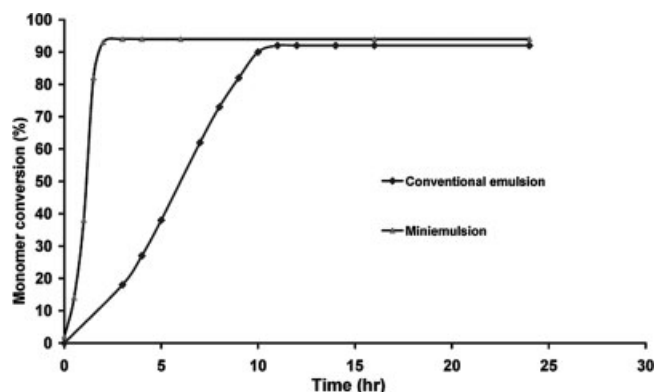
Figure 4 The time variation of overall conversion for emulsifier-free miniemulsion polymerization in Exp. No. 3 and the conventional emulsion in Exp. No. 4 in details.

Study on the rate of polymerizations also showed that the rate of polymerization of monomer in miniemulsion polymerization systems is significantly higher than that in conventional emulsion polymerization. Figure 4 shows the time evolution of conversions for the emulsifier-free miniemulsion polymerization with conditions of Exp. No. 3 and for conventional emulsifier-free emulsion polymerization with conditions of Exp. No. 4 in details in both cases. As Figure 4 shows, the rate of polymerization of monomer in miniemulsion polymerization (using KPS) is significantly higher than that of conventional emulsion polymerization and the monomer conversion of this system reaches up to 92% after 2 h while the polymerization progresses only less than 15% in conventional emulsion polymerization in the same time and reaches up to the conversion about 92% after 11 h (using the same initiator). These results are in accordance with results of our previous work,[27] emulsifier-free emulsion and miniemulsion polymerizations of styrene using V50 as a cationic initiator, and as it have been shown, the rate of polymerization of monomer in emulsion polymerization systems is directly related to the number of formed monomer particles (or droplets) and increases with increasing the number of monomer particles.

GPC data for miniemulsion polymerization (like Exp. No. 3) were compared with those of emulsion polymerization (like Exp. No. 4). The samples at about 92% monomer conversion (at about the end of the conversion of monomer), i.e., polymerization in 3 h (conversion of 94%) and 11 h (conversion of 92%) for miniemulsion and conventional emulsion polymerization, respectively, were analyzed. The GPC data for these systems are given in Table II. The results showed a significant increase in the number–average molecular weight (M_n) and a decrease in the weight–average molecular weight (M_w), and as a result, the molecular weight distribution (M_w/M_n) decreased in miniemulsion polymerization in com-

parison with conventional emulsion polymerization under the same conditions except for the sonication. These results were probably due to monodisperse and small size of particles in miniemulsion polymerization and in these conditions most of the monomers are exposed in the same homogenous conditions in polymerization and the molecular weight distribution becomes narrower. These results are also in accordance with results of our previous work,[27] emulsifier-free emulsion and miniemulsion polymerizations using V-50.

Encapsulation of nanoparticles

Then, we attempted to encapsulate the oleic acid-coated magnetite nanoparticles with polystyrene via miniemulsion polymerizations in the absence of emulsifier using KPS. To achieve the incorporation of magnetite nanoparticles into polystyrene, as described in the Experimental section, the encapsulation of magnetite nanoparticles with polystyrene via emulsifier-free miniemulsion polymerization using KPS was investigated by the examination of various parameters such as monomer concentration, initiator concentration, ultrasonic duration, and magnetite amount, and several experiments (a typical of which is Exp. No. 5 in Table I) were carried out, but the whole of the systems in these experiments agglomerated just after few minutes of polymerization. As described in Introduction section, we reported[26] encapsulation of magnetite nanoparticle via emulsifier-free miniemulsion polymerization using a cationic initiator, V-50, and the comparison of these results comes to this fact that interaction of surface of oleic acid-coated magnetite nanoparticles with the oligomeric radicals (with negative sulfate end groups, which are surface active and act as surfactant) probably prevents the performance of the oligomeric radicals as surfactant. So we chose octylsilane-coated titanium dioxide nanoparticles, which we hypothesized that they do not have the undesired interaction for encapsulation with polystyrene via emulsifier-free miniemulsion polymerization using KPS. To achieve the incorporation of TiO$_2$ nanoparticles into polystyrene, as described in the Experimental section and Table I, TiO$_2$ nanoparticles were sonically dispersed in styrene monomer having cetyl alcohol and then these mixtures were sonicated in

TABLE II
GPC Data of Polymers Obtained from Emulsifier-Free Miniemulsion and the Conventional Emulsion Polymerizations (See Text)

Exp. type	$M_n \times 10^{-4}$ (g/mol)	$M_w \times 10^{-5}$ (g/mol)	M_w/M_n
Miniemulsion	7.9	3.0	3.797
EMULSION	6.5	3.8	5.846

water containing KPS and then polymerized at 70°C. The experiment was carried out successfully without aggregation and a white latex without aggregated particles was achieved. Figure 5, TEM micrograph for latex particles in Exp. No. 5, shows that encapsulation of nanoparticles occurred and the latex has polymer particles with 100–400 nm in diameter. The d_n and DI^{-1} of latex particles in this experiment are also given in Table I. This figure also shows that the distribution of the nanoparticles within the polystyrene particles is quite heterogeneous. Although the TiO_2 particles were distributed uniformly in the starting styrene system, they segregated and accumulated at one side of spheres during the miniemulsion preparation or the subsequent polymerization.[8,26] Curve A in Figure 6 is the TGA thermograph of the dried latex obtained in Exp. No 6. It shows that the latex has 9.150 wt % residue showing incorporation of TiO_2 nanoparticles in miniemulsion polymerization at about 500°C. Comparison of residue in TGA analysis with the amount of the added TiO_2 nanoparticles shows that most of the TiO_2 nanoparticles were incorporated with polystyrene in these experiments. Comparison of the results of this work with our previous work (encapsulation of magnetite nanoparticles with polystyrene via emulsifier-free miniemulsion polymerization using a cationic initiator[26]) shows that for encapsulation (incorporation) of magnetite nanoparticles with polymers such as polystyrene in emulsifier-free miniemulsion polymerization procedure, a cationic initiator is needed.

At last, we attempted to encapsulate TiO_2 nanoparticles with polystyrene via conventional emulsifier-free emulsion polymerization method using V-50 as initiator. The details of this procedure, the d_n and
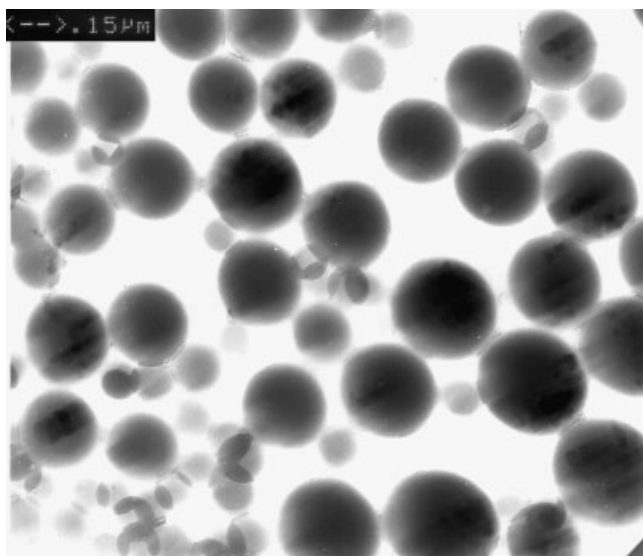

Figure 5 TEM micrograph TiO_2 nanoparticles incorporated in polystyrene particles obtained from Exp. No. 6.
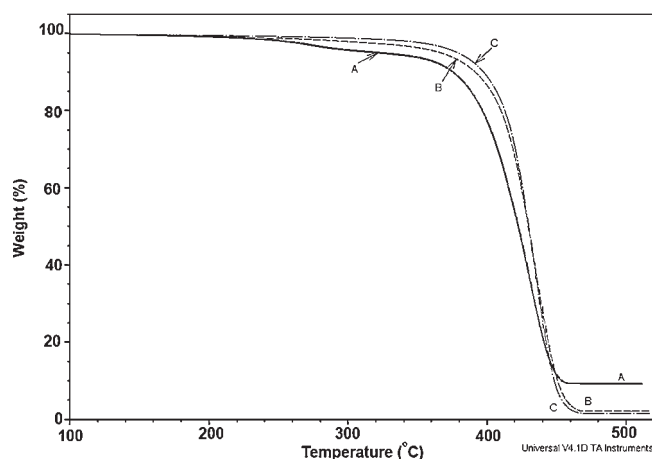

Figure 6 TGA thermographs for experiments: (A) TiO_2 nanoparticles incorporated in polystyrene obtained from Exp. No. 6; (B) emulsion polymerization in the present of TiO_2 nanoparticles obtained from Exp. No. 7; and (C) miniemulsion polymerization in the absence of TiO_2 nanoparticles obtained from Exp. No. 3.

DI^{-1} of latex particles produced in this experiment are also given in Table I (Exp. No. 7). In this method, we obtained a dispersion that consisted of two fractions; the first of which was white polystyrene latex with very little incorporated TiO_2 nanoparticles, whereas the other consisted of large TiO_2 nanoparticles-polystyrene composite particles and TiO_2 aggregates. TGA measurement for this experiment showed that incorporation of nanoparticles in conventional emulsifier-free emulsion polymerization was very insignificant in comparison with emulsifier-free miniemulsion polymerization and the TGA thermogram of this experiment is also shown in Figure 6 (B curve) having 2.162 wt % residue at about 500°C. To better compare TGA data, thermogram of TGA of miniemulsion polymerization in the absence of any add nanoparticles with 1.598 wt % residue at about 500°C (Exp. No. 3 in Table I) is also given in Figure 6 (C curve). By subtracting this amount (1.598%) from the residue amounts in TGA analyses of Exp. No. 6 (9.150 wt %) and No. 7 (2.162 wt %), we can conclude that the contents of TiO_2 in Exps. Nos. 6 and 7 are 7.552 wt % and 0.564 wt %, respectively.

CONCLUSIONS

Emulsifier-free miniemulsion of styrene was conducted to produce latex particles with a size of about 200–250 nm in diameter using an anionic ionizable water-soluble initiator, KPS, and ultrasound waves to shear in the absence of any initially added surfactant. It was shown that sonication time played a key role in controlling particle size and distribution. In short sonication time, there were two mechanisms, that is, emulsifier-free miniemulsion and conventional

emulsifier-free emulsion polymerizations, and in long sonication time, emulsifier-free miniemulsion polymerization takes place. Sonication for above 18 min and subsequently polymerizing the produced miniemulsion gave polystyrene particles with 200–250 nm in diameter. Comparison of this method with conventional emulsifier-free emulsion polymerization under the same conditions showed that this method produced latex particles with smaller particle size and narrower molecular weight distribution. It was found that the rate of polymerization (R_p) in miniemulsion polymerization was significantly higher than that in conventional emulsion due to increasing the particles number. This procedure was also used for the encapsulation of magnetite and titanium dioxide nanoparticles, and the attempt to encapsulate of magnetite nanoparticles failed whereas the encapsulation of titanium dioxide nanoparticles with polystyrene was successfully carried out using KPS as initiator in both cases.

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