

Preparation of Hydrophobic Polymer Particles by Radical Polymerization and Subsequent Modification into Magnetically Doped Particles

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ABSTRACT: The application potential of hydrophobic polymer is numerous. Lauryl methacrylate (LMA) having long alkyl chain is a commercially available hydrophobic monomer. In this investigation, poly-LMA (PLMA) latex particles were prepared by suspension polymerization in aqueous media using 2,2'-azobis(isobutyronitrile) (AIBN) in presence of poly(vinyl alcohol) (PVA) as steric stabilizer. The preparation kinetics was studied in detail in terms of percentage yield and particle size variation. Low glass transition temperature ($\sim -65^{\circ}$ C) associated with high flexibility did not allow electron micrographic observation though ¹H-NMR and particle size measurement confirmed the formation of PLMA latex. To improve the glass transition temperature, aqueous emulsion copolymerization of LMA with methyl methacrylate (MMA) was carried out. The solubility of LMA was improved by adding ethanol to the aqueous phase. Two types of polymeric stabilizers, PVA and poly(vinyl pyrrolidone) (PVP) were used to stabilize the colloidal particles. The nature of the stabilizer affected both morphology and final rate of polymerization. The hydrophobic P(LMA-MMA) copolymer particles were subsequently modified by nanosized magnetic (Fe₃O₄) particles by two different methods. The *in situ* formation of Fe₃O₄ particles in presence of P(LMA-MMA) was found to be suitable for the preparation of magnetic latex particles. Scanning electron microscope (SEM), FTIR, transmission electron microscope (TEM), X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX) were used for the characterization of magnetically doped particles. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Hydrophobic polymers are industrially important; find applications in designing resin for chromatographic separation, water purifier, oil absorbency agent, viscosity modifiers, and oil soluble drag reducers.^{1,2} Limited applications are also there in paper and textile industry to improve the water repelling properties. Lauryl methacrylate (LMA) is one such industrially important monomer which provides hydrophobic polymer because of its long chain alkyl group. The very low water solubility (<<0.01 g/100 g at 25°C) of LMA render this monomer unsuitable for polymerization by conventional emulsion process and often results in poor conversion, formation of suspension polymer particles, poor compositional control in copolymers.³

So far most of the researches reported either polymerization or copolymerization of LMA by atom transfer radical polymerization or group transfer polymerization or reversible additionfragmentation chain transfer polymerization in a medium other than water.⁴⁻¹⁰ Additionally, few reports are available on the solution free radical polymerization/copolymerization based on LMA. Klein and coworker studied the free radical copolymerization of LMA with ethyl methacrylate in propylene glycol using oil soluble 2,2'-azobis(isobutyronitrile) initiator and concluded that the kinetics is very similar to emulsion copolymerization kinetics of water soluble monomers in water.¹¹ Similarly, Vasheghani-Farahani estimated the monomer reactivity ratios in free radical solution polymerization of LMA-isobutyl methacrylate.¹² In another paper, the author reported the possibility of emulsion polymerization of LMA in presence of cyclodextrin which acts as a phase transfer agent.¹³ Cyclodextrin acts as a kind of quite effective cargo transporter due to complexation or solubilization of LMA in its hydrophobic interior. The cyclodextrin-

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LMA complex possessing a hydrophilic outer shell diffuses across the aqueous medium to the polymer particles where the LMA is released.

In the present investigation, attempt was made to prepare PLMA latex particle by suspension polymerization using poly(vinyl alcohol) (PVA) as steric stabilizer. The prime requisite of this process is that the monomer and initiator must be insoluble in the continuous phase so that they form droplets within which the polymerization proceeds. Polymerization yield, stability of the latex and particle size distributions were measured against variable PVA and initiator concentrations. However, the prepared PLMA latex particles were too soft due to higher flexibility, i.e., low glass transition temperature $(\sim -65^{\circ}\mathrm{C})^{14}$ and could not be used for further study or modification. As a consequence, we tried to fabricate the previously prepared poly (LMA-methyl methacrylate) or P(LMA-MMA) latex particles¹⁵ with nanosized Fe₃O₄ particles. The earlier work was done to optimize the condition for the preparation of P(LMA-MMA) latex particles by emulsion polymerization. This work is done to increase the application potential of hydrophobic latex particles in magnetic-support-based separation of heavy metals¹⁶⁻¹⁸ and organic pollutants such as oil, dyes, and volatile organic compounds^{19,20} from water. The magnetic nature would facilitate easy separation from the dispersion or purification media by applying magnetic field instead of time consuming centrifugation or sedimentation technique. In addition the magnetic latex particles have potential in many applications such as contrast agents for magnetic resonance imaging, electronics, building blocks in the fabrication of complex devices, catalysis, etc.

EXPERIMENTAL

Materials and Instruments

MMA of monomer grade, purchased from Fluka, Chemika, Switzerland, was distilled under reduced pressure to remove inhibitors and preserved in a refrigerator until use. LMA of monomer grade obtained from Fluka, Chemika, Switzerland, was purified by washing with 10% aqueous NaOH solution followed by dehydration with CaCl₂. Potassium persulfate (KPS) and 2,2'-azobis(isobutyronitrile) (AIBN) both from LOBA Chem. India were recrystallized from distilled water and methanol, respectively. Poly(vinyl pyrrolidone) (PVP) from Fluka, Chemika, Switzerland, of molecular weight 3.6×10^5 gmol⁻¹ and PVA from Thomas baker (Chemicals) Limited, India of molecular weight 1.4×10^4 gmol⁻¹ were used as a polymeric stabilizer. Ethanol was dehydrated and distilled before use. Ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrade (FeCl₂·4H₂O), NaOH, oleic acid, and other chemicals were of analytical grade.

Scanning electron microscope (LEO Electron Microscopy, UK); Bruker Avance 400 MHz NMR Spectrometer; NICOMP 380 Particle Sizer (USA), Sherwood Scientific Magnetic Susceptibility Balance, thermogravimetry analyzer, TGA (TG209F1 Iris@ASC), X-ray diffractometer (XRD) (Bruker D8 Advance) were used for the characterization of latex particles. EDX measurements were carried out with energy dispersive X-ray spectroscopy adapter "Inca" from Oxford Instruments (UK) to the LEO SEM Gemini 1550 (from Zeiss, Germany).

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Preparation of PLMA Particles by Suspension Polymerization Suspension polymerization of LMA (2.0 g) was carried out at 70°C for 24 h in a two-necked round bottomed flask dipped in an oil bath using AIBN (0.03 g) as oil soluble initiator. Variable amount of PVA based on LMA content was used as polymeric stabilizer. Polymerization was carried out under a nitrogen atmosphere and the reaction mixture was magnetically stirred.

Similarly, using the same conditions, a series of PLMA latexes were prepared with variable amount of AIBN and the PVA content (0.6 g) was kept identical. The monomer content (4% w/w) was kept identical in all the batches based on the dispersion media.

Preparation of P(LMA-MMA) Particles by Emulsion Copolymerization

P(LMA-MMA) particles were prepared by emulsion copolymerization of LMA (2 g) and MMA (2 g) in a three-necked round flask dipped in a thermostat water bath using KPS (0.04 g) as water soluble initiator. The dispersion media comprised 40% (w/w) ethanol in water–ethanol mixture (36 g) and PVA or PVP (0.1 g) was used as polymeric stabilizer. The reaction mixture was mechanically stirred at 100 rpm and polymerization was carried out at 70°C for 12 h.

Polymerization Yield or Overall Monomer Conversion

Polymer samples were withdrawn from the reactor and instilled in a preweighed dried ceramic Petri dish. To prevent further polymerization, the ceramic dish contained a known amount of 1% hydroquinone solution and was rapidly dipped in an ice water bath. Samples were kept in an oven at around 90°C until a constant weight was reached. Then the percentage of yield/ conversion was calculated from the solid content by correcting for the amounts of auxiliary materials.

In the suspension polymerization, PLMA latex particles were partially aggregated into small flocks. At the end of polymerization, the emulsion was filtered through a cellulose net having porosity of around 10 μ m. The residual part was dried in oven to a constant weight to measure the percentage of coagulant.

Measurement of Diameter of PLMA Latex Particles

Intensity weighted average particle diameters were measured by a dynamic laser scattering particle sizer (NICOMP, model 380, Santa Barbara, CA). Before the measurement, the dispersion was diluted to around 0.1% solid using distilled water. Each measurement was repeated twice and the average value is reported in the graphs. The reproducibility was good as in one such experiment PLMA latex prepared with 30% (w/w) PVA was repeatedly measured and the standard deviation was calculated to be around 14.0.

Preparation of Magnetite (Fe₃O₄) Particles

Nanosized magnetite (Fe₃O₄) particles were produced by coprecipitation of Fe²⁺ and Fe³⁺ from their aqueous solution (molar ratio 1: 2) using 5*M* NaOH. The precipitation was carried out in a three-necked flask, magnetically stirred under a nitrogen atmosphere at 85°C for 2 h. Oleic acid was slowly added toward the end of the process to stabilize the Fe₃O₄ dispersion.

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Figure 1. PVA-dependent percent yield and coagulant obtained during preparation of PLMA particles by suspension polymerization. Conditions: 65° C, N₂, 250 rpm for 24 h.

The produced Fe_3O_4 particles were washed by serum replacement with deionized distilled water, followed by 0.1*M* HCl aqueous solution, and again by deionized distilled water in order to remove the residual electrolyte and excess oleic acid.

Preparation of Magnetically Modified P(LMA-MMA) Particles Two routes have been used to prepare magnetically modified P(LMA-MMA) particles. In one route, attempt was made to prepare Fe₃O₄/P(LMA-MMA) composite particles by seeded copolymerization of LMA (2 g) and MMA (2 g) in presence of nanosized Fe₃O₄ particles (0.05 g). Seeded copolymerization was carried out in water-ethanol dispersion media containing 40% (w/w) ethanol while the mixture was mechanically stirred at 70°C for 12 h under a nitrogen atmosphere. It was expected that under the conditions Fe₃O₄ particles would be encapsulated within P(LMA-MMA) shell layer. In another route, attempt was made to prepare P(LMA-MMA)/Fe₃O₄ composite polymer particles by in situ preparation and deposition of nanosized Fe₃O₄ particles on (0.05 g) P(LMA-MMA) latex particles. In this case, it was expected that P(LMA-MMA) latex particles would be covered with nanosized Fe₃O₄ particles. The copolymer particles stabilized by, respectively, PVA and PVP were used for the magnetization.

The prepared magnetically modified composite particles were washed repeatedly by serum replacement to remove any free Fe₃O₄ particles before analyses.

Magnetic Susceptibility

The particles were washed by serum replacement and subsequently separated from the respective dispersion, dried in oven at 70°C for several hours. The dried powders were then placed in the preweighed sample tube and measured the magnetic susceptibility (χ_g) using a Magnetic Susceptibility Balance.

Thermogravimetric Analysis (TGA)

Thermal properties of the dry powdered samples of Fe₃O₄, Fe₃O₄/P(LMA-MMA), and P(LMA-MMA)/Fe₃O₄ microspheres were measured by heating samples (15–30 mg) under flowing nitrogen atmosphere from 40°C to 600°C at a heating rate of 20°C/min and the weight loss was recorded.

RESULTS AND DISCUSSION

PLMA Latex by Suspension Polymerization

Hydrophobic latex particles derived from LMA was synthesized in an aqueous media via suspension polymerization. Within 1 h after starting the polymerization, the clear heterogeneous system turned milky. Figure 1 shows the PVA-dependent yield and coagulant for PLMA particles. It is to be noted that polymer yield included the coagulant. The percent yield increased with the increase in PVA content. A maximum yield of 95% was obtained as the PVA content increased to 30% (w/w) based on total LMA. The percent coagulant decreased with the increase of PVA and a minimum 18% was obtained at 30% (w/w) PVA content. It is evident that lower percentage of coagulant at the PVA content in excess of 20% (w/w) increased the yield of latex particles and hence the polymerization proceeds without much hindrance. Polymeric stabilizer therefore played a vital role in stabilizing the PLMA colloid system. This result implies that higher the PVA added in the system the higher the number of monomer droplets are stabilized, i.e., the locus of polymerization.

The PVA-dependent variation of intensity weighted average diameters of PLMA latex particles prepared with 0.03 g AIBN decreased with the increase in PVA content as shown in Figure 2. This feature is not surprising as the addition of stabilizer increased the stability of the monomer droplets and hence the number of polymerization locus and polymerization proceeds within the droplets without coalescence and breakup of droplets.



Figure 2. Effect of PVA content on intensity weighted average diameter of PLMA latex particles prepared by suspension polymerization. Conditions: 65°C, N₂, 250 rpm for 24 h.

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Figure 3. Effect of AIBN content on percent yield and coagulant obtained during suspension polymerization of LMA in aqueous media. The dotted line is just for guiding the eyes. Conditions: 65°C, N₂, 250 rpm for 24 h.

Figure 3 represents the AIBN-dependent yield and coagulant obtained during the preparation of PLMA latex by suspension polymerization using 30% (w/w) PVA. The percentage of yield did not change much with the increase of [AIBN]; however, the percentage of coagulant increased abruptly as the AIBN increased from 0.06 to 0.1 g. This suggests that as AIBN is increased the concentration of radicals increased and hence the number of polymerization locus. Since [PVA] remained constant, it became insufficient to stabilize the colloidal system due to the increased total surface area of the particles. This behavior is also common in any free radical polymerization.^{21–23}

The change in diameter of PLMA latex particles with AIBN content prepared with 30% (w/w) PVA based on LMA content



Figure 5. ¹H-NMR spectra of PLMA latex particles taken in CDCl₃.

(Figure 4) indicates that the final diameter increased as the AIBN content increased. This confirmed the above observation, i.e., as the number of polymerization locus increased due to the increase in radical concentration, the particles became unstable and aggregated. Hence, the 30% PVA content is not enough to stabilize the system at the highest AIBN content.

¹H-NMR spectra was used to confirm the polymerization of LMA. Before the recording of NMR spectra shown in Figure 5, the latex particles prepared with 30% (w/w) PVA were repeatedly washed to remove any unreacted monomer. The





Figure 4. Effect of AIBN content on intensity weighted average diameter of PLMA latex particles prepared by suspension polymerization. The dotted line is just for guiding the eyes. Conditions: 65° C, N₂, 250 rpm for 24 h.

Figure 6. The percentage of conversion of LMA and MMA into copolymer latex particles prepared by emulsion copolymerization in aqueous media in presence of identical amount of PVA and PVP, respectively. Conditions: 70° C, N₂, 95 rpm for 12 h.



Figure 7. SEM photographs of P(LMA-MMA) latex particles prepared by emulsion copolymerization in presence of stabilizers: (a) PVA and (b) PVP.

characteristic peak of ester protons (CH₂OCO—) appeared at 3.90 ppm. The multiplate signal due to lauryl chain (CH₃—(CH₂)₁₁—) is observed between 0.701 and 1.932 ppm. The signal due to methyl protons attached to the polymer backbone is also observed at 1.281 ppm. Hence, it can be said that LMA monomer is polymerized.

Although the above results confirmed the formation of PLMA latex particles by suspension polymerization, it was not possible to observe electron micrographs due to the complete collapse of the particles in the dried state. This is attributed to the low glass transition temperature of PLMA (~ -65° C). To improve the glass transition temperature of PLMA latex particle, comonomer MMA was used to copolymerize LMA. The homopolymer of MMA has relatively high glass transition temperature (110°C) and it was observed that with increasing LMA in the P(LMA-MMA) copolymer, the T_g changes from 100°C to 80°C.¹⁵ The prepared copolymer latex particles named as P(LMA-MMA) were used to prepare magnetically doped hydrophobic latex particle.

Magnetically Modified P(LMA-MMA) Latex Particles

Two types of P(LMA-MMA) copolymer particles having different morphology were prepared by aqueous emulsion polymerization using either PVA or PVP as polymeric stabilizer. A total of 40% (w/w) ethanol based on total dispersion media was used to increase the solubility of LMA.

Figure 6 shows the time-conversion curves of P(LMA-MMA) latex particles prepared by emulsion copolymerization using identical amounts of either PVA or PVP. The steep increase in conversion upto 55% within the first 60 min shows no differentiation between two different reaction conditions. During the following period, the conversion increased much slower with time. The second stage of conversion-time curves shows a significant difference in dependence of the nature of stabilizer. P(LMA-MMA) polymer particles prepared in presence of PVA reached the final conversion after about 400 min instead of 720 min in presence of PVP.

SEM photographs of P(LMA-MMA) latex particles prepared with PVA and PVP stabilizers are illustrated in Figure 7. For PVP as steric stabilizer, the average particle diameter is less than half of that for PVA. SEM images of copolymer particles prepared in presence of PVA and PVP revealed a rather unusual morphology. It is reasonable to assume that artifacts are not developed during sample preparation as the fluid phase was slowly evaporated at low temperature. The surface of copolymer particles prepared in presence of PVA is heterogeneous, whereas that of particles prepared in presence of PVP is relatively smooth and shape appears to be bowl shaped to certain extent.



Figure 8. SEM photographs of $Fe_3O_4/P(LMA-MMA)$ composite polymer particles prepared by seeded copolymerization in presence of stabilizers: (a) PVA and (b) PVP.



Figure 9. SEM photographs of P(LMA-MMA)/Fe₃O₄ composite polymer particles prepared by *in situ* precipitation of Fe₃O₄ particles on P(LMA-MMA) particles obtained in presence of stabilizers: (a) PVA and (b) PVP.

To prepare magnetically modified hydrophobic latex particles, two different routes have been used. The results are summarized below.

In one route, seeded copolymerization of LMA and MMA was carried out in presence of nanosized Fe_3O_4 particles. The particles were named as $Fe_3O_4/P(LMA-MMA)$ composite particles. Seeded copolymerization was carried out using identical amounts of PVA and PVP, respectively. Under the conditions, it is expected that Fe_3O_4 particles would be encapsulated. However, relative to the size and morphology of the copolymer seed particles (Figure 7), $Fe_3O_4/P(LMA-MMA)$ composite polymer particles illustrated in Figure 8 did not change. High resolution transmission electron micrographs (not shown) also did not show the existence of a different phase inside the particles, i.e., Fe_3O_4 particles are not incorporated within the copolymer shell layer. This may suggest that the surface of Fe_3O_4 particles is not hydrophobic enough for the encapsulation with hydrophobic LMA-MMA copolymer shell layer.

In another route, *in situ* preparation of nanosized Fe_3O_4 particles was carried out in presence of previously prepared P(LMA-MMA) particles. Both PVA and PVP stabilized copolymer latexes were used for the purpose. Under the conditions, Fe_3O_4 particles are expected to deposit on the surface of hydrophobic copolymer latex particles. We called those modified particles as P(LMA-MMA)/Fe₃O₄ composites.

Figure 9 shows the SEM photographs of washed P(LMA-MMA)/Fe₃O₄ composite particles. It is clearly visible that particle morphologies of both copolymer particles have been changed after deposition of Fe₃O₄ particles. Washed magnetically doped composite particles showed positive value of magnetic susceptibility ($\sim 2.2 \times 10^{-4}$) indicating that both are strongly paramagnetic. The particles also visibly moved toward the magnetic field in both emulsion and dried states. The magnetically doped composite particles can therefore be separated from the dispersion by applying magnetic field.

A comparative plot of FTIR spectra of Fe_3O_4 particles and washed P(LMA-MMA)/Fe_3O_4 composite particles stabilized by PVA and PVP is shown in Figure 10. In the FTIR spectrum of Fe₃O₄, the characteristic broad stretching vibrations due to

Fe—O bonds of Fe₃O₄ particles appeared at 582.5 cm⁻¹ and 357 cm⁻¹, respectively, as also reported elsewhere.^{24–26} Both spectra of magnetically doped composite particles exhibited similar but weak signal at 580 cm⁻¹ and 353 cm⁻¹, respectively. The characteristic signal due to carbonyl (CO) group of ester derived from LMA and MMA components is also appeared at 1720 cm⁻¹ in the composite particles. The above results also confirmed that Fe₃O₄ particles have successfully been deposited on the surface of copolymer particles.

Figure 11 shows the TGA thermograms of P(MMA-LMA) and P(MMA-LMA)/Fe₃O₄ microspheres stabilized by PVA (Figure 11A) and PVP (Figure 11B), respectively. It is expected that as the temperature is raised from ambient temperature to 600° C, the organic part of the composite would be burned away and the remaining percentage after calcination would represent the iron oxide content. It is evident that irrespective of copolymers



Figure 10. FTIR spectra of (a and b) washed $P(MMA-LMA)/Fe_3O_4$ composite and (c) Fe_3O_4 particles. The copolymer particles used for composite preparation were obtained in presence of stabilizers: (a) PVA and (b) PVP, respectively.



Figure 11. TGA thermograms of (a) P(LMA-MMA) particles and (b) P(LMA-MMA)/Fe₃O₄ composite polymer particles. Data in A and B represent two different copolymer particles stabilized by PVA and PVP, respectively.

prepared by either PVA or PVP completely burned away at 420°C. On the contrary, for PVA-stabilized P(LMA-MMA)/ Fe₃O₄ composite particles about 79% of the total weight burned away and hence 21% (w/w) magnetic Fe₃O₄ nano particles are precipitated on the copolymer particles. Similarly, about 12% (w/w) magnetic Fe₃O₄ nano particles are deposited on PVP stabilized P(LMA-MMA) copolymer particles. For PVA, the surface heterogeneity of the copolymer particles increased the loading capacity of Fe₃O₄ nano particles. In both systems, the weight loss onset temperature, i.e., degradation temperature for composite particles shifted to higher value. The more the inorganic



Figure 12. XRD patterns of (a) P(LMA-MMA) prepared by using PVA, (b) Fe₃O₄, and (c and d) P(LMA-MMA)/Fe₃O₄ composite particles. The copolymer particles used for composite preparation were obtained in presence of stabilizers: (c) PVA and (d) PVP.

particles deposited on the copolymer particles the greater the shifting of onset temperature to higher value occurred. This indicates that the thermal stability of composite particles improved due to the incorporation of inorganic materials.

Figure 12 shows a comparative XRD patterns for P(LMA-MMA) and Fe_3O_4 particles and washed P(LMA-MMA)/Fe_3O_4 composite polymer particles. The copolymer particles irrespective of stabilizer nature are substantially amorphous in character and a broad reflection centered at around 21° is appeared. Considering the same diffraction pattern, copolymer particles stabilized by PVA is only illustrated in the Figure. In spectra of P(LMA-MMA)/Fe₃O₄ composite particles 2 weak reflections at around 36° and 63° are observed, which are the characteristic peaks normally observed for Fe₃O₄ nano particles.²⁷ The poor signal intensity is attributed to the low concentration of Fe₃O₄ particles. The broad reflection band appeared in copolymer particles almost disappeared in composite polymer. The presence of



Figure 13. EDX spectra of P(LMA-MMA)/Fe₃O₄ composite polymer particles prepared from copolymers stabilized by (a) PVA and (b) PVP, respectively.

noises in all spectra can be explained from the view point of rich amorphous character of the particles.

The EDX spectra of washed P(LMA-MMA)/Fe₃O₄ composite polymer particles were also used to confirm the existence of Fe atom on the surface of copolymer particles (Figure 13). Both particles irrespective of the type of stabilizer showed the presence of a signal due to Fe atom. The elements other than Fe, C, and O came from the glass ware used for the preparation of samples. The amount of Fe (atom %) impregnated on P(LMA-MMA) copolymer particles is higher on PVA stabilized particles ($\sim 14\%$) than on PVP stabilized particles ($\sim 7\%$). This result again supported the earlier observation made in the explanation of TGA thermograms.

CONCLUSIONS

PLMA latex particles were prepared by suspension polymerization in aqueous media using oil soluble initiator and PVA as stabilizer. The percentage yield, particle diameter, and coagulant suggested that PVA played a vital role to get stable suspension. The particles were very soft and the morphology changed while drying due to low glass transition temperature. Stable copolymer latexes (PLMA-MMA) with comparatively higher glass transition temperature were prepared by emulsion copolymerization in aqueous media containing 40% (w/w) ethanol. The nature of stabilizer affected the morphology of the copolymer particles. The surface heterogeneity of the PVA stabilized P(LMA-MMA) latex particles improved the loading capacity of nanosized Fe₃O₄ particles.

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