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Emulsifier-Free Emulsion Polymerization of Methyl Methacrylate Containing Hydrophilic Magnetite Nanoparticles

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Abstract: Emulsifier-free emulsion polymerization of methyl methacrylate was carried out in the presence of hydrophilic magnetite nanoparticles using a persulfate initiator. Before the magnetic nanoparticles were placed into the polymerization system, they were dispersed and stabilized electrostatically with perchloric acid in water (magnetic sol). For magnetic nanoparticles in the sol, the hydrodynamic radius and polydispersity index (PDI) measured by dynamic light scattering was 18.8 nm and PDI of 0.282, respectively. The latex sizes also were determined to be 125 -223 nm with a PDI of 0.009-0.065. Magnetic measurements by vibrating sample magnetometry confirmed that the magnetite nanoparticles and magnetic poly(methyl methacrylate) nanospheres exhibited superparamagnetism with zero coercivity. The saturation magnetization of the magnetic polymeric nanospheres ranged from 0.2 to 1.19 emu/g depending on the magnetite content. The polymer chain terminations were affected by the addition of magnetite nanoparticles to the polymerization system. In addition, the magnetite that reduced the average molecular weight of the polymers obtained by gel permeation chromatography should be defined as a transfer agent.

Keywords: emulsifier-free emulsion polymerization, superparamagnetic latex, magnetic nanoparticles.

Introduction

In recent years, there is a considerable interest in the incorporation of Fe_3O_4 (magnetite) nanoparticles in polymeric nanospheres which is mainly found to be useful in various applications such as magnetic resonance imaging, drug delivery, biomedicine, biosensors, bioprocessing and high-grade magnetic separation.[1-3] The one of the methods that has been proposed for the synthesis of polymeric nanospheres containing magnetite is emulsifier-free emulsion polymerization of monomer *in situ*.[4] In the reports, the surfaces of magnetite nanoparticles were modified by suitable surfactants such as sodium oleate,[5] dodecanoic acid,[6] oleic acid[7,8] and hence the hydrophobic magnetite has been put into polymerization medium for the better interaction with polymer molecules. On the side, the effects of various polymerization parameters such as the monomer concentration, ferrofluid content and initiator concentration on particle size of the magnetic composite latex particles were examined in detail.[4,6,9] To our knowledge, but no research has been focused on the hydrophilic surfaces of magnetite nanoparticles that was treated with perchloric acid in emulsifier-free emulsion polymerization system.

In this study, the main interest was to investigate the effects of the hydrophilic or naked surfaces of magnetite nanoparticles on the properties of the polymers synthesized by emulsifier-free emulsion polymerization system of methyl methacrylate (MMA) in presence of potassium persulfate. For this purpose, an electrostatically stable dispersion of the magnetite nanoparticles synthesized by coprecipitation was prepared with perchloric acid in water and therefore the hydrophilic magnetite was used in the polymerization system as different from literature.[4-9] It was seen that the smaller latex size and poly(methyl methacrylate) (PMMA) with smaller molecular weight was obtained when the magnetite nanoparticles were put into the system. Furthermore, the magnetite concentration was examined to have significant influences on the latex stability and the molecular weight and terminal structures of the PMMA chains.

Experimental

Materials. Methyl methacrylate (MMA) was freed from phenolic inhibitors by shaking with 5% aqueous NaOH, washing with water and drying over Na_2SO_4. The initiator, potassium persulphate (KPS), was a product of Fluka, Ger-

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many. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, >99%), aqueous ammonia (25% NH_3 in water, w/w), perchloric acid ($HClO_4$, % 60) were obtained from Merck. Ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, >99%) were purchased from Fluka. Double distilled water was used in all the stages of the workup. The conductivity of water was measured about 1.0-1.5 μs cm^{-1} at 25 °C.

Synthesis of Magnetite Nanoparticles. Magnetite nanoparticles were prepared by co-precipitation according to the Massart method.[10] Magnetite precipitate formed in the reaction was deposited with a magnet placed under the vessel of the solution, and then supernatant liquid was removed. To obtain magnetic sol, the precipitate was stirred with aqueous 2 M $HClO_4$ and was then isolated by centrifugation. After this process was repeated twice, its peptization was accomplished merely by adding water.

Synthesis of Magnetic Polymeric Nanospheres. Polymerization was carried out at 75 °C in a 1-L round-bottomed, four-necked glass flask equipped with a mechanical stirrer, nitrogen inlet, thermometer (± 0.1 °C), and condenser. The reactor was immersed in a thermostated water bath to maintain constant temperature. Firstly, the appropriate amounts of water and 20 g MMA were charged into the reactor and stirred under N_2 atmosphere for about 60 min to remove O_2 from the reaction system. Temperature equilibrium was attained and the aqueous phase was saturated with monomer. The magnetic sol was added into the reactor and the stirring rate was setup and finally the polymerization process was started with adding 0.5152 g KPS dissolved in 50 mL water. Polymerizations were carried out in total 950 mL water for about 90 min. Synthesis conditions were listed in Table I.

After the polymerization, 10 mL of the latex was removed from the reactor. It was poured into glass vial containing 1% hydroquinone as the inhibitor. The final product was dried in oven at 70 °C. The monomer conversion (X%) was calculated by eq. (1)

$$X\% = \frac{m_L - m_N x W_m}{m_N x W_S - m_N x W_m} \times 100 \tag{1}$$

where m_L is the weight of latex solution taken from reactor; m_N, the weight of dry polymer; W_m and W_S, the weight fraction of magnetite and solid initially in the reaction mixture respectively.

Table I. *Experimental Conditions for PMMA Latexes

Sample	Magnetic Sol (mL)	Deionized Water (mL)	Stirring Rate (rpm)
MP0	0	950	300
MP1	20	930	500
MP2	35	915	400
MP3	50	900	400

*Polymerization temperature: 75 °C, KPS=0.515 g, MMA=~20 g.

Characterizations. The crystalline structure of the nanoparticles was investigated with PANalytical's X'Pert PRO X-ray diffractometer system (XRD). The XRD patterns were taken from 10° to 80° (2θ value) using Cu Kα radiation at room temperature. An ALV/CGS-3 compact goniometer system (Malvern, UK) was used to measure the particle size and size distribution of magnetite nanoparticles in magnetic sol. Total iron concentration in magnetic sol was determined spectrophotometrically[11] after HCl/H_2O_2 induced oxidation Fe^{+2} to Fe^{+3} and addition of potassium thiocyanate followed absorption measurement of the thiocyanate complex at λ = 480 nm. Magnetic properties of the magnetite nanoparticles and the polymeric nanospheres containing magnetite were determined from the hysteresis curves measured at room temperature using a vibrating-sample magnetometer (VSM-ADE EV9 Model). The measurements were performed on the samples that were dried at 70 °C.

To determine amount of free magnetite particles from the polymer particles, magnetic polymeric particles were introduced into aqueous HCl solution (2 M) in volumetric flask for 48 h at room temperature. After the suspension was centrifuged, the upper fraction was restrained for chemical analysis with thiocyanate described earlier. For hydrodynamic radius (R_H) and the polydispersity index (PDI = μ_2/Γ^2) of polymeric nanospheres containing magnetite, dynamic light scattering (DLS) studies were conducted using Zetasizer NanoZS (Malvern Instruments). Before the measurements, the aggregates in the latex were removed by filtration and then polymeric particles were highly diluted; thereafter, the samples were introduced into a thermostated scattering cell at 25 °C. Thermal gravimetric analysis (TGA) with diamond series from PerkinElmer Instruments was used to observe thermal degradation behavior and the weight loss of composite samples. Approximately 10 mg of sample was placed in a aluminum pan and heated from 25 to 600 °C at 20 °C/min. High resolution transmission electron microscope (HRTEM, FEI TECNAI G^2 F30 model) with an accelerating voltage of 300 kV was used to obtain information about the morphology of magnetite nanoparticles and magnetic polymer nanospheres. Samples for HRTEM were prepared by placing a drop of very dilute dispersion on a copper grid covered by Formvar foil and drying.

To separate magnetic nanoparticles from the polymers, the dried composite samples were dissolved in the chloroform and a bit iron powder was added to the solution. The magnetic nanoparticles in the solution adsorbed on the surface of the iron powder due to the effect of the magnetic field produced by a magnet put under the vessel of the solution at about 5 h. It is observed that only the polymers suspended while precipitating the magnetite in the chloroform. The polymer samples were used to determine the average molecular weight (M_n) and polydispersity index (M_w/M_n) using gel permeation chromatography (GPC). The GPC consisted of an Agilent Iso Pump, a refractive index detector, both Mixed ‘D’ and Mixed ‘E’ columns (ex. Polymer Labs) and calibration was carried out using PMMA calibration standards. The GPC eluent was HPLC grade THF stabilized with BHT at a flow rate of 1.0 mL/min.

Results and Discussion

In this study, after the synthesis process, superparamagnetic magnetite nanoparticles, which were characterized by XRD and VSM, were dispersed in the water using $HClO_4$. The mean diameter of the magnetite particles in the sol was measured to be 18.8 nm with PDI: 0.282 using DLS. As seen in Figure 1(b), DLS results of superparamagnetic nanoparticles showed the magnetite nanoparticles were dispersed well in water. In addition, HRTEM picture in Figure 1(a) revealed that the particles have irregular shapes as reported[12] and their average size was about 10 nm. The concentration of magnetite in the sol was calculated as 1.13×10^{-2} g/mL. The various volumes of the magnetic sol were added to the emulsifier-free emulsion polymerization of MMA with KPS initiator and the forming of latexes allowed to proceed for 1.5 h.

Figure 2 shows a HRTEM micrograph and DLS diagram of the synthesized magnetic polymeric nanospheres in MP1 latex. The particle size distribution of latex was seen highly narrow in both of Figure 2(a) and 2(b); however the average size of particles was calculated 118 nm by HRTEM and this value was slightly smaller than DLS result (125 nm) because of Brownian motions.[13] Additionally, inset at the left of Figure 2(a) reveals that the magnetic nanoparticles are in the core of polymeric nanospheres.

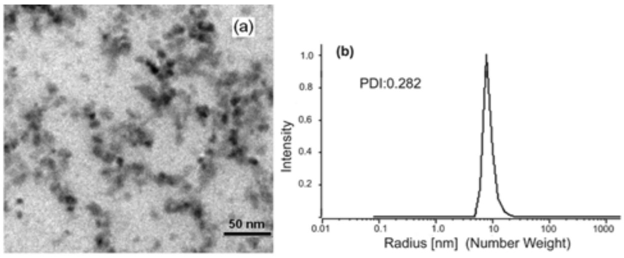

Figure 1. (a) HRTEM picture and (b) DLS diagram of magnetic nanoparticles.

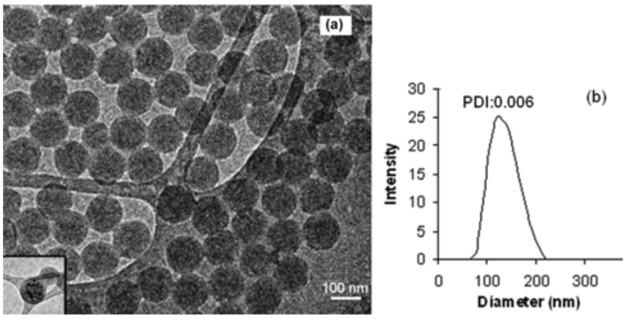

Figure 2. (a) HRTEM picture and (b) DLS diagram of magnetic polymeric nanospheres.

Table II. The Properties of the Synthesized Latexes

Conversion (%)	Aggregate Amount (g)	Magnetite in *p.s. (%)	R_H (nm)	PDI	M_s (emu/g)
98.36	-	-	223	0.009	-
90.23	a few	99.59	125	0.006	0.225
96.27	0.127	97.95	156	0.060	1.191
96.69	0.347	96.84	150	0.065	1.017

*p.s: Polymeric nanospheres.

The PMMA latex without the magnetic sol was also prepared at similar conditions for comparison. The properties of latexes in Table II were examined and discussed depending on the amount of magnetite.

In Table II, all monomer conversions (MP1, MP2, and MP3) containing the magnetic sol were obtained in the range of 90.23% to 96.36%, which were slightly smaller than the pure latex (MP0) in the reaction systems. This is not like the limited conversion effect of magnetite nanoparticles observed by Pich *et al.*,[5] which is probably due to the use of well-dispersed magnetite nanoparticles in our polymerization system. During the polymerization process having the magnetic sol, the aggregations were realized and more pronounced with increasing magnetite amount. The aggregates have been removed from latex by filtration, dried and weighted and then recorded in Table II. The amount of the aggregates increased up to 0.347 g as the amount of magnetic sol increased from 20 to 50 mL. The possible explanation for the observations made here is when the acidic magnetic sol is added to reaction medium H^+ ions which provide surface charge desorb from the surface of magnetite nanoparticles[14] and the nanoparticles adhere together and form agglomerates of increasing size. The percentage of magnetite inside polymeric nanosphere also reduced from 99.59 to 96.84 with the increase of the aggregations as shown in Table II. During the process, it is anticipated that the unstable particles enlarge with polymer molecules and fall in due to gravity. The variation of the saturation magnetization, M_s with the applied magnetic field (hysteresis) provides information on the magnetic properties of the latex. In Table II, M_s values of latexes obtained from the curves of the Figure 3 increased from 0.225 to 1.191 emu/g with increasing the amount of magnetic sol. However, M_s value of MP3 latex reduced to 1.017 emu/g due to the increase of the aggregations. Besides, Figure 3 showed the hysteresis curves of the samples. In the curves, as the magnetic field intensity decreased, the magnetization decreased from the plateau value and reached zero. Therefore, all latexes were seen to have a superparamagnetic property.

The 125-156 nm sized polymeric nanospheres were formed in the polymerization system with magnetic sol, which was

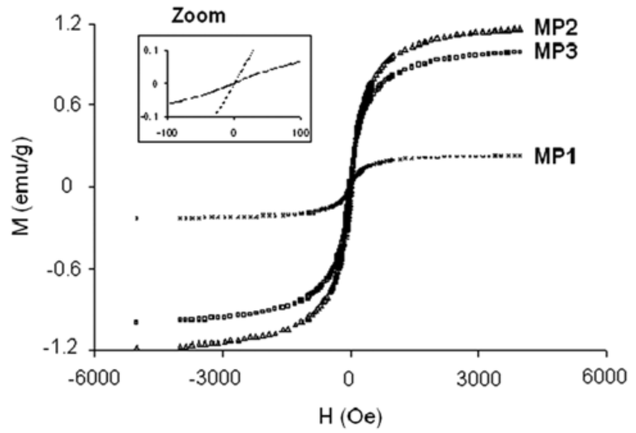

Figure 3. Hysteresis curves of the synthesized superparamagnetic polymeric particles using different amounts of magnetite sol. Inset shows the superparamagnetic nature of the particles with zero coercivity.

smaller than the pure latex (223 nm). In emulsifier-free emulsion polymerization system, the size of polymeric nanospheres depends on the radical concentration strongly.[15] The increased radical concentration led to a higher number of primary particles, so a smaller particle size for resulting nanospheres is obtained.[16] In our study, the Fe^{+2} ions on surface of magnetite nanoparticles can accelerate the decomposition of persulfate initiator and increase radical concentration as the reaction.[17]

$$Fe^{+2} + S_2O_8^{-2} \rightarrow SO_4^{-} \bullet + SO_4^{-2} + Fe^{+3} \qquad (2)$$

According to the above reaction, it should be expected that the size of the magnetic PMMA nanospheres decrease with an increase in the magnetic sol amount. However, the polymeric nanospheres sizes were between 150-156 nm with little change at 400 rpm. The magnetic sol is a strong acid and also an electrolyte consequently the ionic strength of polymerization medium was increased with increasing magnetite amount. Thus, the polymeric nanosphere size was not strongly affected by the concentration of magnetite due to salting-out effect.[18] However, as shown Table II, size (125 nm) of the sample MP1 was measured smaller than the ones of MP2 and MP3 latexes due to the higher stirring rate (500 rpm). The reaction the between the magnetite and the initiator stated in the eq. (2) accelerated as the stirring rate increased, and hence the more radical was produced in the heterogeneous polymerization mixture. Therefore, the smaller sizes of the polymeric nanospheres were obtained with the increase of stirring rate in magnetic-sol used polymerizations. It can be also seen in Table II, the particle size distributions broadened with the increase of the aggregates at the high magnetite concentration.

Under the free radical polymerization, different termination routes result in different terminal groups in PMMA chains. Figure 4 shows thermal degradation behavior of pure PMMA (MP0) sample and the composite PMMA (MP1 and MP3) samples. As seen in Figure 4, all synthesized PMMA latexes have three stages of the thermal degradation. The PMMA chains with different terminal structures would degrade at different temperatures.[19] For example, combination would join two growing chains together to form a single polymer molecule and produces a “head-to-head” (h-h) linkage at the point of coupling (PMMA-hh). Another termination reaction, namely, disproportionation, would result in the formation of an equal number of two polymer molecules, one with a saturated end group (PMMA-H) and the other with an unsaturated end group (PMMA-$CR=CH_2$). In this study, the first stage is in the temperature range from 165 to 270 °C due to the degradation of PMMA-hh, the second stage in the range 270 to 320 °C attributed to the PMMA-$CR=CH_2$ and the last stage in the range 320 to 430 °C caused by the end-initiated depolymerization from PMMA-H chains. The results are in consistent with the degradation temperatures of PMMA-hh, PMMA-$CR=CH_2$, and PMMA-H are about 160, 270, and 360 °C, respectively at a heating rate of 2 °C/min.[19] The proportion of PMMA-$CR=CH_2$ and the weight loss in the second stage increased with the increase of the magnetite concen-

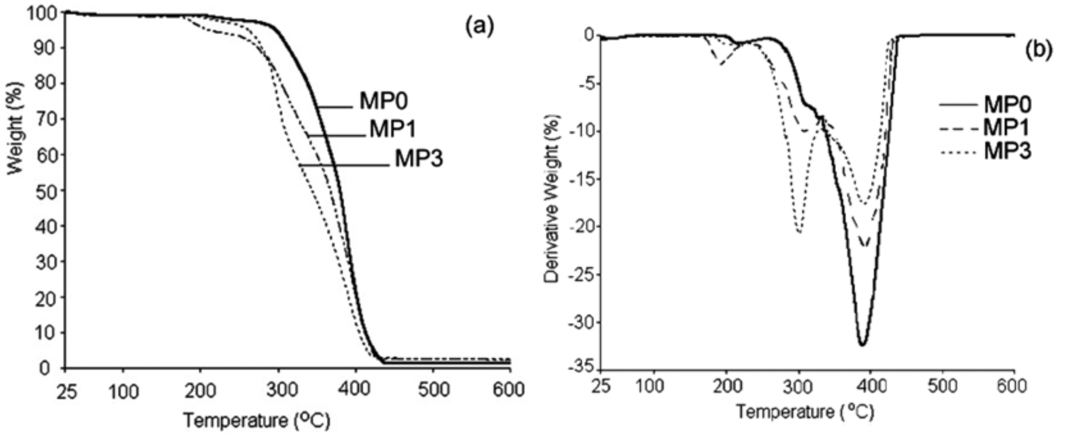

Figure 4. (a) TGA and (b) DTA curves of the magnetic polymeric composites.

tration as it can be easily seen in Figure 4(b). Therefore, the magnetite is presumed to be responsible for the increase of PMMA-CR=CH_2 proportion during polymerization. In other words, it seems that the magnetite acted as a chain transfer agent to terminate growing polymer chains.[20] The DTA curves shown in Figure 4(b) also exhibited that the proportions of the PMMA-hh were enhanced by the magnetite. However, the intensity of the low-temperature peak firstly increased with the adding of magnetite and then decreased because of the radical termination reaction of Fe^{+2} on surface of magnetite with the excess of magnetite amount as in the reaction.[17]

$$Fe^{+2} + SO_4^{-} \bullet \rightarrow Fe^{+3} + SO_4^{-2} \quad (3)$$

It can be said the proportion of PMMA-hh was partially related with the amount of PMMA-CH=CH_2 since Manring[21] has also reported that an active free radical site is formed on the polymer chain end by radical attack at the vinyl terminus of PMMA-CH=CH_2 and the forming of the monomer during degradation process. The thermal degradation and molecular weight properties of PMMA latex is presented in Table III. For MP0 sample, the first (T_{d1}) and the last (T_{d3}) maximum-rate degradation temperature were the highest (222.5 ºC) and the lowest (390.3 ºC), respectively while the second (T_{d2}) maximum-rate was almost the same with the other samples.

Mc Neill[22] found that the sample having higher molecular weight would have higher degradation temperature in the first stages yet lower degradation temperature in the last stage degradation. This phenomenon was also observed and discussed by Grant and Bywater[23] in connection with the results of a number of isothermal degradations. Indeed, the inversion effect caused by the molecular weight was clearly observed where the highest molecular weight (MP0) had the highest T_{d1} and the lowest T_{d3}. On the other hand, the average molecular weight of polymers reduced in the presence of magnetite nanoparticles as resulting from the effect of chain transfer, as also confirmed by thermal analysis. Although Fe^{+2} ion on surface of magnetite nanoparticles is the most common persulfate activator, additions of ferrous iron in excess can lead to the rapid decomposition of persulfate and a loss in remediation performance.[24] In this point of view, the increase of the magnetite amount caused a decrease in the concentration of sulfate radicals which resulted in a high average molecular weight as observed experimentally in Table III. The molecular weight distribution of sample MP1 was found to be the broadest. This is likely due to the high number of chain termination reactions effected by the combination of catalytic and chain transfer agent of magnetite in the latex of MP1. However, the catalytic effect decreased with increasing magnetite concentration as stated in the eq. (3) and hence the lowest M_w/M_n rate 2.60 was obtained for sample MP3. Thus, the results from the molecular weight distribution also verified that the magnetite nanoparticles have a considerable effect on the radical concentration of polymerization.

Table III. Thermal Degradation and the Molecular Weight Properties of the PMMA Latex

Sample	M_n (g/mol)	M_w/M_n	T_{d1} (ºC)	T_{d2} (ºC)	T_{d3} (ºC)
MP0	113,450	2.84	222.5	301.0	390.3
MP1	51,546	3.20	180.1	301.8	398.5
MP2	66,243	2.75	-	-	-
MP3	72,455	2.60	200.2	300.0	396.4

Conclusions

This is most probably the first time that the hydrophilic magnetite nanoparticle that was treated with perchloric acid was used in the synthesis of the superparamagnetic latex by emulsifier-free emulsion polymerization instead of hydrophobic magnetite. The results pointed out that the reactions between the Fe^{+2} ions on the hydrophilic natural surfaces of magnetite and the persulfate also affected the molecular weight of polymer to a significant degree. Therefore, the magnetite nanoparticles not only played a important role in the radical concentration but also acted as a chain transfer agent to terminate growing polymer chains thus producing PMMA-CR=CH_2. Additionally, the magnetite in reaction mixture induced the particle size from 223 to 125 nm and also these superparamagnetic polymeric particles that are prepared without any surfactant are very clean and can be used in potential biomedical applications such as binding of biomolecules.

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