

A new route of emulsifier-free emulsion polymerization for the preparation of polymer coated magnetite nanoparticles

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A new route of emulsifier-free emulsion polymerization based on the homogenous mechanism was investigated to prepare magnetic nanoparticles coated by poly (methyl methacrylate) (PMMA). The experimental results confirm the formation of PMMA thin and unique layers covering magnetite cores. The polymer layer thickness, determined from transmission electron microscopy (TEM) images, increases from 4.3 nm to 6.8 nm with increasing mass ratio of MMA to magnetite from 3:1 to 11:1. The increase of the polymer thickness results in the decrease in magnetization saturation of polymeric coated magnetic particles. However, this reduction, no more than 13 emu g^{-1} , is much lower compared to that in other studies with the presence of surfactants or emulsifiers. Besides, the dispersion stability of the prepared particles is significantly improved.

Keywords: *magnetite; polymer coated nanoparticles; emulsifier-free emulsion polymerization*

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1. Introduction

Coating or encapsulating magnetic particles by polymers have been considered as an effective solution to stabilize the magnetic dispersion and to modify these particles suitable for different applications, in particular clinical and in biotechnology. Various approaches have been used to prepare such polymer encapsulated particles. A commonly used method consists in that magnetic inorganic particles and polymer particles are synthesized separately and then mixed together to enable either physical or chemical adsorption of the polymer onto the magnetic particles [1, 2]. However, in a system where the polymers and the magnetite particles are separately dispersed, the dispersion stability is insufficient and moreover, the polymers can dissociate from the magnetic particles when they are submitted to changes in external conditions such as, for example, an increase of temperature. An alternative method is to suspend magnetic particles in the liquid phase of a polymerizable formulation and polymerize the monomers in the presence of the magnetic particles to form magnetic polymeric particles, including conven-

tional emulsion polymerization [3, 4], miniemulsion polymerization [5–7], dispersion polymerization [8]. In these studies, stabilizers were often preferred to obtain stable colloids. However the residual emulsifier in the particle surface has negative effects on the purification and the properties of the nanoparticles. The literature results [3, 6] report magnetization values of the polymer coated particles that are much lower than those of the bulk. This was attributed not only to the non magnetic polymeric coating but also to the surfactant layer covering magnetic particles.

Therefore, emulsifier-free emulsion polymerization can be thought as a more suitable way to prepare polymer coated magnetic particles. In such polymerization systems, ionizable initiators, hydrophilic or ionic co-monomers stabilize polymer particles instead of surfactants. In order to enhance the interaction between magnetic nanoparticles and polymers, the use of some added components such as emulsifiers, co-stabilizers or crosslinking agents was reported [9, 10]. In a recent study, Beyaz et al. [11] introduced a new route of emulsifier-free emulsion polymerization with only four main components: magnetite nanoparticles, methyl methacrylate, potassium persulfate, and water. Due to the drawbacks of the coagu-

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lation and polydispersity, however, the study had not yielded more than 3.1 % of the initial ratio of magnetite/monomer.

In this study, the preparation of magnetic particles with polymeric encapsulation by the emulsifier-free emulsion polymerization is reported. A novel process, based on a homogenous polymerization mechanism, is presented to synthesize magnetic nanoparticles, coated by PMMA, with high magnetic content. In order to improve the knowledge about this method, the effect of the monomer concentration on the formation of the polymer coated particles and their magnetic property is also investigated.

2. Experimental procedures

2.1. Materials

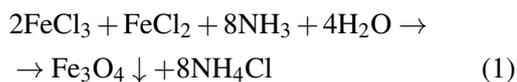
Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, AR) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AR) were procured from BDH Chemicals Ltd. England.

Ammonium hydroxide [AR, 25 % (by mass) NH_3 in water] was purchased from Guangdong Xilong Chemical Co. Ltd. China.

Initiator potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and monomer methyl methacrylate (MMA) of 99 % purity were supplied by Merck.

2.2. Magnetite preparation

In this work, the water based magnetite nanoparticles (MNPs) were prepared by reacting iron (II) and iron (III) ions in an aqueous ammonia solution as follows:



This preparation has been carried out as described in [12] in the following conditions. Solutions of 2 M FeCl_2 in 1 M HCl, 1M FeCl_3 in 2 M HCl and 0.7 M NH_4OH were prepared as stock ones. Stoichiometric 2:1 iron(III)/iron(II) solutions were obtained by mixing 1.0 ml of stock FeCl_2 solution and 4.0 ml of stock FeCl_3 solution. A magnetic stirring bar was introduced in the flask and

vigorous stirring was started. 50 ml of 0.7 M aqueous NH_3 solution was added at a constant rate of 4.6 ml min^{-1} into the flask. The stirring rate of 960 rpm and temperature of 25°C were maintained throughout the addition of the ammonia solution. The reaction was continued after the ammonia addition had been completed for more 30 minutes. The formed precipitate was then decanted and washed several times with deionized water until the pH value dropped to 7.0. A portion of the final product was dried for 4 h at 40°C for the characterization. The other portion was used to prepare magnetic polymeric particles.

2.3. Magnetic polymeric particle preparation

The synthesized precipitate was dispersed, after rinsing, in water at the weight fraction of 2 % by ultrasonication (Elmasonic EH150EL at 37 kHz frequency and 25°C). The dispersion was heated in a thermoregulator until required temperature of $60 \pm 2^\circ\text{C}$ was reached. Then, the appropriate amount of the initiator $\text{K}_2\text{S}_2\text{O}_8$ (5 % of monomer weight) was added. After that the solution of MMA was dropped into the reaction vessel during 4 hours at a constant rate. In order to prepare the magnetic particles with polymer coating layers with different thicknesses the monomer concentration was altered. The investigated monomer concentrations were 6, 10, 16, 22 wt. % equivalent to weight ratios of monomer to magnetite of 3:1, 5:1, 8:1 and 11:1 (samples S1, S2, S3, S4), respectively.

The stirring rate of 300 rpm and nitrogen gas atmosphere were kept constant throughout the polymerization. This process was continued an hour longer after the monomer addition had been completed. The formed polymer coated particles were extracted from the solution by a magnetic particle concentrator to remove the free monomers and polymer. A portion of these isolated particles was dried for the characterization. The other portion was dispersed in water by ultrasonication, in the same manner as in the above mentioned polymerization process. The resulting dispersions were characterized in terms of particle sizes and dispersion stability was evaluated.

2.4. Characterization of particles

The crystalline structure of the magnetic nanoparticles was characterized by X-ray diffraction (XRD). The measurements were performed on powder samples obtained after evaporation of the liquid carrier, using a Siemens diffractometer D5000 with Cu K α radiation at 1.5406 Å.

The formation of the magnetite particles with PMMA coatings was studied by Fourier Transform Infrared Spectroscopy (FTIR, model Impact 400, Nicolet, USA). The polymer coated particles were also evaluated by transmission electron microscopy (TEM) technique with a JEOL EM 1010.

The number-averaged radius of synthesized particles was computed directly from the TEM image by:

$$a_N = \frac{\sum_{i=1}^N a_i}{N} \quad (2)$$

where a_i is the radius of i^{th} particle, N is the total number of particles taken into account.

In addition, the particle sizes were measured with dynamic light scattering (DLS; Otsuka DLS 700). The intensity-averaged radii were calculated from the intensity autocorrelation data by the cumulants method. Also by this technique, the monitoring of the particle size as a function of time was presented to evaluate the stability of dispersion of prepared particles in water.

The mass of polymer coated on the magnetic particle surface was determined by the thermal analysis that was done by a thermo gravimetric analyzer (TGA, NETZSCH STA409 PC/PG instrument) under nitrogen gas with a heating rate of 5 – 10 °C/min from room temperature to 600 °C. Simultaneously with this measurement, the differential thermal analysis (DTA) was also carried out to provide the data on the transformations that had occurred.

Vibrating sample magnetometer (VSM) DMS 880 was used for magnetization measurements. These measurements were taken in the field from –12 to 12 kOe. From the field versus magnetization curves, saturation magnetization values of the samples were determined.

3. Results and discussion

The XRD pattern (Fig. 1) of the nanoparticles synthesized as described in section 2.2 shows the characteristic peaks (220), (311), (400), (422), (511) and (440) corresponding to magnetite from JCPDS card 11-0614. No impurities were detected. Therefore we conclude that magnetite is the main precipitate in our experiments. This conclusion is also supported by the magnetization value of 78 emu g $^{-1}$ obtained for these particles (see the last paragraph) which is very close to the bulk Fe $_3$ O $_4$ (~ 90 emu g $^{-1}$).

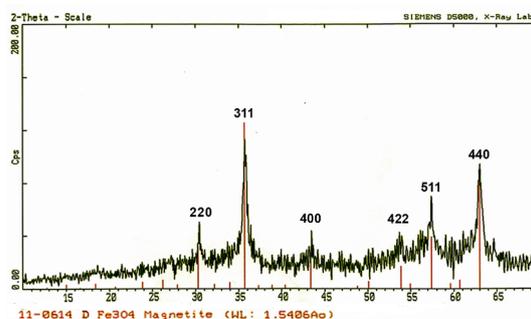


Fig. 1. X-ray diffractogram of synthesized uncoated nanoparticles.

The synthesized magnetite particles have an average radius of 6.6 nm as computed directly from the TEM image (Fig. 2). Meanwhile, the average radius of the particles dispersed in water, determined by DLS is 19.0 nm. Although the DLS intensity averages are often larger than the number averages given by TEM, this result indicates agglomeration. As an approximation, the cubic ratio of these two values yields an average agglomeration number of the magnetite particles in the dispersion equal to 24.

The FTIR spectra of magnetite nanoparticles before and after coating with PMMA (sample S1) are presented in Fig. 3. The absorption band of magnetite at 570 cm $^{-1}$ can be found in both spectra. Meanwhile, the observed C–H stretching bands at just below 3000 cm $^{-1}$ indicate the presence of PMMA on the surface of the magnetite. Moreover, the peak at 1724 cm $^{-1}$ corresponding to C=O groups of PMMA proves the formation of the composite particles.

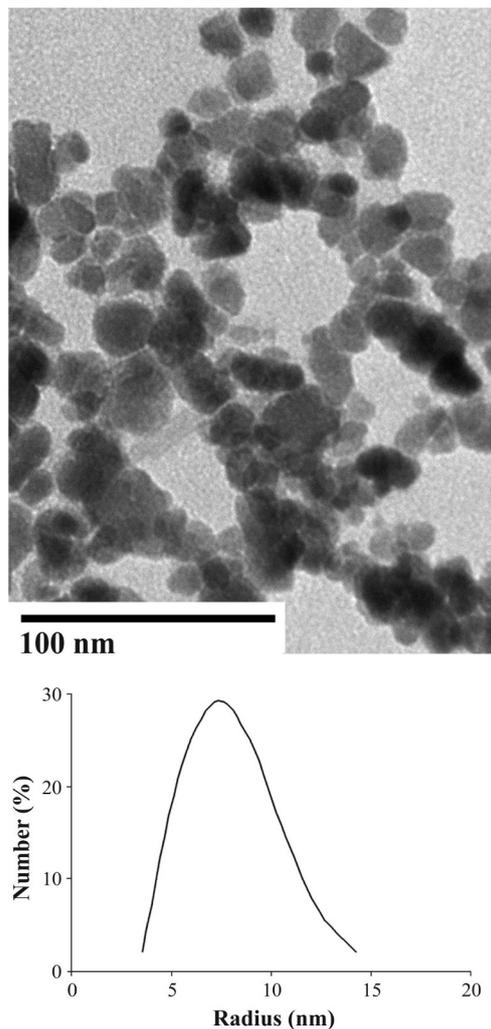


Fig. 2. TEM image and particle size distribution (PSD) of synthesized MNPs.

Fig. 4 shows TEM images of the PMMA coated Fe_3O_4 nanoparticles synthesized at different weight ratios of MMA/ Fe_3O_4 . For all samples, most of magnetite particles are covered by PMMA and the polymer shells have a uniform thickness. The polymer coated particles tend to aggregate into clusters with an agglomeration degree similar to the original particles. This is attested by DLS in which the average size of the agglomerates obtained in all the samples is around of 25 nm and the average agglomeration number is about 16. This implies that the flocculation of the coated particles is determined by that of the initial particles and is independent of the amount of polymer.

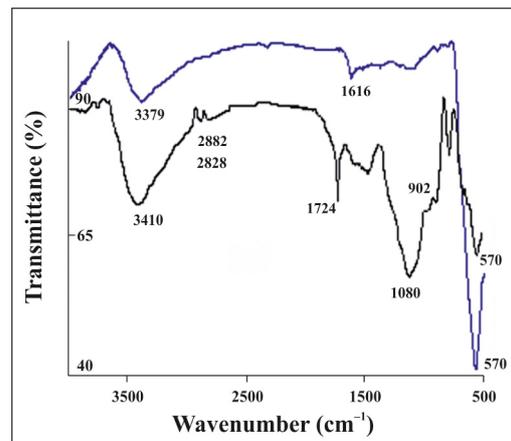


Fig. 3. FTIR spectra of magnetite particles uncoated (above) and coated (below) by PMMA.

The polymer layer thickness can be measured directly in the TEM images and are reported in Table 1. These values are compared to that calculated from TGA measurements. As seen in Fig. 5, the DTA curves of the PMMA coated particles indicate two endothermic peaks at ~ 240 °C and ~ 300 °C, which may be attributed to the evaporation and decomposition of PMMA [3]. The PMMA weight can be estimated by the mass loss from 240 °C to 450 °C revealing the complete decomposition of PMMA. The residual mass is considered as the amount of magnetite in the PMMA coated particles. Assuming that all the bare particles are coated by the polymer films with a uniform thickness t , an individual particle has an initial radius a_i^0 and a radius $a_i^t = a_i^0 + t$ after coating, the weight ratio of the polymer to magnetite from TGA can be expressed as [13]:

$$\chi = \frac{\rho_2 \left[\sum_{i=1}^N (a_i^t)^3 - \sum_{i=1}^N (a_i^0)^3 \right]}{\rho_1 \sum_{i=1}^N (a_i^0)^3} = \quad (3)$$

$$= \frac{\rho_2 \sum_{i=1}^N (a_i^0 + t)^3}{\rho_1 \sum_{i=1}^N (a_i^0)^3} - \frac{\rho_2}{\rho_1} = \frac{\rho_2}{\rho_1} \left[\frac{\sum_{i=1}^N (a_i^0 + t)^3}{\sum_{i=1}^N (a_i^0)^3} - 1 \right]$$

where t is the polymer layer thickness, a_i^0 and a_i^t is the radius of i^{th} uncoated and coated particle, respectively, N is the total number of parti-

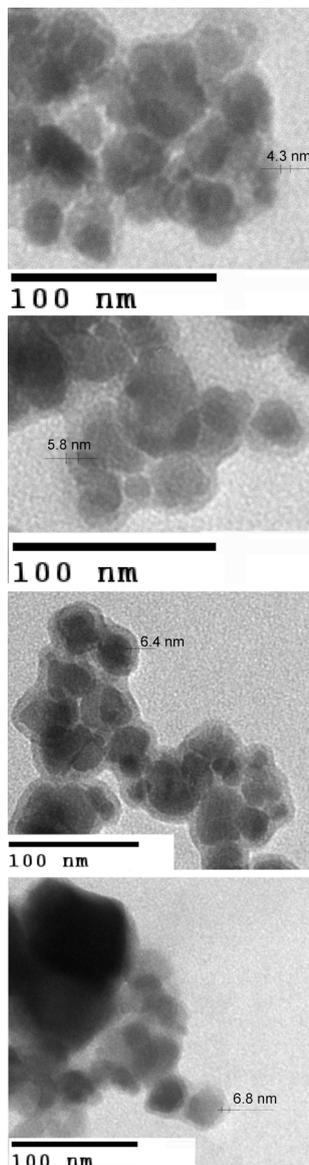


Fig. 4. TEM images of PMMA coated particles prepared at different ratios of MMA/magnetite (S1 top to S4 bottom).

cles taken into account. The densities of magnetite and PMMA are $\rho_1 = 5.20 \text{ g}\cdot\text{cm}^{-3}$ and $\rho_2 = 1.20 \text{ g}\cdot\text{cm}^{-3}$, respectively.

Using Eq. 3, the PSD data determined by TEM (a set of 100 particles) of the original magnetite dispersion (Fig. 2) and the PMMA weight determined by TGA, the polymer shell thickness t is calculated. The results are given in Table 1.

It can be seen that the thickness values esti-

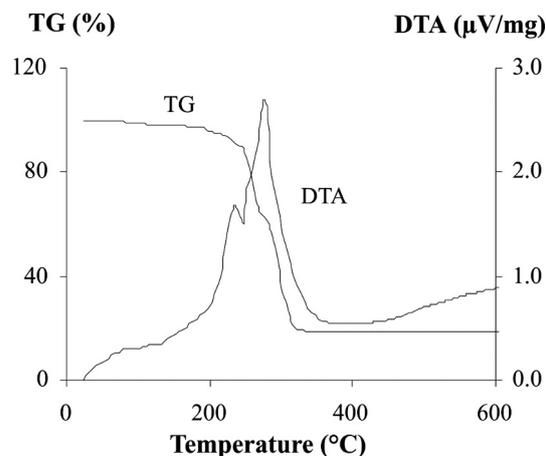


Fig. 5. A typical weight loss curve of PMMA coated particles (sample 2).

mated by TGA are higher by a factor of about 2 than those determined by TEM. This can be explained by the rough surface of the solid particles and by the aggregation of the polymer coated particles which may cause in fact that the total volume of the polymer covering the particle core is larger than the one estimated by $\sum_{i=1}^N (a_i^t)^3 - (a_i^0)^3$ in Eq. 3, resulting in the larger thickness. Nevertheless, the obtained results indicate that a complete and uniform encapsulation is achieved through our process and the thickness values obtained from TEM analysis can be used to evaluate the effect of ratio monomer/magnetite to the formation of PMMA coated particles.

As shown in Table 1, an increase of the polymer film thickness with increasing the ratio of monomer to magnetite is found. The thickness increases approximately 1.6 times when the MMA concentration increases from 6 to 22 %. According to the theory of emulsion polymerization [14], the degree of polymerization (DP) depends on the number of swollen micelles and the initiator concentration. For the emulsifier-free emulsion polymerization, where the initiator also plays the role of surfactants to form micelles, it is clear that the DP as well as the polymer molecular weight (PMW) in the polymer layer is determined by the mass ratio of the monomer to initiator. Note that in our work, this ratio was constant in all the experiments. Hence, a

Table 1. PMMA layer thicknesses determined by TEM and TGA.

Sample	Weight ratio	Initial avg. size	TEM analysis	TGA analysis		Polymerization
	MMA/MNPs	a_N^0 (nm)	t (nm)	PMMA/ MNPs	t (nm)	yield (%)
S1	3/1	6.6	4.3	2.8	9.2	93
S2	5/1		5.8	3.9	11.2	78
S3	8/1		6.4	5.4	13.3	68
S4	11/1		6.8	6.7	14.6	61

possible explanation for the monomer concentration dependence of the formed polymer weight is that the polymerization system in this study is close to homogeneous process. In fact, with the MMA addition rates below 0.09 wt. % ($\sim 9 \times 10^{-3}$ M) per minute and the time of 40 minutes for the complete conversion of 0.3 M MMA [4], the dynamic concentration of MMA in the continuous phase in all the samples (except S4) was always lower than its aqueous solubility of 0.16 M [4] and the polymerization may be considered as a solution polymerization. Due to this mechanism, the DP is proportional to the monomer [M] and initiator concentration [I] as follows [14]:

$$DP = k \frac{[M]}{[I]^{1/2}} \quad (4)$$

Since the ratio of monomer/initiator is constant, the degree is only dependent on the square root of monomer concentration. The experimental results show a linear increase of the thickness with the square root of monomer concentration as presented in Fig. 6. This implies that the polymer layer is formed by the growth of the chain at the surface of magnetite particles and its thickness is determined by the PMW. At the beginning of the reaction, when the amount of MMA is much smaller than initiator concentration, the radical capturing is accelerated to form chain-initiating radicals with sulfate end groups. These elements are surface active and absorb on the surface of magnetic particles. The subsequent polymerization consists in incorporation of the added monomers to the particle surface and forming the structure core-shell. It must be noted that the growth of the coating polymer layers (surface polymer) takes place simultaneously

with the propagation of free active chains in the medium to form bulk polymers. Moreover, experimental studies [15, 17] show that the rate of the bulk polymerization is often faster than that of the surface polymerization, in particular, with the presence of monomer-swollen micelles or monomer droplets. Therefore, the growth of surface polymers is dependent on the active monomer concentration at the surface and the fraction of surface-bound chain radicals (η).

In order to evaluate this competition the polymerization yield has been computed. This parameter is defined by the weight ratio of the polymer formed on the magnetic particle surface to the initial monomer.

$$y = \frac{\chi^0}{\chi} \times 100 \% \quad (5)$$

In Eq. 5, χ^0 and χ are the mass ratios of MAA/Fe₃O₄ and of PMAA/Fe₃O₄, respectively.

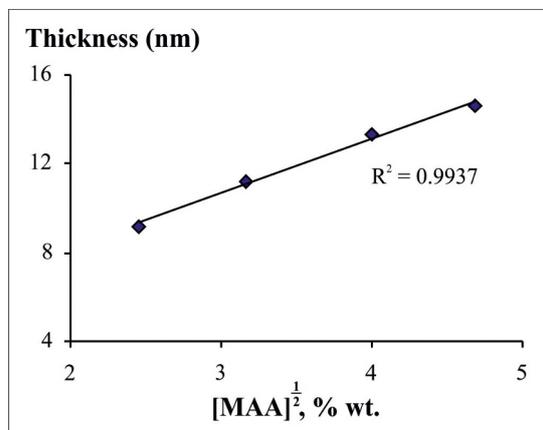


Fig. 6. Polymer layer thickness as a function of square root of monomer concentration.

For sample S1 and sample S2, the polymerization yields are approximately 93 % and 80 % that are in a typical range for pure PMMA synthesized in emulsion polymerization under similar reaction conditions [15]. This means that the surface polymers are prominent and most of the formed polymers are to cover the solid particles. On the other hand, for the remaining samples, where the monomer concentrations and the monomer addition rates are higher, the encapsulation efficiency values are lower than 70 %. Possibly the formation of polymer particles occurs through a monomer swollen micelle mechanism in the solution and these polymer particles have been removed before the characterization. The decrease of the polymerization yield on rising monomer concentration can be explained as follows. Increasing monomer concentration increases the number of monomer molecules reacting in the initiation step [14] and accelerates the decomposition of persulfate [16] that leads to an increase in both size and amount of the active chain radicals. Thereby the fraction of surface-bound chain radicals is decreased, increasing the growth of bulk polymer and resulting in a reduction of the polymerization yield. The experimental results indicate that in the current systems the ratio should be smaller than 5:1 to get $\eta \approx 100\%$ and high polymerization efficiency.

It is striking that the polymerization method used in this study allows preparing PMMA coated particles with the thin polymer coatings and the polymer coating thickness can be simply adjusted by changing the monomer concentration. Furthermore, the prepared particles show magnetic property significantly higher than reported in similar studies [3, 6, 10]. In the room temperature magnetization curves illustrated in Fig. 7, the saturation magnetization of bare Fe_3O_4 nanoparticles at 12 kOe is 78 emu g^{-1} and of PMMA coated magnetite particles is consequently 70, 68 and 65 emu g^{-1} for samples S2, S3 and S4, respectively.

It is clearly observed that the higher the polymer layer thickness the lower the saturation magnetization is. This result can be attributed to the non-magnetic polymer. Nevertheless, compared to the magnetic particles coated by different polymers

such as PMAA, PMMA, PS, the magnetization reduction in this study is much lower than in others. For magnetic particles coated by PMMA, prepared with oleic acid as emulsifier R.Y. Hong *et al.* [6] found magnetization values from 65.6 emu g^{-1} to 23 emu g^{-1} . In addition, the poly ethylene glycol methacrylate (PEG-MA) coated particles of G. Utkan *et al.* [10] showed a sharp reduction in magnetization after polymer coating (from 23 emu g^{-1} to 2.5 emu g^{-1}). A similar result was also observed in [3]. The main difference between our research and the others comes from either too thick polymer layer ($\sim 165 \text{ nm}$) [10] or the presence of surfactant layer [3, 6].

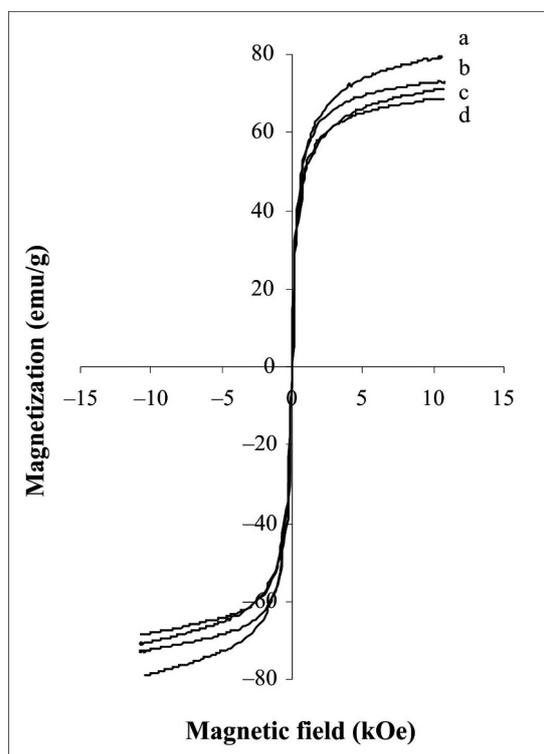


Fig. 7. Room-temperature magnetization curves of MNPs (a) and PMMA coated particles synthesized with different MMA magnetite ratios: (b) 5:1, (c) 8:1 and (d) 11:1.

Besides, the dispersion stability of the prepared coated particles in water is significantly improved as presented in Fig. 8, where the evolution of particle radius with time was measured by DLS for the dispersion of uncoated and PMMA coated particles (sample S2) with the same particle dosage

(2 wt. %). The aqueous dispersion of the coated particles did not show any significant appearance of sedimentation for weeks meanwhile it was obviously observed at the dispersion of the uncoated particles after about a week. The size growth of the uncoated particles was much higher than that of the PMMA coated particles. Clearly, the polymer layers create a spatial effect to protect the magnetic particles against coagulation leading to the improvement of dispersion stability.

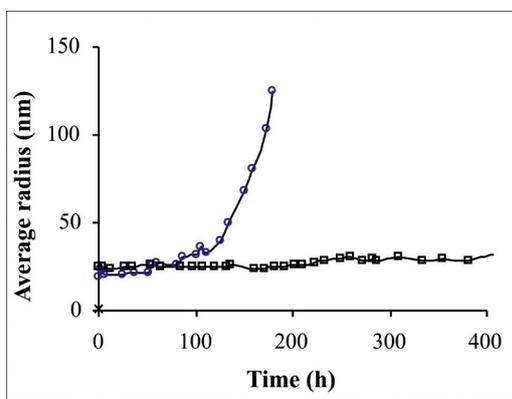


Fig. 8. Evolution of radius with time for the dispersion of uncoated particles (circles) and PMMA coated particles (squares).

4. Conclusions

In this study, magnetic particles coated by PMMA were prepared successfully by the free radical polymerization of MMA monomers without surfactants. The experimental investigations suggest that the polymerization is dominated by homogeneous nucleation in solution and the growth of the chain into the uniform polymer film takes place at the surface of solid particles. By this mechanism, the magnetite particles are encapsulated completely by thin polymeric layers and the layer thickness can be adjusted by altering the mass ratio of monomers to magnetite particles. The PMMA coated nanoparticles enhance the dispersion ability while retaining their magnetic properties at a level much higher than that in other studies.

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