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ATRP-Template Dispersion Polymerization of Methacrylic Acid/PVP*

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Abstract ATRP-template dispersion polymerization of methacrylic acid (MAA) on the template of polyvinyl pyrrolidone (PVP K-30) was carried out in the aqueous solution by using methyl 2-bromopropionate (MBP)/CuCl/2,2′-bipyridine (bpy) as the initiation system. The scanning electron microscopy (SEM), dynamic light scattering (DLS) and gel permeation chromatography (GPC) were employed for evaluating the results of polymerization. As a result, the minimonomer droplets formed due to the H-bond interaction of PVP-MAA. The stability of droplets was dependent on pH and the concentrations of both PVP and MAA. When pH < 2, the coagulum of PVP-MAA formed, whereas when pH > 4.5, the droplets were not observable by DLS. In order to prepare the stable latex, the concentration of PVP should be lower than 9 wt%, whilst the concentration of MAA should be lower than 5.5 wt%. The optimum condition was pH 2.4, PVP 4.76 wt% and MAA 5 wt%, by which the stable latex of *ca.* 50 nm nanoparticles of PMAA/PVP was prepared by ATRP polymerization and simultaneously the molar mass of PVP was duplicated by PMAA according to GPC diagrams. In contrast, by using AIBN, KPS and KPS-Na_2SO_3 redox initiation system, the coagulum accompanying with the larger molar mass of PMAA was obtained, irrespective of pH and concentrations of PVP and MAA.

Keywords: Nanoparticle; ATRP; Dispersion polymerization; Template polymerization; Hydrogel.

INTRODUCTION

Free-radical polymerization is an important synthesis method academically and industrially in the polymer field. Owing to its mild condition and the abundance of monomers, most of commercial polyolefins are produced in industry. However, well-defined polymeric objects are always pursued by chemists. The control of free-radical polymerization inevitably becomes a serious topic in academics. Generally, two aspects are concerned in the free-radical polymerization: 1) the control of molar mass and its distribution, 2) the control of size and its distribution of polymer aggregates (particles). Correspondingly, two strategies in methodology have been adopted to control the polymerization, *i.e.* the active and passive ones. For example, atom transfer radical polymerization[1, 2] (ATRP) and reversible addition-fragmentation chain transfer polymerization[3, 4] (RAFT) can give the well-defined morphologies of polymer chains and narrow distribution of molar mass, whilst the polymerization methods such as the soap-free miniemulsion polymerization[5, 6] and precipitation polymerization[7, 8] can produce the monodispersed particles. Certainly, some combined methods such as ATRP-miniemulsion polymerization[9, 10] and RAFT-miniemulsion polymerization[11] are also developed. These approaches lie on the active strategy. Another strategy is passive, *i.e.* duplication of the well-defined polymer chains that is called template polymerization[12]. It is fascinating, arising from the mimic of example in the nature such as the self-replication of DNA. In general, enhanced rates as well as high selectivity and efficiency

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characterize template reactions in the biological field. As a consequence, both the molecular weight and the sequence of repeat units are strictly predetermined. The polymerization is only a tool to bind the repeat units in a chain. Imitating the natural examples, many works have been done[13, 14]. The ionic interaction, H-bond and even covalent bond are utilized to bind the monomer to the template. Both the free-radical polymerization and ring-opening polymerization have been applied to the template polymerization. Analogous to self-replication of DNA, the mechanism of template polymerization is presumably considered to proceed in two types, *i.e.* type I (zip mechanism) and type II (pick-up mechanism). In the former case, monomer units are connected with a template by strong forces (electrostatic, hydrogen bridges), in the latter case, the monomer is free at the beginning and polymerization starts outside the template. As oligoradical reaches a critical length, the complexes of oligoradical-template form. Thereafter the polymerization proceeds along the template chain by capturing the monomers from the surrounding. Theoretically according to these mechanisms, the molar mass of template should be duplicated by the daughter polymer if the monomer are saturated adsorbed on the template and the oligoradicals generated in the medium are not long. However, unfortunately the molar mass of template is rarely duplicated by the daughter polymer, though the polymerization rate is faster than its blank-polymerization. For example, it is observed that the molar mass of daughter polymer, PMAA, was much smaller than that of its mother polymer, PVP, in the template polymerization in ethanol[15], whereas the molar mass of daughter polymer is 8-fold larger than that of its mother polymer in the template polymerization of *N*-vinyl imidazole (VIM) on PMAA in water[16]. These results are attributed to the combination termination of two radicals and hopping of one template-associated oligoradical to the other like[13]. Accordingly, living radical polymerization, ATRP, should be a proper method to solve the problem of two radicals termination. This is one of the reasons that ATRP-template dispersion polymerization is carried out in this paper. Another reason is based on the knowledge of particle formation. As we know, the nano/mini monomer droplets play the key role in the formation of particles and transfer of monomer[5]. They are the precursors of primary particles and the sources of monomer supplying for the growth of particles. Therefore, if the template polymerization takes place in an isolated nano/mini monomer droplet, especially when a droplet contains one template chain, the hopping of template-associated oligoradical should be stopped.

On the other hand, nanoparticles have been widely applied in various fields[17–21] such as the carriers of drug controlled-releasing system[17], bioactive substances[18], catalysts[19], cosmetics[20], *etc*. PMAA is a conventional building material selected for the construction of bio-applicable nanoparticles due to its excellent biocompatibility and pH-sensitivity[22, 23]. The transition of hydrophobicity-hydrophilicity is an effective factor to capture and excel a molecule from a nanoparticle without any wall hindrance. However, due to the high solubility of PMAA in the aqueous solution, the preparation of microgel containing high composition of PMAA has to be forced to select the environmentally unfriendly approaches such as the precipitation polymerization[22–25], the inverse miniemulsion polymerization[26] and so on, in which a large amount of organic solvent must be used. Therefore, a question naturally arises that whether it is possible to develop a new method applicable for the preparation of particles including migcrogels consisting of water-soluble polymers in the aqueous solution. The answer seems to be serious because it is a common knowledge that the polymer in particles must precipitate from the dispersion medium. Both the monomer of MAA and its polymer of PMAA are water-soluble. However, depending on the pH, the complexes of PVP and PMAA are insoluble in water[15]. It provides us a chance to challenge the preparation of particles rich in PMAA in the aqueous solution. Consequentially, the ATRP-template dispersion polymerization of PVP/MAA was selected in the present paper.

EXPERIMENTAL

Materials

All the chemical reagents used in this paper were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Methacrylic acid (MAA) was purified by distillation under reduced pressure. The template polymer polyvinyl pyrrolidone (PVP K-30, M_n = 30000), the ATRP initiator system methyl 2-bromopropionate

(MBP), CuCl, 2,2′-bipyridine (bpy), the thermally degradable initiators AIBN, potassium persulfate (KPS) and the redox agents, Na_2SO_3/KPS were used without further purification. DDI water was used for all experiments.

Polymerization

Polymerizations were performed in a four-necked 100 mL flask equipped with a thermometer, a condenser (also outlet of N_2), an inlet of N_2 gas and an inlet for charging the chemical reagents, which was settled in a thermostat water bath. A black plastic box was used to cover the polymerization system in order to shade the light. Magnetic stirrer was used.

For ATRP, the molar ratio of initiator system was set at MMA:bpy:CuCl:MBP = 100:2:1:1, referring to the data reported[27]. Formulated PVP aqueous solution and MAA were added first into the flask and pH was adjusted by adding the standard HCl or NaOH solution. Thereafter, the mixture of above solution was deoxygenated by bubbling N_2 for 30 min at the ambient temperature. At the temperature of polymerization, CuCl and bpy were added at first. After all of CuCl dissolved, *i.e.* disappeared at the bottom of flask judging by naked eyes, MBP was charged. This moment was set as the start of polymerization.

As for other polymerizations, the amount of initiators was constant at 2 wt% based on the amount of MAA. The initiator was directly added into the polymerization system at the polymerization temperature, for the redox initiators, it was the room temperature, and for AIBN and KPS, it was 60 °C.

For all polymerizations, the total amount of reaction mixture was always kept at 50 g, and N_2 was bubbled throughout the polymerization.

Characterization

Conversion of MAA was measured gravitimetrically, which commonly applied for the latex[7]. Saturated aqueous solution of K_2SO_4 was used as the agglomerating agent. Due to the difficulty of separation, the conversion of MAA was calculated as following, where m, the total amount of latex, m_{PVP}, the total amount of PVP, m_0, the total amount of MAA, m_1, the amount of latex sample, m_2, the amount of dried latex sample.

$$w\% = \frac{\frac{m}{m_1} \times m_2 - m_{PVP}}{m_0} \times 100$$

It was based on two assumptions. At first, all PVP chains were incorporated into globules and all the globules turned into particles after the template polymerization was completed. At second, the daughter polymer, PMAA, should be picked up by particles, no matter where it was created and how long PMAA chains were.

The dynamic light scattering (DLS) (90plus Particle Sizer/BI-MAS, Brookhaven Instruments Co., US) was employed to measure the hydrodynamic diameters, by which the scattering light at 90° was collected, thereby the diameters were automatically calculated. The solution (or latex) was directly used for DLS measurements without dilution and all measurements were performed at 20 °C. SEM images of particles were also taken (JSM-6360LV JEOL, Japan), and the operations were described elsewhere[8].

The molar mass of polymer was measured by GPC (PL-200, Premium Line Co. Ltd, Germany). The dried samples retained by conversion measurement were directly used for the detection of GPC without separation of PVP and PMAA. Phosphate buffer solution, pH10, was used as the solvent and elution phase as well.

RESULTS AND DISCUSSION

Determination of Template Concentration and MAA Concentration

As aforementioned in the Introduction section, in order to stop the hopping of the template-associated oligoradicals, the locus of template polymerization should be isolated individually. However, as we know[28], distinct from the small molecules, the polymer chains are characterized as the entanglement. At the low concentration, polymer chains are free, but as the concentration increases, the entanglement of chains occurs. The heavy entanglement may make the entire solution be a network of chains. At meanwhile, in the template polymerization, the template adsorbs the monomer by interactions, thus an isolated chain of template containing

monomer may be looked as a globule. Therefore, an isolated globule is ideal for stopping the hopping of free-radicals and the duplication of molar mass, presumably that the polymerization solely happens in a globule. On the other hand, the isolated globule is also the primary factor for the success of particle preparation. Therefore, a proper concentration of PVP is not only the insurance of the stability of PMAA nanoparticles, but also the requirement of stopping hopping.

Actually the gyrate radii of PVP chains measured by the static laser light scattering (SLLS) are the proper criteria to judge whether the chains entangle or not. However, it is complicated and unavailable in our lab. Therefore, conductimetry was employed in this paper. As we know, conductimetry is usually applied for the determination of CMC of surfactant. The loss of ion mobility renders the conductivity of surfactant system to decrease. Analogously, it is assumed that the conductivity of PVP aqueous solution is dominantly attributed to PVP chains, the conductivity should be related to the mobility of PVP chains. Figure 1 exhibits the changes of conductivity when the concentration of PVP was diluted from 16 wt% to 4.5 wt% with DDI water. As shown in Fig. 1, from 4.5 wt% to 6.5 wt%, the conductivity linearly increased with the increase of PVP concentration, and then the data deviated from linearity. The linear increase of conductivity indicated that PVP chains were isolated, whilst the deviation implied the occurrence of entanglement. At high concentration of PVP (14 wt%–16 wt%), the conductivity became unstable while stirring. We think it was possibly attributed to the formation of big networks of PVP chains. When it passed through the cell of conductance meter, the conductivity was low. As the concentration of PVP decreased (6.5%–14%), the networks degraded, thus the decrease of conductivity exhibited somewhat linearity.

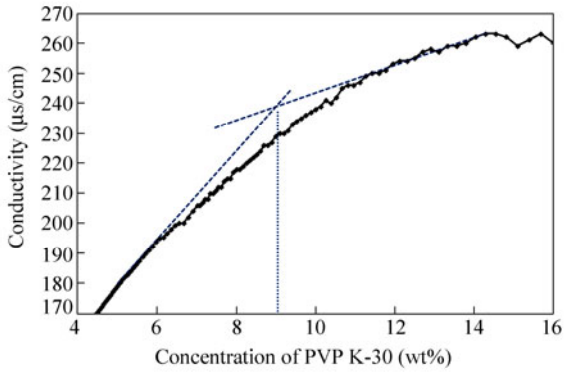

Fig. 1 Conductivity versus the concentration of PVP K-30

In analogous to those of determination of CMC, as shown in Fig. 1, *ca*. 9 wt% PVP determined by the crossover point of two lines was considered as the critical concentration. We considered that it reflected the severity of chain entanglement, or in other words, the independent (isolated) degree of networks. It did work since the particles were not prepared with 10 wt% of PVP K-30 regardless to the concentration of MAA, which will be reported later.

Figure 2 shows the change of conductivity when MAA was added into PVP K-30 aqueous solution. It was normal that the conductivity increased as the concentration of MAA increased since the free MAA in the aqueous solution dissociated, though the mobility of PVP decreased as MAA molecules were adsorbed. The nonlinearity of curves reflected the characteristics of adsorption. On the other hand, as shown in Fig. 2, corresponding to the same concentration of MAA, the lower PVP K-30 concentration gave the higher conductivity. It indicated that the contribution of free MAA was significant due to the adsorption amount of MAA increased as PVP increased.

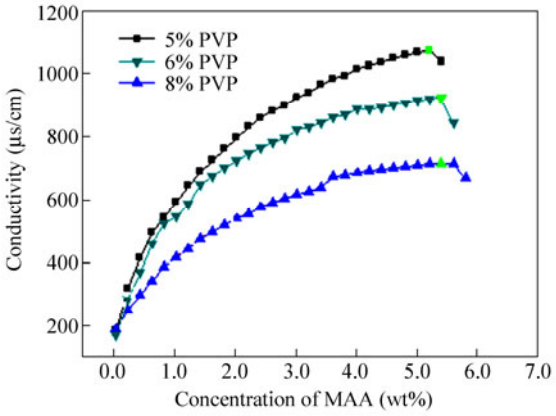

Fig. 2 Conductivity of PVP K-30 solution versus the concentration of MAA

However, all solutions became turbid when the concentration of MAA attained about 5.5 wt% (blank points in Fig. 2). Some big species precipitated irrespective of the concentration of PVP. Thereafter, the conductivity commenced to dramatically decrease with the increase of MAA. The globules were formed by the adsorption of MAA on PVP. The equilibrium ratio of [MAA]/[VP unit] was reported to be around 1/1 in the aqueous solution[29, 30]. Accordingly, the ratio of [MAA]/[VP unit] was calculated at the critical concentration, 5.5 wt% MAA. Corresponding to 5 wt%, 6 wt% and 8 wt% PVP, it was 1.42, 1.18 and 0.89, respectively. This result implied that the instability of globules might not be resulted from the saturated adsorption of MAA on PVP. At 5 wt% PVP, [MAA]/PVP was much more than 1, whereas at 8 wt% PVP, it was less than 1. Therefore, the reason was unclear by now.

Figure 3 shows the size distribution of globules at different pH and concentrations of PVP. It was observed that the intensity with the bigger size increased with the increase of pH, whereas it increased with the decrease of concentration of PVP. This result was understandable readily because the lower pH depressed the dissociation of MAA, whilst the more PVP chains produced more globules.

ATRP Template Dispersion Polymerization

ATRP template dispersion polymerizations were carried out at different pHs. As a result, the latex was only prepared in the pH range of 2 < pH < 4.5. When pH < 2, the coagulum was obtained, whereas pH > 4.5, the transparent aqueous solution was prepared. Here, it should be remarked that the concentration of MAA, 4.76 wt% was selected because it was the highest concentration which gave stable latex.

It was interesting that pK_a of MAA was also around 4.5[31].

$$pK_a = \lg\frac{[MAA]}{[MMA^-]} + pH$$

Accordingly, it implies that if approximately [MAA] < [MAA^-] (pH > 4.5) or [MAA] > 100[MAA^-] (pH < 2), the stable latex cannot be prepared. Presumably pH of polymerization system was solely contributed by the dissociation of free MAA in the continuous phase and the globules of PVP/MAA were created by the molecular interaction of MAA-PVP. The following equilibriums should coexist in the system.

$$H^+ + MAA^- \Leftrightarrow MAA \Leftrightarrow MAA/PVP{-}Complexes$$

The adsorption of MAA was balanced by the dissociation of free MAA. The lower pH the more MAA molecules were, thus the bigger globules were. However, the high H^+ strength pressed the volume of globules, thereby destroyed the electrostatic double layer which led the globules to coagulate. Inversely, when [MAA] < [MAA^-], the equilibrium of adsorption of MAA was destroyed due to the low concentration of free MAA in the aqueous phase. Consequentially, the globules were not formed.

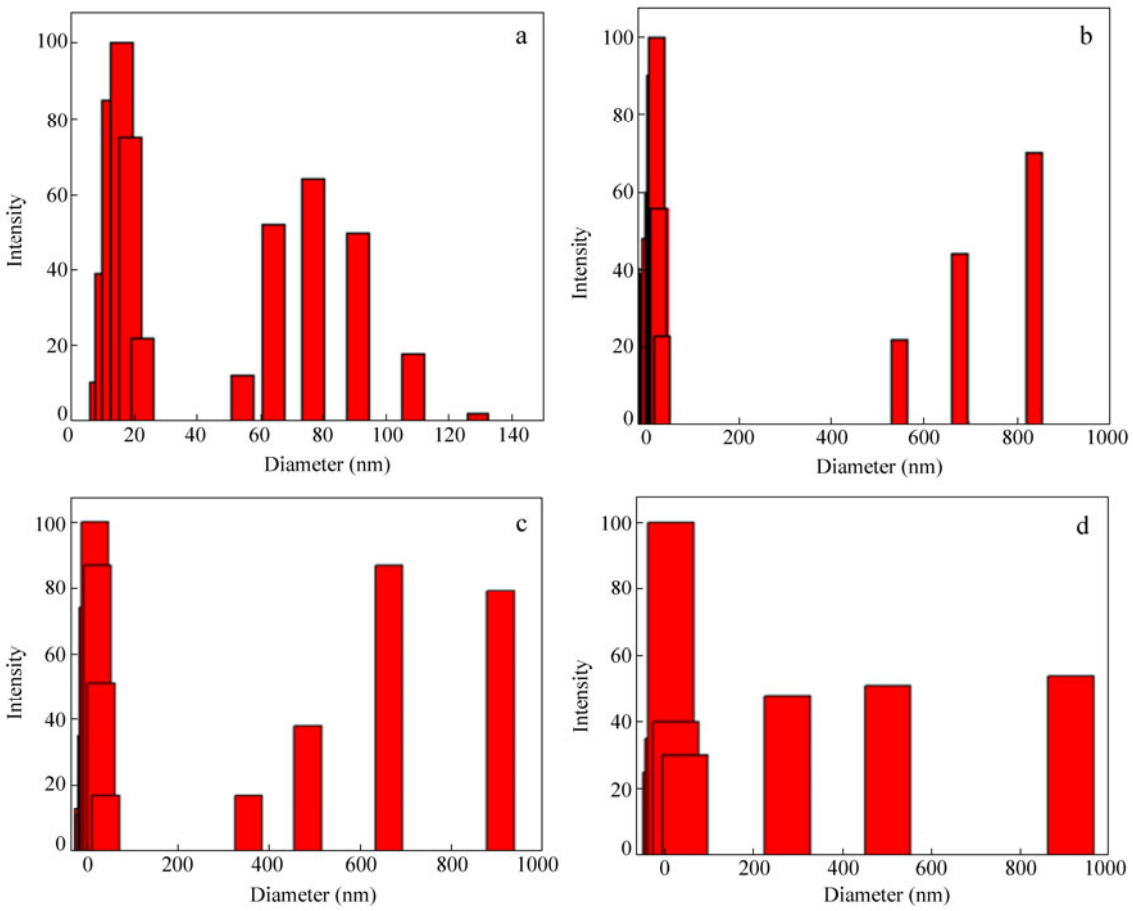

Fig. 3 Size distributions of PVP/MAA globules at different pH and concentrations of PVP (PVP, 4.85 wt%; MAA, 4.17 wt%; (a) pH = 2.4 and (b) pH = 3.2) (pH = 2.4; MAA 4.76 wt%; (c) PVP 5.0 wt% and (d) PVP 6.0 wt%)

Figure 4 shows the conversion of MAA versus the polymerization time of ATRP template dispersion polymerization at pH 2.4. The conversion increased with the increase of polymerization time, but the highest conversion of MAA was only 34% in 6 h. It was possibly attributed to the calculation method of conversion as mentioned in the Experimental section. Namely, it was assumed that all the globules turned into particles. However, as we know, it is a common knowledge[5] that only a part of globules can turn into particles in both the miniminiemulsion polymerization and microminiemulsion polymerization. Moreover, compared with the mini/micro miniemulsion polymerization by using thermally degradable initiator, ATRP-template dispersion polymerization exhibited two features. At first, the formation of globules depended on the adsorption of MAA on PVP. The equilibrium of adsorption was not affected when MAA turned into PMAA in the globules. Therefore, the transfer of MAA from the aqueous phase into the growing particles was inhabited. Secondly, in the mini/micro miniemulsion radical polymerization, the new radicals were continuously supplied throughout the polymerization, whereas in ATRP, the radicals were generated in a short time. In fact, in order to increase the conversion of MAA, the trials increasing the amount of ATRP initiator were carried out. However, the conversion was not significantly increased probably due to the insolubility of BMP. SEM photos of nanoparticles prepared are shown in Fig. 5. The averaged diameter of particles was about 50 nm. It was much smaller than the size of globules measured by DLS (Fig. 3a).

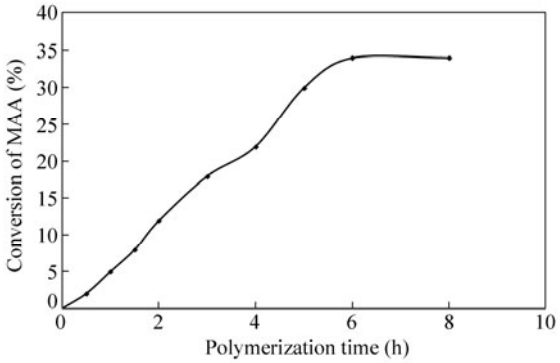

Fig. 4 Conversion of MAA versus ATRP template dispersion polymerization time at pH 2.4 (PVP, 5.0 wt%, MAA, 4.76 wt%)

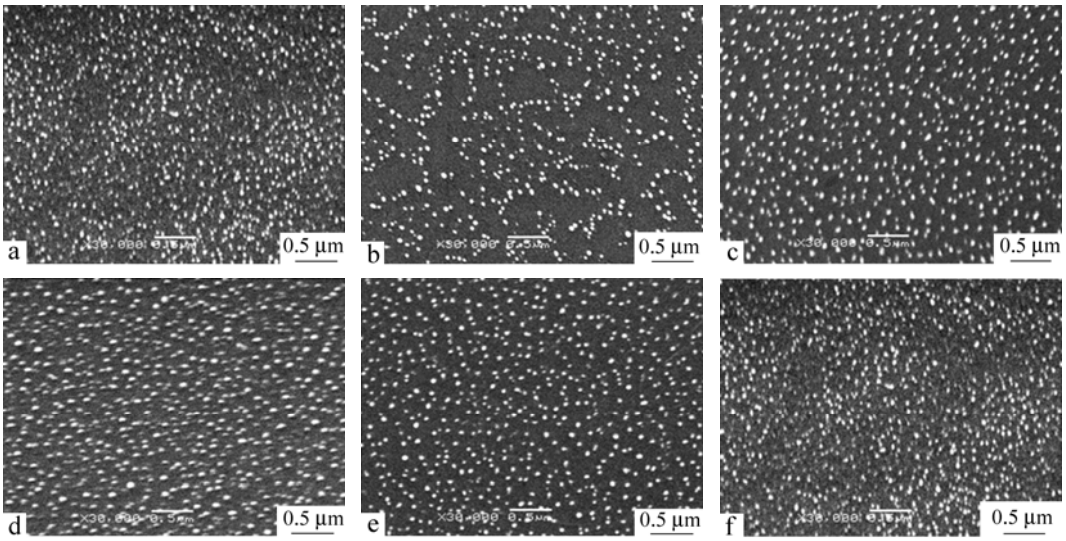

Fig. 5 SEM images of PVP/PMAA nanoparticles prepared by ATRP template dispersion polymerization (a) PVP, 5.0 wt%, MAA, 4.76 wt%, pH = 2.4 (b) PVP, 4.0 wt%, MAA, 4.0 wt%, pH = 3.0 (c) PVP, 3.0 wt%, MAA, 4.0 wt%, pH = 3.0 (d) PVP, 5.0 wt%, MAA, 3.0 wt%, pH = 3.0 (e) PVP, 6.0 wt%, MAA, 4.0 wt%, pH = 3.0 (f) PVP, 4.0 wt%, MAA, 4.0 wt%, pH = 3.7

Effects of pH on the Polymerization

As discussed above, pH was critical to the formation and stability of globules as well. Figure 6 gives the conversions of MAA prepared at different pHs. It was clear that the conversion was almost at the same level, around 30% when $2 < pH < 3$, but then dramatically decreased as pH increased from 3.2 to 4.2. It was coincident to the above result that the adsorption of MAA was dependent on the concentration of free MAA.

The most interesting was the particle size and its distribution measured by DLS. As shown in Fig. 7, the number-averaged diameters decreased as pH increased. For example, at pH 2.4, the diameter was about 428 nm, while at pH 3.7, the diameter was 172 nm. Compared with the diameter of 50 nm obtained by SEM, it was concluded that the particles of PVP/PMAA in the aqueous solution were actually the sponge balls swollen by water if they were spherical. As shown in Fig 5, the similar situation was also found in other polymerization systems. Of course, the defect of DLS simulation model was also one of the reasons for exaggerating the size of soft globules, in which the scattering objects suspended in water were considered as the solid and rigid balls. Due to this reason, perhaps it was the truth that the size of particles at pH 3.7 was smaller than that at pH 2.4, because the scattering was related to the density of objects. The size might be estimated to be small due to the high swollen degree. The fuzzy image of particles (Fig. 5f) and the buried particles (Fig. 5d) supported this

explanation when the amount of MAA was small.

On the other hand, as shown in Fig. 7, the distribution of particle size changed from the dual distribution to monodispersed when pH increased. It was also attributed to the swollen degree of particles at higher pH.

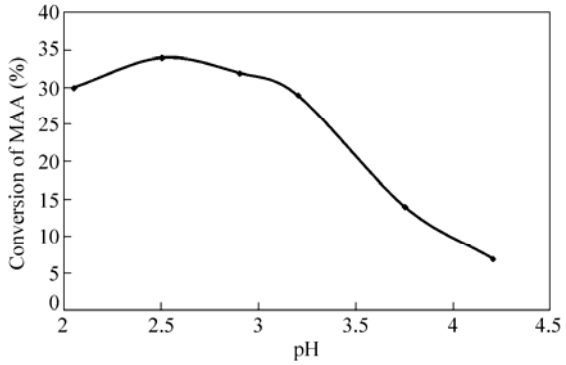

Fig. 6 Effect of pH on the conversion of MAA (PVP, 5.0 wt%, MAA, 4.76 wt%)

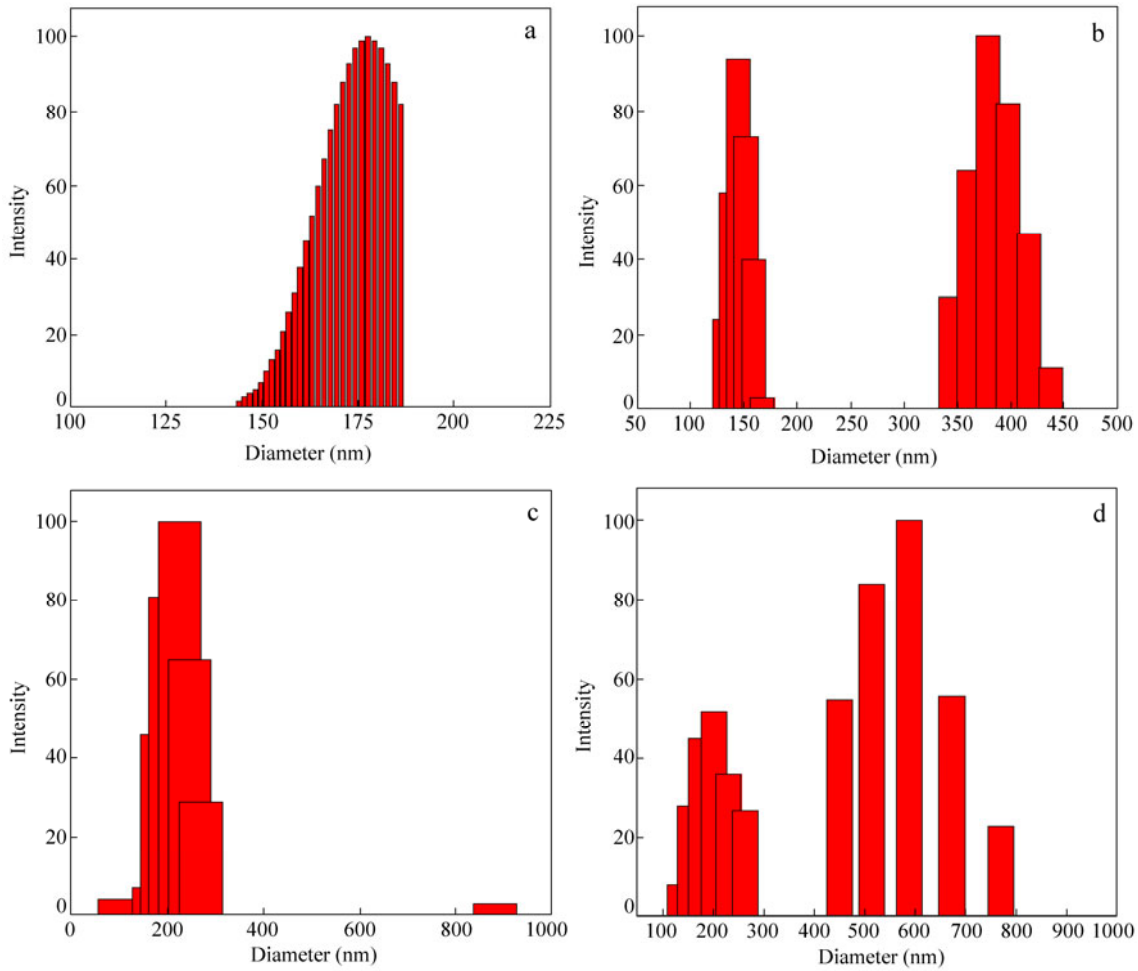

Fig. 7 Effects of pH on the distribution of particle size: (a) pH = 3.7, (b) pH = 3.2, (c) pH = 3 and (d) pH= 2.4 (MAA 4.76 wt%, PVP 5.00 wt%)

Effects of Polymerization Factors on the Conversion of MAA

Various polymerization factors possibly affecting the polymerization were investigated at pH2.4. As shown in Fig. 8(a) (MAA, 4.76 wt%), the concentration of PVP affected the conversion of MAA. From 3 wt% to 5 wt% PVP, the conversion of MAA increased as PVP concentration increased, because the adsorbed amount of MAA increased with the increase of PVP chains. With the concentrations ranged from 5 wt% to 7 wt%, the conversion was almost leveled off. It indicated the saturated adsorption of MAA. When the concentration of PVP was larger than 7 wt%, it should be anticipated that the conversion of MAA increased due to the higher adsorption of MAA. However, unexpectedly, the conversion of MAA commenced to decrease as PVP increased. A possible reason was the limitation of equation calculating the conversion of MAA (in section of Characterization). An assumption was that all PVP chains were incorporated into the particles. However, when a larger number of PVP existed in the polymerization system, the number of MAA molecules shared by each PVP chain decreased. For a PVP chain picking up fewer MAA molecules, the PVP/PMAA complexes might be not precipitated or their sizes were too small to be precipitated due to the short PMAA chains. This was also the reason that, as shown in Fig. 8(b), when the concentration of MAA was as low as 1 wt% and 2 wt%, the conversion of MAA was low. From 3 wt% to 5 wt%, it was normal that the conversion of MAA increased with the increase of MAA concentration. Anyway, it was common that the template polymer was hard to separate from its daughter polymer. Therefore, the error of calculation was unavoidable.

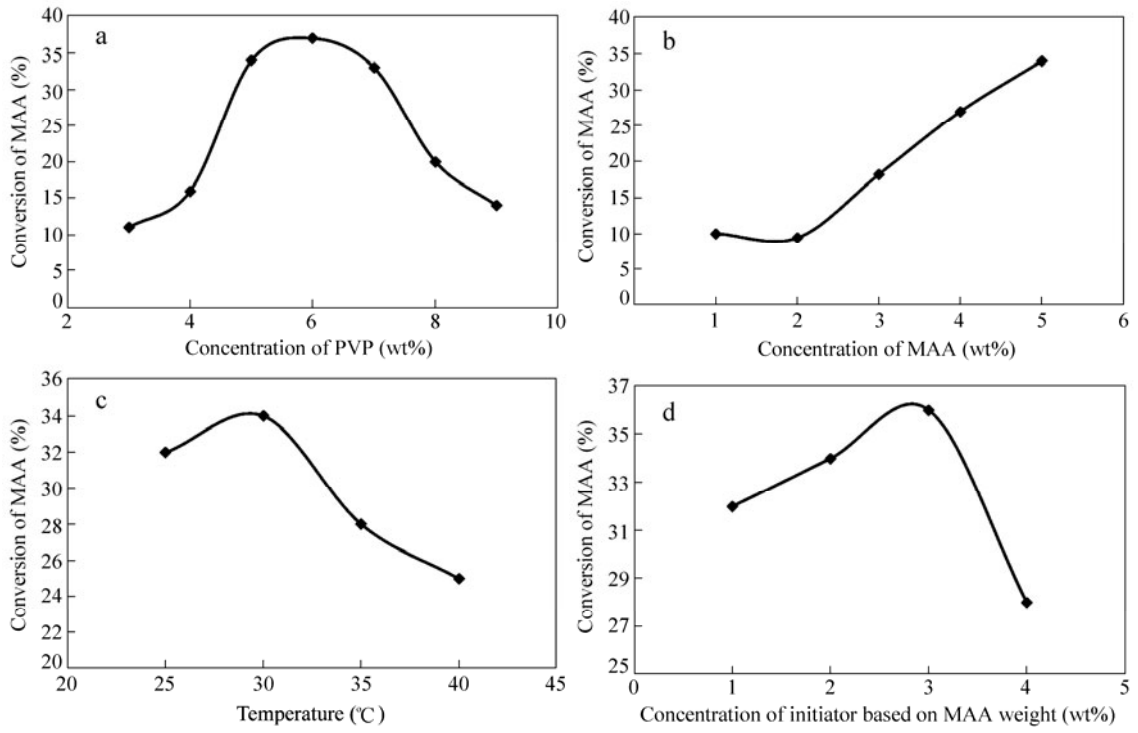

Fig. 8 Effects of polymerization factors on the conversion of MAA: (a) MAA 4.76 wt%, pH 2.4, (b) PVP 5 wt%, pH 2.4, (c) MAA 4.76 wt%, PVP 5 wt%, pH 2.4 and (d) MAA 4.76 wt%, PVP 5 wt%, pH 2.4

The polymerization temperature also affected the conversion of MAA. As shown in Fig. 8(c), at 40 °C, the conversion of conversion slightly decreased due to the deactivation of ATRP living center. Adding more initiator slightly increased the conversion of MAA. However, as shown in Fig. 8(d), when 4 wt% based on the amount of MAA was added, the conversion decreased to *ca*. 27%. It might be that the excess amount of initiator might decrease the molar mass of MAA.

Molar Mass of PMAA

As comparisons, the conventional initiators were also used to carry out the template polymerization. They were AIBN, an oil-soluble initiator, KPS, a water-soluble initiator and KPS-Na_2SO_3, a redox initiation system. Surprisingly, the nanoparticles were not prepared by any initiator. Instead, the coagulum was obtained no matter what concentrations of PVP and MAA were applied at pH < 4.5. At pH > 4.5, the transparent solution was obtained. The conversion of MAA was as high as almost 100%. The GPC diagrams of polymers are shown in Fig. 9. As shown in Fig. 9, two peaks are clear. The peak at the elution time near 7 min indicated the daughter polymer of PMAA with a large molar mass, whilst the peak near 10 min corresponded to the mother polymer of PVP. This result was consistent to the references[13]. It was reported that the molar mass of daughter polymer was sometimes higher than that of its mother polymer, arising from the combination termination of two different template-associated chain radicals and/or from the hopping of a growing daughter polymer from one template to another like. For example, in the template polymerization of *N*-vinyl imidazole (VIM) on PMAA in water, the molar mass of PVIM was 8-fold larger than that of the template PMAA (M_n = 89000)[15]. Theoretically, hopping could be suppressed by a transfer agent or by increasing the initiator concentration. However, this has not been experimentally explored. Therefore, the complete duplication of molar mass of template polymer was still a dream by the radical polymerization. That was why the template polymerization was displaced by the matrix polymerization.

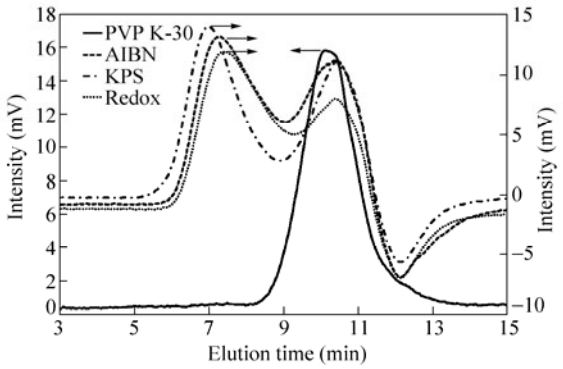

Fig. 9 Effects of initiator types on the molar mass of products prepared by template dispersion polymerization

In principle, ATRP, a living polymerization, can extinct the combined termination of two radicals. Figure 10 shows the GPC diagrams of polymers prepared by ATRP template dispersion polymerization at different pHs. As shown in Fig. 10, at pH 2.4, the distribution peak of molar mass of polymers, *i.e.* PVP and PMAA, almost overlapped that of the template PVP, except for a small shoulder appearing in the range of high molar mass. The main peak was located at 10.1 min of elution time. However, at pH 3.5, the main peak displaced to 10.6 min. It implies that at pH 3.5, a large amount of PMAA with the smaller molar mass was created accompanying with a small amount of PMAA with the larger molar mass. As aforementioned, the amount of adsorbed MAA decreased as pH increased. Hence, both the conversion of MAA and the molar mass of PMAA decreased with the increase of pH. All these results indicated that ATRP template polymerization was an effective way to duplicate the molar mass of template. Of course, the duplication was affected by the conditions. As shown in Fig. 11, at the same level of PVP 5 wt%, the main peak displaced to the longer elution time as the concentration of MAA decreased, indicating the decrease of molar mass. Moreover, at MAA 4.76 wt%, there was a shoulder corresponding to the high molar mass, whereas at MAA 3 wt%, it disappeared, instead a shoulder referring to the lower molar mass appeared. Furthermore, at the same level of MAA 4.76 wt%, the shoulder became bigger and its onset point moved to the shorter elution time, which meant to the larger molar mass, as the concentration of PVP decrease from 5 wt% to 3 wt%. It implies that the insufficient amount of template PVP led to more PMAA with large molar mass.

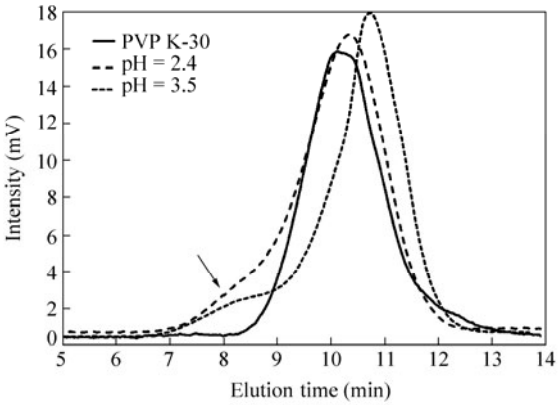

Fig. 10 GPC diagrams of products prepared by ATRP-template dispersion polymerization at different pHs

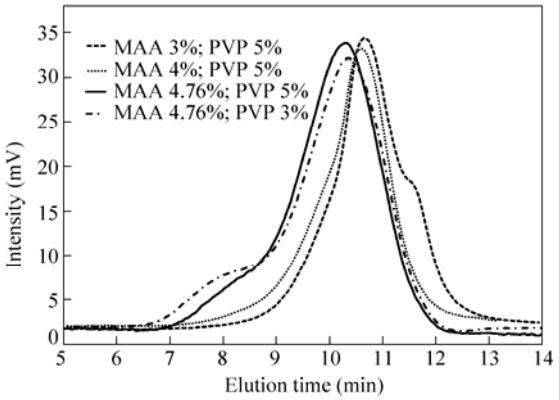

Fig. 11 GPC diagrams of products prepared at different concentrations of PVP and MAA

According to these data, a mechanism of polymerization was suggested. The loci of polymerization depended on the partition of initiator in the globules and the continuous phase. By using KPS and redox initiator, the initiators dominantly existed in the continuous phase. Therefore, a lot of oligoradicals were primarily generated in the continuous phase. These oligoradicals bridge-coagulated the growing particles and produced the larger molar mass. However, by ATRP polymerization, MBP was insoluble in water, thus most of MBP was partitioned in the globules. The polymerization within the globules of PVP/MAA complexes was dominant. Additionally, the partition of MBP in the continuous phase was very little, hence fewer oligoradicals were generated. They produced a small amount of polymer with a larger molar mass but not affected the stability of particles.

This mechanism seemed to contradict the fact that the stable nanoparticles were not prepared by using AIBN, an oil-soluble initiator. However, taking account into the behavior of chain transfer of free radicals, especially the chain transfer to monomers which was called as hopping effect of free radicals in the template polymerization systems, it should be understandable readily. The polymer generated in the aqueous phase bridge-coagulated the nanoparticles.

CONCLUSIONS

The ATRP-template dispersion polymerization of MAA on PVP was carried out. The stable nanoparticles were prepared and the molar mass of PVP was simultaneous duplicated by MAA. For the stability of globules and particles, the concentration of PVP K-30 should be lower than 9 wt% because of chain entanglement. At meanwhile, the concentration of MAA should be lower than 5.5 wt%. pH was a key factor to prepare the stable latex. At pH < 2, the coagulum was obtained, whereas pH > 4.5, the transparent solution was prepared by ATRP-template dispersion polymerization. The SEM size of particles was around 50 nm and monodispersed. As for the duplication of molar mass, the insoluble initiator was essential. By using AIBN, KPS and KPS-Na_2SO_3 redox initiation system, the concentration of initiator partitioned in the continuous phase was high enough to produce sufficient oligoradicals. These oligoradicals resulted in the bridge-coagulation of particles and the lager molar mass of PMAA, regardless to pH. However, by using ATRP initiator of MBP/Cucl/bpy, the polymerization dominantly took place within the globules due to the poorest solubility of MBP in water. Additionally, since the globules of MAA/PVP were formed by the molecular interactions, pH and the concentrations of MAA and PVP were also important to the duplication of molar mass. In this paper, the condition of pH 2.4, 5 wt% of PVP K-30 and 4.76 wt% of MAA was optimum.

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