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Preparation of monodisperse poly(methyl methacrylate) particles by radiation-induced dispersion polymerization using vinyl terminus polysiloxane macromonomer as a polymerizable stabilizer

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Abstract

Monodisperse poly(methyl methacrylate) particles were prepared directly by radiation-induced dispersion polymerization in hexane–ethanol media using vinyl terminus polysiloxane (PSI) macromonmer as a polymerizable stabilizer at room temperature. This method takes advantage of the specialties of radiation-induction, which may result in the formation of uniform polymer particles. The gel effect is evident from the polymerization kinetics curves. Vinyl terminus PSI macromonomer acted as not only a comonomer, but also as a stabilizer. The characterization of PMMA particles was carried out by the scanning electron microscope (SEM), FT-IR, ^{1}H-NMR and X-ray photoelectron spectroscope (XPS). XPS results show that the graft PSI macromonomers were anchored on the surface of PMMA particles to provide a steric stabilization to the PMMA particles.

Keywords: Radiation-induced dispersion polymerization; Poly(methyl methacrylate) monodisperse particles; Vinyl terminus PSI macromonomer

1. Introduction

Since Vanderhoff and his coworkers firstly announced their preparation of polystyrene particles with highly uniform particles size in 1995 [1], monodisperse polymer particles have found a wide variety of application in coating, inks, dry toners, instrument calibration, chromatography, and biomedical treatment [2–5]. The preparation of monodisperse particles in the micron range is particularly challenging because it is just between the limits of particles size by conventional emulsion polymerization and suspension polymerization. Various type of methods have been employed to prepare monodisperse particles, such as multi-stage swollen emulsion polymerization [6,7], successive seed emulsion polymerization [8,9], and suspension polymerization [10,11]. However, the above-mentioned procedures are time-consuming and often difficult to carry out. Dispersion polymerization is a simple effective method for preparing monodisperse polymer particles, which suits not only a wide variety of monomers, but also permits easy functionalization.

Stabilizer plays a very important role in dispersion polymerization for preparing monodisperse particles. Polymeric stabilizers designed for steric stabilization are anchored on colloidal particles either by chemical graft or by physical absorption to the particles surface. In general, chemical graft is a more effective means of stabilization than physical absorption, due to the permanence of the covalent bond between particle and stabilizer. The mechanism of chemical graft stabilization in dispersion polymerization is well established, copolymer chains resulting from the copolymerization of macromonomer with the monomer grow until reaching a critical size, after which, they are no longer soluble in the media and then coagulate with other insoluble oligomer or are captured by existing particles.

Since Paine prepared monodisperse latex particles in the range of 1–18 μm using poly(*N*-vinylpyrrolidone) (PVP) as polymerizable stabilizer in polar solvents [12,13], most studies devoted to stabilization of colloidal particles by macromonomer either using poly(ethylene oxide) (PEO) chains functionalized with methacryloyl, styryl, maleate, and thiol reactive groups [14–18], or using poly(ethylene

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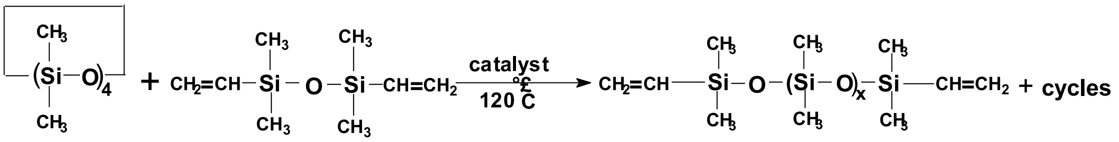

Fig. 1. Schematic diagrams of synthesis of vinyl terminus PSI macromonomer.

glycol) (PEG) chain functionalized with an acrylate terminus [19–21]. But there are few report about hydrophobic polysiloxane (PSI) macromonomer using as steric stabilizer in dispersion polymerization [22,23].

In this work, γ-rays from ^{60}Co source were used to initiate dispersion polymerization; such work has scarcely been reported before [24,25]. Generally speaking, radiation polymerization is one of the most convenient methods owning to its non-temperature dependent initiation and extremely large yield of radiation chemistry, which can easily result in the shorter nucleation stage during the whole polymerization. Additionally, the radiation process can easily prepare monodisperse polymer particles without the pollution of chemical initiators.

In this paper, first we successfully synthesized a special PSI macromonomer chain functionalized with vinyl terminus using as polymerizable stabilizer. After that monodisperse poly(methyl methacrylate) particles in the range of 2.0 ~ 4.0 μm were prepared by radiation-induced dispersion polymerization in hexane–ethanol media using vinyl terminus PSI macromonomer as the polymerizable stabilizer.

2. Experimental

2.1. Materials

MMA was purified at 10 mm Hg to remove inhibitor and was stored at −10 °C before polymerization. Octamethyl cyclotetrasiloxane (D4), and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane were purchased from BengPu Organic Silicone Factory, China. Hexane and ethanol were chemically pure grade and used without further purification.

2.2. Synthesis of vinyl terminus PSI macromonomer

A difunctional vinyl terminus PSI was obtained by anion ring-opening polymerization of D_4 and functionalized 1,3-divinyl-1,1,3,3-tetramethyldisiloxane as end-capped using potassium hydroxide (KOH) as catalyst under stirring for 18 h at 120 °C (Fig. 1). Cyclic compounds and unreacted chain stopper were removed by distillation at 160 °C and 20 mm Hg.

Table 1
Standard recipe for radiation-induced dispersion polymerization of MMA

	Material	Weight ratio (wt%)
Monomer	MMA	20.0
Stabilizer	PSI macromer	4.0
Dispersion media	Hexane	61.0
Dispersion media	Ethanol	15.0

Dose rate: 70.5 Gy/min.

2.3. Preparation of poly(MMA) microspheres by radiation-induced dispersion polymerization

The preparation of polymer particles was performed by γ-ray radiation induced dispersion polymerization in hexane/ethanol media, in which the monomer and stabilizer are easily soluble. Purified nitrogen was bubbled through the mixture for about 20 min to get rid of oxygen. After that the solution was directly fed into a sealed glass ampoule and subjected to the γ-ray radiation using ^{60}Co source at room temperature. The standard recipe used in this paper is given in Table 1.

2.4. Characterization

The proton NMR spectrum was recorded with a Bruker ACF (400 MHz) spectrometer using $CDCl_3$ as a solvent. The infrared spectrum was recorded with VECTOR22 FT-IR using a KBr pellet. The morphology and the size of produced PMMA particles were observed by a Nicolet SEM X-65 scanning electron microscopy. The surface analysis of PMMA particle was carried out in a VG ESCALAB MKΦ spectrometer (XPS) with Mg Kα X-ray source (1253.6 ev) and with an energy analyzer set at a constant retardation ratio of 20. The molecular weight of the PMMA was determined in benzene solution with a Ubbelode Capillary viscometer at 30 °C. The average molecular weight of PMMA particle can be calculated from the following equation [26]: $[\eta] = 0.104 \times 10^{-3} M_n^{0.23}$ ml/g.

3. Results and discussion

3.1. Characterization of vinyl terminus PSI macromonomer

Vinyl terminus PSI macromonomer was prepared by anionic ring-opening polymerization of D_4 using potassium hydroxide (KOH) as catalyst. The FT-IR spectrum of vinyl terminus PSI macromonomer is shown in Fig. 2, from which we observed that the absorption peak at 1596 cm^{-1} reveals the existence of vinyl group. The proton NMR spectrum as shown in Fig. 3 is another evidence to confirm the structure of vinyl terminus PSI macromonomer. The three broad

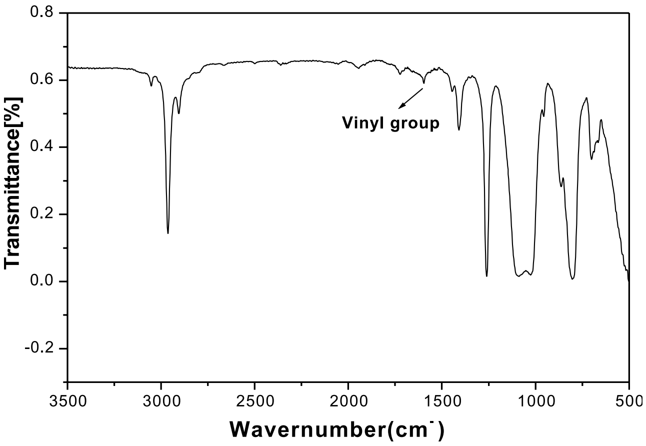

Fig. 2. FT-IR spectrum of vinyl terminus PSI macromonomer.

absorption peaks located between 5.80 and 6.20 ppm primarily represent the vinyl protons and the strong absorption peaks at 0 ppm arise from the methyl protons. The molecular weight of PSI macromonomer will be determined in benzene solution with an Ubbelode Capillary viscometer at 20 °C. The average molecular weight can be calculated with the Mark–Houwink relation [26]: $[\eta] = 12 \times 10^{-3} M_n^{0.68}$ ml/g, and is about 5300.

3.2. Variation of polymerization conversion and polymer molecular weight with irradiation time

Fig. 4 shows the polymerization conversion against irradiation time and polymer molecular weight against irradiation time, respectively. The irradiation time dependence of the conversion is represented by S-shaped curves. After a short initial period, the polymerization rate increase until the higher conversion. This feature can be explained by the existence of the gel effect. At the early polymerization stage, polymerization mainly occurred in the continuous phase, and the growing oligomers formed mainly in the continuous phase. As conversion increased, the viscosity with each particle built up, decreasing the rate of diffusion-controlled of termination, and in turn accelerating the rate of propagation, which results in the presence of the gel effect. Similar behavior has been reported for the dispersion polymerization in which polystyrene-b-poly(ethylene oxide) [27] and poly(ethylene oxide) [18] macromonomer was used as reactive surfactants.

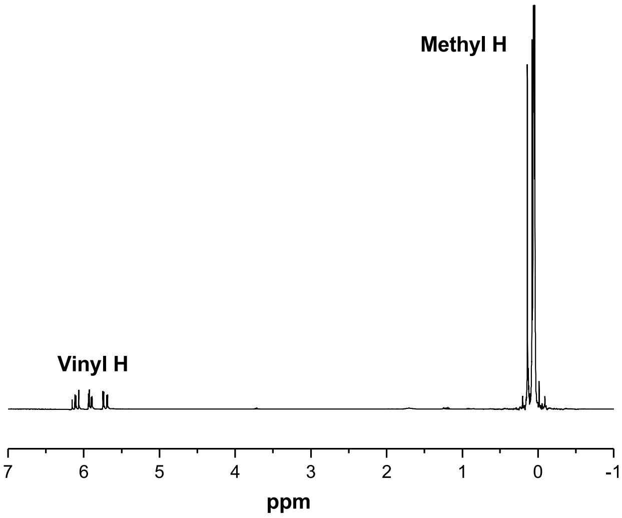

Fig. 3. ^{1}H-NMR spectrum of vinyl terminus PSI macromonomer.

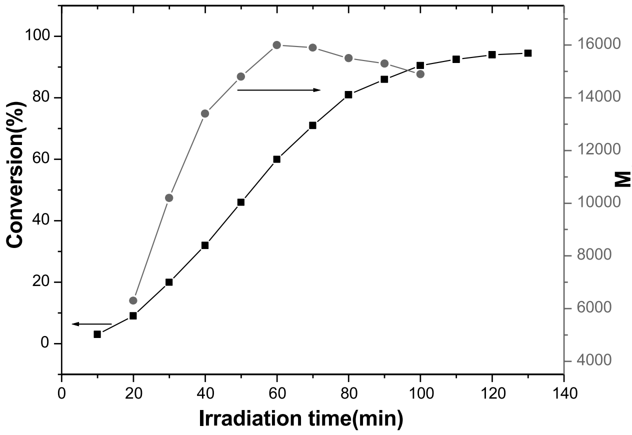

Fig. 4. Polymerization conversion versus irradiation time and polymer molecular weight versus irradiation time curve. Dose rate: 70.5 Gy/min; MMA: 20 wt%; hexane/ethanol: 65/11; vinyl terminus PSI-22 stabilizer: 4 wt%; 298 K.

The polymer molecular weight increases with irradiation time in the early stages and then reaches a steady value, which is also an indicative of the existence of the gel effect. From Fig. 4, we can see that when the conversion increases from 10 to 65%, the average molecular weight of polymer increases from 6000 to 14,000.

3.3. Characterization of polymer particles by SEM

Colloidal particles of the polymer at 30% conversion and at 96% conversion photographed by scanning electron microscopy are shown in Fig. 5(a) and (b), respectively. The particles size in diameters of the polymer latex was estimated to be around 2.2 ± 0.1 and 3.8 ± 0.15 μm, respectively. The size distribution of these particles is quite narrow. The monodispersity of the colloidal dispersion

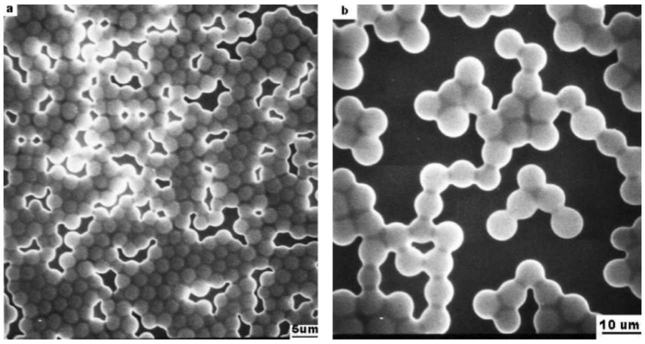

Fig. 5. Scanning electron microscope photographs of poly(MMA) microspheres: (a) 30% conversion; (b) 94% conversion.

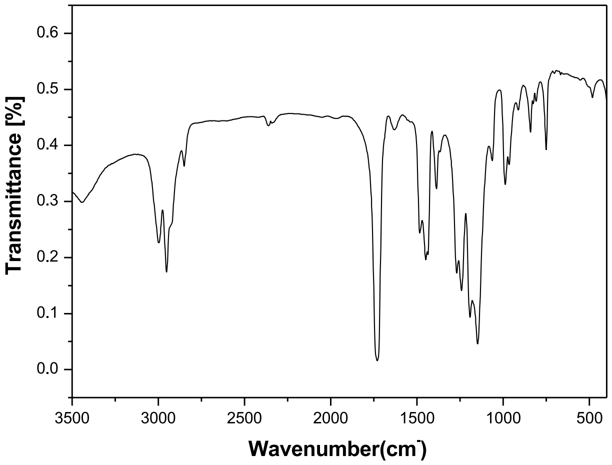

Fig. 6. FT-IR spectrum of polymer particles.

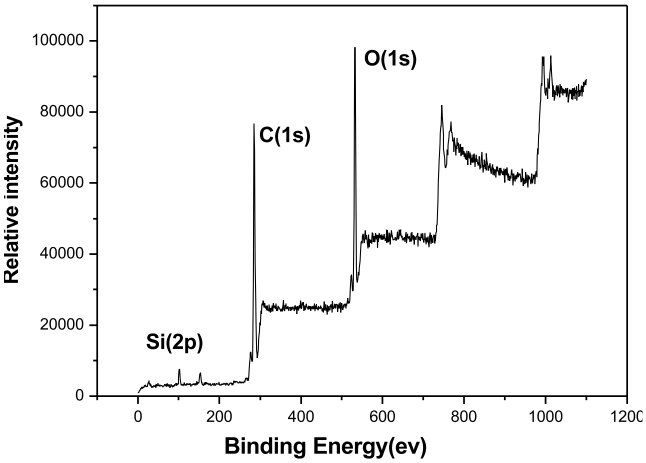

Fig. 8. XPS spectrum of polymer particles.

has been discussed by Lamer and Dineager previously [28]. They claimed that the monodispersity is only obtained when the initiation and nucleation stage is very short compared with the overall reaction period. At the same time, the period of repetitive nucleation must be made so short that monodispersity arise from subsequent uniform growth on the existing nuclei. In the radiation-induced polymerization, the gamma ray produces a higher rate of free radicals formation and initiation and the formation of nuclei is finished in a very short time (about 10^{-6} s) after radiation [29]. After the nuclei formation step, the number of the particles becoming constantly, so all of which result in the formation of monodisperse particles in the radiation-induced dispersion polymerization.

3.4. Characterization of polymer particles by FT-IR and ^{1}H-NMR spectroscopy

All samples before measurements were washed with hexane for several times to remove stabilizer absorbed physically in the particle surface and then dried in vacuum at room temperature. Fig. 6 shows the FT-IR spectrum of the polymer particles. The absorption peak at 850 cm^{-1}, corresponding to silicone–oxygen bands is clearly observed, which indicate that the grafted copolymer indeed existed in the final product. The strong absorption peak at 1720 and 1150 cm^{-1} arise from the stretching vibrations of C=O and C–O, respectively. The proton NMR spectrum as shown in Fig. 7 is another evidence to confirm that PSI macromonomer was grafted onto the PMMA backbone by radiation-induced dispersion polymerization. The proton peak of Si–CH_3 group appears at 0 ppm, the peak at 3.6 ppm indicates the presence of the OCH_3 group in polymers. Therefore, we can conclude that PSI macromonomer acted not only as stabilizers in radiation-induced dispersion polymerization, but also acted as a comonomer.

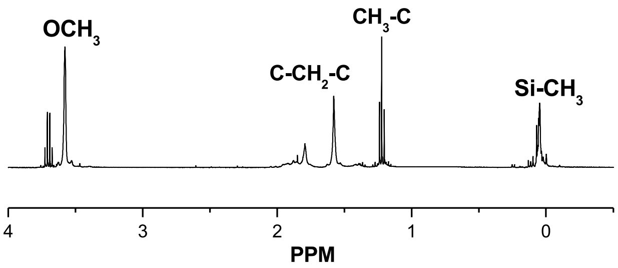

Fig. 7. ^{1}H-NMR spectrum of polymer particles.

3.5. Characterization of polymer particles by XPS

The composition on the particles surface was analyzed by X-ray photoelectron spectroscope (XPS). XPS uses X-rays to irradiate the particles surface and generate photoelectron whose energy is characteristic of each element. Fig. 8 shows XPS spectrum with a strong carbon and oxygen peak together with a weak silicone peak in the polymer powder. The atomic concentrations can be calculated based on these peak areas, from which the surface composition of the particles can be estimated. From Fig. 8, we can conclude that PSI macromonomer cover only parts of surface of the PMMA particles. This is consistent with Deslandes's model [30], which said that only a fraction of a particle surface covered by a stabilizer is sufficient to stabilize the latex particles.

4. Conclusion

Monodisperse PMMA particles in the range of 2.0–4.0 μm were obtained by radiation-induced dispersion polymerization of MMA monomer in the hexane–ethanol media using vinyl terminus PSI macromonomer as polymerizable stabilizer. The gel effect is evident from the increase in the molecular weight and the polymerization conversion versus irradiation time. PSI macromonomer in this system acted not only as a stabilizer, but also as a comonomer. The vinyl groups in the PSI terminus enable grafting of the macromonomer to the surface of PMMA particles, which provide a steric stabilization to the PMMA particles.

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