

Synthesis of Poly(vinyl acetate) Containing Diblock Copolymer by DPE Method

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ABSTRACT: Diblock copolymer poly(methyl methacrylate)-*b*-poly(vinyl acetate) (PMMA-*b*-PVAc) was prepared by 1,1-diphenylethene (DPE) method. First, free-radical polymerization of methyl methacrylate was carried out with AIBN as initiator in the presence of DPE, giving a DPE containing PMMA precursor with controlled molecular weight. Second, vinyl acetate was polymerized in the presence of the PMMA precursor and AIBN, and PMMA-*b*-PVAc diblock copolymer with controlled molecular weight

was obtained. The formation of PMMA-*b*-PVAc was confirmed by ¹H NMR spectrum. Transmission electron microscopy (TEM) and dynamic light scattering (DLS) were used to detect the self-assembly behavior of the diblock polymer in methanol. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1581–1587, 2009

Key words: 1,1-diphenylethene; block copolymers; controlled radical polymerization; self-assembly

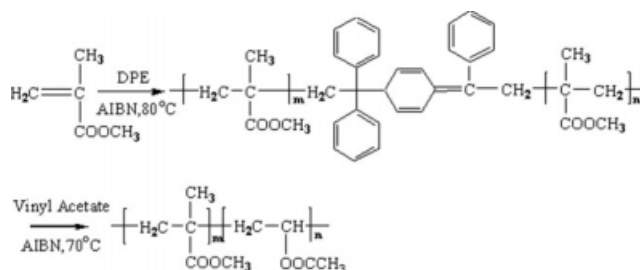
INTRODUCTION

Because of the stability of poly(vinyl acetate) (PVAc) with respect to thermal and photochemical degradation, interests in block copolymers containing PVAc block increased during the past years. Some of these copolymers, such as poly(methyl methacrylate)-*b*-poly(vinyl acetate) (PMMA-*b*-PVAc), can be used as compatibilizer for blend pairs such as PMMA/PVAc. Although recent progress in controlled radical polymerization opens a new way to prepare well-defined block copolymers, the synthesis of PVAc block containing diblock copolymers is still difficult due to the low radical reactivity of VAc. Qin and Qiu¹ prepared well-defined poly(vinyl acetate-*b*-styrene-*b*-vinyl acetate) utilizing diethyl 2,3-dicyano-2,3-di(*p*-*N,N*-diethyldithiocarbamylmethyl)phenylsuccinate as a multifunctional iniferter. Huang et al.^{2–6} synthesized diblock and triblock copolymers of PVAc by successive photo-induced charge-transfer polymerization. Matyjaszewski and coworkers⁷ prepared block copolymers of PVAc by combining atom-transfer radical polymerization (ATRP) and conventional radical polymerization by the use of azo compounds containing activated halogen atoms, such as 2,2'-azobis[2-methyl-*N*-(2-(4-chloromethylbenzoyloxy)ethyl)propionamide]. Several groups^{8–12} reported the synthesis of PVAc containing block

copolymers by ATRP using trichloromethyl-end-grouped PVAc as a macroinitiator which was prepared via telomerization of VAc with CCl₄ as a telogen. Zou et al.¹³ synthesized PVAc diblock copolymer by stable free-radical polymerization, but the PVAc block was very short. Sawamoto and coworkers¹⁴ prepared block copolymers containing PVAc by ATRP in the presence of iron catalysts. Kaneyoshi and Matyjaszewski¹⁵ prepared poly(butyl acrylate-*grad*-VAc)-*b*-PVAc by cobalt-mediated radical copolymerization of butyl acrylate and VAc when the copolymerization was carried out under the VAc-rich condition in the initial feed. Jérôme and coworkers¹⁶ obtained well-defined PVAc containing diblock copolymers by combining cobalt-mediated radical polymerization with ATRP. In Jérôme's work, PVAc was first end capped with an activated bromide by the addition of a α -bromoester or a α -bromoketone containing nitroxide and then was converted into effective macroinitiator for ATRP of styrene, ethyl acrylate or methyl methacrylate. However, all the afore-mentioned methods were too complicated, and the reaction conditions were very rigorous.

Since Nuyken's group¹⁷ reported the 1,1-diphenylethene (DPE) system in 2001, there have been a lot of articles on this novel controlled radical polymerization system^{18–31}. It was found that many conventional radical polymerization systems became controlled if a small amount of DPE was added. Its polymerization conditions are very close to conventional free-radical polymerization system, and there

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Scheme 1 Synthesis of diblock copolymer PMMA-*b*-PVAc.

is no use of any catalyst as in ATRP or expensive agents as in NMRP and RAFT. The DPE method appears to be a useful alternative to prepare block copolymers. Nuyken et al.¹⁹ synthesized diblock of PVAc and PS using the DPE method. In their report, one monomer was first polymerized by conventional radical polymerization in the presence of DPE to prepare the precursor. The second monomer was then polymerized in the presence of the precursor. However, the polymerization temperature was so high (110°C) that the molecular weights of the obtained diblock polymers were not controlled well enough.

In this article, we prepared PMMA-*b*-PVAc block copolymers by utilizing the DPE method. First, free-radical polymerization of methyl methacrylate (MMA) was carried out with AIBN as initiator in the presence of DPE to prepare the PMMA precursor which contained unique semiquinoid structure. Second, VAc was polymerized in the presence of the PMMA precursor and a small amount of AIBN. To make the reaction conditions mild and improve the controllability of block copolymer structure, the blocking polymerization temperature was reduced to 70°C (Scheme 1).

EXPERIMENTAL

Materials

MMA (>99%) and VAc (>99%) were all dried over CaH₂ and MgSO₄ overnight, respectively and then distilled under reduced pressure. DPE was synthesized according to the method reported by Anschütz and Hilbert³² and distilled under reduced pressure. All other reagents were used as received without any further purification.

Characterization

Monomer conversion was obtained gravimetrically. Molecular weights and molecular weight distributions of PMMA and its block copolymers were measured by gel permeation chromatography (GPC)

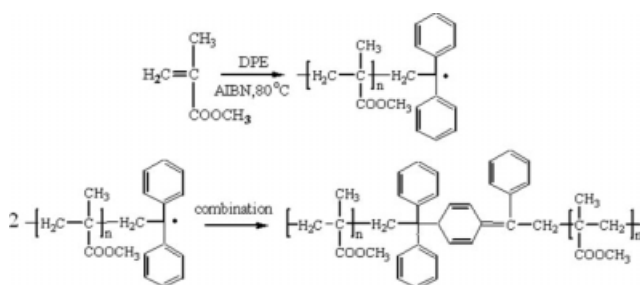
on a Tosoh HLC 8220 GPC (column: TSK-Gel Super HZM-M ×2) with THF as the eluent (40°C) at a flow rate of 0.35 mL/min. Narrow PMMA standards were used to generate the calibration curve. ¹H NMR spectra were recorded on a Bruker AV600-MHz NMR spectrometer. CDCl₃ or CD₃COCD₃ was used as solvent. Dynamic light scattering (DLS) measurements were done by using Brookhaven BI-200SM operated at 532 nm at an angle of 90° and at 25°C. Solutions for light scattering measurements were prepared by dissolving the block copolymers in previously filtered and distilled methanol. All solutions were filtered through 0.45 μm filters before analysis. Transmission electron microscopy (TEM) was carried out with a Hitachi H-800 microscope operated at an acceleration voltage of 200 kV. Samples were prepared by dropping a droplet of latex (formed by self-assembly of the block copolymer in methanol) on a copper TEM grid, which was coated with thin films of Formvar and carbon successively, and methanol was let to evaporate under ambient atmosphere for 1 h.

Synthesis of DPE-containing PMMA precursor

In a typical experiment, 20 g (0.2 mol) of MMA, 432 mg (2.4 mmol) of DPE, 196.8 mg (1.2 mmol) of AIBN were added into a 100 mL dry round-bottomed flask equipped with a magnetic stirrer and degassed by five freeze-pump-thaw cycles. The polymerization was carried out at 80°C. After polymerization, the polymer was obtained by precipitation in methanol and dried under vacuum to constant weight.

Synthesis of diblock copolymer PMMA-*b*-PVAc

In a typical experiment, 1.02 g (0.1 mmol) of PMMA precursor ($M_{n, GPC} = 10200$, $M_w/M_n = 1.34$), 4.3 g (0.05 mol) of VAc, 8.2 mg (0.05 mmol) of AIBN, and 10 mL of toluene (or benzene) were added to a 50 mL dry round-bottomed flask equipped with a magnetic stirrer. After five freeze-pump-thaw cycles, the flask was placed in an oil bath thermostated at 70°C. At definite time intervals, portions of the sample were withdrawn from the flask using an argon-filled gas-tight syringe to determine monomer conversions and molecular weights. The polymerization was stopped by pouring the reaction mixture into a large amount of cold methanol. PVAc homopolymer could be dissolved in methanol, whereas PMMA homopolymer precipitated from methanol. As for PMMA-*b*-PVAc diblock copolymer, it could be dispersed in methanol at room temperature. However, when the temperature was lower than -5°C, it would also precipitate from methanol.



Scheme 2 Semiquinoid structure of PMMA precursor.

RESULTS AND DISCUSSIONS

Preparation of PMMA precursor

The free-radical polymerization in the presence of DPE has been investigated by Nuyken's group. In this system, DPE reacted with growing chains and the activity of growing chain radicals reduced. Combination termination of two DPE-ended radicals formed a unique semiquinoid structure as shown in Scheme 2.

In our experiment, 20 g (0.2 mol) of MMA was polymerized in bulk at 80°C in the presence of 196.8 mg (1.2 mmol) of AIBN and 432 mg (2.4 mmol) of DPE. After 3 h of polymerization, monomer conversion reached 18%, and the reaction mixture was poured into methanol. The ¹H NMR spectrum of the purified PMMA precursor is shown in Figure 1.

As shown in Figure 1, in addition to the large absorptions of the protons of main chain repeating units from 1.2 to 2.0 ppm and that of methoxyl protons at 3.6 ppm, the polymer also shows the characteristic signals of the phenyl proton at 7–7.5 ppm and the protons of semiquinoid ring at 5.4–6.1 ppm. On the assumption that one polymer chain contains one semiquinoid structure and taking the molecular

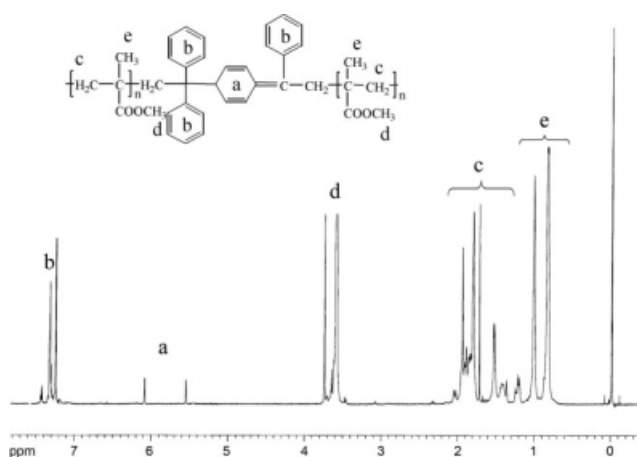


Figure 1 ¹H NMR spectrum of PMMA precursor ($M_{n,GPC} = 10,200$, $M_w/M_n = 1.34$). Solvent: $CDCl_3$.

weight of the semiquinoid unit into consideration, the number-average molecular weight of PMMA precursor can be calculated from the peak intensity ratio of the phenyl protons and that of methoxyl protons using the following equation.

$$M_{n,NMR} = 100 \times 5I_d/I_b + 360 = 9860$$

where I_b and I_d are the integral values of the protons of phenyl and methoxyl protons, respectively. The molecular weight of MMA and semiquinoid unit are 100 and 360, respectively.

This value was in good agreement with that obtained with GPC calibrated by standard PMMA samples, confirming that there was indeed one semiquinoid structure in each PMMA chain.

Free-radical polymerization of VAc in the presence of PMMA precursor

The PMMA precursor ($M_{n,GPC} = 10,200$, $M_w/M_n = 1.34$) obtained earlier was added to the free-radical polymerization system of VAc to prepare PMMA-*b*-PVAc diblock copolymer. In all the blocking polymerization experiments, 1.02 g (0.1 mmol) of PMMA precursor, 4.3 g (50 mmol) of VAc, and 10 mL of toluene were used, and the polymerization was carried out at 70°C. The amount of AIBN was 8.2 mg (0.05 mmol) or 16.4 mg (0.1 mmol) in two different runs. Samples were withdrawn at regular intervals to determine monomer conversion and molecular weight.

Figure 2 shows the GPC curves of the crude products obtained at different reaction time when the amount of AIBN was 0.05 mmol. These samples were not purified by separation process. The GPC traces showed that the molecular weight shifted to higher molecular weight direction with unimodal

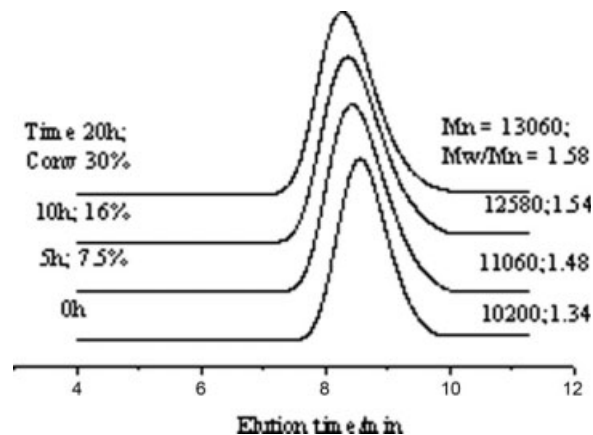


Figure 2 GPC curves of PMMA precursor and block copolymers obtained at different monomer conversions. Conditions: 50 mmol of VAc, 0.1 mmol of PMMA precursor, 0.05 mmol of AIBN, and 10 mL of toluene.

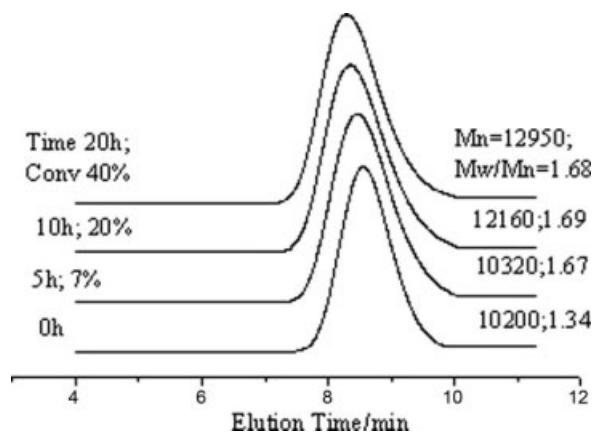


Figure 3 GPC curves of PMMA precursor and block copolymers obtained at different monomer conversions. Conditions: 50 mmol of VAc, 0.1 mmol of PMMA precursor, 0.1 mmol of AIBN, and 10 mL of toluene.

shape, indicating that the blocking polymerization of VAc proceeded in a controlled fashion. The unimodal shape of the GPC traces throughout the polymerization process and no visible residue of the PMMA precursor suggested good reinitiating efficiency of the PMMA precursor and successful formation of PMMA-*b*-PVAc block copolymers.

When the amount of AIBN increased to 0.1 mmol, similar results were obtained as shown in Figure 3. But the molecular weight distributions were broader than those obtained at lower AIBN amount (0.05 mmol). Furthermore, the polymerization rate at higher AIBN concentration was greater than that at lower AIBN concentration. For example, the monomer conversion reached 40% in 20 h with 0.1 mmol of AIBN, whereas that with 0.05 mmol of AIBN only reached 30% in the same polymerization time.

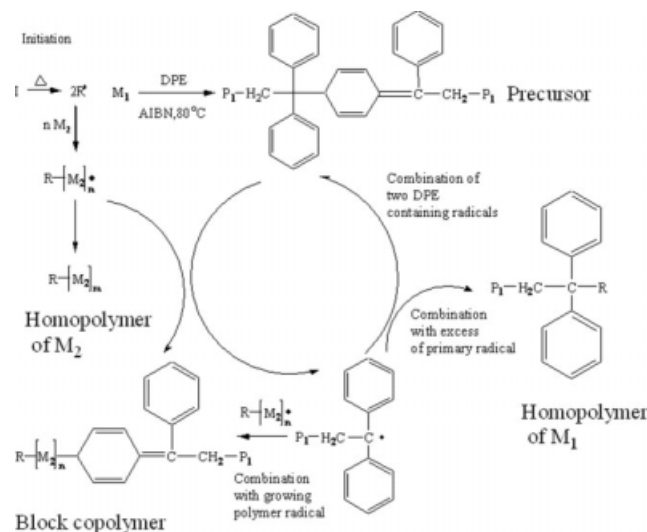
According to the mechanism proposed by Viala et al. in Refs. 24 and 26, the formation process of block copolymers can be shown in Scheme 3. Different from the other CRP techniques, the DPE method was a two-step procedure. In the first step, a precursor polymer containing semiquinoid structure, which was used as active species in the second polymerization step, was prepared in the presence of DPE. Second, the primary radicals generated by the added initiator started the polymerization of the second monomer, generating polymeric radicals which led to the decomposition of the semiquinoid structure of PMMA precursor. Therefore, DPE-ended radical was generated, and block copolymer was formed at the same time. The DPE-ended radical was inactive and could not initiate polymerization of the second monomer. The recovery of the semiquinoid structure of PMMA precursor would be achieved through the combination of two DPE-ended radicals; therefore, the controllability of the polymerization was preserved.

The concentration of PMMA precursor, AIBN, and VAc were all of crucial importance for the block copolymer yielding efficiency. When PMMA precursor was in excess compared with AIBN, the recombination of two DPE ended polymeric radicals predominated with the formation of PMMA-*b*-PVAc and recovery of the PMMA precursor. Hence, the polymerization process was well controlled, and the blocking efficiency was high.

When the concentration of AIBN was higher than that of PMMA precursor, side reaction between DPE-ended radical and PMMA radical was favored. Because DPE-ended polymeric radical was consumed, the molecular weight distribution of the crude product became broad. When PMMA precursor was consumed up, residual AIBN led to the formation of PVAc homopolymer.

PVAc homopolymer could be dissolved in methanol, but methanol was nonsolvent for PMMA homopolymer. So, block copolymer PMMA-*b*-PVAc could self-assemble in methanol if VAc segment was long enough. Temperature had great influence on the dissolving behavior of PMMA-*b*-PVAc in methanol. At room temperature, PMMA-*b*-PVAc could form stable dispersion in methanol. When the temperature was lower than -5°C , PMMA-*b*-PVAc could not be dispersed in methanol. When methanol was heated, PMMA-*b*-PVAc self-assembled gradually and stable dispersion formed again. On the other hand, temperature had little effect on the dissolving behavior of PVAc homopolymer. So, we used this difference between PMMA-*b*-PVAc block copolymer and PVAc homopolymer for the purification of the crude products.

At low AIBN concentration (0.05 mmol was added.), the composition of the crude product obtained at 30% monomer conversion was that 68%



Scheme 3 Mechanism of block copolymer formation.

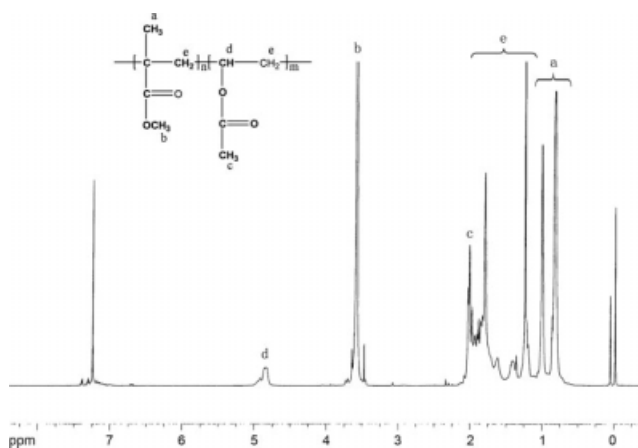


Figure 4 ^1H NMR spectrum of the PMMA-*b*-PVAc diblock copolymer in CDCl_3 . PMMA precursor: $M_{n,\text{GPC}} = 10,200$, $M_w/M_n = 1.34$. The product of blocking polymerization obtained at 7.5% monomer conversion: $M_{n,\text{GPC}} = 11,060$, $M_w/M_n = 1.48$ (before purification); $M_{n,\text{GPC}} = 11,480$, $M_w/M_n = 1.43$ (after purification).

weight percent of the polymer obtained was block copolymer, and the other 32% was PVAc homopolymer. At high-AIBN concentration (0.1 mmol was added.), 61% weight percent of the crude product obtained was block copolymer, and the other 39% was PVAc homopolymer. This indicated that the blocking efficiency became low when the concentration of AIBN increased.

The formation of PMMA-*b*-PVAc block copolymer was confirmed by the ^1H NMR spectrum. It can be seen from Figure 4 that in addition to the large absorptions of the methyl protons at 0.85 and 1.02 ppm (a), the protons of main chain repeating units at from 1.2 to 2.0 ppm (c), and the methoxyl protons at 3.6 ppm (b), the polymer also showed the

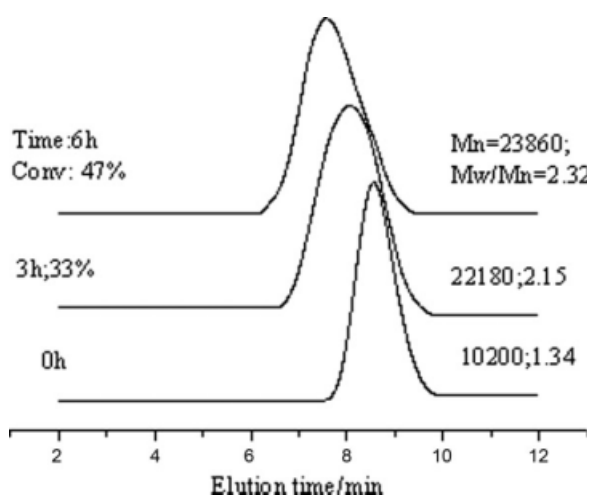


Figure 5 GPC curves of PMMA precursor and block copolymers obtained at different monomer conversions. Conditions: 50 mmol of VAc, 0.1 mmol of PMMA precursor, 0.1 mmol of AIBN, and 10 mL of benzene.

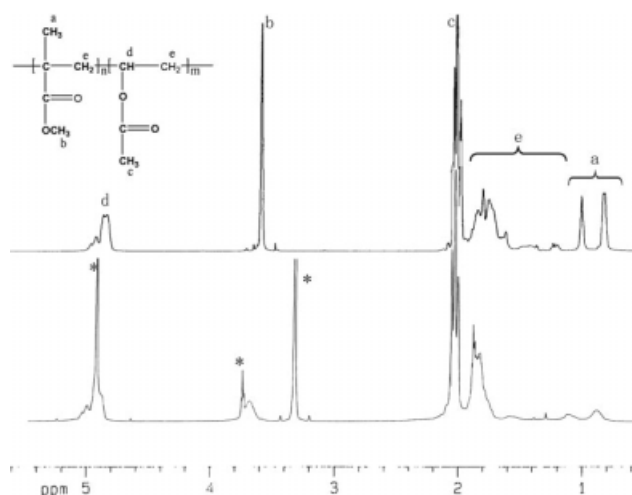


Figure 6 ^1H NMR spectra of PMMA-*b*-VAc diblock copolymer in CDCl_3 (upper) and CD_3OD (bottom). (PMMA precursor: $M_{n,\text{GPC}} = 10,200$, $M_w/M_n = 1.34$. PMMA-*b*-PVAc: $M_{n,\text{GPC}} = 28,580$, $M_w/M_n = 2.16$). *Because of water and methanol in deuterated CD_3OD .

characteristic signal of the methine proton adjacent to acetyl group at 4.88 ppm (d).

Effect of solvent on blocking efficiency

For polymerization of VAc, when toluene is used as the solvent, the chain-transfer constant to solvent (C_s) is 29.2×10^{-4} at 70°C . When benzene is used as the solvent at the same temperature, the C_s is only 5.27×10^{-4} . Therefore, we used benzene to replace toluene to get longer VAc segment and higher blocking efficiency. The results are shown in Figure 5.

It can be seen that after toluene was replaced by benzene, the polymerization speed became very

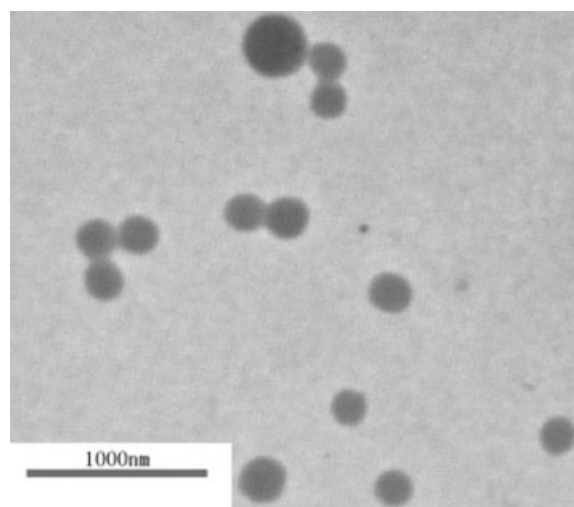


Figure 7 TEM picture for the particles formed in methanol by PMMA-*b*-PVAc diblock copolymer (PMMA precursor: $M_{n,\text{GPC}} = 10200$, $M_w/M_n = 1.34$. PMMA-*b*-PVAc: $M_{n,\text{GPC}} = 28,580$, $M_w/M_n = 2.16$).

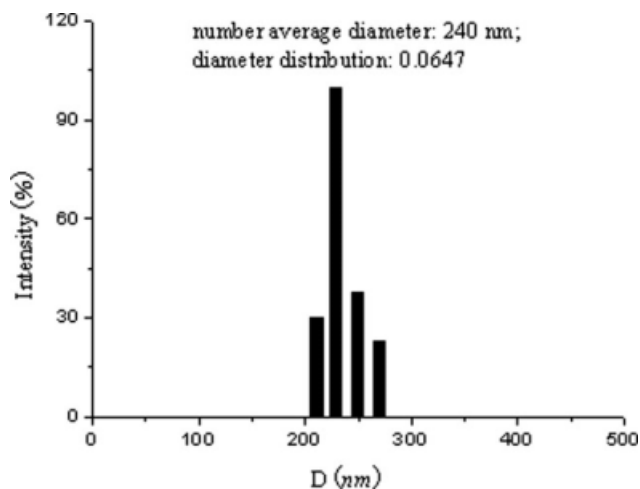


Figure 8 DLS result for the particles formed in methanol by PMMA-*b*-PVAc diblock copolymer (PMMA precursor: $M_{n, GPC} = 10,200$, $M_w/M_n = 1.34$; PMMA-*b*-PVAc: $M_{n, GPC} = 28,580$, $M_w/M_n = 2.16$).

high. The monomer conversion reached 47% in 6 h. Furthermore, the molecular weight of the obtained block copolymer was much higher than that of PMMA precursor, indicating that the PVAc segment was longer.

The blocking efficiency also increased greatly when toluene was substituted by benzene. For the sample obtained at 47% monomer conversion, 88% weight percent of the crude product obtained was block copolymer and only 12% was PVAc homopolymer.

Self-assembly of PMMA-*b*-PVAc diblock copolymers in methanol

The formation of latex via aggregating and its structure depend on many parameters, such as the nature and molecular weights of the blocks and solvent interaction. For PMMA-*b*-PVAc diblock copolymer, PVAc segment could be dissolved in methanol, but methanol was nonsolvent for PMMA segment. Therefore, PVAc block would form the shell of latex and PMMA block would be sheltered in the core of latex. For PMMA-*b*-PVAc block copolymer with $M_{n, GPC}$ 28580 and M_w/M_n 2.16 (after purification to remove PVAc homopolymer), its ^1H NMR spectrum (Fig. 6) in CD_3OD showed that the characteristic signals of methyl protons (0.85 and 1.02 ppm) and methoxyl protons (3.60 ppm) for PMMA segment was very weak compared with those in CDCl_3 . This provided direct evidence for the self-assembly of PMMA-*b*-PVAc in methanol.

TEM and DLS were used to characterize the sizes and size distributions of the aggregates of the PMMA-*b*-PVAc block copolymer in methanol. Figure 7 shows the typical morphology of PMMA-*b*-PVAc

aggregates in methanol at a concentration of 2.5 mg/mL. It can be seen that the PMMA-*b*-PVAc aggregates showed spherical shape, and that the average diameter was about 215 nm. The result of DLS was given in Figure 8. The number-average diameter of the aggregates obtained with DLS was a little bigger than that obtained by TEM.

CONCLUSIONS

Free-radical polymerization of VAc initiated by AIBN with PMMA precursor as active species, which was obtained by free-radical polymerization of MMA in the presence of DPE, resulted in PMMA-*b*-PVAc diblock copolymer. At low-AIBN concentration, the blocking efficiency was higher and less PVAc homopolymer was generated. When benzene was used as solvent to substitute toluene, the polymerization speed and the blocking efficiency all increased greatly. PMMA-*b*-PVAc diblock copolymers could self-assemble into spherical particles in methanol.

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