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Synthesis of poly(methyl methacrylate)-*b*-poly(acrylic acid) by DPE method

*Dong Chen, Ruixue Liu, Zhifeng Fu, Yan Shi**

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China; e-mail: shiyan@mail.buct.edu.cn

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Abstract: Amphiphilic diblock copolymer poly(methyl methacrylate)-*b*-poly(acrylic acid) (PMMA-*b*-PAA) was prepared by 1,1-diphenylethene (DPE) method. Firstly, 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. *tert*-Butyl acrylate (*t*BA) was then polymerized in the presence of the PMMA precursor, and PMMA-*b*-P*t*BA diblock copolymer with controlled molecular weight was prepared. Finally, amphiphilic diblock copolymer PMMA-*b*-PAA was obtained by hydrolysis of PMMA-*b*-P*t*BA. The formation of PMMA-*b*-PAA was confirmed by ^{1}H NMR spectrum and gel permeation chromatography. Transmission electron microscopy and dynamic light scattering were used to detect the self-assembly behavior of the amphiphilic diblock polymers in methanol.

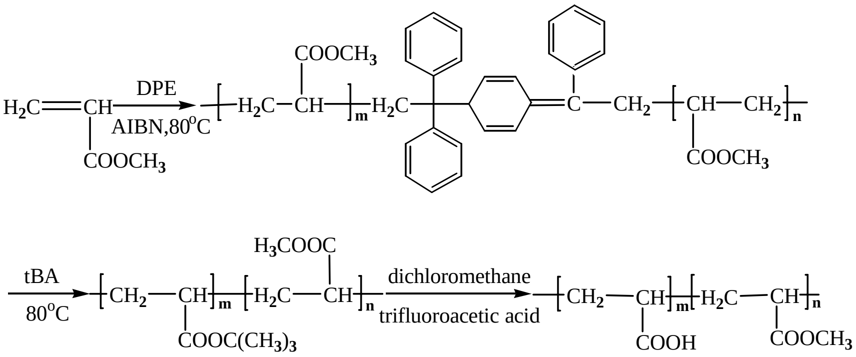
Key Words: living free radical polymerization, amphiphilic diblock copolymers, self-assembly, 1,1-diphenylethene.

Introduction

Amphiphilic block copolymers containing poly(acrylic acid) (PAA) segments have recently attracted increasing interest [1]. Traditionally, well-defined block copolymers containing PAA segments were synthesized by sequential living anionic polymerization of protected monomers, such as *tert*-butyl acrylate (*t*BA), followed by hydrolysis [2, 3]. However, the anionic polymerization needs to be carried out under rigorous conditions. Recently controlled radical polymerization has become an established method to prepare block copolymers under mild conditions. Block copolymers containing PAA segment have been successfully synthesized by using atom transfer radical polymerization (ATRP) [4-11], reversible addition fragmentation chain transfer polymerization (RAFT) [12-14], and stable free radical polymerization (SFRP) [15, 16] techniques, or via combination of these controlled radical polymerization methods [17-19]. The iodide-mediated radical polymerization was also employed by our group for the synthesis of block copolymers containing PAA segment [20].

In 2001, Nuyken's group reported a novel controlled radical polymerization system [21-27]. They found that many conventional radical polymerizations became controlled if a small amount of 1,1-diphenylethene (DPE) was added. Furthermore, the polymerization conditions are very close to conventional free radical polymerization and there is no use of any catalyst as in ATRP, which need to be removed, or no use of expensive agents as in NMRP and RAFT. The DPE method appears to be a useful alternative to prepare block copolymers. Nuyken [21] and his coworkers have synthesized polystyrene-*b*-poly(vinyl acetate), polystyrene-*b*-

poly(methyl methacrylate), poly(N-vinylpyrrolidone)-*b*-polystyrene, poly(N-vinylpyrrolidone)-*b*-poly(methyl methacrylate) and poly(N-vinylpyrrolidone)-*b*-poly(vinylacetate) using DPE system. But there is still no report on the synthesis of poly(methyl methacrylate)-*b*-poly(acrylic acid) (PMMA-*b*-PAA) block copolymers using this method. In this paper we utilized the DPE method to prepare PMMA-*b*-PAA through the following steps as shown in Scheme 1. Firstly, 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. *tert*-Butyl acrylate (*t*BA) was then polymerized in the presence of the PMMA precursor, and PMMA-*b*-P*t*BA diblock copolymer with controlled molecular weight was prepared. Finally, amphiphilic diblock copolymer PMMA-*b*-PAA was obtained by hydrolysis of PMMA-*b*-P*t*BA.

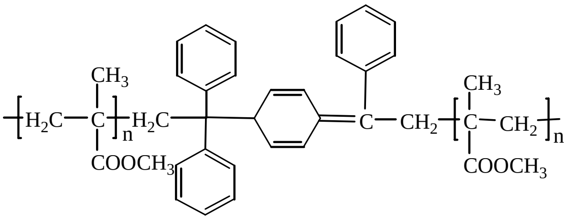


Scheme 1. Synthesis of amphiphilic diblock copolymer PMMA-*b*-PAA.

Results and discussion

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.



Scheme 2. Semiquinoid structure of PMMA precursor.

In our experiment, 20 g of MMA (0.2 mol) was polymerized in bulk at 80 °C in the presence of DPE with AIBN as initiator. The molar ratio of AIBN to MMA was 0.6 %, and that of AIBN to DPE was 0.5. After polymerization for 3 h, the reaction mixture was poured into methanol. The ^1H NMR spectrum of purified PMMA is shown in Fig. 1.

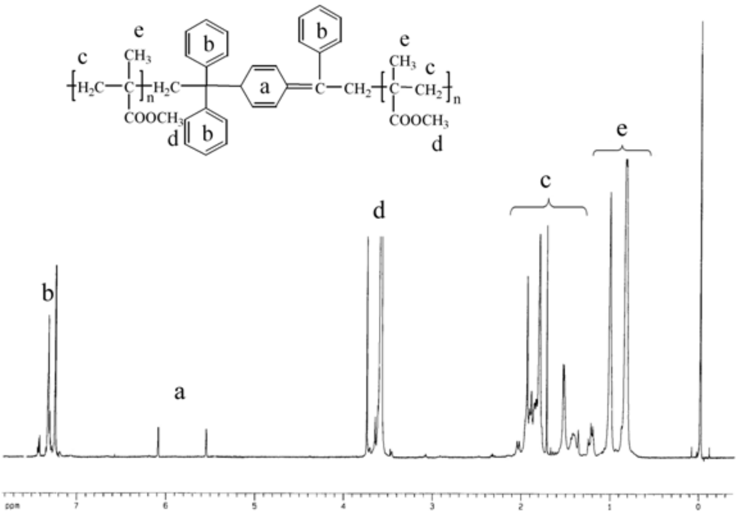


Fig. 1. ^{1}H NMR spectrum of PMMA precursor ($M_{n,\ GPC}$ = 10400, M_w/M_n = 1.34). Solvent: $CDCl_3$. For detailed preparation conditions, see the text.

As shown in Fig. 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 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 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, 100 and 360 are the molecular weight of MMA and semiquinoid unit respectively.

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

Preparation of PMMA-b-PtBA block copolymer

The PMMA precursor ($M_{n,\ GPC}$ = 10400, M_w/M_n = 1.34) obtained above was added to the free radical polymerization system of *t*BA in order to prepare PMMA-*b*-P*t*BA diblock copolymer. Solution polymerization of *t*BA in toluene was carried out at 80 °C. In all the blocking polymerization experiments, 0.5 g of PMMA precursor and 10 mL of toluene were used, and the polymerization time was 6 h. But 1.0 g, 2.5 g and 5.0 g of *t*BA were added respectively in three different experiments. Furthermore, no radical initiator was added to the polymerization system.

After polymerization, the mixture was poured into a large amount of cold methanol and the precipitated product was obtained by filtration. Fig. 2 (A) shows the ^{1}H NMR spectrum of one of the obtained products. It can be seen from Fig. 2(A) that in addition to the large absorptions of the methoxyl protons of MMA repeating units at 3.6 ppm (a), the polymer also shows the characteristic signals of *t*BA repeating units at 1.42 ppm (b). At the same time, the protons of semiquinoid ring in PMMA precursor at 5.4-6.1 ppm disappeared, indicating that all semiquinoid structure in the PMMA precursor was consumed. Furthermore, the ratio of I_a/I_b is about 1:9.3, where I_a and I_b are the integral values of the characteristic methoxyl protons of MMA and the *tert*-butyl protons of *t*BA, respectively. Therefore we could calculate that the mole ratio of MMA unit to *t*BA unit is about 1:3.1, which is in good agreement with that (1:3.13) determined from monomer conversion. This indicates that no P*t*BA homopolymer formed.

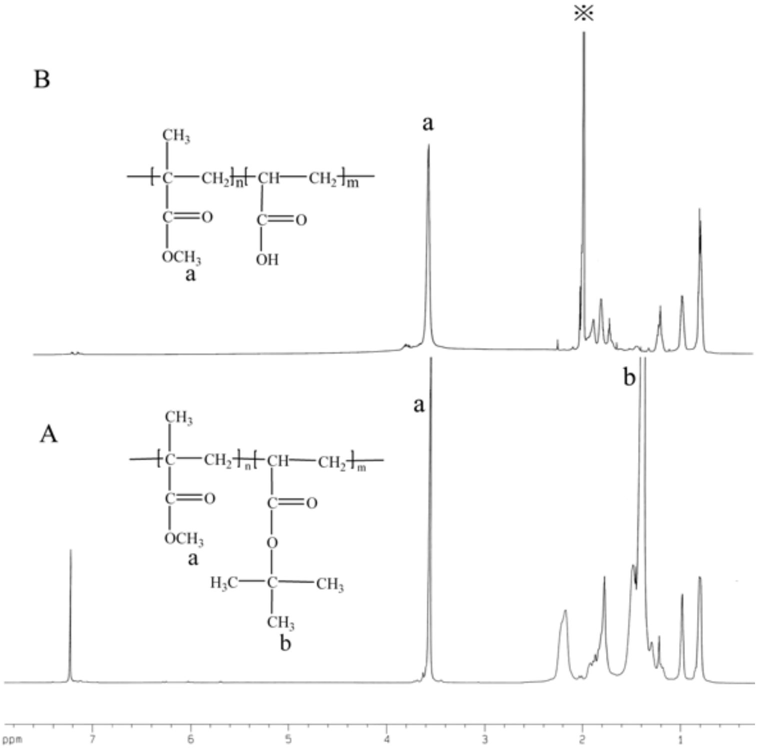


Fig. 2. ^{1}H NMR spectra of the PMMA-*b*-P*t*BA diblock copolymer in $CDCl_3$(A) and the PMMA-*b*-PAA diblock copolymer in CD_3COCD_3(B). (PMMA precursor $M_{n,\ GPC}$ = 10400, M_w/M_n = 1.34; PMMA-*b*-P*t*BA block copolymer $M_{n,\ GPC}$ = 21700, M_w/M_n = 1.89).   Attributed to CH_3COCH_3 in CD_3COCD_3.

Fig. 3 shows GPC curves of PMMA precursor and crude products of three blocking polymerizations. It should be pointed that the samples were withdrawn from the polymerization system and diluted with THF directly.

At lower amount of *t*BA (Run 1), the GPC curve was symmetrical and shifted to higher molecular weight direction, showing good blocking efficiency of the PMMA precursor and successful formation of PMMA-*b*-P*t*BA block copolymer.

At medium amount of *t*BA (Run 2), the molecular weight polydispersity index was much broader than that of PMMA precursor and the GPC curve was unsymmetrical, indicating that a relative large amount of PMMA precursor still existed.

At higher amount of *t*BA (Run 3), although the GPC curve shifted to higher molecular weight direction very clearly, there was a small shoulder peak at low molecular weight direction. This indicated that the blocking efficiency of PMMA precursor became lower.

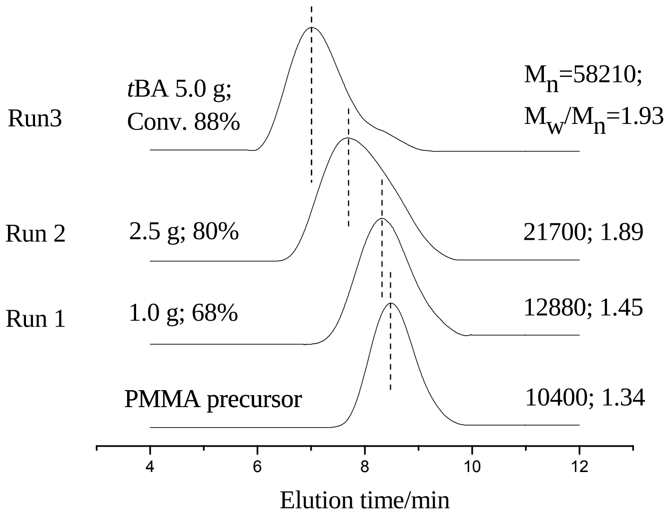


Fig. 3. GPC curves of PMMA precursor and block copolymers obtained with different amount of *t*BA. For detailed reaction conditions, see the text.

Tab. 1 summarizes the results for the three experiments. It can be seen that although the blocking efficiency of PMMA precursor became lower at higher *t*BA concentrations, the number-average molecular weights determined by GPC and ^{1}H NMR were still in good agreement with the theoretical values, further confirming that no P*t*BA homopolymer was generated.

Tab. 1. Results for PMMA-*b*-P*t*BA diblock copolymer synthesis.

Exp. No.	$[M]_0/[I]_0$[1]	Conversion (%)	Mn,th[2]	$M_{n,\ GPC}$	$M_{n,NMR}$[3]
Run 1	162.50	68.0	12270	12880	12050
Run 2	406.25	80.0	26000	21700	25830
Run 3	812.50	88.0	50960	58210	50060

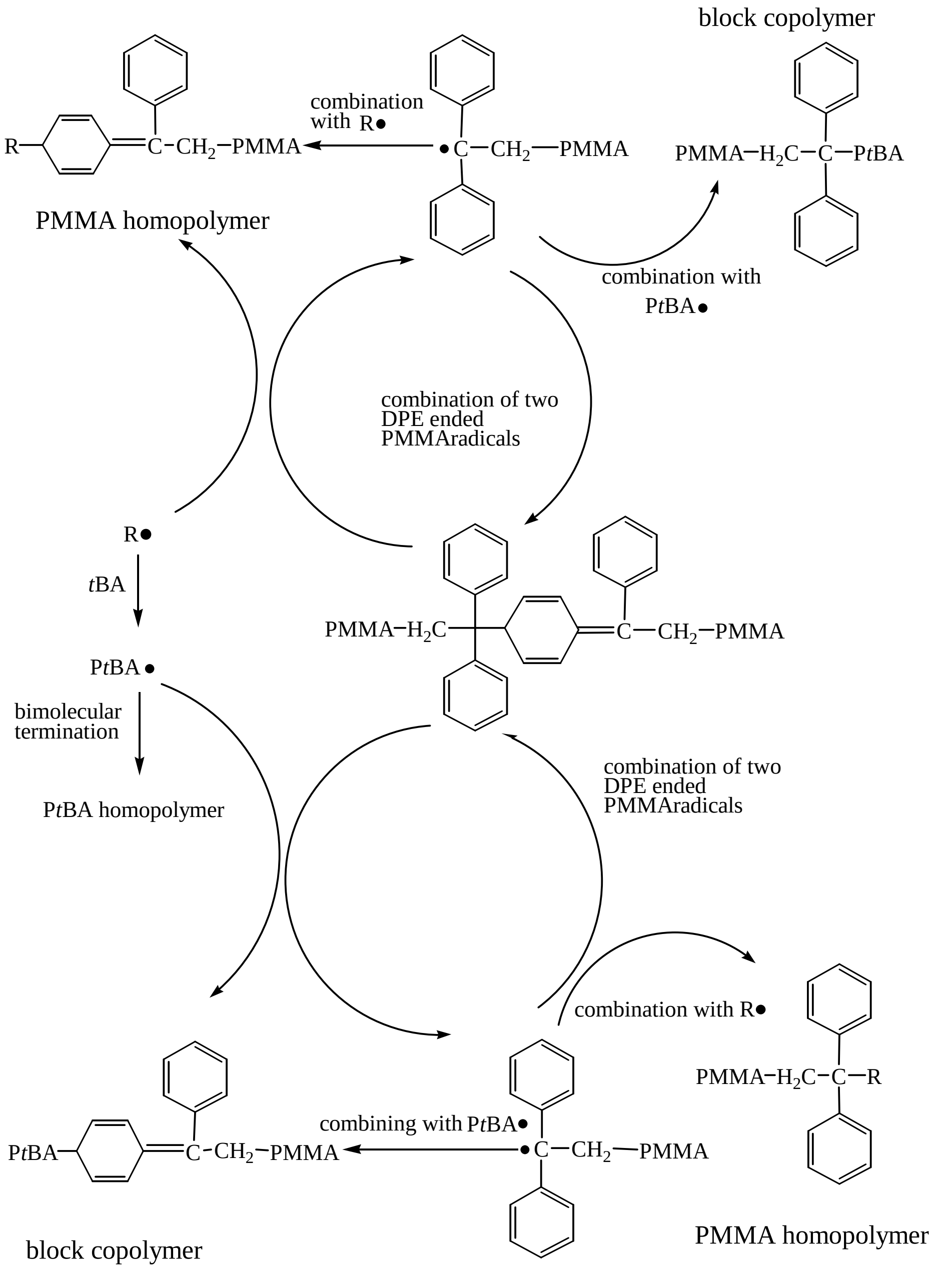
[1] $[M]_0$ and $[I]_0$ are the initial concentrations of monomer *t*BA and PMMA precursor respectively.

[2] $Mn,th = M_{n,PMMA}/2 + ([M]_0 \times Conversion \times 128)/([I]_0 \times 2)$, where Mn,PMMA and 128 are number-average molecular weights of PMMA precursor and monomer *t*BA respectively. This equation is based on the assumption that one PMMA precursor chain generates two PMMA-*b*-P*t*BA diblock copolymer chains.

[3] $M_{n,NMR} = [(I_b/3I_a) \times 1.28 + 1] \times (M_{n,PMMA}/2)$, where I_a and I_b are the integral values of the characteristic methoxyl protons of MMA and the *tert*-butyl protons of *t*BA espectively, and 1.28 is the ratio of molecular weight of *t*BA to that of MMA.

In order to explain the above results, according to the mechanism proposed in Ref. [24, 25], the following mechanism for block copolymer formation was suggested. The semiquinoid structure of the PMMA precursor was attacked by a growing or a primary radical ("P*t*BA·" or "R·" in Scheme 3), which might be formed from small amount of residual oxygen in the polymerization system, leading to decomposition of the band between two DPE units in the PMMA precursor. Therefore DPE ended radical was generated, at the same time, PMMA-*b*-P*t*BA block copolymer formed if PMMA precursor was attacked by a growing radical, or PMMA homopolymer formed if

PMMA precursor was attacked by a primary radical. The DPE ended radical was inactive and could not initiate polymerization of *t*BA. However, on one hand, the recovery of the semiquinoid structure precursor would be achieved through the combination of two DPE ended radicals. On the other hand, DPE ended radical reacted with primary radical or growing radical, generating PMMA homopolymer and PMMA-*b*-P*t*BA block copolymer respectively. The concentrations of PMMA precursor, *t*BA, primary radical R· and growing radical P*t*BA· were all of crucial importance for the block copolymer yield.



Scheme 3. Mechanism of block copolymer formation.

When the precursor polymer was in excess compared with R· and P*t*BA·, the recombination of two DPE terminated polymeric radicals predominated, and recovery of the semiquinoid structure took place. Hence, the polymerization process was well controlled, and the block efficiency was high.

When the concentration of R· was higher comparing with the precursor polymer, side reactions between DPE ended radical and primary radical were favored, and thus PMMA homopolymer was produced. This can be seen clearly in the GPC curves of the crude products obtained in Run 2 and 3.

Hydrolysis of PMMA-b-PtBA Diblock Copolymer

Cleavage of the *tert*-butyl ester groups was achieved by the PMMA-*b*-P*t*BA diblock copolymers being treated in dichloromethane with trifluoroacetic acid at room temperature under stirring for 48 h. Fig. 2 (B) shows the ^{1}H NMR spectrum of hydrolyzed products in CD_3COCD_3. Compared with Fig. 2 (A), the signal at 1.42 ppm, which was attributed to the *tert*-butyl protons of the P*t*BA block, disappeared almost completely, indicating that PMMA-*b*-P*t*BA diblock copolymer had successfully transformed into PMMA-*b*-PAA amphiphilic diblock copolymer.

Self-assembly of PMMA-b-PAA Diblock Copolymer

PAA homopolymer can be dissolved in methanol, but methanol is nonsolvent for PMMA homopolymer. Therefore, PMMA-*b*-PAA block copolymer can self-assemble when it is put into methanol and form latex like emulsion (not precipitated) if the PAA block is long enough.

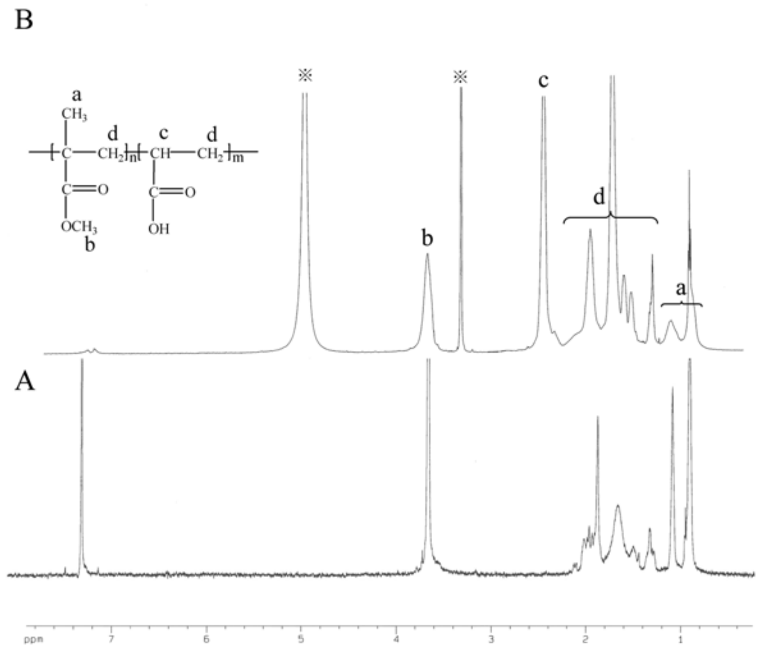


Fig. 4. ^{1}H NMR spectra of the hydrolyzed PMMA-*b*-PAA in $CDCl_3$(A) and CD_3OD (B). PMMA precursor $M_{n,\,GPC}$ = 10400, M_w/M_n = 1.34; PMMA-*b*-P*t*BA block copolymer $M_{n,\,GPC}$ = 21700, M_w/M_n = 1.89. Attributed to CH_3OH and H_2O in CD_3OD.

Furthermore, PAA block should form the shell of the latex and PMMA block should be sheltered in the core of the latex. On the contrary, PMMA homopolymer can be dissolved in chloroform, while PAA homopolymer would precipitate in chloroform. Therefore, PMMA-*b*-PAA diblock copolymer would self-assemble into latex with PAA block as the core and PMMA block as the shell. We used ^{1}H NMR to investigate the self-assembly behavior of PMMA-*b*-PAA diblock copolymer in CD_3OD and $CDCl_3$

respectively. In Fig. 4 (A) of ^{1}H NMR spectrum of PMMA-*b*-PAA in $CDCl_3$, the characteristic signal are nearly the same as those of pure PMMA homopolymer, indicating that PAA block is really sheltered in the core. In Fig. 4 (B) of ^{1}H NMR spectrum of PMMA-*b*-PAA in CD_3OD, beside the characteristic signals of PMMA block, there is a new sharp signal at 2.5 ppm, which is attributed to the proton adjacent to carboxyl of AA repeating unit. This confirms that PAA block was rich in the shell.

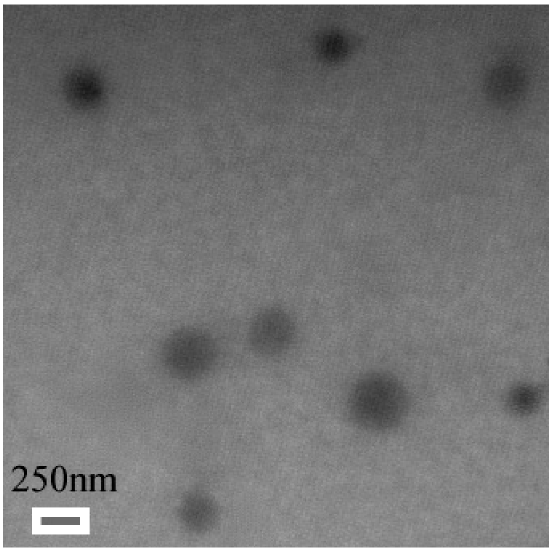


Fig. 5. TEM picture for the latex of PMMA-*block*-PAA in methanol. (PMMA-*b*-P*t*BA block copolymer $M_{n,\ GPC}$ = 21700, M_w/M_n = 1.89; PMMA precursor $M_{n,\ GPC}$ = 10400, M_w/M_n = 1.34).

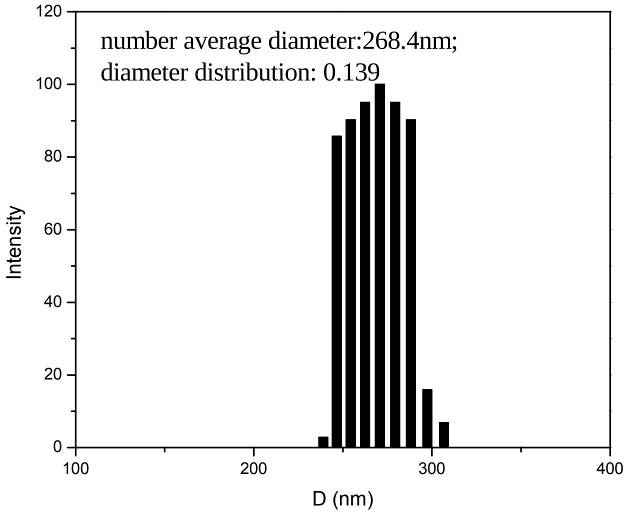


Fig. 6. Diameter distribution of the particles formed by PMMA-*block*-PAA in methanol. (PMMA-*b*-P*t*BA block copolymer $M_{n,\ GPC}$ = 21700, M_w/M_n = 1.89; PMMA precursor $M_{n,\ GPC}$ = 10400, M_w/M_n = 1.34).

We also used TEM and DLS to detect the self-assembly behavior of the PMMA-*b*-PAA block copolymer in methanol. Latex samples were investigated using transmission electron microscopy (TEM) with an H-800 Hitachi microscope at an accelerating voltage of 200 kV. Fig. 5 shows the typical morphology of PMMA-*b*-PAA aggregates in methanol. It can be seen that PMMA-*b*-PAA aggregates were spherical in shape. Their diameter was about 220-300 nm.

The result of DLS is given in Fig. 6. It can be seen that the diameter of the aggregates obtained with DLS is in good agreement with that obtained by TEM.

Conclusions

The DPE technique is a very successful method for the synthesis of PMMA-*b*-P*t*BA diblock copolymers, the formation of PMMA-*b*-P*t*BA was confirmed by ^{1}H NMR spectrum and GPC. In the free radical polymerization of *t*BA in the presence of PMMA precursor, at lower amount of *t*BA, the GPC curve of the resulted product was symmetrical and shifted to higher molecular weight direction, showing successful formation of PMMA-*b*-P*t*BA block copolymer. At medium amount of *t*BA, the molecular weight polydispersity index of the resulted product was much broader than that of PMMA precursor and the GPC curve was unsymmetrical. At higher amount of *t*BA, although the molecular weight of the resulted product was very high, there was a clear shoulder peak at low molecular weight direction, and the blocking efficiency of PMMA precursor became lower. Amphiphilic diblock copolymer PMMA-*b*-PAA was then obtained by hydrolysis of the resulted PMMA-*b*-P*t*BA. The resulting block copolymer can self-assemble in methanol and form spherical aggregates with PAA block at the shell and PMMA block being sheltered in the core.

Experimental part

Materials

MMA (>99%) and *t*BA (>99%) were from Beijing Chemical Reagent Co., dried over CaH_2 (Aldrich, 90-95%) overnight, and then distilled under reduced pressure. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Fluka) was recrystallized from ethanol. DPE was synthesized according to the method reported by Anschütz and Hilbert [28] and distilled under reduced pressure. All other reagents were used as received without any further purification.

Preparation of PMMA precursor

In a typical experiment, 10.0 g (0.1 mol) of MMA, 65.6 mg (0.4 mol% to MMA) of AIBN and 108 mg (0.6 mol% to MMA) of DPE 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 ^{o}C. After polymerization, the polymer was obtained by precipitation in methanol, and purified by dissolution/precipitation from chloroform into methanol.

Preparation of PMMA-b-PtBA

In a typical experiment, 0.5 g of PMMA precursor ($M_{n,\ GPC}$ = 10400, M_w/M_n = 1.34), 2.50 g of *t*BA (19.5 mmol), and 10 mL of toluene were added to a 50 mL dry round-bottomed flask equipped with a magnetic stirrer. No initiator was added. After five freeze-pump-thaw cycles, the flask was placed in an oil bath thermostated at 80 ^{o}C.

The polymerization was stopped by pouring the reaction mixture into a large amount of cold methanol and the precipitated block copolymer was obtained by filtration.

Hydrolysis of PMMA-b-PtBA

0.5 g of PMMA-*b*-P*t*BA ($M_{n,\ GPC}$ = 21700, M_w/M_n = 1.89) was dissolved in 40 mL of dichloromethane completely, and then 0.5 mL of trifluoroacetic acid was added slowly under stirring. After hydrolysis at room temperature for 48 h, the solution was filtered to remove insoluble impurities. The filtrate was concentrated by rotary evaporator and the white powdered polymer was recovered by precipitation in cyclohexane.

Characterization

Monomer conversion was obtained gravimetrically. Molecular weights and molecular weight distributions were measured using a Tosoh HPLC 8220 gel permeation chromatograph (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 polystyrene standards were used to generate the calibration curve. ^{1}H NMR spectra were recorded on a **Bruker** AV600-MHz NMR spectrometer. $CDCl_3$ or CD_3COCD_3 was used as solvent. Dynamic light scattering measurements were done by using Brookhaven BI-200SM operated at 532 nm at an angle of 90^o and at 25 ^oC. Solutions for light scattering measurements were prepared by dissolving the block copolymer in previously filtered and distilled THF. 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 THF) on a copper TEM grid, which was coated with thin films of Formvar and carbon successively, and THF was let to evaporate under ambient atmosphere for 1 h.

Acknowledgements

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