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Synthesis of Amphiphilic Diblock Copolymers by DPE Method

Dong Chen, 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; Fax: +86 010 6442 3811

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Summary

Amphiphilic diblock copolymers, poly(methyl methacrylate)-*b*-poly(acrylic acid) (PMMA-*b*-PAA) and polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA), were prepared by 1,1-diphenylethene (DPE) method under mild conditions. Firstly, free radical polymerization of *tert*-butyl acrylate (*t*BA) was carried out with AIBN as initiator in the presence of DPE, giving a DPE-containing precursor, P*t*BA, with controlled molecular weight. Secondly, methyl methacrylate and styrene were polymerized in the presence of P*t*BA precursor, and PS-*b*-P*t*BA and PMMA-*b*-P*t*BA diblock copolymers with controlled molecular weights were obtained respectively. Finally, amphiphilic diblock copolymers, PMMA-*b*-PAA and PS-*b*-PAA, were prepared by hydrolysis of PS-*b*-P*t*BA and PMMA-*b*-P*t*BA. The formation of PS-*b*-PAA and PMMA-*b*-PAA was confirmed by ^{1}H NMR. Transmission electron microscopy (TEM) and dynamic light scattering (DLS) were used to detect the self-assembly behavior of the amphiphilic diblock polymers in tetrahydrofuran (THF).

Introduction

Amphiphilic block copolymers containing poly(acrylic acid) (PAA) segment have attracted increasing interests because PAA is weak polyelectrolyte and its dissociation degree can be governed by the pH and ionic strength of aqueous solution [1]. Traditionally, well-defined block copolymers containing PAA segment were synthesized by sequential living anionic polymerization [2, 3] or group transfer polymerization [4] of protected monomers, such as *tert*-butyl acrylate (*t*BA), followed by hydrolysis. Teyssie *et al.* [2] have prepared AB and ABA type block copolymers by sequential anionic polymerization of styrene and *t*BA in the presence of LiCl in THF at -78°C and subsequently eliminated *tert*-butyl groups by hydrolysis using *p*-toluene sulfonic acid as catalyst. However, the anionic polymerization need to be carried out under rigorous conditions such as in high-vacuum, highly purified monomers and solvents. Recent progress in controlled radical polymerization, especially nitroxide-mediated radical polymerization (NMRP), [5, 6] atom transfer radical polymerization (ATRP), [7, 8] and reversible addition-fragmentation chain transfer polymerization (RAFT) [9] opens a new way to prepare well-defined block copolymers under mild conditions. Block copolymers containing PAA segment have been successfully synthesized by using ATRP [10-22], RAFT [23-25], and NMRP [26, 27], or via combination of these controlled radical polymerization methods [28-30]. But metal catalysts or expensive stable radicals or RAFT agents were used in these controlled radical polymerization methods. We recently reported the synthesis of PAA containing block copolymers by the use of iodide-mediated radical polymerization, but the iodide containing chain transfer agent was very sensitive to light and heat [31].

Recently, Nuyken's group reported a novel controlled radical polymerization system [32-40]. They found that many radical polymerizations became controlled if a small amount of 1,1-diphenylethene (DPE) was added. For the preparation of block copolymers, the first monomer, initiator and DPE were heated at 60 to 110°C to get the DPE containing precursor, and then the second monomer was polymerized in the presence of the precursor at 60 to 110°C, this process can be carried out batchwise or in a one-pot process.

The DPE method appears to be a useful alternative to prepare block copolymers because the polymerization conditions for DPE method are very close to conventional free radical polymerization and there is no use of catalyst as in ATRP, which need to be removed, or no use of expensive agent as in NMRP and RAFT. We herein reported the synthesis of polystyrene-*b*-poly(*tert*-butyl acrylate) (PS-*b*-P*t*BA) and poly(methyl methacrylate)-*b*-poly(*tert*-butyl acrylate) (PMMA-*b*-P*t*BA) diblock copolymers *via* DPE method, in which *t*BA was used as the first monomer and styrene (St) or methyl methacrylate (MMA) as the second monomer. The amphiphilic diblock copolymers, PS-*b*-PAA and PMMA-*b*-PAA, were then obtained through hydrolysis of PS-*b*-P*t*BA and PMMA-*b*-P*t*BA with trifluoroacetic acid. Transmission electron microscopy (TEM) and dynamic light scattering (DLS) were used to study the self-assembly behavior of the amphiphilic diblock polymers in THF.

Experimental

Materials

St (Polymerization grade, Yanshan Petrochemical Co.), MMA (99%, Beijing Chemical Plant) and *t*BA (Analytical grade, Shanghai Chemicals Plant) were dried over anhydrous $MgSO_4$, then distilled under reduced pressure and stored in brown glass bottles at -15°C. 2,2'-Azobis(isobutyronitrile) (AIBN, 98 %, Fluka) was recrystallized from ethanol. DPE was synthesized according to the method reported by Anschütz and Hilbert [41] and distilled under reduced pressure. ^{1}H NMR ($CDCl_3$, δ): 5.47 ppm (=CH_2), 7.2-7.4 ppm (aromatic protons).

Synthesis of DPE containing PtBA precursor

In a typical experiment, 12.8 g (0.1 mol) of *t*BA, 108 mg (0.6 mol% to *t*BA) of DPE, 65.6 mg (0.4 mol% to *t*BA) of AIBN and 5 mL of toluene were added into a 100 mL dry round-bottom flask equipped with a magnetic stirrer and degassed by five freeze-pump-thaw cycles. The polymerization was carried out at 80°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. After polymerization, the polymer was obtained by precipitated in methanol/water mixture, and purified by dissolution/precipitation from chloroform into methanol/water mixture. The polymer was dried in a vacuum oven.

Synthesis of Diblock Copolymers PS-b-PtBA and PMMA-b-PtBA

In a typical experiment, 0.5 g of P*t*BA precursor ($M_{n,\,GPC}$ = 8360, M_w/M_n = 1.63), 2.50 g (24 mmol) of St, and 12 mL of toluene were added to a 50 mL dry round-bottom 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°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 and the precipitated block copolymer was obtained by filtration.

Hydrolysis of PS-b-PtBA and PMMA-b-PtBA

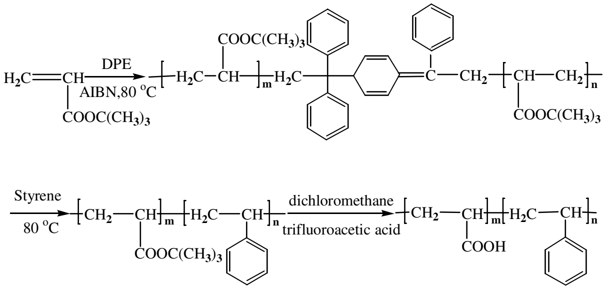
0.5 g of block copolymer was dissolved in 40 mL of dichloromethane completely, and then 0.5 mL of trifluoroacetic acid was added slowly under stirring. After hydrolyzed at room temperature for 48 h, the solution was filtered to remove insoluble impurities. The filtrate was concentrated by rotary evaporator and the white powdered polymer was recovered by precipitation in cyclohexane.

Instruments

Monomer conversion was obtained gravimetrically. Molecular weights and molecular weight distributions of P*t*BA and its block copolymers were measured using a Tosoh HPLC 8220 gel permeation chromatography (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° and at 25°C. 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.

Results and Discussions

The amphiphilic diblock copolymers PS-*b*-PAA and PMMA-*b*-AA were synthesized in three steps as shown in Scheme 1.
Firstly, free radical polymerization of *t*BA was carried out with AIBN as initiator in the presence of DPE to get the P*t*BA precursor containing unique semiquinoid structure. Secondly, free radical polymerization of St or MMA was carried out using the P*t*BA precursor obtained above as active specie to prepare PS-*b*-P*t*BA or PMMA-*b*-P*t*BA block copolymers. Finally, amphiphilic diblock copolymers PS-*b*-PAA and PMMA-*b*-PAA were obtained by hydrolysis of PS-*b*-P*t*BA and PMMA-*b*-*t*BA respectively.



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

Free Radical Polymerization of tBA via DPE method

*t*BA was polymerized in toluene at 80°C with the molar ratio of *t*BA to AIBN to be 250:1. By varying the molar ratio of DPE to AIBN and the amount of solvent toluene, four experiments were carried out. The logarithmic conversion data, $\ln([M]_0/[M])$ ([M] is the monomer concentration at time *t*), plotted against time *t* are shown in Fig. 1. It can be seen that when a larger amount of solvent was used straight lines passing through the origin were obtained.

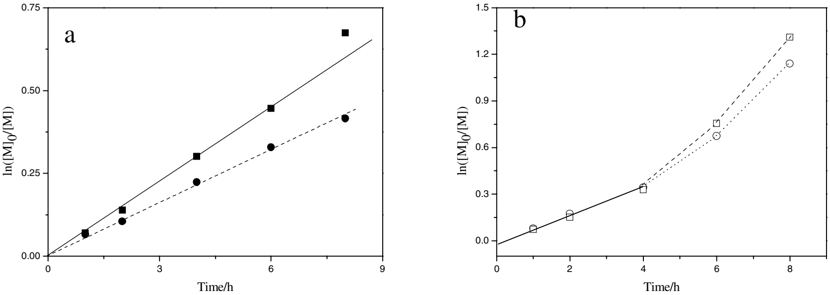


Fig. 1. Logarithmic conversion data $\ln([M]_0/[M])$ ([M] is the monomer concentration at time *t*), plotted against time for the polymerization of *t*BA with DPE in toluene at 80°C.
(a) 10 mL of toluene, 12.8 g of *t*BA (0.1 mol). ●: $[DPE]_0/[AIBN]_0/[tBA]_0$ = 0.8%:0.4%:1;
■: $[DPE]_0/[AIBN]_0/[tBA]_0$ = 0.6%:0.4%:1. (b) 5 mL of toluene, 12.8 g of *t*BA (0.1 mol).
○: $[DPE]_0/[AIBN]_0/[tBA]_0$ = 0.8%:0.4%:1; □: $[DPE]_0/[AIBN]_0/[tBA]_0$ = 0.6%:0.4%:1.

However, when less solvent was used the curve of logarithmic conversion data plotted against time became steep when the conversion increased to about 30%. This means that a gel effect took place when the monomer conversion reached a certain value in this polymerization system. Furthermore, the reason why polymerization rate decreased with the increase of the molar ratio of DPE to AIBN was that DPE reacted with growing chains and therefore the activity of growing chain radicals decreased.

Fig. 2 shows the number-average molecular weights (M_n), the polydispersity indexes (M_w/M_n) and molecular weight distribution curves of the P*t*BA obtained at different amounts of DPE and toluene. The molecular weight distribution curves were unimodal and the molecular weight shifted to higher molecular weights, which showed the character of controlled radical free polymerization. But the polydispersity indexes of the polymers obtained were broader than those by other controlled free radical polymerization methods, such as ATRP and RAFT. The polydispersity indexes became broader and the number-average molecular weights did not increased proportionally to monomer conversion especially at higher monomer conversions. All these results demonstrated that the controlled ability of the DPE system was not good enough.

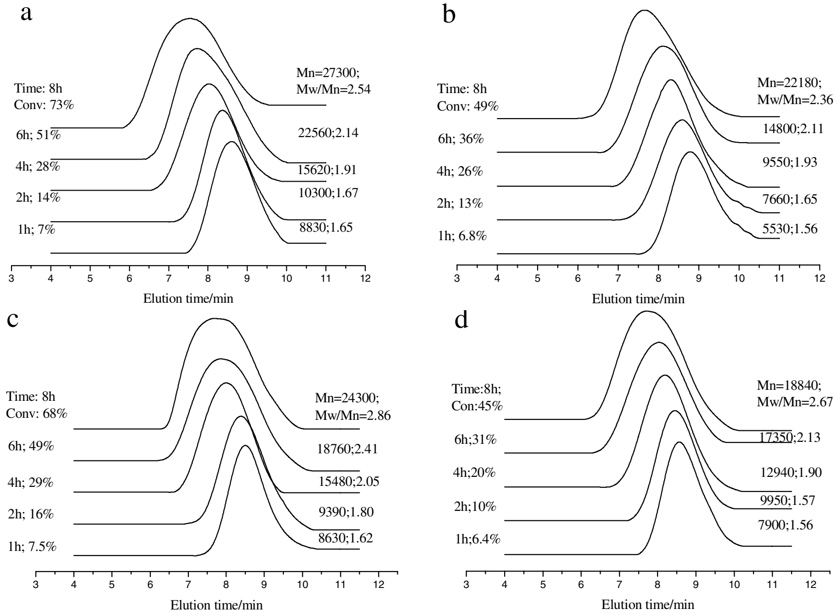


Fig. 2. GPC traces of P*t*BA obtained at different monomer conversions. Reaction conditions: (a) 5 mL of toluene, 12.8 g of *t*BA (0.1 mol), $[DPE]_0/[AIBN]_0/[tBA]_0$ = 0.6%:0.4%:1; (b) 10 mL of toluene, 12.8 g of *t*BA (0.1mol), $[DPE]_0/[AIBN]_0/[tBA]_0$ = 0.6%:0.4%:1; (c) 5 mL of toluene, 12.8 g of *t*BA (0.1 mol), $[DPE]_0/[AIBN]_0/[tBA]_0$ = 0.8%:0.4%:1; (d) 10 mL of toluene, 12.8 g of *t*BA (0.1 mol), $[DPE]_0/[AIBN]_0/[tBA]_0$ = 0.8%:0.4%:1.

The structure of the obtained P*t*BA precursor was analyzed by ^{1}H NMR spectroscopy. Fig. 3 shows the typical spectrum of P*t*BA, which was prepared at the following conditions: 10 mL of toluene, 12.8 g of *t*BA, $[DPE]_0/[AIBN]_0/[tBA]_0$ = 0.8%:0.4%:1, polymerization time 0.5 h, polymerization temperature 80°C, monomer conversion 3 %, $M_{n,GPC} = 3860$, $M_w/M_n = 1.52$.

As shown in Fig. 3, in addition to the large absorptions of the repeated units of *t*BA at 1.42 ppm (a) and the large absorptions of the protons of main chain repeated units from 0.8 to 2.4 ppm (b), the polymer shows the characteristic signals of the phenyl protons at 7-7.5 ppm (c) and the protons of semi-quinoid ring at 5.4-6.1 ppm (d). On the assumption that one molecule contains one semi-quinoid unit in the polymer chain, the number-average degree of polymerization is calculated from the peak intensity ratio of the protons of phenyl proton and methyl protons of the *tert*-butyl: $15I_a/9I_c$, where I_a and I_c are the integral values of methyl protons of the *tert*-butyl and the protons of phenyl respectively. Taking the semi-quinoid unit into consideration, the number-average molecular weight $M_{n},_{NMR}$ will be:

$$M_{n},_{NMR} = 128\times 15I_a/9I_c + 360 = 2640$$

Compared with 3860 ($M_{n,\ GPC}$) from GPC calibrated against standard polystyrene samples, $M_{n,\ NMR}$ was much smaller. The reason for such a great deviation may be that the $M_{n,GPC}$ value was based on the calibration of PS standards.

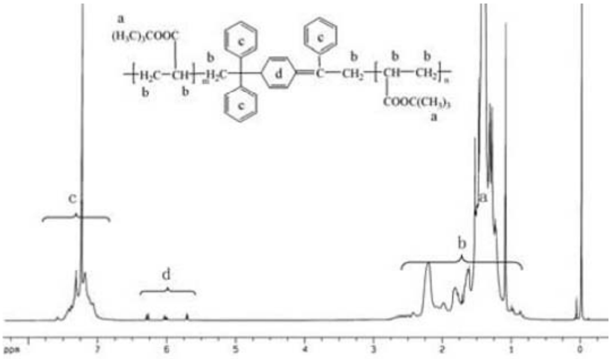
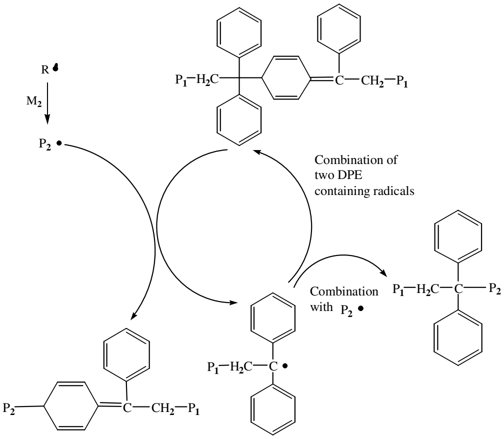


Fig. 3. ^{1}H NMR spectrum of P*t*BA precursor ($M_{n,\ GPC}$ = 3860, M_w/M_n = 1.52). Solvent: $CDCl_3$. For detailed preparation conditions, see the text.

Free Radical Polymerization of St and MMA in the Presence of PtBA Obtained above as Macro-initiator

According to the mechanism proposed in Ref. [35, 36], the formation process of the block copolymers can be shown in Scheme 2.



Scheme 2. Mechanism of block copolymer formation via DPE method.

Different from the conventional CRP-techniques, the DPE method is a two-step procedure. In the first step a precursor polymer is prepared by conventional free radical polymerization in the presence of DPE (the semi-quinoid structure is introduced into the resulting precursor polymer). This precursor polymer is then used as active specie in the second step. The second step polymerization reaction is started with the attack of a growing radical (P_2 in Scheme 2) to the band between two DPE unit of the semiquinoid structure in the precursor polymer. The attack of growing radicals can lead to the decomposition of the semiquinoid structure, and thus block copolymer and DPE containing macro-radical will be generated. These macro-radicals are inactive and can not initiate chain growth of the second monomer. But the recovery of the precursor is achieved through the combination of two DPE containing macro-radicals and the controllability is reserved. DPE ended macro-radicals can also react with growing radicals via bimolecular termination to form block copolymers. The concentration of the precursor polymer, growing radical, and monomer (M_2) are all of crucial importance for the block copolymer yield. In our experiment, although no initiator was added in the second polymerization step, the polymerization was started with thermal initiation.

In this study, two P*t*BAs (A and B) with different molecular weights were used in the free radical polymerization of monomer St and MMA. Their number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were 8360 and 1.63 (A), and 27150 and 2.52 (B), respectively.

GPC traces of the crude products obtained at different monomer conversions are shown in Fig. 4.

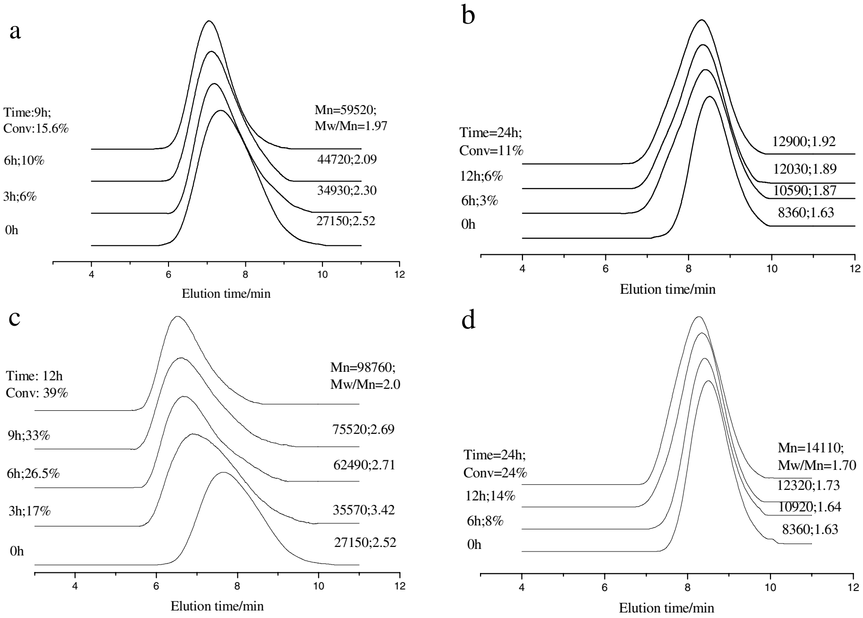


Fig. 4. GPC curves of P*t*BA precursor and block copolymers obtained at different monomer conversions in 6 mL of toluene at 80°C. Reaction conditions: (a) 1.25 g of St, 0.25 g of precursor B; (b) 1.25 g of St, 0.25 g of precursor A; (c) 1.25 g of MMA, 0.25 g of precursor B; (d) 1.25 g of MMA, 0.25 g of precursor A.

The GPC traces showed that the molecular weights shifted to higher molecular weight direction. The unimodal shape of the GPC traces throughout the polymerization process and no visible residence of the P*t*BA precursor especially at higher monomer conversions suggested good reinitiating efficiency of the P*t*BA precursor and successful formation of PS-*b*-P*t*BA and PMMA-*b*-P*t*BA block copolymers. It should be also pointed that no PS or PMMA homopolymer were detected by GPC. This may be because the polymerization was stopped at not very high monomer conversions.

Fig. 5 shows the ^{1}H NMR spectra of the resulting block copolymer of free radical polymerization of St and MMA in the presence of P*t*BA precursor. It can be seen from Fig. 5(A) that in addition to the large absorptions of the repeated units of *t*BA at 1.42 ppm (c) and large absorptions of the protons of main chain repeated units from 1.2 to 2.0 ppm (b, d, e), the polymer showed the characteristic signals of the phenyl proton of St repeated units at 6.3-7.3 ppm (a). At the same time, the protons of semi-quinoid ring at 5.4-6.1 ppm disappeared, indicating that all semi-quinoid structure in the precursor polymer chain was consumed. Furthermore, the ratio of I_a/I_c was about 5/11, where I_a and I_c are the integral values of the characteristic phenyl protons and the *tert*-butyl protons of the block copolymer respectively. We can calculate that the molar ratio of St segment to *t*BA segment ($9I_a/5I_c$) was about 0.8, which was in good agreement with that calculated from the monomer conversion. In Fig. 5(B), the ratio of I_b/I_c was about 19/30, where I_b and I_c are the integral values of the methoxyl protons and the *tert*-butyl protons of the block copolymer respectively. Therefore, the molar ratio of MMA segment to *t*BA segment ($3I_a/I_c$) was about 1.9, which was also in good agreement with that calculated from the monomer conversion.

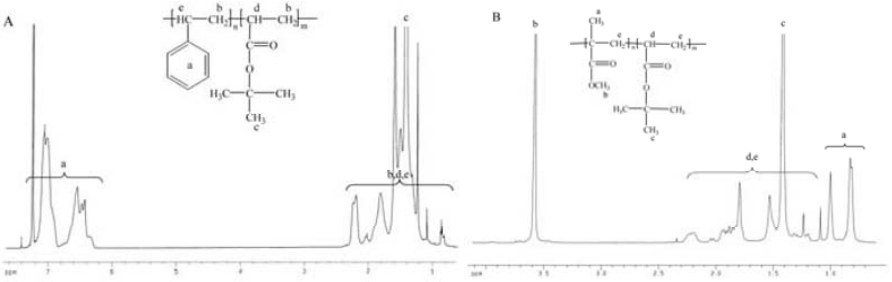


Fig. 5. ^{1}H NMR spectra of PS-*b*-P*t*BA and PMMA-*b*-P*t*BA. (A) PS-*b*-P*t*BA ($M_{n,GPC}$ = 59520, M_w/M_n = 1.97, P*t*BA precursor: $M_{n,GPC}$ = 27150, M_w/M_n = 2.52). (B) PMMA-*b*-P*t*BA ($M_{n,GPC}$ = 98760, M_w/M_n = 2.0, P*t*BA precursor: $M_{n,GPC}$ = 27150, M_w/M_n = 2.52). Solvent: $CDCl_3$.

Hydrolysis of PS-b-PtBA and PMMA-b-PtBA Diblock Copolymers

Cleavage of the *tert*-butyl ester groups was achieved by the PS-*b*-P*t*BA and PMMA-*b*-P*t*BA diblock copolymers being treated in dichloromethane with trifluoroacetic acid at room temperature under stirring for 48 h. Fig. 6 shows the ^{1}H NMR spectra of hydrolyzed products. The signal at 1.42 ppm, attributed to the *tert*-butyl protons of the P*t*BA block, disappeared almost completely, indicating that the PS-*b*-P*t*BA and PMMA-*b*-P*t*BA diblock copolymers had successfully transformed into PS-*b*-PAA and PMMA-*b*-PAA amphiphilic diblock copolymers respectively.

Self-assembly of PS-b-PAA and PMMA-b-PAA in THF

The formation of micelles via aggregating and the structure of these molecular assemblies depend on different parameters, including the nature and molecular weights of the block, solvent interaction, and the architecture of the block copolymer. For PS-*b*-PAA and PMMA-*b*-PAA amphiphilic diblock copolymers, the PS and PMMA segment can be dissolved in THF, but THF was nonsolvent for PAA segment. Therefore, PS-*b*-PAA and PMMA-*b*-PAA block copolymers can form latexes like suspension (not precipitated) in THF if PS or PMMA segment was long enough. Furthermore, PMMA or PS segment should form the shell of the latex and the PAA segment should be sheltered in the core.

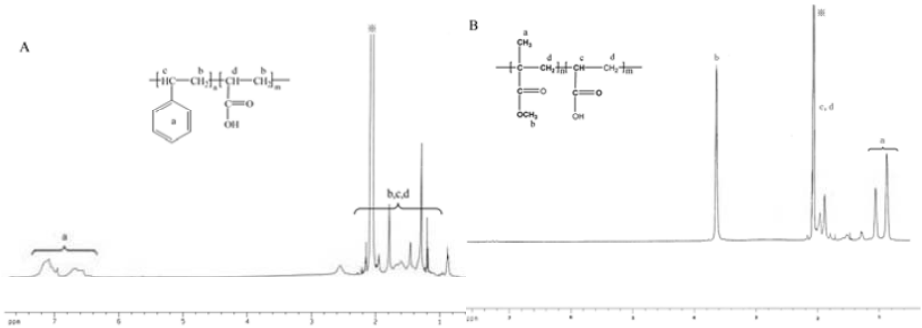


Fig. 6. ^{1}H NMR spectra of PS-*b*-PAA and PMMA-*b*-PAA. (A) PS-*b*-PAA (PS-*b*-P*t*BA: $M_{n,GPC}$ = 59520, M_w/M_n = 1.97); (B) PMMA-*b*-PAA (PMMA-*b*-P*t*BA: $M_{n,GPC}$ = 98760, M_w/M_n = 2.0). Solvent: CD_3COCD_3. ※ Attributed to CH_3COCH_3 in CD_3COCD_3.

TEM and DLS were used to characterize the sizes and size distributions of the aggregates of the hydrolyzed product in THF. Fig. 7(a) shows the typical morphology of PS-*b*-PAA aggregates in THF at a concentration of 1 mg/mL. PS-*b*-PAA aggregates showed spherical shape, and their diameter was about 80-170 nm. Fig. 7(b) shows the typical morphology of PMMA-*b*-PAA aggregates in THF at the same concentration, PMMA-*b*-PAA aggregates also showed spherical shape, and their diameter was about 70-150 nm. The results of DLS were given in Fig. 8. The results obtained with DLS and TEM also demonstrated the block structure of the hydrolyzed products.

Additionally, we also replaced THF with aqueous NaOH solution, and the similar results were observed.

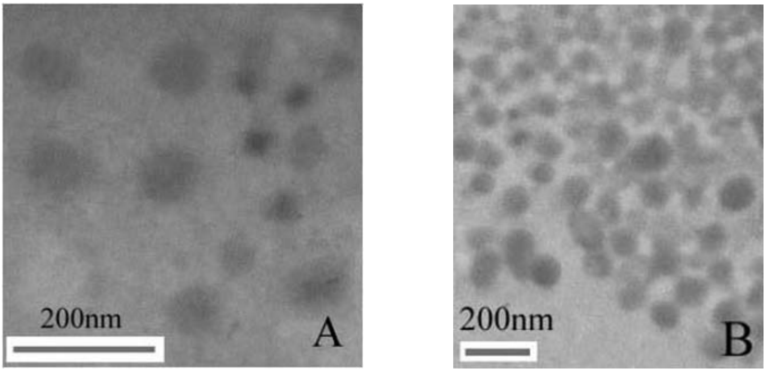


Fig. 7. TEM pictures for the particles formed by PS-*b*-PAA and PMMA-*b*-PAA in THF. (a) PS-*b*-PAA; (b) PMMA-*b*-PAA.

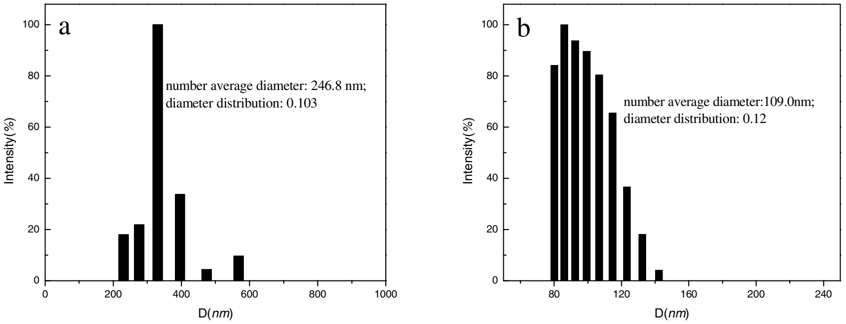


Fig. 8. Diameter distribution of the particles formed by PS-*b*-PAA and PMMA-*b*-PAA in THF (a) PS-*b*-PAA; (b) PMMA-*b*-PAA.

Conclusion

The DPE technique is a universal method for the synthesis of designed block copolymers. This paper reported the successful synthesis of PAA containing block copolymers: *t*BA was first polymerized with AIBN as initiator in the presence of DPE, yielding DPE containing P*t*BA precursor with controlled molecular weight, which could be used as an initiator for the further copolymerization. St and MMA were then polymerized respectively in the presence of the PtBA precursor to prepare PS-*b*-P*t*BA and PMMA-*b*-P*t*BA diblock copolymers. With the increase of monomer conversion, the molecular weight distribution curves of PS-*b*-P*t*BA and PMMA-*b*-P*t*BA diblock copolymers shifted to higher molecular weight direction without visible trace of P*t*BA homopolymer being detected by GPC. Amphiphilic block copolymers PMMA-*b*-PAA and PS-*b*-PAA were obtained by hydrolysis of PS-*b*-P*t*BA and PMMA-*b*-P*t*BA with trifluoroacetic acid. The resulting block copolymers can self assemble into spherical shape latexes in THF.

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