Synthesis of Amphiphilic Polystyrene-*b*-Poly(acrylic acid) Diblock Copolymers by Iodide-Mediated Radical Polymerization

Bingyi LI, Yan SHI, Wanchao ZHU, Zhifeng FU,[†] and Wantai YANG

*Key Laboratory of Science and Technology of Controllable Chemical Reactions Ministry of Education,
Beijing University of Chemical Technology, Beijing 100029, China*

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ABSTRACT: Amphiphilic polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) diblock copolymers were prepared by iodide-mediated radical polymerization. Firstly, free radical polymerization of styrene was carried out with AIBN as initiator and iodoform as chain-transfer agent, giving iodine atom-ended polystyrene with controlled molecular weights. Secondly, *tert*-butyl acrylate (*t*BA) was polymerized using above obtained polystyrenes as macro-chain-transfer agents and PS-*b*-*Pr*BA diblock copolymers with controlled molecular weights were obtained. Finally, amphiphilic PS-*b*-PAA diblock copolymers were prepared by hydrolysis of PS-*b*-*Pr*BA under the acid condition. The formation of PS-*b*-*Pr*BA and PS-*b*-PAA diblock copolymers was confirmed by the use of gel permeation chromatography and ¹H NMR spectroscopy. [DOI 10.1295/polymj.38.387]

KEY WORDS Living Radical Polymerization / Iodide-Mediated Radical Polymerization / Amphiphilic Block Copolymers / Styrene / *tert*-Butyl Acrylate /

Amphiphilic block copolymers have been extensively investigated both theoretically and practically in past few decades. Among them, block copolymers containing poly(methacrylic acid) (PMAA) and poly(acrylic acid) (PAA) segments have attracted increasing research interest because PMAA and PAA are weak polyelectrolytes and their dissociation degree can be governed by the pH and ionic strength of aqueous solution.¹

Traditionally, well-defined block copolymers containing PMAA or PAA segments have been synthesized by sequential living anionic polymerization or group transfer polymerization of protected monomers, such as *tert*-butyl methacrylate (*t*BMA) and *tert*-butyl acrylate (*t*BA), with subsequent elimination of protecting groups.^{2–9} For example, Teyssie *et al.*² 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, followed by hydrolysis using *p*-toluene sulfonic acid as catalyst. However, the anionic polymerization or group transfer polymerization need to be carried out under rigorous conditions such as in high-vacuum, highly purified monomers and solvents, making large-scale production by these processes impractical. Recent progress in controlled radical polymerization, especially nitroxide-mediated radical polymerization (NMRP),¹⁰ atom transfer radical polymerization (ATRP),^{11,12} and reversible addition-fragmentation chain transfer polymerization (RAFT),¹³ opens a new channel to prepare well-defined block copolymers at much mild reaction conditions. Block copolymers containing PMAA or PAA

segments have been successfully synthesized using ATRP,^{14–22} RAFT,^{23,24} and NMRP^{25,26} techniques. The so-called iniferter-based living radical polymerization was also employed for the synthesis of block copolymers containing PMAA segment.²⁷

Iodide-mediated living radical polymerization was discovered by Tatemoto *et al.* in 1984.²⁸ Degenerative transfer mechanism for this polymerization was first proposed by Matyjaszewski *et al.*^{29–31} in 1995, and later this polymerization was investigated in detail by Fukuda *et al.*³² In this system, a conventional radical initiator is needed together with the specific transfer agent, and a great advantage of the reversible transfer technique is that the experimental conditions can be very close to conventional ones, in terms of temperature, concentrations and processes. The synthesis of block copolymers using iodide-mediated radical polymerization in bulk and mini-emulsion systems has been described.^{29,33–35} Nevertheless, to the best of our knowledge, the preparation of PS-*b*-PAA amphiphilic block copolymer using this technique has not been reported. Because the reaction conditions for iodide-mediated radical polymerization are very close to conventional ones and there is no use of catalyst as in ATRP which is need to be removed or expensive agent as in NMRP and RAFT, we herein reported the synthesis of polystyrene-*b*-poly(*tert*-butyl acrylate) (PS-*b*-*Pr*BA) diblock copolymer *via* iodide-mediated radical polymerization, in which styrene was used as the first monomer to prepare the macro-transfer agent with iodine atom terminal group and *t*BA as the second monomer. The amphiphilic diblock

[†]To whom correspondence should be addressed (E-mail: fuzf@mail.buct.edu.cn).

copolymer, PS-*b*-PAA, was then obtained through hydrolysis of (PS-*b*-PtBA) under acid condition.

EXPERIMENTAL

Materials

Styrene (Polymerization grade, Yanshan Petrochemical Co.) and *t*BA (Analytical grade, Shanghai Chemicals plant) were dried over anhydrous MgSO₄, then distilled under reduced pressure and stored in brown glass bottles at -15 °C. α, α' -Azobisisobutyronitrile (AIBN, 98%, Fluka) was recrystallized from ethanol. Iodoform (Analytical grade, Beijing Chemicals plant) and all other reagents were used without further purification.

Synthesis of Macro-transfer Agent (PS-I)

In a typical experiment, 0.1642 g (1.0 mmol) of AIBN, 1.9743 g of iodoform (5.0 mmol) and 25.01 g of styrene (240.0 mmol) and 27.5 mL of benzene were added to a 100 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 65 °C. At definite time intervals, portions of the sample were withdrawn from the flask using argon-filled gas-tight syringes 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 polystyrene was obtained by filtration.

Synthesis of Diblock Copolymer (PS-*b*-PtBA)

In a typical experiment, 0.0328 g of AIBN (0.20 mmol), 2.11 g of PS-I (1.0 mmol, $M_{n, GPC} = 2100$, $M_w/M_n = 1.42$), 5.00 g of *t*BA (39 mmol) and 15.0 mL of benzene were added to a 100 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 65 °C. At definite time intervals, portions of the sample were withdrawn from the flask using 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

One gram of PS-*b*-PtBA block copolymer was dissolved in 80 mL dioxane, and then 10 mL of HCl (5 M) was added slowly under stirring to prevent the precipitation of the block copolymer. After being heated under reflux condition 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 of macro-chain-transfer agent and block copolymers were measured using gel permeation chromatography (GPC), on a system equipped with a Waters 515 pump, three columns (Styragel HR1, Styragel HR3 and Styragel HT4) and a 2410 differential refractometer detector. The eluent was THF and the flow rate was 1 mL/min. Narrow polystyrene standards were used to generate the calibration curve. ¹H NMR spectra were obtained using a Bruker AV600-MHz NMR spectrometer. CDCl₃ or CD₃COCD₃ was used as solvent. The FT-IR spectra were recorded at room temperature on a Nicolet Nexus-670 spectrometer using KBr tablets.

RESULTS AND DISCUSSION

The amphiphilic diblock copolymer PS-*b*-PAA was synthesized in three steps (Scheme 1). Firstly, free radical polymerization of styrene was carried out with AIBN as initiator and iodoform as chain-transfer agent to prepare iodine atom-ended polystyrene, PS-I. Secondly, free radical polymerization of *t*BA was carried out using the above obtained iodine atom-ended polystyrene obtained above as macro-chain-transfer agent to prepare PS-*b*-PtBA block copolymer. Finally, amphiphilic diblock copolymer PS-*b*-PAA was obtained by hydrolysis of PS-*b*-PtBA under the acid condition.

Free Radical Polymerization of Styrene with Iodoform as Chain-Transfer Agent

Styrene was polymerized in benzene at 65 °C with the molar ratio of iodoform to AIBN to be 5:1. By

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

Figure 1. First-order plots for the polymerization of styrene in benzene at 65 °C. Reaction conditions: [St] = 4.61 M. (a) [St]:[CHI₃]:[AIBN] = 240:5:1. (b) [St]:[CHI₃]:[AIBN] = 480:5:1. (c) [St]:[CHI₃]:[AIBN] = 960:5:1.

varying the molar ratio of styrene to iodoform, three experiments were carried out. As shown in Figure 1, the logarithmic conversion data, $\ln([M]_0/[M])$ ([M] is the monomer concentration at time t), plotted against time t , gave straight lines passing through the origin, which shows constant concentrations of the growing species during the polymerizations. Furthermore, the reason why polymerization rate decreased with the increase of the molar ratio of styrene to iodoform was that the concentration of AIBN decreased at the same time.

Figure 2 shows the number-average molecular weights (M_n), the polydispersity indexes (M_w/M_n) and molecular weight distribution curves of the polystyrenes obtained at different CHI₃ concentrations. The molecular weight distribution curves were unimodal throughout the polymerizations, although the polydispersity indexes were broader than those for other controlled free radical polymerization methods, such as ATRP and RAFT. The polydispersity indexes of the polystyrenes obtained at higher CHI₃ concentrations were relatively low.

The number-average molecular weights increased in direct proportional to monomer conversion, and agreed well with the theoretical ones, $M_{n,th}$, which were calculated from the amount of the consumed monomer ($\Delta[St]$), the amount of iodoform added ([CHI₃]) and the molecular weight of styrene (104) using the following equation.

$$M_{n,th} = \Delta[St]/[CHI_3] \times 104 \quad (1)$$

The terminal structures of the obtained polystyrenes were then analyzed by ¹H NMR spectroscopy.

Figure 3 shows the spectrum of one polystyrene prepared in benzene at 65 °C ([St] = 4.61 M; [St]:[CHI₃]:[AIBN] = 240:5:1; polymerization time, 15 h; conversion, 45.0%; $M_{n,GPC}$ = 2100, M_w/M_n = 1.42). Besides the large absorptions of the repeating units of styrene, there are characteristic signals originating from CHI₃. The methine proton (a) at the α -end of polymer chain, which was derived from CHI₃, was seen at 4.30 ppm. The peaks at 4.51 to 4.65 ppm were ascribed to the methine proton (b) at the ω -end adjacent to the iodine atom.³⁶ Furthermore, the ratio of I_a/I_b was 1:1.18, which was close to 1:1, where I_a and I_b are the integral values of methine proton at the α -end derived from CHI₃ and that at the ω -end adjacent to the iodine atom, respectively, indicating that the obtained polystyrene indeed had CHI₃ moiety at one end and an iodine atom at the other end.

The molecular weight of this polystyrene sample was determined from the peak intensity ratio of the methine proton adjacent to the iodine atom at ω -end to the aromatic protons of main chain ($I_c/5I_b$). Taking into the end groups from CHI₃, the number-average molecular weight was 2200, which was in excellent agreement with the value ($M_{n,GPC}$ = 2100) from GPC calibrated against standard polystyrene samples. This result further confirmed that there was an iodine atom at the ω -end for every polystyrene chain.

Free Radical Polymerization of *tert*-Butyl Acrylate with Polystyrene Obtained Above as Macro-Chain-Transfer Agent

Compared with 1-phenylethyl iodide, the iodine atom at the ω -end of polystyrene obtained above

Figure 2. M_n , M_w/M_n and molecular weight distribution curves of polystyrenes obtained with different concentrations of CHI_3 in benzene at 65°C . For reaction conditions, see Figure 1.

had the same chemical environment. Therefore, it can be used as macro-chain-transfer agent to control free radical polymerization, which have been reported by Matyjaszewski *et al.*³¹ and Farcet *et al.*³³ In this study, two polystyrenes with different molecular weights were used in the free radical polymerization of *t*BA. Their number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were 2100 and 1.42, and 6600 and 1.42, respectively. The narrow molecular weight distributions were attributed to the precipitation treatment of crude products in methanol.

Figure 4 shows the kinetic plot of $\ln([M]_0/[M])$ vs. time for *t*BA polymerization with AIBN as initiator and polystyrenes obtained above as macro-chain-transfer agents. The straight lines indicate that the polymerization proceeded with an approximately constant concentration of active species, therefore the contribution of termination reactions could be neglected.

GPC traces of the products obtained at different monomer conversions are shown in Figure 5. It can be seen that GPC curves were unimodal throughout the polymerizations and the molecular weight shifted

Figure 3. ^1H NMR spectrum of polystyrene ($M_{n,\text{GPC}} = 2100$) prepared in benzene at 65°C . Solvent: CDCl_3 . For detailed preparation condition, see the text.

Figure 4. First-order plots for the polymerization of *t*BA in benzene at 65°C . Reaction conditions: $[t\text{BA}] = 1.7\text{ M}$. (a) $M_{n,\text{GPC}}$ and M_w/M_n of PS-I were 2100 and 1.42, respectively. $[t\text{BA}]:[\text{PS-I}]:[\text{AIBN}] = 195:5:1$. (b) $M_{n,\text{GPC}}$ and M_w/M_n of PS-I were 6600 and 1.42, respectively. $[t\text{BA}]:[\text{PS-I}]:[\text{AIBN}] = 390:5:1$.

to higher molecular weights without any trace of the polystyrene macro-chain-transfer agents, indicating successful formation of PS-*b*-PtBA block copolymers. Furthermore, the number-average molecular weights of PS-*b*-PtBA block copolymers increased in direct proportional to monomer conversion, although their polydispersities were somewhat broader than those of polystyrene macro-chain-transfer agents. In addi-

tion, no PtBA homopolymer was detected by GPC. This may be because the chain-transfer constant of PS-I was large enough and only a little amount of PtBA homopolymer was produced.

Figure 6 shows the ^1H NMR spectrum of the product of *t*BA free radical polymerization with AIBN as initiator and PS-I as macro-chain-transfer agent. It can be seen that the signal at 4.51–4.65 ppm correspond-

Figure 5. M_n , M_w/M_n and molecular weight distribution curves of PS-*b*-PtBA block copolymers obtained at different monomer conversions in benzene at 65 °C. For reaction conditions, see Figure 4.

Figure 6. ^1H NMR spectrum of PS-*b*-PtBA diblock copolymer. Solvent: CDCl_3 .

ing to the methine proton of polystyrene adjacent to the iodine atom disappeared completely, while a new signal at 4.21 ppm appeared, which was attrib-

ed to the methine proton of PtBA segment adjacent to the iodine atom. This shows that all PS-I took part in the chain-transfer reaction. In addition, the signal at

Figure 7. The FT-IR spectra of diblock copolymer PS-*b*-PtBA and PS-*b*-PAA.

Figure 8. ^1H NMR spectrum of amphiphilic diblock copolymer PS-*b*-PAA. Solvent: CD_3COCD_3 . *Due to water in the deuterated CD_3COCD_3 . For detailed preparation condition, see the text.

4.30 ppm corresponding to the methine proton at the α -end of polymer chain, which was derived from CHI_3 , still existed. Furthermore, the ratio of I_a/I_e was about 1.0, where I_a and I_e are the integral values of methine proton at the α -end derived from CHI_3 and that at the ω -end of PtBA adjacent to the iodine atom, respectively, indicating that well-defined PS-*b*-PtBA diblock copolymer was successfully synthesized.

Hydrolysis of PS-*b*-PtBA Diblock Copolymer

Cleavage of the *tert*-butyl ester groups was achieved by the PS-*b*-PtBA diblock copolymers being treat-

ed in dioxane with HCl at reflux temperature. IR spectra of PS-*b*-PtBA diblock copolymer and its hydrolyzed product PS-*b*-PAA are shown in Figure 7. It can be seen that the absorption at 1728 cm^{-1} disappeared completely and a new absorption at 1707 cm^{-1} due to the carboxyl group of PAA block appeared. Figure 8 shows the ^1H NMR spectrum of hydrolysis product. The signal at 1.42 ppm, resulting from the *tert*-butyl protons of the PtBA block, disappeared almost completely, indicating that the PS-*b*-PtBA diblock copolymer had successfully transformed into PS-*b*-PAA amphiphilic diblock copolymer.

CONCLUSIONS

Free radical polymerization of styrene was carried out with AIBN as initiator and iodoform as chain-transfer agent, giving iodine atom-ended polystyrene with controlled molecular weights. *tert*-Butyl acrylate was then polymerized using polystyrenes obtained above as macro-chain-transfer agents and PS-*b*-PtBA diblock copolymers with controlled molecular weights were obtained. The number-average molecular weights of PS-*b*-PtBA diblock copolymers increased in direct proportional to monomer conversion, and the molecular weights shifted to higher molecular weight direction without any trace of the polystyrene macro-chain-transfer agents. In addition, no PtBA homopolymer was detected by GPC. The PS-*b*-PAA amphiphilic diblock copolymers were successfully obtained by hydrolysis of PS-*b*-PtBA under acid condition.

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