ABC Triblock Copolymers

Synthesis of Poly(*tert*-butyl acrylate)-*block*-Polystyrene-*block*-Poly(4-vinylpyridine) by Living Anionic Polymerization**

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Amphiphilic block copolymers, such as polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) and polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP), can self-assemble to form various aggregates, which include vesicles, in aqueous solutions.[1] It was demonstrated recently that vesicles were formed from a mixture of PS-*b*-PAA (with a relatively short PAA block) and PS-*b*-P4VP (with a longer P4VP block) in which the PAA was on the inner interface of the vesicle while P4VP was on the outer interface.[2] Recently, our interests have focused on the study of triblock copolymers with the composition PAA-*b*-PS-*b*-P4VP, which contain the hydrophobic PS block between two hydrophilic blocks, and might yield the same types of aggregates as those formed with amphiphilic block copolymers. The precursor for PAA-*b*-PS-*b*-P4VP is PtBA-*b*-PS-*b*-P4VP (PtBA = poly(*tert*-butyl acrylate)). Many methods, such as living anionic polymerization,[3] group-transfer polymerization (GTP),[4] and atom-transfer radical polymerization (ATRP)[5] have been employed in the preparation of ABC triblock copolymers. However, the synthesis of the PtBA-*b*-PS-*b*-P4VP triblock is very difficult because of the significantly different reactivities of the monomers in that neither PtBA nor P4VP ions can initiate styrene polymerization, especially in anionic polymerization reactions, and because the PS is located between the PtBA and P4VP blocks. *tert*-Butylacrylate and 4-vinylpyridine are much more reactive than styrene; therefore, styrene has to be polymerized first, followed by the polymerization of either *tert*-butyl acrylate or 4-vinylpyridine.[6] This method was employed by Giebeler and Stadler[3d] to prepare a PS-*b*-PVP-*b*-PtBMA triblock in which styrene was polymerized first; however, the sequence in this triblock is different from that needed in our polymer. Techniques, such as GTP[4] and living cationic polymerization,[7] allow only the polymerization of monomers with similar chemistry, and consequently similar reactivities, and therefore are not suitable for the preparation this particular triblock copolymer. ATRP was used by Davis and Matyjaszewski[5a] in the preparation of ABC triblock copolymers, which includes an example of a similar polymer, PtBA-*b*-PMMA-*b*-P4VP (PMMA = polymethyl methacrylate), in which there is a hydrophobic PMMA sequence between hydrophilic blocks. This polymer was prepared with a 16% conversion of 4VP and a polydispersity of 1.43. Herein, we report a new method for preparing PtBA-*b*-PS-*b*-P4VP triblock copolymers starting with a PtBA macromonomer that contains a styrene end group. The macromonomer is used in the initiation of the anionic polymerization of styrene (st), followed by 4VP polymerization by sequential monomer addition (Figure 1). Polymers prepared by this method have a well-defined structure, low polydispersity, and quantitative conversion.

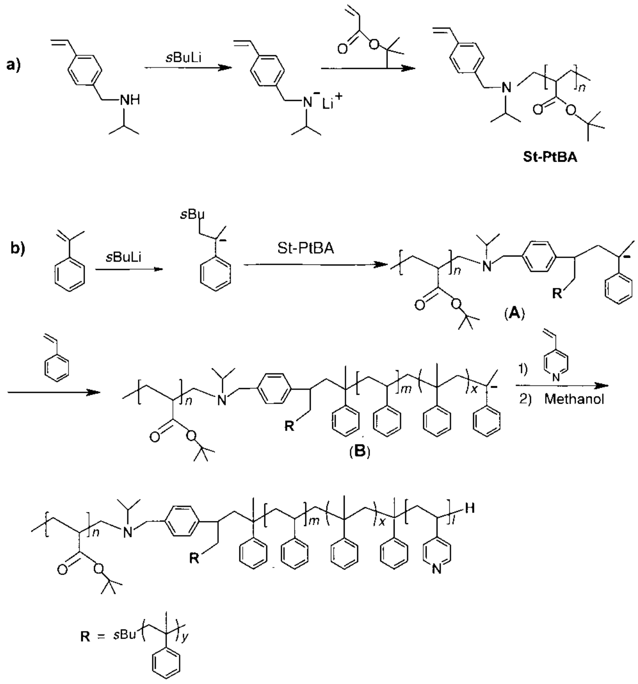

Figure 1. a) Reaction scheme for the synthesis of macromonomer poly(*tert*-butyl acrylate) with a styrene end group. b) Schematic representation for the synthesis of triblock poly(*tert*-butyl acrylate)-*b*-polystyrene-*b*-poly(4-vinylpyridine).

The PtBA macromonomer with a styrene functional end group (St-PtBA) was prepared by the living anionic polymerization of tBA and was initiated with a nitro ion (Figure 1a), by using a published procedure.[8] Three different samples ($\bar{M}_n = 3380$, $\bar{M}_w/\bar{M}_n = 1.07$; $\bar{M}_n = 2320$, $\bar{M}_w/\bar{M}_n = 1.13$; and $\bar{M}_n = 2270$, $\bar{M}_w/\bar{M}_n = 1.16$; $\bar{M}_n$ = number-average molar mass, $\bar{M}_w$ = weight-average molar mass) were prepared. An analysis

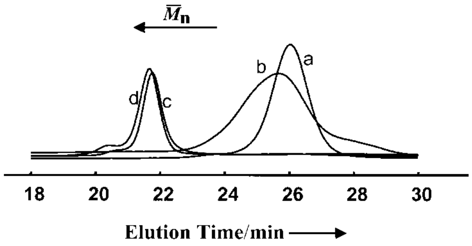

Figure 2. GPC traces: a) PtBA macromonomer; b) the reaction product of macromonomer with α-methylstyryllithium; c) PtBA-*b*-PS diblock copolymer; and d) PtBA-*b*-PS-P4VP triblock copolymer.

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of the product by gel-permeation chromatography (GPC; Figure 2 trace a) shows a narrow molecular-weight distribution for the first sample ($\bar{M}_n = 3280$, equivalent to 26 repeat units with $\bar{M}_W/\bar{M}_n = 1.07$), the other two samples, not shown, are similar. Resonance signals arising from protons of the vinyl functional group in this macromonomer are seen in the range between 5.0 and 7.0 ppm of the ^{1}H NMR spectrum, while resonance signals from *tert*-butyl protons ($\text{-C(C}H_3)_3$) appear at 1.44 ppm (Figure 3 A). The number of repeat units of tBA in this sample was calculated to be 25, based on integrated values for protons in the vinyl group and the *tert*-butyl group and this number is in good agreement with the result obtained by GPC. This sample was used for the next step of the polymerization. For the macromonomer/styrene polymerization, an attempt was made to initiate the vinyl group on the macromonomer with *s*BuLi. Unfortunately, the anions generated by this reaction "died" quickly, their deactivation being attributed mostly to side reactions of the butyl ion with the acrylate ester of PtBA. α-Methylstyryllithium ($\alpha\text{-MS}^-\text{Li}^+$), the reaction product of *s*BuLi with a few units of α-methylstyrene, is less reactive than the styryl ion, and has been employed to prepare diblock copolymers such as PS-*b*-PtBA[9] and PS-*b*-P4VP;[1d] thus, $\alpha\text{-MS}^-\text{Li}^+$ was used to react with the vinyl group of the macromonomer. The GPC trace of the resulting product (Figure 2, trace b) shows a broader peak compared with that of the macromonomer. A lower-molecular-weight peak, corresponding to an elution time of 28 min, is evident. The peak arises, most likely, from short α-methylstyrene chains that were formed by the reaction of the *s*BuLi with α-methylstyrene and terminated by impurities from the macromomoner solution prior to the initiation of the styrene terminated macromonomer. The primary peak in trace b is broader than that in trace a and reflects the higher-molecular-weight component. The increased molecular weight for **A** (Figure 1 b) arises from the reaction of the activated macromonomer with some additional α-methyl styrene.

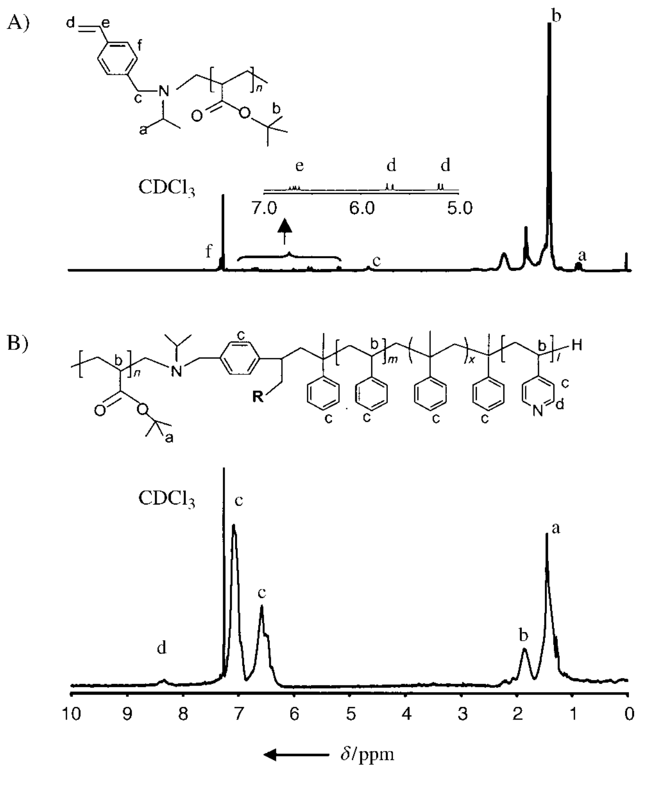

Figure 3. ^{1}H NMR spectra for a) PtBA macromonomer in CDCl$_3$; b) triblock PtBA$_{26}$-PS$_{450}$-P4VP$_{23}$ in CDCl$_3$.

A fast polymerization occurred upon the addition of styrene to the reaction mixture, as seen from the increased viscosity and successive color changes (red to yellow to red). The results of GPC analysis showed a sharp peak (Figure 2 trace c) and a complete peak shift from trace b, which indicates the effective initiation and polymerization of styrene. The length of the second block (PS) can be controlled by a further addition of styrene. The third block (P4VP) can be formed by the addition of 4-vinylpyridine to the reaction diblock copolymer (**B** in Figure 1 b); a sharp single GPC peak was observed for this triblock (Figure 2 trace d). The small shoulders representing a high molar-mass component were observed in trace c and trace d (especially the latter) of Figure 2. These shoulders might arise from infrequent coupling of polymer anions during the withdrawal of the samples for GPC analysis.[6b] The increased molecular weight between the diblock and triblock (trace c versus trace d) is very small because only a short vinylpyridine segment was wanted. The length of the PVP segment was estimated from chemical compositions by ^{1}H NMR spectroscopy and the molecular weight of the precursor PtBA by GPC; see below.

Notably, the presence of α-methylstyrene is essential to the success of the polymerization. If the α-methylstyrene had been polymerized completely before the addition of the styrene, the styrene could still be polymerized. However, in this reaction, the yellow from the polystyryl anions was found to fade gradually, and no further polymerization of vinylpyridine was detected by GPC or by ^{1}H NMR analysis of the final product. This fact suggests the existence of interfering side reactions of the polystyryl anions in the presence of PtBA. To guarantee that α-methylstyrene monomer is present throughout the whole polymerization in sufficient amounts to provide a short-chain segment at the end of the styrene polymerization, the α-methylstyrene should be present in excess and the reaction of the macromomer with the $\alpha\text{-MS}^-\text{Li}^+$ should not be allowed to proceed for too long. A direct indication for the existence of free α-methylstyrene is obtained by observing the reaction mixture, as the poly(α-methylstyryl) anions are deep red, while the polystyryl anions are yellow. As long as the PS chain is capped by an α-methylstyrene molecule, the polymerization of 4VP can proceed.

The PtBA-*b*-PS-*b*-P4VP triblock copolymers were further characterized by ^{1}H NMR spectroscopy. The presence of the different components in the triblock copolymer is shown for a typical sample, PtBA$_{26}$-*b*-PS$_{450}$-*b*-P4VP$_{23}$, in Figure 3 B (^{1}H NMR (CDCl$_3$, 300 HMz): $\delta = 1.44$, ($\text{-C(C}H_3)_3$), 6.5, 7.0 (C_6H_5 and C_6H_4N), 8.5 (C_6H_4N)). The compositions were calculated from the integrated values of the proton peaks. For the molecular-weight calculation, the method used by Giebeler and Stadler[3d] was employed. The molecular weights were calculated from the molecular weight of the PtBA

Table 1: Molecular weights and molecular distributions of triblock copolymers and their corresponding precursors.

Sample[a]	StPtBA		[StPtBA][b]		PtBA-*b*-PS		PtBA-PS-P4VP	
	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[e]	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[e]
$PtBA_{26}$-*b*-PS_{450}-*b*-$P4VP_{23}$	3280	1.07	3890	1.18	50200	1.07	52600	1.11
$PtBA_{26}$-*b*-PS_{370}-*b*-$P4VP_{11}$	3280	1.07	4140	1.20	41900	1.14	43000	1.18
$PtBA_{26}$-*b*-PS_{890}-*b*-$P4VP_{25}$	3280	1.07	3900	1.16	96000	1.06	98600	1.09

[a] The numbers refer to the final compositions determined by methods shown below.[b] [StPtBA] refers to the reaction product of PtBA macromonomer with α-methylstyryllithium. The broadened molecular-weight distribution reflects the presence of some low molecular-weight poly-(α-methylstyrene). [c] Determined by GPC, calibrated against PtBA standards. For the StPtBA, the molecular weight of the styrene end group was subtracted. [d] Determined from the molecular weight of the PtBA precursor and the composition from ^{1}H NMR spectroscopy. The α-methylstyrene is counted as styrene because its chemical shifts are similar to those of styrene and its low triblock content. [e] Determined by GPC, calibrated against PS standards.

precursor along with the chemical compositions obtained from ^{1}H NMR spectra. The molecular characteristics are shown in Table 1; narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.07$–$1.20$ were obtained for the PtBA-*b*-PS-*b*-P4VP triblock copolymer and their PtBA and PtBA-*b*-PS precursors.

In conclusion, we have developed a method to prepare PtBA-*b*-PS-*b*-P4VP triblock copolymers. These are examples of ABC or asymmetric ABA triblock copolymers in which A does not initiate B, but B does initiate A and C. The advantage of this method is that the polymers have controlled block lengths and narrow polydispersity, and the conversion of monomers is quantitative. The novelty of this method is that polystyrene can be formed as the second block by a two-step anionic polymerization. This method can be used to prepare a range of ABC or ABA triblock copolymers.

Experimental Section

Reagents and solvents: LiCl and monomers, such as *tert*-butyl acrylate, styrene, α-methylstyrene, and 4-vinylpyridine were purified by standard procedures.[9] The initiator used in this study was the reaction product of *s*BuLi with a few units of α-methylstyrene, which gave a red solution, and was prepared in the glass reactor that was to be used for the polymerization.

Macromonomer (St-PtBA) preparation and purification: The poly(*tert*-butyl acrylate) macromonomer with the vinyl functional group was prepared according to literature procedures,[8] and purified as follows: Macromonomer (0.66 g, 0.19 mmol of vinyl groups) was dissolved in benzene, then freeze dried in the presence of P_2O_5 for 6 h. The macromonomer was further dried under vacuum at 60 °C for 3 h, then dissolved by introducing freshly distilled THF (10 mL) under nitrogen. It was then ready for polymerization.

Polymerization: THF (≈800 mL) and α-methylstyrene (2 mL) were added to a flask containing LiCl (0.2 g, 4.7 mmol). After the LiCl had completely dissolved, the solution was titrated with *s*BuLi until the solution turned light red, then a further portion of *s*BuLi was added (0.15 mL, 0.19 mmol). After 15 min, this solution was cooled to −78 °C, and the solution of macromonomer was quickly added through a stainless steel capillary. The deep-red solution changed rapidly to deep yellow and then changed to red, which indicated the completion of the reaction between the macromonomer and initiator. After 15 min, the calculated amount of pure styrene was introduced to the reaction mixture; again, the reaction mixture changed from red to deep yellow to red, which indicated the end of styrene polymerization. The polymerization was allowed to proceed for another 10 min, and then 10 mL of the reaction medium was extracted for GPC analysis to determine the degree of polymerization of the polystyrene block. Upon the addition of a few drops of 4VP to the reaction medium, the red from the poly(α-methylstyryllithium) anions changed instantaneously to yellow. The polymerization was allowed to proceed for another 1 h, before being terminated by the addition of degassed methanol (1 mL). As we reported previously,[1d] the precise degrees of polymerization of the P4VP blocks can not be determined by GPC because of some absorption of the P4VP block in the GPC column. The polydispersities determined by GPC for the triblocks containing P4VP should be broader than the real polydispersities, and thus should be considered as the upper limits. ^{1}H NMR spectroscopy was used to measure the degree of polymerization of the P4VP blocks by referring to the PtBA and PS blocks. The final triblock copolymers were recovered by precipitation into cold petroleum ether and dried under vacuum for 48 h.

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