

Synthesis of poly(styrene-*b*-isobutylene-*b*-styrene) triblock copolymer by ATRP

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Summary

A poly(styrene-*b*-isobutylene-*b*-styrene) triblock copolymer has been prepared by a two-step process. Polyisobutylene with $M_n = 6600$ and $M_w/M_n = 1.12$ functionalized with phenol at both ends was reacted with 2-bromopropionyl chloride to form a macroinitiator for atom transfer radical polymerization (ATRP). The synthesized difunctional PIB macroinitiator was subsequently heated with styrene xylene solution in the second step to 110°C under conditions for ATRP using the copper coordination complex CuBr/bipyridine. Both the macroinitiator and the triblock copolymer were characterized by ¹H NMR and SEC. The triblock copolymer with around 25% polystyrene was found to have a narrow molecular weight distribution of 1.20.

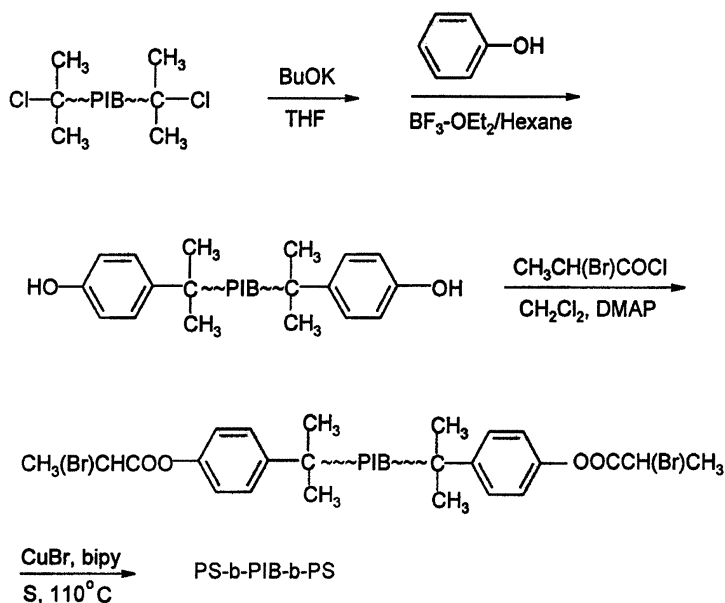
Introduction

After the living carbocationic polymerization of isobutylene had been demonstrated¹ efforts were directed towards synthesizing the triblock copolymer poly(styrene-*b*-isobutylene-*b*-styrene (PS-*b*-PIB-*b*-PS). Eventually the polymerization was developed to the point where well-defined triblock copolymers could be prepared by sequential monomer addition.² Such thermoplastic elastomers have mechanical properties which are comparable to those prepared by anionic living polymerization techniques.³ However, the polyisobutylene based materials have saturated elastomeric parts and therefore better oxidation stability. These systems have been further studied,^{4,6} and other triblock copolymers with PIB as the middle block also prepared from other cationically polymerizable monomers.^{7,8} By combination of the living cationic polymerization technique with other types of polymerizations other triblock copolymers may be synthesized. The transformation of cationic to anionic polymerization was accomplished by changing the end group quantitatively into polymerization active anions after the living carbocationic polymerization was completed.^{9,10} The transformation from cationic to polymerization by radical mechanism is of particular interest due to the large number of different monomers that will polymerize by this mechanism. In one approach for synthesizing block copolymers, PIB with a central azo group was prepared from an azo radical initiator which carried *tert*-ether groups for cationic initiation of polymerization of isobutylene.¹¹ Subsequent heating of the active PIB polymer in the presence of monomer yielded block copolymers by uncontrolled radical polymerization, however not a triblock with PIB as the middle segment. The recent development of controlled radical polymerization has opened for new ways of synthesizing block copolymers. Atom transfer radical polymerization, ATRP¹² was used in the synthesis of PS-*b*-PIB-*b*-PS by transformation of living carbocationic into living radical polymerization.¹³⁻¹⁵ In this case a few units of styrene were added to living difunctional polyisobutylene after the isobutylene

had reacted. The isolated polyisobutylenes could act as difunctional macroinitiators for ATRP since they had active chloro groups in α -positions in the styryl end groups. Several structures have been found to be active as initiators in ATRP¹². Very recently, PIB-g-PS with properties as thermoplastic elastomer was synthesized by initiating ATRP from *p*-bromomethylstyrene units in a copolymer with isobutylene¹⁶. We have demonstrated that amphiphilic PS-*b*-PEG-*b*-PS could be prepared from a difunctional poly(ethylene glycol) (PEG) macroinitiator prepared by quantitative esterification of the hydroxyl groups of PEG as 2-bromo- or 2-chloropropionic esters.¹⁷ Such ester compounds have been used in the preparation of other types of macroinitiators.¹⁸

In this paper the synthesis of a new PIB difunctional macroinitiator and the corresponding PS-*b*-PIB-*b*-PS triblock copolymer obtained therefrom by ATRP (Scheme 1) is presented. PIB functionalized with phenol at both ends was quantitatively reacted with 2-bromopropionyl chloride. The resulting difunctional PIB macroinitiator was subsequently heated with styrene in xylene solution in a second step to 110°C under conditions for ATRP, and in this way the PS-*b*-PIB-*b*-PS triblock copolymer was prepared. By this route other triblock copolymers with PIB may be synthesized by ATRP from end positioned activated ester groups. In comparison with the in-situ formation of the initiating groups by addition of styrene to living polyisobutylene¹³⁻¹⁵ the capping with short blocks of polystyrene may thus be avoided..

Scheme 1



Experimental

Materials

Styrene (Riedel-de Haen) was passed through a column filled with activated Al_2O_3 (Aldrich, neutral, Brockmann I, standard grade, ~ 150 mesh, 58\AA) remove the inhibitor, stored over CaH_2 and then vacuum distilled before polymerisation. All other chemicals were purified as described elsewhere^{17,19} or used as received. 4-phenol telechelic PIB (HOPh-PIB-PhOH) prepared as previously described¹⁹ by dehydrochlorination of PIB ($M_n=6600$, $M_w/M_n=1.12$) with *t*-BuOH in THF followed by phenolation using $\text{BF}_3\cdot\text{OEt}_2$ as catalyst.

Synthesis of 2-Bromopropionate telechelic PIB (Br-PIB-Br)

A 0.017 g (0.14 mmol) sample of 4-(dimethylamino)pyridine (DMAP) in 10 mL of dry methylene chloride was mixed with 0.13 mL (0.79 mmol) of triethylamine (TEA). The solution was transferred into a 250 mL three-neck round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer. After cooling to 0°C , 0.10 mL (0.93 mmol) freshly distilled 2-bromopropionyl chloride (techn. grade) in 10 mL CH_2Cl_2 was added, followed by slowly dripping of 3.00 g (0.45 mmol) of phenolated PIB in 50 mL of dry CH_2Cl_2 under dry nitrogen. After 1h the temperature was allowed to rise to room temperature. The reaction was continued under stirring overnight and the solvent was removed by rotavapor. The crude product was dissolved in hexane and the polymer solution was filtered off from the solid. The polymer was precipitated once from hexane/methanol, twice from CH_2Cl_2 /methanol and dried in vacuum.

Synthesis of PS-*b*-PIB-*b*-PS triblock copolymer

PS-*b*-PIB-*b*-PS triblock copolymer was synthesized by ATRP of styrene in xylene. Thus, a glass tube was charged with 0.350 g (0.052 mmol) Br-PIB-Br, 0.015 g (0.104 mmol) of CuBr and 0.049 g (0.312 mmol) of 2,2' - bipyridine (bipy). 1mL (8.721 mmol) of styrene and 5 mL of xylene were added, and the system was degassed three times and then heated at 110°C under nitrogen for 20 hours. The crude product was dissolved in THF, filtered, and precipitated in methanol. The polymer was further purified by precipitation from CH_2Cl_2 /methanol and dried in vacuum. The yield was determined gravimetrically and was 33.8 %.

Instrumental analysis

The molecular weights of polymer samples were determined by SEC analysis (Viscotek Model 200 equipped with Nucleosil columns: 50\AA , 100\AA , and 500\AA), using polystyrene and polyisobutylene standards for calibration, THF as eluent with flow rate of 1 ml/min at room temperature.

The structure of the macroinitiator and block copolymers was characterized by ^1H NMR, using a Bruker 250 MHz spectrometer and CD_2Cl_2 as solvent. Block copolymer composition was determined by either the yield of the copolymer or the ratio of the signal intensity of phenyl peak region (6.4-6.7ppm) so that of methyl peak region (0.9-1.2ppm).

Differential scanning calorimetry (DSC) was carried out using a Seiko Instruments DSC 220CU. The sample was cooled to -100°C and then heated at 5°C min^{-1} up to -10°C and further heated at $10^\circ\text{C min}^{-1}$ to a temperature of 170°C .

Results and discussion

The synthesis of the PS-*b*-PIB-*b*-PS triblock copolymer is outlined in Scheme 1. In the first step under the reaction conditions previously described¹⁹ PIB with $M_n=6600$ and $M_w/M_n=1.12$

had quantitatively been converted to the 4-phenol telechelic PIB. This functionalized PIB was then reacted with 2-bromopropionyl chloride in methylene chloride. The reaction conditions were similar to those used before for functionalization of poly(ethylene glycol)¹⁷ and carried out as given under Experimental. However, because of the higher reactivity of the phenolic end groups compared to the hydroxymethyl groups of the PEG only catalytic amount of DMAP was used in the esterification reaction. The complete substitution of the phenolic groups was proved by ¹H NMR spectroscopy. The OH singlet of HOPh-PIB-PhOH in CD₂Cl₂ at 4.55 ppm was found to disappear after the esterification and a new signal in a form of quadruplet appeared at 4.6-4.7 ppm, due to the CH₃CHBr protons in the Br-PIB-Br (Figure 1). Their ratio to all kinds of aromatic protons in the Br-PIB-Br was correct. The two resonances around 7.0 and 7.4 ppm are due to the protons in the aromatic endgroups, which are shifted downfield from the originally phenolic groups.¹⁹ The singlet at 7.2 ppm is due to four symmetric protons of the central aromatic ring. SEC analysis shows the following molecular weight characteristics for the synthesized Br-PIB-Br macroinitiator: M_n=6730 and MWD=1.12, which means, that the introduction of initiating groups in the PIB showed the expected result of a small increase of the molecular weight and no change in the MWD.

The telechelic macroinitiator was used to initiate the ATRP of styrene. In order to introduce short segments of PS in the triblock copolymer the polymerisation was carried out in solution of xylene to slow down the rate and exert a better control of the reaction. Before the actual synthesis a model experiment with 2-bromo propionic ethylester (EBP) as initiator under the selected conditions gave a 55% yield after 20 h and M_n=3200 for the PS corresponding to 87% initiation efficiency based on a theoretical value of M_n=2800. Using the synthesized macroinitiator only a 34% yield was achieved. A similar yield was obtained before by us,¹⁴ using another PIB macroinitiator for ATRP of styrene in solution.

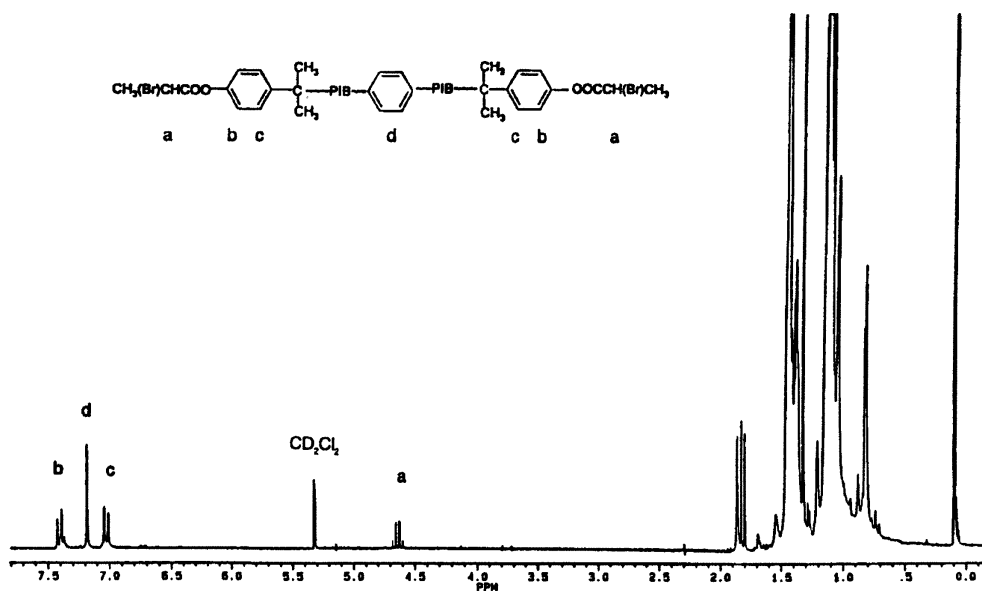


Figure 1. ¹H NMR spectrum of difunctional PIB macroinitiator in CD₂Cl₂.

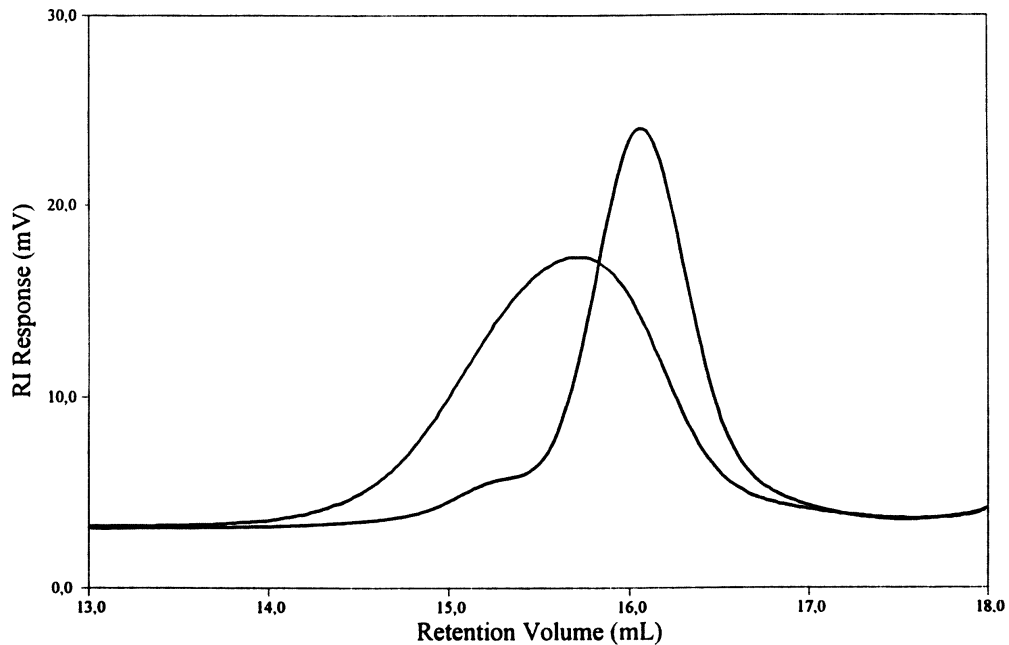


Figure 2. GPC traces of PIB macroinitiator and the corresponding PS-*b*-PIB-*b*-PS triblock copolymer.

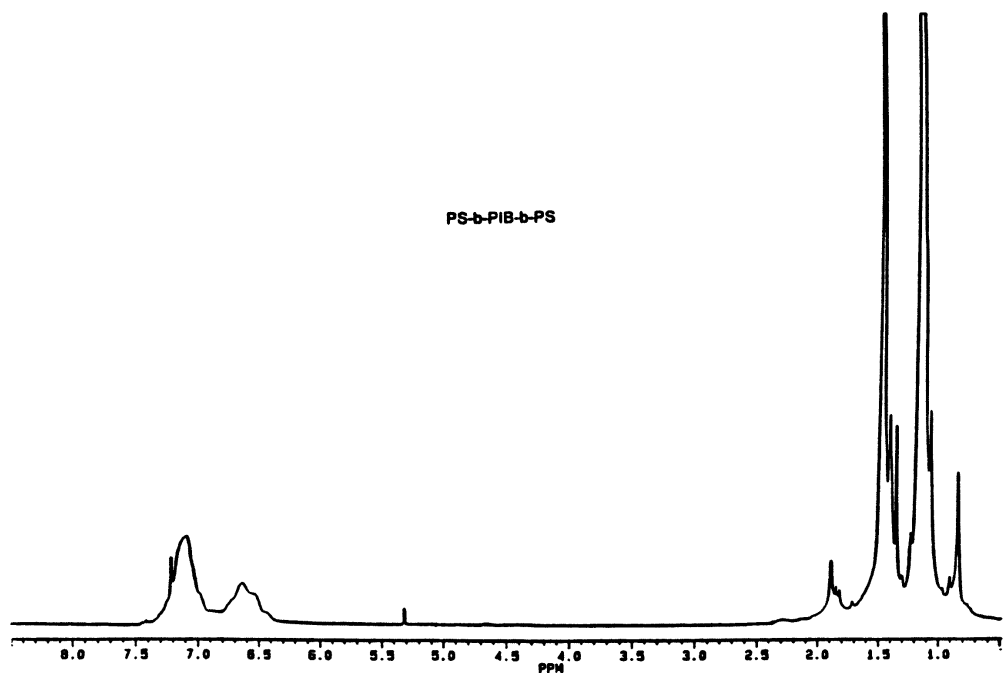


Figure 3. ¹H NMR spectrum of PS-*b*-PIB-*b*-PS triblock copolymer in CD₂Cl₂.

Figure 2 shows the GPC traces of the Br-PIB-Br macroinitiator and the resulting PS-*b*-PIB-*b*-PS triblock copolymer. The elution volume is shifted towards higher molecular weights and the SEC trace remains monomodal after the blocking reaction. This shows the involvement of the Br-PIB-Br chains in initiating ATRP of styrene and in the formation of the PS-*b*-PIB-*b*-PS triblock copolymer. The MWD remains narrow (1.20) and no detectable PS formed by thermal polymerisation was obtained.

In Figure 3 the ^1H NMR spectrum of the PS-*b*-PIB-*b*-PS triblock copolymer is presented. Integration of the aromatic and aliphatic peak regions gave 26.8% PS content, where the calculation of the PS content after the SEC analysis gave 23.0%.

DSC analysis of the representative PS-*b*-PIB-*b*-PS triblock copolymer indicates two-phase morphology. Clear changes in sample heat capacities for the PIB and PS blocks were observed. For the PIB segment, T_g is determined to -58°C , and for the PS phase the T_g is $+95^\circ\text{C}$, in good agreement with that reported elsewhere.²

Conclusions

A PS-*b*-PIB-*b*-PS triblock copolymer may be prepared from PIB functionalized with phenol at the ends by first preparing a macroinitiator by esterification with 2-bromopropionyl chloride. This difunctional PIB macroinitiator is found to be initiator for the ATRP of styrene to yield the well defined triblock copolymer. DSC analysis indicated a two-phase morphology of the synthesized triblock copolymer.

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