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Living Cationic Sequential Block Copolymerization of Isobutylene with 4-tert-Butoxystyrene: Synthesis and Characterization of Poly(p-hydroxystyrene-*b*-isobutylene-*b*-p-hydroxystyrene) Triblock Copolymers

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The living polymerization of p-*tert*-butoxystyrene (tBuOS) was studied in methylcyclohexane (MeChx)/methylchloride (MeCl) 60/40 v/v solvent mixture at −80°C. The model initiator 1,1,-ditolylethylene (DTE) capped 2-chloro-2,4,4-trimethylpentane (TMPCl) was formed *in situ* in conjunction with $TiCl_4$. Lowering the Lewis acidity by the addition of $Ti(OIp)_4$ was necessary to induce a rapid and controlled polymerization of tBuOS. Well-defined polymers with controlled molecular weights, however, were only obtained at a narrow $[Ti(OIp)_4]/[TiCl_4] = 0.83–0.86$ ratio. Above this ratio, the polymerization of tBuOS was slow and became absent at $[Ti(OIp)_4]/[TiCl_4] \geq 1.18$. At ratios lower than 0.83, the polymerization was too rapid and the initiator efficiency was lower than 100%. The living polymerization of tBuOS was also studied with $SnBr_4$ as Lewis acid. After capping TMPCl with DTE, $Ti(OIp)_4$ was added to reach $[Ti(OIp)_4]/[TiCl_4] = 1.2$, followed by the addition of tBuOS and $SnBr_4$. $SnBr_4$ induced a well-controlled living polymerization approximately first order in $[SnBr_4]$, and the polymers exhibited close to theoretical M_ns and low polydispersity indices (PDI < 1.2). The success of the method was also demonstrated by the clean synthesis of poly(isobutylene-*b*-p-*tert*-butoxystyrene) PIB-*b*-PtBuOS diblock copolymers. PtBuOS-*b*-PIB-*b*-PtBuOS triblock copolymer thermoplastic elastomers were prepared by employing 5-tert-butyl-1,3-bis(1-methoxy-1-methylethyl)benzene (DCE) as a difunctional initiator for the living polymerization of IB followed by capping with DTE and substitution of $TiCl_4$ with $SnBr_4$ for the polymerization of tBuOS. Deprotection of the triblock copolymer in the presence of catalytic amount of HCl yielded poly(p-hydroxystyrene-*b*-isobutylene-*b*-p-hydroxystyrene) (PHOS-*b*-PIB-*b*-PHOS). PHOS-*b*-PIB-*b*-PHOS with 39.3 wt% p-hydroxystyrene content exhibited typical characteristic of a thermoplastic elastomers (TPEs) with tensile strength of 18 MPa and ultimate elongation of 300%.

Keywords: carbocationic polymerization; block copolymer; poly(p-hydroxystyrene-*b*-isobutylene-*b*-p-hydroxystyrene); thermoplastic elastomer

1 Introduction

With the development of the living carbocationic polymerization of isobutylene (IB) (1) and styrenic monomers (2, 3), the synthesis of triblock copolymer thermoplastic elastomers (TPEs) with polyisobutylene (PIB) as rubbery middle segment and styrenic polymers as plastic outer segments with well-defined architecture, predictable molecular weight and narrow molecular weight distributions became possible. In particular, PIB based TPEs have attracted considerable attention in biomedical applications (2). Poly(styrene-*b*-isobutylene-*b*-styrene) (SIBS) triblock copolymer is currently employed as the drug carrier matrix for the TAXUS Express Paclitaxel-Eluting Coronary Stent system (Boston Scientific Corporation) (4).

We have recently reported on the synthesis of poly(p-hydroxystyrene-*b*-isobutylene-*b*-p-hydroxystyrene) (PHOS-*b*-PIB-*b*-PHOS) by deprotection of poly(p-(*tert*-butyldimethylsilyloxy)styrene-*b*-isobutylene-*b*-p-(*tert*-butyldimethy lsilyloxy)styrene) with tetrabutylammonium fluoride. The preparation of this precursor triblock copolymer was accomplished by living sequential block copolymerization of IB and p-(*tert*-butyldimethylsiloxy)styrene (TBDMS) utilizing the capping-tuning technique in a one-pot procedure in MeChx/MeCl (60/40, v/v) at −80°C. This procedure involved the living cationic polymerization of IB with the

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5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene/$TiCl_4$ initiating system and capping of the living difunctional PIB chain ends with 1,1-ditolylethylene (DTE) followed by the addition of titanium (IV) isopropoxide ($Ti(OIp)_4$) to lower the Lewis acidity before the introduction of TBDMS. The disadvantages of this technique are the limited availability and high cost of TBDMS and the high sensitivity of the polymerization to the $[TiCl_4]/[Ti(OIp)_4]$ molar ratios. Rapid polymerization of TBDMS yielding complete monomer conversions in less than 2 min and close to theoretical M_n were obtained at a narrow range of $[TiCl_4]/[Ti(OIp)_4] = 0.92-1.24$ ratios. When the $[TiCl_4]/[Ti(OIp)_4]$ ratio is higher, the propagation of TBDMS is much faster than initiation, which leads to incomplete initiation and hence low initiator efficiency. On the other hand, polymerization was practically absent in 30 min at lower $TiCl_4/Ti(OIp)_4$ ratios. The PHOS-*b*-PIB-*b*-PHOS triblock copolymer with 31 wt% *p*-hydroxystyrene content exhibited a tensile strength of 8 MPa and ultimate elongation of 500%. The low tensile strength of the triblock copolymer relative to that reported for SIBS and other PIB based TPEs (5) was attributed to insufficient development of the phase-separated morphology and/or by the possible diblock copolymers contamination estimated to be 4–10 wt% (6).

A readily available alternative monomer is *p*-tert-butoxystyrene (tBuOS), moreover the polymer PtBuOS can be easily deprotected to PHOS by treatment with acids (7). The living cationic polymerization of tBuOS has already been reported. Higashimura et al. reported the living cationic polymerization of tBuOS in CH_2Cl_2 at $-15°C$, using HI/ZnI_2 in the presence of nBu_4NI as common ion salt (8). Satoh et al. (9) have found that BF_3 OEt_2 also induces the living cationic polymerization of tBuOS in the presence of a fairly large amount of water in a CH_3CN/CH_2Cl_2 (4/1 v/v) solvent mixture at 0°C, although the polymerization became slower in the later stage and complete conversion was not reached even after 5 h. Both of these publications, however, report M_ns well below 10000, and the polymerization systems are not applicable for IB.

In this article, we report the living cationic polymerization of tBuOS using $TiCl_4/Ti(OIp)_4$ or $SnBr_4$ in MeChx/MeCl (60/40 v/v) at $-80°C$. These methods have also been applied for the synthesis of PIB-*b*-PtBuOS diblock and PtBuOS-*b*-PIB-*b*-PtBuOS triblock copolymers, which were subsequently hydrolyzed to PHOS-*b*-PIB-*b*-PHOS.

2 Experimental

2.1 Materials

4-*tert*-butoxystyrene (tBuOS, Aldrich, 99%) was dried over CaH_2 and distilled under reduced pressure and stored under nitrogen at $-20°C$, and just before use it was again distilled from CaH_2 under reduced pressure. 5-*tert*-Butyl-1,3-bis(1-methoxy-1-methylethyl)benzene were prepared as described by Wang and coworkers (10). 2-Chloro-2,4,4-trimethylpentane (TMPCl) was obtained from 2,4,4-trimethyl-1-pentene (Aldrich, 99%) by hydrochlorination with hydrogen chloride gas in dry dichloromethane in at 0°C. The 1,1-di-p-tolyethylene (DTE) was prepared as described earlier (5). Methyl chloride (MeCl) and isobutylene (IB) (Matheson) were passed through in-line gas purifier columns packed with barium oxide/Drierite and were condensed inside the glove box at $-80°C$ prior to polymerization. Methanol was distilled before use. Titanium tetrachloride ($TiCl_4$, Aldrich, 99.9%), tin IV bromide ($SnBr_4$, Aldrich, 99%), 2,6-di-tert-butyl pyridine (DtBP, Aldrich, 97.5%), methylcyclohexane (MeCHx, Aldrich, anhydrous grade), tetrahydrofuran (Aldrich, 99%) and toluene (Aldrich, 99%) were used as received without further purification.

2.2 Polymerization

Polymerizations were carried out under a dry nitrogen atmosphere in an MBraun 150-M glove box (Innovative Technology Inc., Newburyport, MA). The experiments were carried out in 75 mL culture tubes or in 2 L reaction flasks fitted with overhead stirrer set at 450 rpm, in MeCHx/MeCl 60/40 (v/v) solvent mixture, at $-80°C$.

2.3 Homopolymerization of tBuOS with $Ti(OIp)_4/TiCl_4$

In large (75 ml) culture tubes, the reagents were added in the following order: MeCHx (4.7 ml), TMPCl (0.5 ml, 0.04 M in MeCHx), DtBP (0.5 ml, 0.0803 M in MeCHx), MeCl (3.9 ml), $TiCl_4$ (0.5 ml, 0.072 M in MeCHx/MeCl 60/40 v/v solvent mixture) and DTE (1.0 ml, 0.04 M in MeCHx/MeCl 60/40 v/v solvent mixture). After 1 h reaction time, the $Ti(OIp)_4$ stock solution (1.0 ml, 0.0432 M in MeCHx/MeCl 60/40 v/v solvent mixture) and 0.9 ml of tBuOS in solution in 1.1 ml MeCHx/MeCl (60:40 v:v) were added under vigorous stirring. The total volume of the solution was 16 mL. After 1 h, 1 mL of pre-chilled methanol was added to the reaction mixture to quench the polymerization. Then, 10 mL of toluene was added and the quenched reaction mixture was washed with water until neutral. The polymer solution was dried over $MgSO_4$, filtered, and the solvent was evaporated. The polymer was purified by reprecipitation from tetrahydrofuran/methanol twice. The monomer conversions were determined by gravimetric analysis.

PIB-*b*-PtBuOS and PtBuOS-*b*-PIB-*b*-PtBuOS were prepared by a procedure similar to that described above.

2.4 Homopolymerization of tBuOS with $SnBr_4$

In large (75 ml) culture tubes, the reagents were added in the following order: MeCHx (4.7 ml), TMPCl (0.5 ml, 0.04 M in MeCHx), DtBP (0.5 ml, 0.0803 M in MeCHx), MeCl (3.9 ml), $TiCl_4$ (0.5 ml, 0.072 M in MeCHx/MeCl 60/40 v/v solvent mixture) and DTE (1.0 ml, 0.04 M in MeCHx/MeCl 60/40 v/v solvent mixture). After 1 h reaction time, the $Ti(OIp)_4$ stock solution (1.0 ml, 0.0432 M in MeCHx/MeCl 60/40 v/v solvent mixture) and 0.9 ml of tBuOS at room temperature was added followed by the addition of 0.7 ml of MeCHx and 0.4 ml of MeCl. Finally, under vigorous stirring, the $SnBr_4$ stock solution (2.0 ml, 0.2867 M in MeCHx/MeCl 60/40 v/v solvent mixture) was introduced. The total volume of the solution was 16 mL. After predetermined times (2, 6, 10, 15, 20, 30, 40, 60 min) 1 mL of pre-chilled methanol was added to the reaction mixture to quench the reaction. Then, 10 mL of toluene was added and the quenched reaction mixture was washed with water to remove the organic salts until neutral. The polymer solution was dried over $MgSO_4$ filtered and the polymer was recovered by evaporation of the solvent. It was purified by reprecipitation from tetrahydrofuran/methanol twice. The monomer conversions were determined by gravimetric analysis.

2.5. Synthesis of PIB-b-PtBuOS

In large (75 ml) culture tubes, the reagents were added in the following order: MeChx (6.4-V_{IB}x0.6 ml), TMPCl (1.0 ml, 0.03 M in MeCHx), DtBP (1.0 ml, 0.06 M in MeCHx), MeCl (5.6–V_{IB}x0.4 ml), IB (V_{IB} ml) and $TiCl_4$ (1.0 ml, 0.539 M in MeCHx). The total volume of the solution was 15 mL. IB was polymerized for 90 min and then DTE stock solution was added (1.0 ml, 0.06 M in MeCHx/MeCl 60/40 v/v mixture solvent). After 1 h reaction time, $Ti(OIp)_4$ stock solution (1.0 ml, 0.65 M in MeChx/MeCl 60/40 v/v mixture solvent) was introduced. After ~ 2 min, 0.2 mL of the reaction mixture was taken and quenched with 2 mL of pre-chilled methanol for molecular weight measurement of the PIB segment. After ~ 1 min, the required amount of tBuOS (V_{tBuOS} mL) in solution in (5-V_{tBuOS}) ml of MeCHx/MeCl 60/40 v/v mixture solvent was added dropwise. Under vigorous stirring, the $SnBr_4$ stock solution (3.0 ml, 2.0478 M in MeCHx/MeCl = 60/40 v/v) was added last. The total volume of the solution was 24.8 mL. After 90 min, the polymerization was terminated by adding prechilled methanol followed by the addition of 15 ml of toluene. The quenched reaction mixture was washed with water until neutral and dried over $MgSO_4$. The polymer was then recovered by evaporating the solvent and purified by reprecipitation from tetrahydrofuran/methanol twice.

2.6. Synthesis of PtBuOS-b-PIB-b-PtBuOS

In a 2 liter reactor fitted with overhead stirrer, the reagents were added in the following order: MeCHx (144.5 ml at room temperature), MeCl (103 mL), HDCE (6.0 mL, 0.05 M in MeCHx), DtBP (4.0 mL, 0.45 M in MeChx), IB (37.5 ml) and $TiCl_4$ (5.0 mL, 0.072 M in MeCHx). The total volume of the solution was 300 mL. IB was polymerized for 90 min and then DTE stock solution was added (24 mL, 0.05123 M in MeCHx/MeCl 60/40 v/v mixture solvent). After 1 h reaction time, $Ti(OIp)_4$ stock solution (20 ml, 0.648 M in MeCHx/MeCl = 60/40 v/v) was added. After ~ 2 min, 2 mL of the reaction mixture was taken and quenched with 2 mL of pre-chilled methanol for molecular weight measurement of the PIB middle segment (M_n= 90,000 g/mol; Mw/Mn = 1.1). After ~2 min, 27.0 ml of tBuOS in solution in 90 ml of MeCHx/MeCl 60/40 v/v mixture solvent was added. Under vigorous stirring, the $SnBr_4$ stock solution (19.0 ml, 0.885 M in MeCHx/MeCl 60/40 v/v mixture solvent) was added. After 90 min, 10 mL of pre-chilled methanol was added to the reaction mixture to quench the reaction. Then, 200 mL of toluene was charged into the flask and the quenched reaction mixture was washed with water and dried over $MgSO_4$. The solution was filtered and the polymer was then recovered by evaporation of the solvent and purified by reprecipitation from tetrahydrofuran/methanol twice.

2.7 Hydrolysis

The triblock copolymer (2.5 g) was dissolved in 50 mL of THF at room temperature. 1 mL of concentrated hydrochloric acid was added dropwise and the solution was refluxed. The solution became hazy. After 3 h, the solution was cooled down and 25 ml of a saturated sodium bicarbonate solution was added to neutralize the acidity. After 1 h, the organic layer containing the polymer was poured into 200 mL of water. The precipitation was repeated from THF into 200 mL of water. The polymer was filtered and dried in a vacuum oven. Yield = 1.57 g (91%).

2.8 Characterization

Molecular weights were measured with a size-exclusion chromatography system equipped with a model 510 HPLC pump, a model 410 differential refractometer, a model 441 UV/visible detector, and online multiangle light scattering (MALLS) detector (Minidawn, Wyatt Technology Inc.) and five ultra-styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5 and 100 Å. Samples were eluted in tetrahydrofuran (THF) at a flow rate of 1.0 ml/min at room temperature. The measurements were carried out at room temperature. Specific refractive index increment (dn/dc) measurements were performed at 25°C on an OPTILAB DSP Interferometric Refractometer (Wyatt Technology Inc.), operating at $\lambda = 690$ nm in THF, using a P10 flow cell (1 mm path length). For PtBuOS $dn/dc = 0.15$ mL/g and for PHOS $dn/dc = 0.208$ mL/g have been determined. For block copolymers, the dn/dc was calculated from the dn/dc and weight fraction of the components.

The composition of the block copolymers was measured by ^{1}H-NMR spectroscopy using a Bruker 250 or 500 MHz instrument.

2.9 Mechanical Properties

Tensile strength properties measured on films using a Texture Analyzer TA.XT2i from stable Micro Systems with serrated grips. The PHOS-*b*-PIB-*b*-PHOS films were obtained by slow (7 days) casting from tetrahydrofuran at room temperature. The films were kept under vacuum at room temperature for 4 days to remove residual solvent.

3 Results and Discussion

3.1 Living Cationic Polymerization of tBuOS with $Ti(OiPr)_4/TiCl_4$

First, the capping reaction of the model compound TMPCl with DTE in conjunction with $TiCl_4$ in MeCHx/MeCl (60/40 v/v) at -80°C was carried out. After 1 h, varying amounts of $Ti(OIp)_4$ was added to decrease the Lewis acidity in order to find the optimum ratio for the living polymerization of tBuOS, followed by the addition of the monomer. The results are shown in Table 1.

Complete conversion in 30 min and close to theoretical M_ns were obtained at $[Ti(OIp)_4]/[TiCl_4] = 0.83–0.86$. At ratios lower than 0.83, the polymerization is too rapid and the initiator efficiency is lower than 100% and at ratios higher than 0.86 the polymerization becomes slow and eventually stops.

Using the optimal ratios di- and triblock copolymers with M_ns close to theoretical values and narrow polydispersity index (PDI < 1.2) have also been successfully prepared. Figures 1 and 2 show the GPC RI traces of the precursor PIBs and the final products. However, while we succeeded to replace TBDMS with the more readily available tBuOS, the polymerization is even more sensitive to the $[Ti(OIp)_4]/[TiCl_4]$ ratio than that reported with TBDMS. Since impurity (e.g., H_2O) levels may depend on the source of chemicals, condition of glove box, etc. the optimal ratio was rather irreproducible. Therefore we set out to find a more robust polymerization method for tBuOS.

3.2 Living Cationic Polymerization of tBuOS with $SnBr_4$

We recently reported that $SnBr_4$ is the most suitable Lewis acid for the living cationic polymerization of p-methoxystyrene (11).

Table 1. Polymerization of tBuOS at varying $TiCl_4/Ti(OiPr)_4$ molar ratios. [TMPCl] = 2 mM, [DTBP] = 6 mM, [TiCl4] = 36 mM, [DTE] = 4 mM, time: 30 min, total volume: 12.5 ml Solvent: MeCHx/MeCl = 60/40 v/v, temp: -80°C

$Ti(OiPr)_4/TiCl_4$	Conv. (%)	$M_{n\,GPC}$ g/mol	PDI	I_{eff}
0.752	99	64000	2.2	58
0.781	99	71000	1.8	53
0.806	99	41000	1.9	91
0.834	97	38000	1.4	98
0.862	98	38000	1.4	98
0.893	15	—	—	—
0.917	16	—	—	—

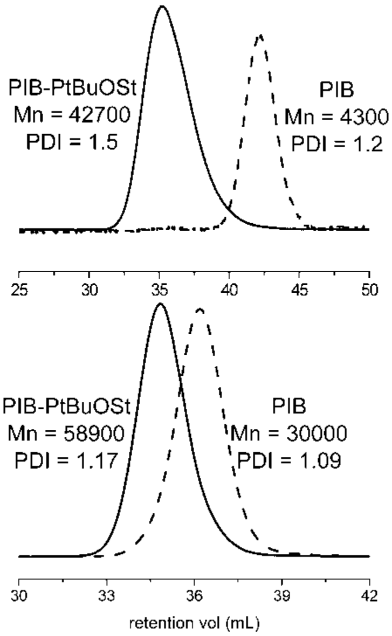


Fig. 1. SEC RI traces of (—) PIB-*b*-PtBuOS and (– – –) PIB precursor polymers.

As the reactivity of tBuOS is expected to be similar, we planned to employ this Lewis acid for the polymerization following a procedure we first reported for poly(IB-*b*-α-methylstyrene) (12). In this procedure, as depicted in Scheme 1, after the capping reaction of living PIB $TiCl_4$ is deactivated by the addition of $Ti(OIp)_4$ followed by the addition of $SnBr_4$ and tBuOS. To identify the most appropriate $Ti(OIp)_4/TiCl_4$ molar ratios where the polymerization of tBuOS does not take place first IB was polymerized by the $TMPCl/TiCl_4$ initiating system in MeChx/MeCl (60/40, v/v) at -80°C. After 90 min (complete conversion, $M_n = 45200$ g/mol, PDI = 1.08) the living PIB chains end was capped with DTE ([DTE]/[TMPCl] = 2) for 1 h, followed by the

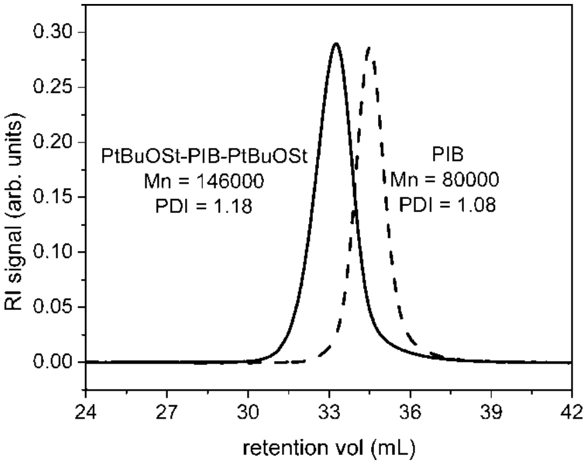
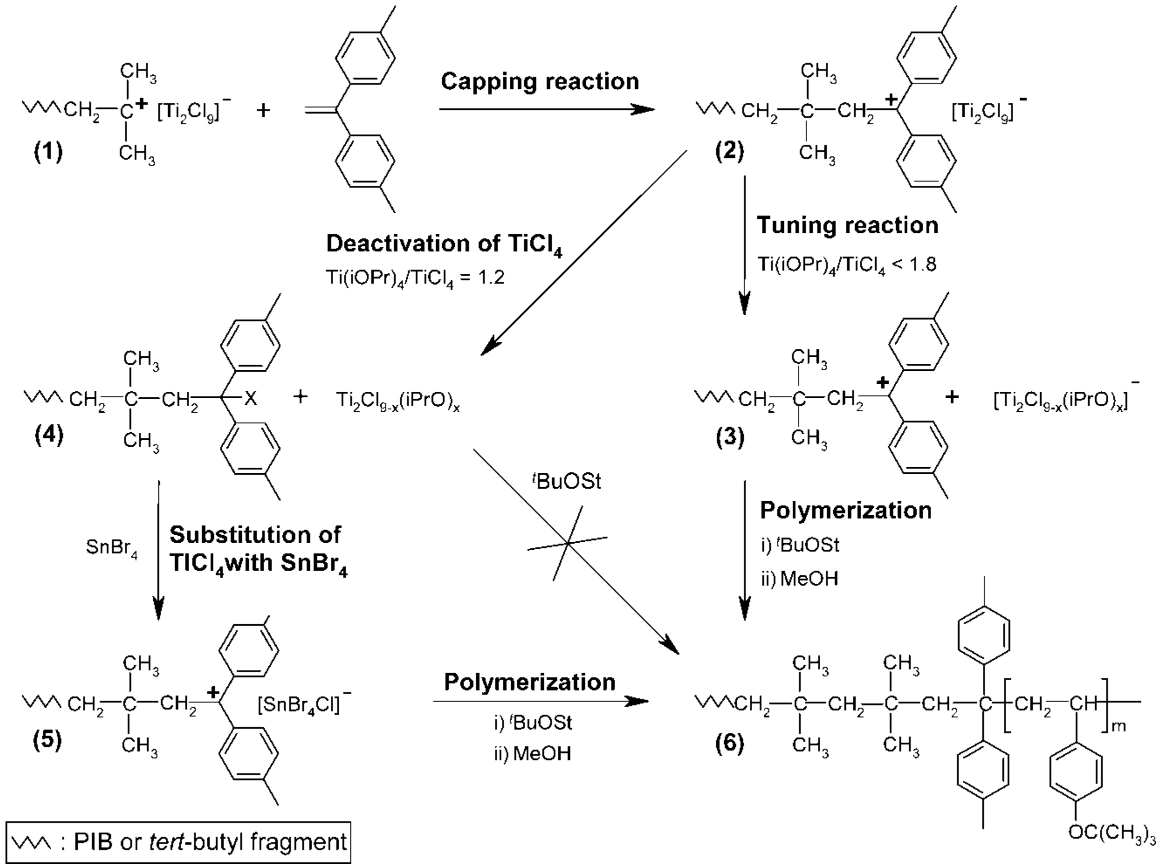


Fig. 2. SEC RI traces of (—) PtBuOS-*b*-PIB-*b*-PtBuOS and (– – –) PIB precursor.



Sch. 1. Capping-tuning process for block copolymerization of IB with tBuOS.

addition of $Ti(OIp)_4$ and finally, tBuOS. The polymerizations were quenched 2 h after the addition of tBuOS.

With $[Ti(OIp)_4]/[TiCl_4] = 1, 1.1, 1.12$ and 1.14, conversions of 30%, 17%, 11% and 5% were obtained, respectively and at $[Ti(OIp)_4]/[TiCl_4] \geq 1.18$ the polymerization of tBuOS was completely absent. Therefore, in all subsequent experiments after the capping reaction of living PIB with DTE $Ti(OIp)_4$ was added to reach the $[Ti(OIp)_4]/[TiCl_4] = 1.2$ ratio. Based on results of preliminary experiments (Table 2) with different $[SnBr_4]$ that suggested that the polymerization is first order in $[SnBr_4]$, further detailed experimentation was carried out with $SnBr_4 = 0.036$ M for which the M_n *vs.* conversion plot and the first order plot of $\ln([M]_0/[M])$ *vs.* time are shown in Figures 3 and 4.

As shown in Figure 3, the $M_{n\ (GPC)}$ values are in acceptable agreement with those calculated with the assumption that each molecule of TMPCl initiates one living polymer chain, and the molecular weight distribution was narrow (PDI $\sim$ 1.1 at complete conversion). According to the linear first order plot (Figure 4) termination is undetectable in this molecular weight range. The SEC traces of the polymers are shown in the Figure 5.

Table 2. Synthesis of PIB-*b*-tBuOS at different $[SnBr_4]$

	PIB segment				PIB-*b*-PtBuOS		
Diblock Sample	Mn_{GPC} g/mol	PDI	$[SnBr_4]$ Mol/l	Conv. %	$M_{n\,theo.}$ g/mol	$M_{n\ GPC}$ g/mol	PDI
—	28055	1.13	0	0	—	—	—
1	28045	1.10	0.01	72.4	47200	47350	1.11
2	28075	1.09	0.02	93.7	52800	52900	1.13
3	29090	1.08	0.036	98	55700	55570	1.14

TMPCl (30 μmol), DtBP (60 μmol), IB (15.3 mmol), TiCl4 (540 μmol), DTE (60 μmol), $Ti(OiPr)_4$ (648 μmol), tBuOS (4.5 mmol) and $SnBr_4$ (573 μmol). Time is 90 min for PIB, 60 min for capping reaction, 10 min for tuning reaction, 60 min for tBuOS polymerization after $SnBr_4$ addition.

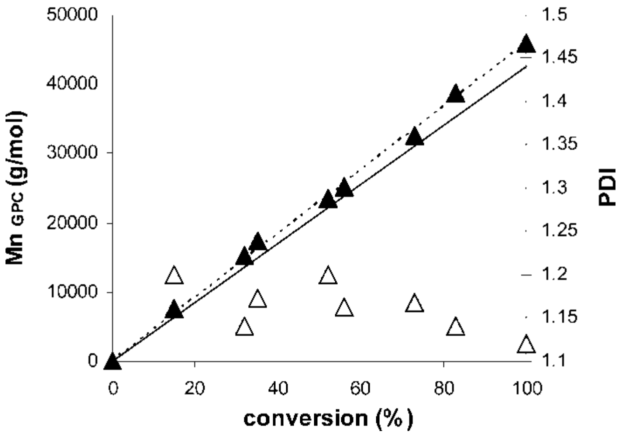


Fig. 3. Dependence of $M_{n\ (GPC)}$ (▲) and $M_w/M_{n\ (GPC)}$ (△) on conversion for the polymerization of tBuOS with TMPCl/TiCl$_4$/DTE/Ti(OiPr)$_4$/SnBr$_4$ initiating system in MeCHx/MeCl 60:40 (v/v) at −80°C. TMPCl (20 μmol), DTBP (40 μmol), TiCl4 (360 μmol), DTE (40 μmol), Ti(OiPr)$_4$ (432 μmol), tBuOS (10.66 mmol), SnBr$_4$ (573 μmol), and volume of reaction (15 ml). (-----) is the dependence of M_n *vs.* conversion computed from GPC data (slope = 460.14). (—) is the theoretical dependence of M_n *vs.* conversion (slope = 426.00).

3.3 Synthesis of the PIB-b-PtBuOS Diblock Copolymers

Based on the above results, diblock copolymers with different composition were prepared according to the methodology described in Scheme 1 via the substitution of TiCl$_4$ with SnBr$_4$ (Figure 6). All samples were quenched 90 min after the addition of tBuOS. The M_n, PDI and composition of copolymers are summarized in Table 3. All diblock copolymers exhibited narrow molecular weight distribution and $M_{n(GPC)}$'s close to theoretical.

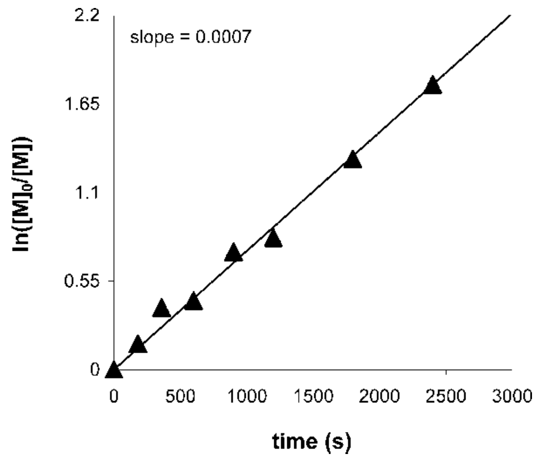


Fig. 4. First order ln([M]$_o$/[M]) *vs.* time for the polymerization of tBuOS with TMPCl/TiCl$_4$/DTE/Ti(OiPr)$_4$/SnBr$_4$ in MeCHx/MeCl 60/40 (v/v) at −80°C.TMPCl (20 μmol), DTBP (40 μmol), TiCl4 (360 μmol), DTE (40 μmol), Ti(OiPr)$_4$ (432 μmol), tBuOS (10.66 mmol), SnBr$_4$ (573 μmol), and total volume (15 ml).

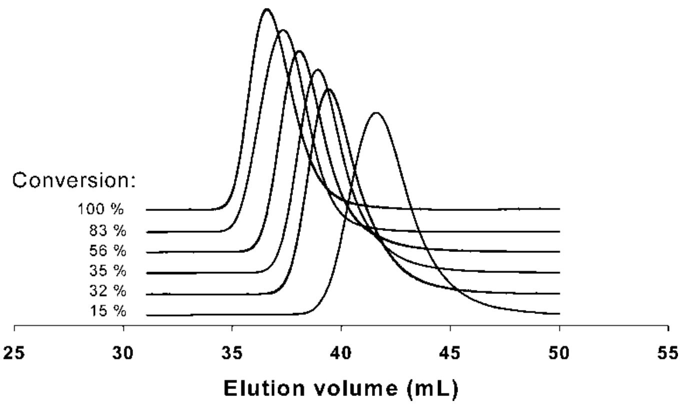


Fig. 5. SEC RI traces in the cationic polymerization of tBuOS with TMPCl/TiCl$_4$/DTE/Ti(OiPr)$_4$/SnBr$_4$ initiating system at −80°C in 6/4 (v/v) MeCHx/MeCl. TMPCl (20 μmol), DTBP (40 μmol), TiCl$_4$ (360 μmol), DTE (40 μmol), Ti(OiPr)$_4$ (432 μmol), tBuOS (10.66 mmol), SnBr$_4$ (573 μmol), and volume of reaction (15 ml).

3.4 Synthesis of the PtBuOS-b-PIB-b-PtBuOS Triblock Copolymers

The triblock copolymer synthesis was carried out as described above, except DCE was used instead of TMPCl as difunctional initiator. First, IB was polymerized by the DCE/TiCl$_4$ initiating system to yield living PIB ($M_n \sim 90000$ g/mol and PDI < 1.12). [IB] = 1.6 M, [DCE] = 0.001 M, [DtBP] = 0.004 M, [TiCl$_4$] = 0.036 M. After 90 min, the living PIB chain end was capped with DTE ([DTE]/[TMPCl] = 2) followed by the addition of Ti(OIp)$_4$ to reach [Ti(OIp)$_4$]/[TiCl$_4$] = 1.2. Then, tBuOS in MeChx/MeCl (60/40 v/v) was added followed by the addition of SnBr$_4$ in MeChx/MeCl (60/40 v/v). The GPC traces of PIB precursor and the triblock copolymer are shown in the Figures 7 and 8. The data summarized in the Table 4 show that the M_ns are close to the theoretical values and the molecular weight distributions are narrow (PDI < 1.2).

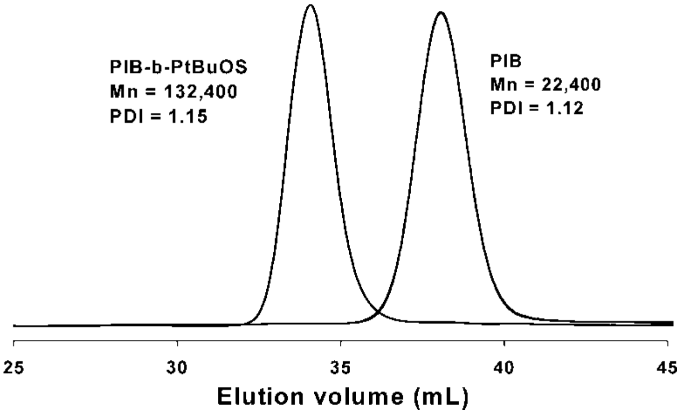


Fig. 6. SEC RI traces of (—) PIB-*b*-PtBuOS (Table 3, Polymer Sample 1) and its (———) PIB precursor.

Table 3. Characteristics of PIB precursor and PIB-*b*-PtBuOS

PIB segment			PIB-*b*-PtBuOS				
$M_{\mathrm{n\,GPC}}$ g/mol	PDI	$M_{\mathrm{n\,targeted}}$ g/mol	$M_{\mathrm{n\ theo}}$ g/mol	$M_{\mathrm{n\,NMR}}$ g/mol	$M_{\mathrm{n\ GPC}}$ g/mol	PDI	PIB wt. % ^{1}H NMR
22,400	1.12	19,950	131,950	131,450	132,400	1.15	16
29,500	1.06	30,000	53,700	53,350	53,170	1.13	55.5
43,200	1.09	45,000	86,800	86,660	83,400	1.14	52

TMPCl (30 μmol), DTBP (60 μmol), IB (10.6 (sample 1), 16.04 (sample 2) and 24.05 (sample 3) mmol), TiCl4 (540 μmol), DTE (60 μmol), Ti(OiPr)$_4$ (648 μmol), tBuOS (19.16 (sample 1), 3.95 (sample 2) and 6.55 (sample 3) mmol) and SnBr$_4$ (573 μmol). Time is 90 min for PIB, 60 min for capping reaction, 10 min for tuning reaction, and 90 min for tBuOSt polymerization after SnBr$_4$ addition.

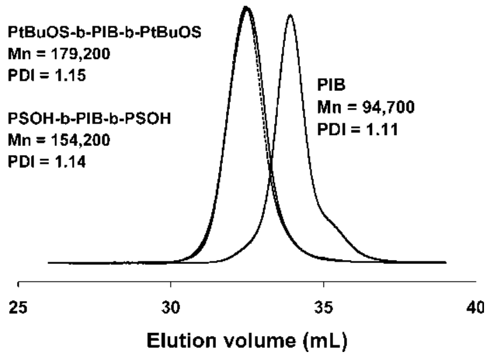


Fig. 7. SEC RI traces of (—) PtBuOS-*b*-PIB-*b*-PtBuOS (Table 4, Polymer Sample 1) triblock, its (·—) PIB precursor and of the hydrolyzed (----) PSOH-*b*-PIB-*b*-PSOH.

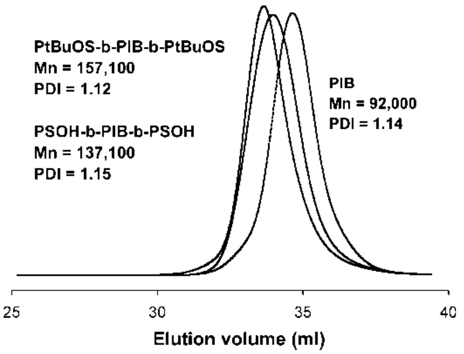


Fig. 8. SEC RI traces of (—) PtBuOS-*b*-PIB-*b*-PtBuOS (Table 4, Polymer Sample 2) triblock, its (·—) PIB precursor and the hydrolyzed (– – –) PSOH-*b*-PIB-*b*-PSOH.

3.5 *Hydrolysis of PtBuOS-b-PIB-b-PtBuOS Triblock Copolymers*

The deprotection of PtBuOS-*b*-PIB-*b*-PtBuOS triblock copolymers was carried out using catalytic amount of concentrated aqueous HCl, which yielded PHOS-*b*-PIB-*b*-PHOS with M_{n}s close to the theoretical values and the molecular weight distribution remained narrow. The data are summarized in the Table 4. The SEC traces before and after hydrolysis is shown in the Figures 7 and 8.

3.6 *NMR Spectroscopy of the Triblock Copolymers*

^{1}H-NMR spectra of PtBuOS-*b*-PIB-*b*-PtBuOS and PHOS-*b*-PIB-*b*-PHOS are shown in the Figure 9. The *t*-butyl group at ~ 1.3 ppm in PtBuOS-*b*-PIB-*b*-PtBuOS completely disappears after hydrolysis. The new peak at 7.9 ppm corresponds to the phenolic proton.

3.7 *Mechanical Properties*

The solution cast film of PHOS-*b*-PIB-*b*-PHOS triblock copolymer (entry 1 in Table 4) exhibited 16 MPa average tensile strength and 300% elongation at break. This tensile strength value is lower than the 24–26 MPa reported for SIBS, but is substantially better than that reported for the PSOH-*b*-PIB-*b*-PSOH triblock copolymer obtained by hydrolysis of PTBMS-*b*-PIB-*b*-PTBMS (6).

Table 4. Characteristics of the PIB middle segment, PtBuOS-*b*-PIB-*b*-PtBuOS and the hydrolyzed product PSOH-*b*-PIB-*b*-PSOH

PIB segment		PtBuOS-*b*-PIB-*b*-PtBuOS				PSOH-*b*-PIB-*b*-PSOH			
$M_{\mathrm{n\,GPC}}$ g/mol	PDI	$M_{\mathrm{n\,NMR}}$ g/mol	$M_{\mathrm{n\ GPC}}$ g/mol	PDI	PIB wt% H NMR	$M_{\mathrm{n\,NMR}}$ g/mol	$M_{\mathrm{n\ GPC}}$ g/mol	PDI	PIB wt% H NMR
91,000	1.10	182,800	179,200	1.15	50.7	154,100	153,200	1.14	60.7
92,00	1.14	153,000	157,000	1.12	59.8	132,000	137,100	1.15	69.7

DCE (0.3 mmol), DTBP (1.2 mmol), IB (37.5 ml), TiCl4 (10.8 mmol), DTE (1.2 mmol), Ti(OiPr)$_4$ (12.9 mmol), tBuOS (27.3 (sample 1), 3.95 (sample 2) ml) and SnBr$_4$ (14.3 mmol). Time is 90 min for PIB, 60 min for capping reaction, 10 min for tuning reaction, 90 min for tBuOS polymerization after SnBr$_4$ addition.

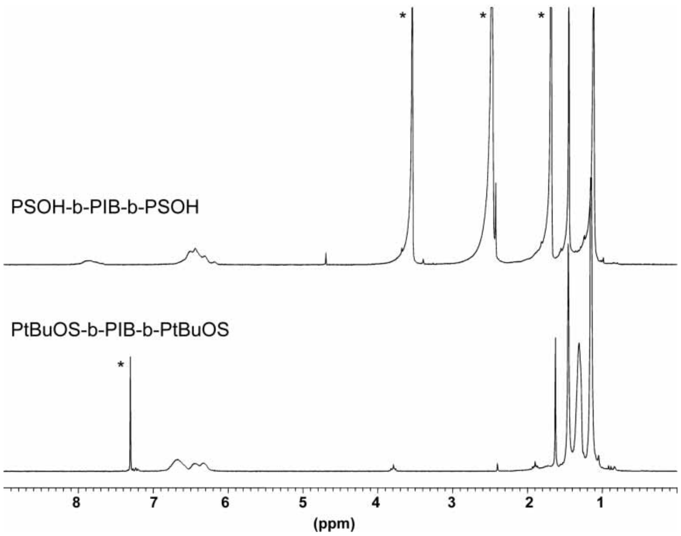


Fig. 9. ^{1}H-NMR spectrum of PtBuOS-*b*-PIB-*b*-PtBuOS (Table 4, sample 1, solvent: $CDCl_3$) (bottom) and PSOH-*b*-PIB-*b*-PSOH (Table 4, sample 1, solvent d^8-THF) (top). Solvent peaks and water are marked by asterix.

4 Conclusions

The homopolymerization a tBuOS and sequential block copolymerization of IB with tBuOS can be accomplished using the capping-tuning method. Employing $SnBr_4$ for the polymerization of tBuOS, however, yields a more robust procedure than tuning the Lewis acidity by the addition of $Ti(iOp)_4$. PtBuOS-*b*-PIB-*b*-PtBuOS triblock copolymers could be easily hydrolyzed by concentrated hydrochloric acid to yield PHOS-*b*-PIB-*b*-PHOS triblock copolymers. The PHOS-*b*-PIB-*b*-PHOS triblock copolymers obtained by this method exhibited 16 MPa tensile strength, much higher than that reported before for the PHOS-*b*-PIB-*b*-PHOS triblock copolymers obtained by hydrolysis of PTBMS-*b*-PIB-*b*-PTBMS indicating lower diblock contamination.

5 Acknowledgment

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