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Cite this: *RSC Adv.*, 2017, 7, 5948

Preparation of polystyrene–polyolefin multiblock copolymers by sequential coordination and anionic polymerization†

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Block copolymers of polyolefins (PO) and polystyrene (PS) are attractive materials that are not synthesized directly from the olefin and styrene monomers. A strategy for construction of PS-*b*-PO-*b*-PS triblock units directly from the olefin and styrene monomers is disclosed herein. PO chains (ethylene/1-octene or ethylene/1-pentene copolymers) were grown from dialkylzinc species bearing the α -methylstyrene moiety (*i.e.*, [4-(isopropenyl)benzyl]₂Zn) by 'coordinative chain transfer polymerization (CCTP)' using a typical *ansa*-metallocene catalyst, *rac*-[Me₂Si(2-methylindenyl)₂]ZrCl₂ activated with modified-methylaluminoxane (MMAO). PS chains were subsequently grown from the Zn-alkyl sites and from the α -methylstyrene moieties of the resulting PO chains by switching to anionic polymerization. When *n*BuLi(tmeda)₂ was fed into the system as an initiator in a quantity fulfilling the criterion [Li] > [Zn] + [Al in MMAO], *n*BuLi(tmeda)₂ successfully attacked the α -methylstyrene moieties to initiate the anionic styrene polymerization at both ends of the PO chains generated in the CCTP process. However, in model studies, the attack of *n*BuLi(tmeda)₂ on α -methylstyrene in the presence of (hexyl)₂Zn consumed two molecules of α -methylstyrene per *n*BuLi to afford mainly R-CH₂C(Ph)(Me)-CH₂C(Ph)(Me)Li, where R is either an *n*butyl or hexyl group originating from *n*BuLi or (hexyl)₂Zn, respectively. This observation suggests that the block copolymer does not simply comprise the PS-*b*-PO-*b*-PS triblock, but instead comprises a multiblock containing PS-*b*-PO-*b*-PS units. The molecular weight of the polymer increased after performing anionic polymerization. Even though the phase separation of the PS and PO blocks observed in the TEM images is less regular in the multiblock copolymers, the elastomeric property of the multiblock copolymers observed in the hysteresis testing is better than that of the diblock analogue.

Received 26th October 2016
 Accepted 9th January 2017

DOI: 10.1039/c6ra25848d

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Introduction

Block copolymers comprised of polyolefins (PO) and polystyrene (PS) are attractive materials that have drawn significant attention in industry and academia.^{1–6} The triblock copolymer, PS-*block*-poly(ethylene-*co*-1-butene)-*block*-PS (SEBS) is a thermoplastic elastomer. Glassy PS blocks form spherical domains that are uniformly distributed in a rubbery poly(ethylene-*co*-1-butene) matrix. SEBS is commercially produced on a scale of several hundred thousand ton per year and advertised to be the material of choice for production of soft and strong compounds for handles and grips, elastic components in diapers, oil gels for telecommunications and medical applications, impact modifiers of engineering thermoplastics, and flexibilizers and tougheners for clear polypropylene. The unique and attractive properties have led to a massive increase in its demand, but its use is limited by

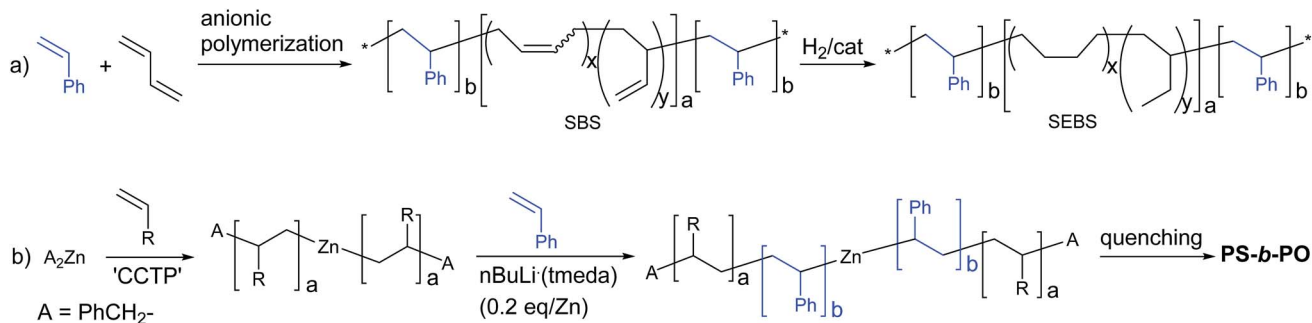
the high manufacturing cost. In industry, SEBS is not produced directly from olefin and styrene monomers, but, instead, is generated *via* hydrogenation of PS-*block*-poly(1,4-butadiene)-*block*-PS (SBS), which is produced by anionic living polymerization of 1,4-butadiene and styrene (Scheme 1(a)).^{7–10} The hydrogenation process is not an easy task and is a significant contributor to the manufacturing cost in the production of SEBS. Hence, preparation of PO–PS block copolymers directly from olefin and styrene monomers is a worthwhile and formidable pursuit.^{11–14}

Recently, we disclosed a novel method for direct preparation of PO–PS diblock copolymers using olefin and styrene monomers, where coordination and anionic polymerizations were sequentially performed in one-pot (Scheme 1(b)).¹⁵ The polyolefin chains were grown from dialkylzinc sites by the so-called 'coordinative chain transfer polymerization (CCTP)',^{16–20} which is a useful tool for precise architectural design of polyolefin chains.^{21–32} The PS chains were subsequently grown from the zinc sites attached to the PO chains by feeding styrene monomer and a sub-stoichiometric amount of *n*BuLi(tmeda) (tmeda: *N,N,N',N'*-tetramethylethylenediamine) initiator (0.2 eq./Zn) into the system. Reversible formation of zincate species *via*

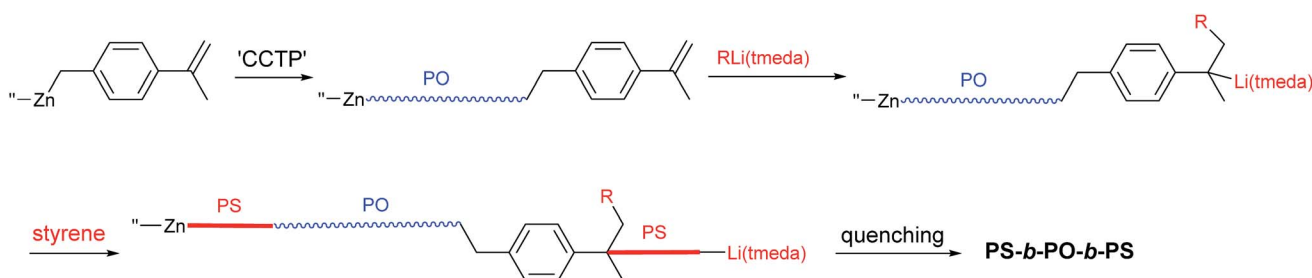
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† Electronic supplementary information (ESI) available: NMR spectra, mass data, GPC curves, and DSC thermogram. See DOI: 10.1039/c6ra25848d





Scheme 1 Preparation of PO-PS block copolymers.

Scheme 2 Strategy for direct preparation of PS-*block*-PO-*block*-PS using olefin and styrene monomers.

the reaction between the dialkylzinc species and the chain-growing alkylolithium sites may be responsible for the growth of PS chain from the zinc sites. Coordination of tmeda enhances the reactivity of the alkylolithium species, playing a key role in the formation of the zincate species in the aliphatic hydrocarbon solvent in which the anionic polymerization is performed. In this work, we report the preparation of PS-PO multiblock copolymers that mimic the chain structure of SEBS (Scheme 2). Preparation of PO-based block copolymers is currently highly topical.³³⁻⁴³

Results and discussion

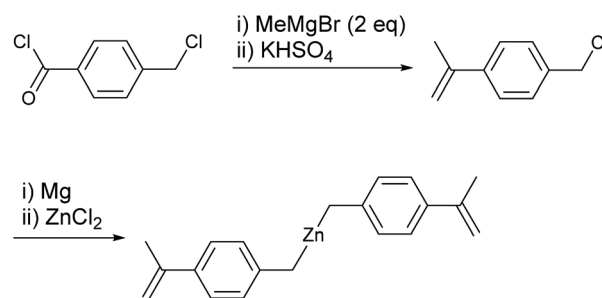
Strategy for preparation of PS-*block*-PO-*block*-PS

The present strategy for preparation of the PS-*block*-PO-*block*-PS copolymer is summarized in Scheme 2. The PO chains were grown from dialkylzinc species bearing an α -methylstyrene moiety, *i.e.*, [4-(isopropenyl)benzyl]₂Zn, by the established CCTP method, and the PS chains were subsequently grown from both the zinc sites and the α -methylstyrene moieties by switching to anionic polymerization. The prerequisite for success of the strategy is that the α -methylstyrene moiety should remain intact during the coordination polymerization process. The styrene monomer readily acts as a chain terminating agent or becomes incorporated into polymer chains during the coordination polymerization,^{11,12} but, α -methylstyrene does not interfere in the ethylene/1-octene copolymerization carried out using the typical *ansa*-metallocene catalyst *rac*-[Me₂Si(2-methylindenyl)₂]ZrCl₂ activated with modified-methylaluminum (MMAO); the

polymerization behaviour did not change in the presence or absence of α -methylstyrene.

The key material in the strategy, [4-(isopropenyl)benzyl]₂Zn, was prepared in a straightforward manner from 4-(chloromethyl)benzoyl chloride (Scheme 3). Thus, addition of two equivalents of MeMgBr to 4-(chloromethyl)benzoyl chloride (*p*-ClC(O)C₆H₄CH₂Cl) and subsequent treatment of the resulting *tert*-benzylic alcohol (4-(Me₂C(OH))C₆H₄CH₂Cl) with the weak acid KHSO₄ at 140 °C afforded 4-(isopropenyl)benzyl chloride in good yield (76%).⁴⁴ Generation of the Grignard reagent using the prepared 4-(isopropenyl)benzyl chloride and subsequent addition of half equivalent of ZnCl₂ in diethyl ether afforded the desired [4-(isopropenyl)benzyl]₂Zn. Purification of dibenzylzinc derivatives is sometimes problematic, but in this case, extremely pure [4-(isopropenyl)benzyl]₂Zn was obtained through recrystallization in hexane.⁴⁵⁻⁴⁷

In the previous studies focusing on the preparation of PO-PS diblock copolymers, a minimal amount of *n*BuLi(tmeda) ([Li]/

Scheme 3 Synthesis of [4-(isopropenyl)benzyl]₂Zn.

[Zn] = 0.2) was used to minimize the generation of PS homopolymers (Scheme 1(b)); however, in the present strategy to prepare PS-*b*-PO-*b*-PS triblock copolymers (Scheme 2), a significant amount of RLi(tmeda) ([Li]/[Zn] = 2) should be fed into the system to attack the α -methylstyrene moieties. Gratifyingly, PS chains were effectively grown from almost all the Zn-alkyl sites, even when the [Li]/[Zn] ratio was as high as 1.0, 1.5, and 2.0. The ([PS growth sites] – [Li])/[Zn] values determined from the measured PS- M_n values (*i.e.*, ([PS growth sites] – [Li])/[Zn] = {styrene}/DP – [nBuLi(tmeda)]/[Zn], where DP = PS- M_n /104) were close to the value of 2.0 that is expected when PS chain growth occurs from all the Zn-alkyl sites (1.89, 1.97, and 1.82 for [Li]/[Zn] feed ratios of 1.0, 1.5, and 2.0, respectively) (2–4 in Table 1). Additionally, the molecular weight distributions were narrower at high feed ratios of *n*BuLi(tmeda) (M_w/M_n , 1.26, 1.27, and 1.23 for [Li]/[Zn], 1.0, 1.5, and 2.0, respectively) compared with the M_w/M_n value (1.52) observed when the [Li]/[Zn] ratio was low at 0.20 (entry 1). Addition of two equivalents tmeda per *n*BuLi afforded similar results at [Li]/[Zn] ratios of 1.0 and 1.5; PS chains were effectively grown from most of the Zn-alkyl sites with narrow molecular weight distributions ([PS growth sites] – [Li])/[Zn], 2.12 and 1.73; M_w/M_n , 1.32 and 1.29; entries 5 and 6). However, growth of the PS chain from the zinc sites was not very effective when the [Li]/[Zn] ratio was high at 2.0 ([PS growth sites] – [Li])/[Zn] = 1.23) (entry 7).

Initiation of α -methylstyrene

It was reported that *tert*-BuLi reacts with α -methylstyrene in aliphatic hydrocarbon solvent to form a 1 : 1 adduct (*t*Bu-CH₂C(Ph)(Me)Li).⁴⁸ Less reactive *n*BuLi does not react with α -methylstyrene, but *n*BuLi(tmeda) rapidly attacks α -methylstyrene; ¹H NMR studies in deuterated cyclohexane indicate that the 1 : 1 adduct (*n*Bu-CH₂C(Ph)(Me)Li) and the 1 : 2 adduct (*n*Bu-CH₂C(Ph)(Me)-CH₂C(Ph)(Me)Li) were generated (Fig. 1(a)). The xylolithium species *p*-MeC₆H₄CH₂Li(tmeda), which is generated cleanly through α -lithiation of *p*-xylene using *n*BuLi(tmeda), also attacks α -methylstyrene. Analyses of the generated organolithium species itself and the protonated organic compounds (two spots in TLC studies) by 1D and 2D NMR also indicated formation of the 1 : 1 and 1 : 2 adducts (MeC₆H₄CH₂-CH₂C(Ph)(Me)Li and MeC₆H₄CH₂-CH₂-C(Ph)(Me)-CH₂C(Ph)(Me)Li (see ESI†). Higher adducts, 1 : 3

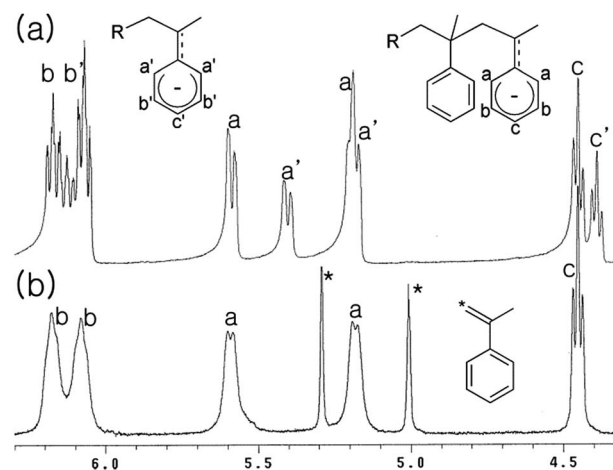


Fig. 1 ¹H NMR spectra for the reactions of α -methylstyrene with *n*BuLi(tmeda) (a) and *n*BuLi(tmeda)₂ in the presence of (hexyl)₂Zn (b).

adduct, *etc.*, were not generated; that is, α -methylstyrene can only be inserted successively twice, but further insertion of three or more units is not allowed. These observations agree with the fact that homopolymerization of α -methylstyrene is not feasible, especially at a high temperature due to its low ceiling temperature (T_c , 66 °C),^{49–51} and that the maximum α -methylstyrene content attainable in α -methylstyrene/styrene anionic copolymerization is limited to *ca.* 70 wt% (*i.e.*, 2 : 1 α -methylstyrene/styrene mole ratio).⁵²

For success of the present strategy, the alkylolithium species should be able to attack the α -methylstyrene moieties in the presence of dialkylzinc species. Disappointingly, the reactivity of *tert*-BuLi, *n*BuLi(tmeda), and *p*-MeC₆H₄CH₂Li(tmeda) toward α -methylstyrene was extinguished in the presence of an equivalent amount of (hexyl)₂Zn; formation of Li–Zn aggregates may reduce the reactivity. However, when [Li] > [Zn], consumption of α -methylstyrene was observed, with generation of the characteristic orange-red colour of the styryl anion. However, the reaction rate was rather slow; only ~50% consumption of α -methylstyrene was observed at the reaction time of 30 min using the feed ratio of [nBuLi(tmeda)] : [(hexyl)₂Zn] : [α -methylstyrene] = 1.5 : 1 : 2. Addition of *n*BuLi(tmeda)₂ instead of *n*BuLi(tmeda) leads to acceleration of the reaction rate and almost all the α -methylstyrene was consumed within 30 min. In the ¹H

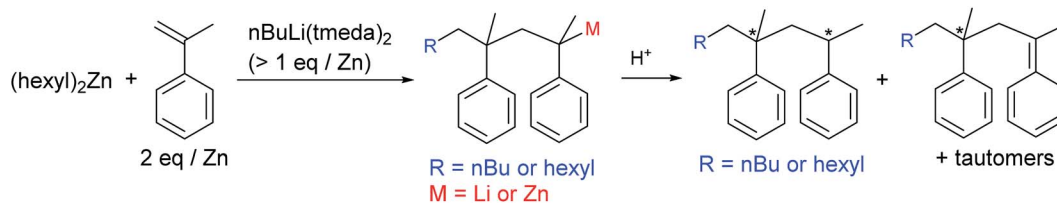
Table 1 Anionic styrene polymerization in the presence of (hexyl)₂Zn^a

| Entry | Initiator | [Li]/[Zn] | Time ^b (h) | M_n^c (Da) | M_w/M_n | ([PS growth sites] – [Li])/[Zn] ^d |
|-------|-----------------------------------|-----------|-----------------------|--------------|-----------|--|
| 1 | <i>n</i> BuLi(tmeda) | 0.20 | 2.0 | 25 100 | 1.52 | 1.87 |
| 2 | <i>n</i> BuLi(tmeda) | 1.0 | 2.0 | 18 000 | 1.26 | 1.89 |
| 3 | <i>n</i> BuLi(tmeda) | 1.5 | 1.0 | 15 000 | 1.27 | 1.97 |
| 4 | <i>n</i> BuLi(tmeda) | 2.0 | 1.0 | 13 600 | 1.23 | 1.82 |
| 5 | <i>n</i> BuLi(tmeda) ₂ | 1.0 | 1.0 | 16 700 | 1.32 | 2.12 |
| 6 | <i>n</i> BuLi(tmeda) ₂ | 1.5 | 1.0 | 16 100 | 1.29 | 1.73 |
| 7 | <i>n</i> BuLi(tmeda) ₂ | 2.0 | 1.0 | 16 100 | 1.18 | 1.23 |

^a Polymerization conditions: styrene in methylcyclohexane (25 wt%, 2.5 g, 24 mmol), (hexyl)₂Zn (11.3 mg, 0.048 mmol, [styrene]/[Zn] = 500), 90 °C.

^b Time not optimized for full conversion. ^c Measured by GPC at 40 °C using THF eluent and PS-standards. ^d Calculated as ([styrene]/[Zn])/DP – [nBuLi(tmeda)]/[Zn], where DP = M_n /104.



Scheme 4 Reaction of $n\text{BuLi}(\text{tmeda})_2$ with α -methylstyrene.

NMR spectrum, only signals assignable to the 1 : 2 adduct ($\text{R}-\text{CH}_2\text{C}(\text{Ph})(\text{Me})-\text{CH}_2\text{C}(\text{Ph})(\text{Me})\text{Li}$) were observed, with no appearance of the signals assignable to the 1 : 1 adduct ($\text{R}-\text{CH}_2\text{C}(\text{Ph})(\text{Me})\text{Li}$) (Fig. 1(b) and Scheme 4). After quenching with acidic water, full analyses of the protonated organic compound (one spot in TLC analysis) using NMR and mass spectral data further supported primary generation of 1 : 2 adduct attached *via* either *n*-butyl or hexyl group (*i.e.*, $\text{R} = n\text{Bu}$ or hexyl in $\text{R}-\text{CH}_2\text{C}(\text{Ph})(\text{Me})-\text{CH}_2\text{C}(\text{Ph})(\text{Me})\text{Li}$) originating from $n\text{BuLi}$ or $(\text{hexyl})_2\text{Zn}$, respectively (see ESI†). When styrene monomer was added to the generated the $\text{R}-\text{CH}_2\text{C}(\text{Ph})(\text{Me})-\text{CH}_2\text{C}(\text{Ph})(\text{Me})\text{Li}$ species in the NMR cell, rapid and full consumption of styrene monomer was observed, indicating the generated lithium species acts well as an initiator for the styrene anionic polymerization.

Preparation of multiblock copolymers

Based on the aforementioned background studies, preparation of multiblock copolymers containing PS-*b*-PO-*b*-PS units was attempted (Table 2). The olefin polymerization was performed using a typical *ansa*-metallocene catalyst ($\text{rac}[\text{Me}_2\text{Si}(2\text{-methylindenyl})_2\text{ZrCl}_2]$) activated with MMAO, which was reported to be effective in the CCTP with suppression of the undesirable β -elimination process.^{15,53,54} Olefin polymerization was performed by feeding ethylene gas into the system containing 1-octene or 1-pentene monomer. The catalyst worked efficiently, leading to consumption of almost all of the α -olefin monomers, once the zinc species $[\text{4}-(\text{isopropenyl})\text{benzyl}]_2\text{Zn}$ is sufficiently pure. The molecular weights of the generated POs (M_w , 115–147 kDa) were similar to the M_w (140 kDa) observed for PO generated in the presence of $(\text{benzyl})_2\text{Zn}$, indicating that $[\text{4}-(\text{isopropenyl})\text{benzyl}]_2\text{Zn}$ works as effectively as $(\text{benzyl})_2\text{Zn}$ in the CCTP while the α -methylstyrene moieties do not interfere in the olefin polymerization (entry 4 *versus* others).

Anionic polymerization of styrene was subsequently performed in one-pot by successive feeding of $n\text{BuLi}(\text{tmeda})_2$ and styrene monomer into the system with a lag time of 1 h. The time lag was introduced to allow $n\text{BuLi}(\text{tmeda})_2$ to attack the α -methylstyrene moieties fully. $n\text{BuLi}$ forms 1 : 1 aggregates with alkylaluminum species (MMAO), preventing initiation of the anionic polymerization when $[\text{Li}] < [\text{Al}]$. However, when the $[\text{Li}]/[\text{Al}]$ ratio exceeds 1.0, styrene polymerization is initiated, but the PS-chains grow from all of $n\text{BuLi}$ fed into the system, including $n\text{BuLi}$ units trapped by alkylaluminum species and dialkylzinc sites.⁵⁵ PS chains grown from $n\text{BuLi}$ form the undesired PS homopolymer (homo-PS), while those grown from Zn sites form the desired block copolymers.

Attack of $n\text{BuLi}(\text{tmeda})_2$ on the α -methylstyrene moieties that are attached to the end of PO chains results in formation of PS-*b*-PO-*b*-PS triblock units. In this one-pot process, a substantial amount of $n\text{BuLi}(\text{tmeda})_2$ is needed for the reaction between $n\text{BuLi}(\text{tmeda})_2$ and α -methylstyrene (*i.e.*, $[\text{Li}] > [\text{Al}] + [\text{Zn}]$) since some portion of the $n\text{BuLi}(\text{tmeda})_2$ fed into the system remains unreacted with α -methylstyrene moieties by becoming trapped by aggregation with the Al and Zn sites; consequently, formation of a substantial amount of PS-homopolymers is inevitable.

The PS homopolymer can be selectively extracted from the generated block copolymers using chloroform and acetone (1 : 2 w/w). When the amount of $n\text{BuLi}(\text{tmeda})_2$ (300 μmol) was less than $[\text{Zn}] + [\text{Al}]$ (*i.e.*, $200 + 200 = 400 \mu\text{mol}$), $n\text{BuLi}(\text{tmeda})_2$ did not attack the α -methylstyrene moieties, as indicated by the lack of appearance of the characteristic orange colour of the styryl anion. The number of homo-PS growth sites calculated as '(homo-PS weight)/PS- M_n ' was 310 μmol , which is consistent with the amount of $n\text{BuLi}(\text{tmeda})_2$ fed into the system. This agreement indicates that PO-*b*-PS diblock copolymers were generated and the α -methylstyrene moieties did not participate in the anionic styrene polymerization (entry 1). However, when the amount of $n\text{BuLi}(\text{tmeda})_2$ fed into the system was 500 μmol , which exceeds the sum of $[\text{Zn}]$ and $[\text{Al}]$ (*i.e.*, $[\text{Li}] > [\text{Zn}] + [\text{Al}]$), the colorless solution became red-orange, indicating generation of the styryl anion *via* attack of $n\text{BuLi}(\text{tmeda})_2$ on the α -methylstyrene moieties; the homo-PS growth sites (320 μmol) were less than the amount of $n\text{BuLi}(\text{tmeda})_2$ used as feed (500 μmol) (entry 3). When the zinc species do not bear α -methylstyrene moieties, *i.e.*, when $(\text{benzyl})_2\text{Zn}$ was used instead of $[\text{4}-(\text{isopropenyl})\text{benzyl}]_2\text{Zn}$, the quantity of homo-PS growth sites (510 μmol) again agreed well with the amount of $n\text{BuLi}(\text{tmeda})_2$ used as feed (500 μmol) (entry 4). In all other cases where $[\text{Li}] > [\text{Zn}] + [\text{Al}]$, some portion of the fed lithium species reacted with the α -methylstyrene moieties, and the quantity of homo-PS growth sites was less than the amount of the lithium species used as feed (entries 5, 7, and 12). As the amount of $n\text{BuLi}(\text{tmeda})_2$ fed into the system increased from 300 to 400, and 500 μmol , the polydispersity (PDI, M_w/M_n) of the extracted homo-PS gradually decreased from 1.82 to 1.66 and 1.46; however, the PDI increased (1.66) with a further increase of the $n\text{BuLi}(\text{tmeda})_2$ feed to 600 μmol (entries 1–3 and 5). In all cases, the polymerization rate was fairly high and the styrene monomers were completely consumed within 1.5 h.

The fraction of extracted homo-PS declined when a small amount of divinylbenzene (0.25–1.0 mol% per styrene), which may connect the homo-PS chains with the block copolymer



Table 2 Data for preparation of PS-*b*-PO-*b*-PS multiblock copolymers^a

| Entry | RLi(tmeda) ₂ (μmol) | Consumed monomers | | | Homo-PS ^c (g; %) | PS- <i>M</i> _n (PDI) ^d (kDa) | Homo-PS growth sites ^e (μmol) | PO- <i>M</i> _w (PDI) ^f (kDa) | Block copolymer- <i>M</i> _w (PDI) ^f (kDa) |
|----------------|-----------------------------------|-------------------|--------------------------------------|-----------------------------|--------------------------------|---|--|--|---|
| | | 1-Alkene (g) | C ₂ H ₄ (g) | Styrene ^b (g) | | | | | |
| 1 | <i>n</i> Bu; 300 | C8; 10.0 | 15.4 | 10.4 | 4.4 (42) | 14.3 (1.82) | 310 | 129 (4.06) | 143 (2.60) |
| 2 | <i>n</i> Bu; 400 | C8; 10.0 | 19.0 | 10.4 | 4.6 (44) | 11.4 (1.66) | 400 | 135 (4.57) | 150 (2.92) |
| 3 | <i>n</i> Bu; 500 | C8; 10.0 | 18.4 | 10.4 | 4.6 (45) | 14.5 (1.46) | 320 | 115 (3.02) | 145 (2.51) |
| 4 ^g | <i>n</i> Bu; 500 | C8; 10.0 | 17.4 | 10.4 | 5.5 (53) | 10.7 (1.65) | 510 | 140 (3.55) | 148 (3.37) |
| 5 | <i>n</i> Bu; 600 | C8; 10.0 | 18.0 | 10.4 | 5.7 (55) | 11.2 (1.66) | 510 | 134 (3.76) | 155 (2.68) |
| 6 | Benzyl; 400 | C8; 10.0 | 16.7 | 10.4 | 5.4 (52) | 12.0 (1.56) | 450 | 133 (3.33) | 138 (2.86) |
| 7 | Benzyl; 500 | C8; 10.0 | 20.1 | 10.4 | 5.0 (48) | 14.3 (1.65) | 350 | 142 (3.61) | 154 (3.19) |
| 8 | <i>n</i> Bu; 500 | C8; 10.0 | 19.3 | 10.4 (0.25) | 3.1 (30) | 16.1 (1.54) | | 147 (2.96) | 162 (3.68) |
| 9 | <i>n</i> Bu; 500 | C8; 10.0 | 18.3 | 10.4 (0.50) | 3.1 (29) | 11.3 (1.79) | | 132 (3.15) | 157 (2.54) |
| 10 | <i>n</i> Bu; 500 | C8; 10.0 | 19.1 | 10.4 (0.75) | 2.0 (19) | 11.1 (1.56) | | 136 (3.09) | 146 (2.42) |
| 11 | <i>n</i> Bu; 500 | C8; 10.0 | 19.8 | 10.4 (1.0) | 1.5 (14) | 10.1 (1.66) | | 130 (3.05) | 155 (3.28) |
| 12 | <i>n</i> Bu; 500 | C5; 10.0 | 15.8 | 10.4 | 5.0 (48) | 14.5 (1.51) | 340 | 119 (3.65) | 134 (2.98) |
| 13 | <i>n</i> Bu; 500 | C5; 10.0 | 16.2 | 10.4 (0.25) | 3.7 (36) | 14.8 (1.74) | | 126 (3.22) | 140 (3.20) |
| 14 | <i>n</i> Bu; 500 | C5; 10.0 | 19.0 | 10.4 (0.50) | 2.8 (27) | 11.5 (1.78) | | 129 (2.92) | 153 (3.19) |

^a Polymerization conditions: *rac*-[Me₂Si(2-methylindenyl)₂]ZrCl₂ (1.0 μmol), MMAO (200 μmol-Al), initial ethylene charge at 30 bar and then regulation at 10–20 bar, 120 °C, 20 min for the first step CCTP; [styrene]/[Zn] = 500, 120–130 °C, 1.5 h (complete conversion of styrene) in the second step anionic polymerization. ^b Values in parentheses indicate mol% of additional divinylbenzene per styrene. ^c Filtrate portion extracted with acetone and chloroform (2 : 1 weight ratio); percentage value = (extracted PS weight)/(consumed styrene weight). ^d Measured with GPC at 40 °C eluting with THF using PS-standards. ^e (Homo-PS weight)/PS-*M*_n. ^f Measured with GPC at 160 °C eluting with 1,2,4-trichlorobenzene using PS-standards. ^g (Benzyl)₂Zn was used instead of [4-(isopropenyl)benzyl]₂Zn.

chains during the course of anionic polymerization, was used as the feed. In fact, by feeding divinylbenzene in quantities of 0.25, 0.50, 0.75, and 1.0 mol%, the fraction of homo-PS fraction gradually declined from 45% to 30%, 29%, 19%, and 14%, respectively (entries 8–11). The extracted homo-PS *M*_n values gradually decreased from 16.1 to 11.3, 11.1, and 10.1 kDa with an increase of the amount of divinylbenzene from 0.25 mol% to 0.50, 0.75, and 1.0 mol%.

Formation of the block copolymers was evident from comparison of the molecular weights of the samples before and after anionic polymerization (*i.e.*, PO-*M*_w and block copolymer-*M*_w). The refractive index (RI) detector response of the GPC instrument is opposite for the PO and PS samples (see ESI[†]), which complicates the analyses, but the retention time should be shortened by attaching the PS-blocks, which leads to increase of the molecular weight, even though the actual value of the increment may not be fully reliable. When [Li] was less than '[Al] + [Zn]', where PO-*b*-PS diblock copolymers are the main species generated, the *M*_w increased from 129 to 143 kDa after anionic polymerization (entry 1); the increment of the *M*_w values (ΔM_w) was 14 kDa, which is almost similar to the measured molecular weight of homo-PS (*M*_n, 14.3 kDa). In the GPC curves plotted in the log(molecular weight) scale (Fig. 2(a)), the shift is substantial at the low molecular end while it is insubstantial at the high molecular weight end, and the molecular weight distribution is narrowed after the anion polymerization (*M*_w/*M*_n, 2.60 *versus* 4.06). In the step of anion polymerization, the molecular weight distribution of PS fraction is not as narrow as that in the living polymerization (*M*_w/*M*_n 1.82) and some low molecular weight portion below 10 kDa is observed in the GPC curve of the generated block copolymer.

When the amount of *n*BuLi was 500 μmol to meet the criterion '[Li] > [Al] + [Zn]', where PO-PS multiblock copolymers are generated by the attack of *n*BuLi on the α -methylstyrene moieties (entry 3), ΔM_w was significant, *i.e.*, 30 kDa, which is almost double of the *M*_n value obtained for homo-PS (14.5 kDa). In the GPC curves plotted in the log(molecular weight) scale (Fig. 2(b)), the shift is substantial at both the low molecular and the high

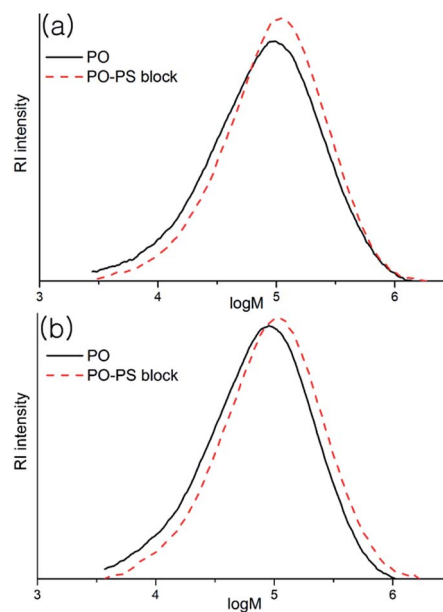


Fig. 2 GPC curves before and after the anionic polymerization for the generation of PO-PS diblock copolymer (a, entry 1 in Table 2) and multiblock copolymer (b, entry 3 in Table 2).



molecular weight ends, which suggests that the generated copolymer is not a simple triblock but, instead, a multiblock copolymer. In contrast, ΔM_w was marginal (8 kDa) when $(\text{benzyl})_2\text{Zn}$ was used instead of $[\text{4-(isopropenyl)benzyl}]_2\text{Zn}$ under the identical conditions; the α -methylstyrene moieties must play a role in obtaining the high ΔM_w value. The ΔM_w values were relatively small (5 or 12 kDa) when $\text{benzyl-Li}(\text{tmeda})_2$ was fed as an initiator in amounts of 400 and 500 μmol ; $\text{benzyl-Li}(\text{tmeda})_2$ is not as good an initiator as $n\text{BuLi}(\text{tmeda})_2$ for successful execution of the strategy. When divinylbenzene is used, much higher ΔM_w values are expected due to connection of the growing block copolymer chains; however, the observed ΔM_w values were not so very high (10–25 kDa). The polymerization solution turned turbid at an early stage of the anionic polymerization, indicating that the generated block copolymers are insoluble and form micelles. In this situation, connection between the growing block copolymer chains may not be feasible. In the case of ethylene/1-pentene copolymerization, the molecular weight also increased after anionic polymerization (ΔM_w , 14–24 entries 12–14). In most cases, the molecular weight distributions became narrow after anionic polymerization.

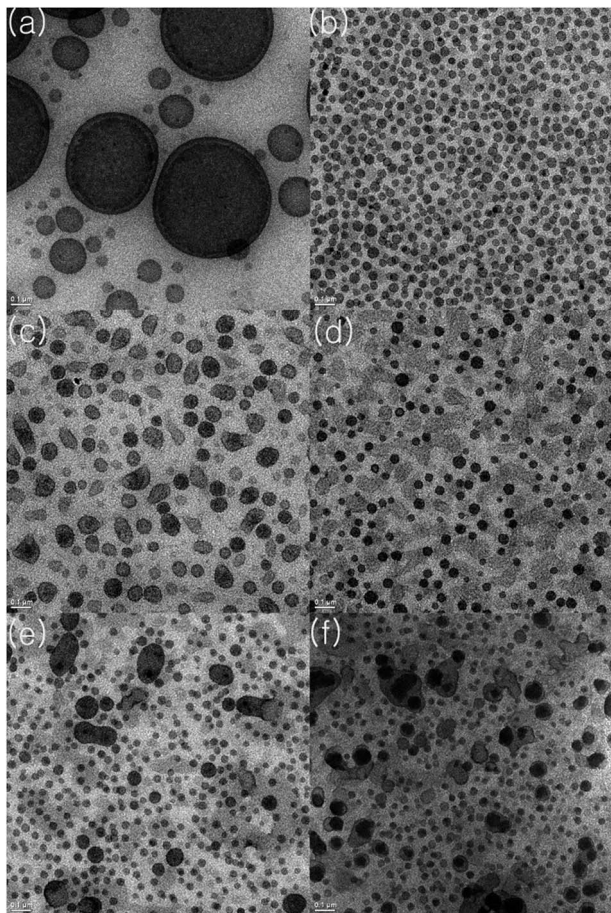


Fig. 3 TEM images (1500 nm \times 1500 nm) of thin films prepared using a blend of poly(ethylene/1-octene) and PS (a) and PO-PS block copolymers (entry 1 (b), entry 3 (c), entry 8 (d), entry 9 (e), entry 10 (f) in Table 2).

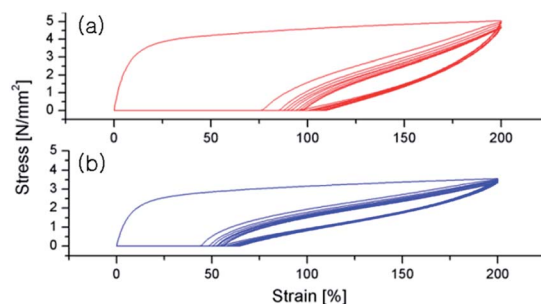


Fig. 4 Plots of hysteresis experiment for the PO-PS diblock copolymer (a, entry 1 in Table 2) and PO-PS multiblock copolymer (b, entry 3 in Table 2). Ten cycles at 200% strain were performed.

Formation of the block copolymers was evident from investigation of the TEM images of the thin films after staining with RuO_4 . Because PS is immiscible with PO, phase separation occurs and the PS domains selectively stained by RuO_4 are clearly seen as a dark image. In contrast with the image of the PO-PS blend (Fig. 3(a)), the PO-*b*-PS diblock copolymers generated under the condition $[\text{Li}] < [\text{Al}] + [\text{Zn}]$ (entry 1) formed spherical PS domains with an average 40 nm; these domains were regularly distributed in the PO matrix (Fig. 3(b)). However, the shape of the PS domains was rather blurred and irregular for the multiblock copolymers generated by the attack of $n\text{BuLi}(\text{tmeda})_2$ on the α -methylstyrene moieties under the condition $[\text{Li}] > [\text{Al}] + [\text{Zn}]$ (Fig. 3(c)). When divinylbenzene was fed in the system, the shape of the PS domains became much more blurred and irregular. Specifically, large domains were observed when the amount of divinylbenzene feed was high (0.50 and 0.75 mol% per styrene) (Fig. 3(e) and (f)). The PS-domains are very regularly distributed with uniform sizes in the case of the related triblock copolymer SBS.⁵⁶ Generation of multiblock instead of triblock copolymers may deteriorate the regularity of the phase separation of PS and PO blocks.

The polymer samples were compressed between hot plates at 110 °C to make films with 400–500 μm thickness and the films, after cutting with 100 \times 10 mm² size, were subjected to hysteresis testing where each sample was extended to 200% strain over 10 cycles to determine elastic recovery. Both the PO-PS diblock (entry 1 in Table 2) and multiblock copolymers (entry 3 in Table 2) exhibit the elastomeric property; the first cycle results in the most significant amount of permanent deformation, followed by minimal deformation on subsequent cycles (Fig. 4). However, the multiblock copolymer shows better elastomeric property than the diblock analogue; the permanent deformation of the multiblock copolymer is significantly less than that of the diblock analogue.

Conclusion

Dialkylzinc bearing an α -methylstyrene moiety (*i.e.*, $[\text{4-(isopropenyl)benzyl}]_2\text{Zn}$) was prepared for the use in so-called ‘coordinative chain transfer polymerization (CCTP)’ using a typical *ansa*-metallocene catalyst, $\text{rac}[\text{Me}_2\text{Si}(2\text{-methylindenyl})_2]\text{ZrCl}_2$ activated with modified-methylaluminoxane (MMAO) to grow PO



chains attached to zinc at one end and bearing the α -methylstyrene moiety at the other end. Switching to anionic polymerization by adding $n\text{BuLi}(\text{tmeda})_2$ in an amount to meet the criterion $[\text{Li}] > [\text{Zn}] + [\text{Al in MMAO}]$ with subsequent addition of the styrene monomer enabled growth of PS chains from the Zn-alkyl sites and α -methylstyrene moieties, thereby generating PS-*b*-PO-*b*-PS triblock units. A PS growth site was generated from the α -methylstyrene moiety by the attack of $n\text{BuLi}(\text{tmeda})_2$ and the PS growth sites on the other side were generated from the Zn-alkyl sites *via* alkyl exchange between the zinc and lithium species. Formation of a substantial amount of PS homopolymers grown from $n\text{BuLi}(\text{tmeda})_2$ was inevitable (40–50%). The amount of homo-PS was reduced due to the consumption of some $n\text{BuLi}(\text{tmeda})_2$ by the reaction with α -methylstyrene moieties and was further significantly reduced by up to 14% upon addition of a small amount of divinylbenzene (0.25–1.0 mol% per styrene). The molecular weights increased after anionic polymerization, supporting formation of the block copolymers. However, in the model reaction of $n\text{BuLi}(\text{tmeda})_2$ with α -methylstyrene in the presence of $(\text{hexyl})_2\text{Zn}$, the 1 : 2 adduct, $\text{R}-\text{CH}_2\text{C}(\text{Ph})(\text{Me})-\text{CH}_2-\text{C}(\text{Ph})(\text{Me})\text{Li}$, where R is either *n*-butyl originating from $n\text{BuLi}$ or hexyl from $(\text{hexyl})_2\text{Zn}$, was generated. This observation suggests that simple PS-*b*-PO-*b*-PS triblock copolymers were not generated, but, instead, multiblock copolymers containing PS-*b*-PO-*b*-PS units might be formed. Generation of multiblock beyond triblock deteriorates the regularity of the phase separation of PS and PO blocks.

Experimental section

General remarks

All manipulations were performed under an inert atmosphere using a standard glove box and Schlenk techniques. Methylcyclohexane and 1-octene were purchased from Sigma-Aldrich and purified over a Na/K alloy. Ethylene was purified by contact with molecular sieves and copper at 40 bar pressure. Styrene was purchased from Sigma-Aldrich. N,N,N',N' -Tetramethylethylenediamine (tmeda) was purchased from Sigma-Aldrich and purified over CaH_2 . The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a Varian Mercury Plus 400 instrument. The gel permeation chromatograms (GPC) were obtained in THF at 40 °C using a Waters Millennium apparatus or in 1,2,4-trichlorobenzene at 160 °C using a PL-GPC 220 system at Korea Polymer Testing & Research Institute. Transmission electron microscopes (TEM) images were recorded on an FEI Tecnai G2 F30 S-Twin instrument. Differential scanning calorimetry (DSC) data were collected from the second heating, performed at a heating rate of 10 °C min^{-1} using a Thermal Analysis Q10 instrument. 1-Chloromethyl-4-isopropenylbenzene was prepared by the method reported in the literature.⁴⁴

Synthesis of [4-(isopropenyl)benzyl] $_2\text{Zn}$

1-Chloromethyl-4-isopropenylbenzene (6.00 g, 36.0 mmol) in diethyl ether (20 mL) was added dropwise to a flask containing magnesium (1.31 g, 54.0 mmol) in diethyl ether (40 mL). After stirring for 4 h, the remaining Mg was removed by filtration over

Celite. ZnCl_2 (2.70 g, 18.0 mmol) was subsequently added to the filtrate. The white solids that precipitated after stirring for three days were removed by filtration over Celite. The solvent was removed under vacuum to yield a yellowish residue, which was dissolved in methylcyclohexane (200 g). After removal of the residual solid by filtration, the white solid was isolated by evaporation of the solvent under vacuum (5.31 g, 90%); the solid was pure based on ^1H and ^{13}C NMR spectral analyses. For use in polymerization as a chain transfer agent, the isolated product was recrystallized from hexane at -30 °C two additional times. ^1H NMR (400 MHz, C_6D_6): δ 7.36 (d, $J = 8.0$ Hz, 4H), 6.86 (d, $J = 8.0$ Hz, 4H), 5.44 (s, 2H), 5.00 (s, 2H), 2.04 (s, 6H), 1.55 (s, 4H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 144.21, 143.42, 127.24, 126.19, 110.63, 23.91, 22.28 ppm.

Typical procedure for anionic polymerization of styrene in the presence of $(\text{hexyl})_2\text{Zn}$ (entry 5 in Table 1)

$n\text{BuLi}$ (3.07 mg, 48 μmol) and tmeda (11.2 mg, 96 μmol) were successfully added to a flask containing $(\text{hexyl})_2\text{Zn}$ (11.3 mg, 48 μmol) and methylcyclohexane (1.0 g) inside a glove box. Styrene (2.5 g, 24 mmol) dissolved in methylcyclohexane (6.5 g) was added and the anionic polymerization was performed at 90 °C for 2 h. Complete conversion of the styrene monomer was evident from the analysis of the ^1H NMR spectrum of the sample. Aqueous HCl (2 N, 0.3 mL) was added and the resulting solution was stirred for 30 min at 90 °C to destroy the zinc species. The solution was filtered through a short pad of silica gel that was thoroughly washed with toluene. Toluene was removed by using a rotary evaporator to isolate PS; the isolated sample was dried in a vacuum oven at 130 °C for 1 h. The weight of isolated PS was identical to that of the styrene monomer fed into the system.

Typical procedure for synthesis of PO-PS block copolymers (entry 3 in Table 2)

A bomb reactor (125 mL) was charged with a solution of MMAO (AkzoNobel, 7.0 wt%-Al in heptane, 77 mg, 200 μmol -Al) in methylcyclohexane (17.0 g). After stirring for 1 h at 100 °C using a mantle, the solution was removed using a cannula. This washing procedure was performed to clean up any catalyst poisons with the MMAO solution. The reactor was again charged with a solution of 1-octene (10.0 g) and $[(4\text{-isopropenyl)benzyl}]_2\text{Zn}$ (65.6 mg, 0.200 mmol) in methylcyclohexane (17.0 g) under an inert atmosphere. The catalyst solution was prepared by reacting *rac*- $[\text{Me}_2\text{Si}(2\text{-methylindenyl})_2]\text{ZrCl}_2$ (0.48 mg, 1.0 μmol) and MMAO (77 mg, 200 μmol -Al) in methylcyclohexane (2.0 g) for 40 min. After injection of the catalyst solution with a syringe at 60 °C, ethylene gas was immediately charged into the system at 30 bar. Even though the reactor was cooled in an ice bath, the temperature increased to ~ 130 °C within 5 min due to the exothermic nature and the pressure gradually decreased due to the consumption of ethylene. Whenever the pressure reached 10 bar, ethylene gas was fed to a pressure of 15 bar and the temperature was self-controlled within the range of 120–130 °C. Twenty minutes after injection of ethylene gas, the stirring rate was decreased from 300 to 15 rpm by formation of a thick viscous solution. The olefin polymerization was



terminated by venting the remaining ethylene gas and an aliquot of the sample was taken to measure the molecular weight of the generated PO. When the ethylene feed was disconnected, the temperature decreased. When the temperature reached 90 °C, a solution of *n*BuLi(tmeda)₂ prepared by mixing *n*BuLi (32.0 mg, 0.500 mmol) and tmeda (116.2 mg, 1.00 mmol) in methylcyclohexane (2.0 g) was added to the reactor. The temperature was increased to 120 °C by heating with a mantle for 1 h under stirring, after which styrene (10.4 g, 100 mmol) was injected. The temperature was controlled in the range of 100–130 °C using a mantle. The viscosity gradually increased to reach an almost unstirrable state after 1.5 h. Full conversion of styrene and 1-octene was evident from ¹H NMR analysis of an aliquot of the reaction mixture. After complete conversion of styrene, the reactor was cooled and the generated polymers were broken into pieces with scissors. The polymer pieces were dispersed in chloroform (290 g) containing HCl (2 N, 5 mL), and the resulting mixture was refluxed overnight. When acetone (580 g) was added, the block copolymers precipitated, whereas the PS-homopolymer is soluble in the resulting co-solvent of chloroform and acetone (1 : 2 w/w). The block copolymers were isolated by filtration, and were thoroughly dried in a vacuum oven at 80 °C for several hours. The PS-homopolymers were isolated by evaporation of the solvent in the filtrate using a rotary evaporator. The residual PS-homopolymers was redissolved in chloroform and precipitated by adding methanol. The PS-homopolymers isolated by filtration were thoroughly dried in a vacuum oven at 80 °C for several hours. The weight of consumed ethylene (18.4 g) was calculated by subtracting the weights of 1-octene (10.0 g) and styrene (10.4 g) fed into the system (both of which were completely converted to polymers) from the weight of total isolated polymers [multiblock-copolymer (34.2 g) + PS-homopolymer (4.6 g)]. The GPC and TEM studies were carried out using the isolated multiblock-copolymers after separation of the PS-homopolymer.

Sample preparation for transmission electron microscopy (TEM)

The multiblock copolymer (10 mg) was completely dissolved in toluene (5 mL) by stirring at 100 °C for 20 min. A drop of the hot solution was loaded on a carbon-coated copper TEM grid (400 mesh). After evaporation of toluene at room temperature, the sample was completely dried in a vacuum oven at 130 °C for 1 h. The sample was annealed in an oven at 150 °C for 12 h. The sample was stained with RuO₄ by suspending the TEM grid coated with the film for 1 h in a closed chamber containing an aqueous solution of RuO₄, which was prepared by reacting RuO₂ (30 mg) with NaIO₄ (0.20 g) in water (5 mL) at 0 °C for 3 h.⁵⁷

Acknowledgements

This work was supported by the Korea CCS R&D Center (KCRC) grant (No. 2012-0008935) and the Priority Research Centers Program (No. 2012-0006687) funded by the Korean Government (Ministry of Science, ICT and future planning).

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