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Synthesis and Characterization of ABC Block Copolymers with Glassy (α-Methylstyrene), Rubbery (Isobutylene), and Crystalline (Pivalolactone) Blocks

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The synthesis of ternary semicrystalline poly(α-methylstyrene-b-isobutylene-b-pivalolactone) poly(αMeSt-b-IB-b-PVL) linear triblock copolymers has been accomplished for the first time, taking advantage of living cationic sequential block copolymerization and site-transformation technique from living cationic to anionic ring-opening polymerization (AROP). Poly(αMeSt-b-IB) diblock copolymer with ω-methoxycarbonyl group was successfully prepared by sequential addition of IB to living PαMeSt chain ends modified with p-chloro-α-methylstyrene, followed by capping with 1,1-diphenylethylene and in-situ quenching with 1-methoxy-1-trimethylsiloxy-propene. The poly(αMeSt-b-IB) diblock macroinitiator, prepared by subsequent hydrolysis of ω-methoxycarbonyl group, initiated AROP of PVL in conjunction with 18-crown-6 in THF at 60°C. Characterization by ^{1}H NMR spectroscopy and DSC confirmed that poly(αMeSt-b-IB-b-PVL) copolymers consisted of three microphases, low glass transition ($T_g = -66°C$) rubbery PIB, amorphous glassy PαMeSt, and high melting ($T_m = 232 \sim 235°C$) PPVL with 72 ∼ 92% of crystallinity normalized for the content of PPVL.

Keywords ABC triblock copolymer, semicrystalline, living cationic polymerization, anionic ring-opening polymerization, site-transformation

Introduction

The ability of block copolymers to self assemble into a variety of nanoscale ordered structures has been well documented. There has been recent interest in these organized structures in the newly emerging field of nanotechnology (1, 2). Successful efforts have also been reported to align and/or orient the desired defect-free morphology over macroscopic dimension at interfaces or in bulk state for use in future applications (3, 4).

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The morphology of all amorphous binary AB diblock and ABA triblock copolymers is determined by two factors: the degree of segregation of each blocks expressed in terms of the overall degree of polymerization (N) and the Flory-Huggins interaction parameter (χ), and the volume fraction of the copolymer (ϕ). Depending on the factors mentioned previously, alternating lamellae, hexagonally-packed cylinders, body-centered cubic ordered spheres, double gyroid, and perforated lamellae have been obtained below the order-disorder transition temperature (5). By introducing an additional C block to an AB diblock copolymer, tremendous morphological complexity in amorphous ternary ABC linear triblock copolymers has been revealed experimentally (6–11) and described theoretically (12, 13). The morphology of amorphous ternary ABC block copolymers in the strong segregation limit is governed by the overall degree of polymerization (N), three binary interaction parameters (χ_{AB}, χ_{BC}, χ_{AC}), two independent volume fractions (ϕ_A, ϕ_B), and the block sequence (ABC – BAC – ACB). Therefore, the self-assembly of ternary ABC block copolymers provides a unique way to create novel fascinating nanostructures which are not attainable in binary block copolymers.

Amorphous/crystalline block copolymers exhibit additional complexity of microphase morphologies as the interplay of crystallization and microphase segregation greatly influences the final equilibrium ordered states when the crystallization process takes place from the melt state of the block copolymers (14–18). If the crystallization of the crystallizable block takes place in a microphase separated melt, whole scale rearrangement of the microdomain morphology may take place. On the other hand, crystallization must proceed within the pre-existing microdomain space defined by the relative volume fractions of the components, when the crystallization proceeds below the T_g of amorphous block (19).

Compared to many experimental and theoretical works on amorphous ternary ABC block copolymers as described previously, studies on semicrystalline ternary ABC linear block copolymers have been somewhat fewer due to difficulties in the synthesis of well-defined ternary block copolymers with at least one semi-crystalline segment, as well as in the characterization of complicated self-assembled morphologies.

The first report on the synthesis of poly(styrene-*b*-butadiene-*b*-ε-caprolactone) (PSt-PB-PCL) copolymer via sequential anionic polymerization by Stadler et al. (20) stimulated research on semi-crystalline ABC linear triblock copolymers. In the case of PSt-PB-PCL copolymer, however, crystallinity of the PCL segment was relatively low (~50% based on PCL block), (21) and since the PSt and PCL blocks were predicted to be in the weak segregation regime, a considerable reduction of the T_g of PSt block was observed. The effect of block sequence on the phase behavior of linear ABC triblock copolymers was studied using polyisoprene (PI), PSt, and poly(ethylene oxide) (PEO) segments by Bates et al. (22). While PI-PSt-PEO triblock copolymer showed three distinct morphologies such as two-domain lamellae, a three-domain non-cubic triply periodic network structure, and three-domain lamellae, on the other hand, PSt-PI-PEO exhibited four different morphologies with increasing PEO content. Morphological studies (23, 24) on poly(styrene-*b*-(ethylene-*alt*-propylene)-*b*-ethylene) (PSt-PEP-PE) copolymer, prepared by catalytic hydrogenation of PSt-PI-PB copolymer, revealed the formation of cylindrical PSt microphases and crystalline PE lamellae surrounded by PEP matrix at room temperature, which was attributed to the miscibility of PEP and PE segments in the melt. However, the crystallinity of the PE segment (~30%) and the melting point was significantly lower than that of high density PE, due to the presence of the ethyl branches. Similar results were reported from the studies on crystallization in ABC linear triblock copolymers with two different crystalline end blocks (25). While the crystallization of PEO ($\leq$20 wt% of PEO) in PE-PEP-PEO triblock copolymer was confined within isolated microdomains, crystallization of PE (10–20 wt% of PE) occurred without confinement from a homogeneous melt of PE and PEP segments. In addition, PS-PE-PCL copolymer (26) exhibited considerably decreased crystallinity and T_m of PE block, and a confined crystallization of the PCL block especially when the PCL component in the ABC triblock copolymers was present as a minor phase.

Importantly, while ABA block copolymers show the existence of non-load bearing loop conformations with two ends in the same microphase domain, loop formation is absent in strongly segregated ternary ABC block copolymers, which show improved elastic behavior. For all amorphous ABC triblock copolymers relatively high molecular weight of A and C blocks is necessary to induce phase separation between the end blocks. However, ABC triblock copolymers with crystallizable end blocks are expected to show high incompatibility even at low molecular weights of the end blocks, since crystallization is a strong driving force for microphase separation. Mechanical studies on ABC triblock copolymers containing two crystallizable end blocks revealed (27) that PSt-PEP-PE triblock copolymers exhibited improved elastic properties, which was attributed to restricted loop formation. It was reported, however, that PE-PEP-PEO triblock copolymers exhibited insufficient mechanical properties as TPEs due to the low crystallization temperature of PEO block segment ($T_{c,PEO} <$ room temperature) at PEO contents below 30 wt%.

Although studies on ternary block copolymers have been promising as seen previously, the synthesis of novel model semicrystalline ternary block copolymers with high T_m, high crystallinity, and strongly segregated microphase separation even in the melt state, remains to be a challenge.

In this article, we report on the synthesis of a novel ternary semicrystalline ABC linear block copolymers based on rubbery polyisobutylene mid-block (B) with an amorphous glassy poly(α-methylstyrene) (A) and crystalline polypivalolactone (C) end-blocks. This synthetic methodology is principally based on the combination of sequential living cationic polymerization and site-transformation from living cationic to AROP, since living cationic sequential block copolymerization is unsuitable for the synthesis of amorphous/crystalline block copolymers due to the lack of suitable vinyl monomers that give rise to a crystallizable segment by cationic polymerization. As the effect of crystallization behavior on properties of block copolymers is a matter of great interest, some preliminary results on thermal and mechanical characterization are also given.

Experimental

Materials

αMeSt was purified by washing with 10% aqueous NaOH (w/w) solution three times, followed by distilled water until neutral, then dried over $MgSO_4$. After treatment with dibutylmagnesium (1.0 M solution in heptane) the monomer was finally vacuum distilled and stored at -20°C until use. Isobutylene (IB) was dried in a gaseous state by passing it through in-line gas purifier columns packed with BaO/Drierite®. It was condensed in the cold bath of a glovebox at -80°C just prior to use. Pivalolactone (PVL) was prepared by reaction of 3-chloropivalic acid (Aldrich, 99%) with sodium hydroxide according to the procedure described by Lorenz, (28) and distilled under reduced pressure. PVL was additionally dried over calcium hydride (CaH_2) for 48 h and distilled under reduced pressure just before use. *p*-Chloro-α-methylstyrene (*p*ClαMeSt) was purified by vacuum distillation after the treatment with dibutylmagnesium. 1-Methoxy-1-trimethylsiloxy-propene (MTSP) was synthesized according to Anisworth et al. (29)

2-Chloro-2,4-diphenyl-4-methylpentane (DiαMeSt◆(HCl) was prepared by hydrochlorination of 2,4-diphenyl-4-methyl-1-pentene (30). All other chemicals and solvents were purified as described previously (31, 32) or used as received.

Synthesis of Poly(α-methylstyrene-b-isobutylene) Diblock Macroinitiator

Living cationic polymerization of αMeSt was carried out at $-80°C$ under dry ($[H_2O] < 1.0$ ppm) nitrogen atmosphere in an Mbraun 150-M glovebox (Innovative Technology Inc.). A representative polymerization procedure of αMeSt was as follows: $[\alpha\text{MeSt}] = 0.17$ M, [2,6-di-*tert*-butylpyridine, DTBP] $= 3 \times 10^{-3}$ M as a proton trap, and [DiαMeSt◆(HCl)] $= 2 \times 10^{-3}$ M as an initiator in methylcyclohexane (MeChx)/ methyl chloride (MeCl) (60/40 v/v) were added to a prechilled 75 mL test tube. Then polymerization of αMeSt was initiated by adding $[BCl_3] = 6 \times 10^{-3}$ M of stock solution.

After complete polymerization of αMeSt, two different strategies of continuing the living cationic sequential block copolymerization with IB were performed.

1) Simple sequential IB addition: the second monomer [IB] = 1.4 M was transferred to the polymerization solution of αMeSt, followed by addition of $[TiCl_4] = 3.64 \times 10^{-2}$ M of stock solution.
2) Chain modification with *p*ClαMeSt, followed by sequential IB addition (33): a small amount of [*p*ClαMeSt] $= 2.0 \times 10^{-2}$ M, corresponding approximately 10 monomeric units at every PαMeSt chain ends, was added and further polymerized for additional 15 min. Then [IB] = 1.4 M was introduced, followed by addition of $[TiCl_4] = 3.64 \times 10^{-2}$ M of stock solution.

After 3 h of block copolymerization, the capping reaction of living poly(αMeSt-*b*-IB) diblock copolymer was accomplished by adding 2 equiv. of 1,1-diphenylethylene (DPE) stock solution. For subsequent *in-situ* chain-end functionalization, 2 equiv. of MTSP stock solution was added into the above reaction mixture. After 1 h reaction time, the reaction mixture was quenched with prechilled methanol and poured in NH_4OH/ methanol (10/90 v/v) to neutralize the reaction mixture. The obtained ω-methoxycarbonyl functionalized poly(αMeSt-*b*-IB) diblock copolymer was purified by repeated precipitation from hexane(Hex) into methanol, followed by drying in vacuum.

The ω-carboxylate potassium salt of poly(αMeSt-*b*-IB) diblock copolymer was obtained by the hydrolysis of methyl ester group of the above polymer: Into the reactor containing a stirred solution of polymer (2.5 g, $\overline{M}_n = 58{,}010$ g/mol, $\overline{M}_w/\overline{M}_n = 1.15$) in 35 mL of toluene, 25 mL of saturated solution of KOH (8.3%, w/v) in hexanol/water (98/2 v/v) was added. The solution was maintained at 100°C for 48 h and precipitated into methanol. The precipitated polymer was filtered and purified by repeated dissolution/precipitation in Hex/Methanol.

Synthesis of Poly(αMeSt-b-IB-b-PVL) Copolymers

Into the reactor containing [ω-carboxylate poly(αMeSt-*b*-IB) macroinitiator] $= 3.8 \times 10^{-3}$ M and 18-crown-6 with the same concentration as the initiator in THF, the required amount of PVL was added. After a specified period of time at 60°C, the obtained polymer was precipitated in acidic methanol or Hex. Then the polymer was washed, recovered by filtration, and dried under vacuum at 50°C.

Characterization

Molecular weights and molecular weight distributions of the PαMeSt homopolymer and poly(αMeSt-*b*-IB) diblock macroinitiator were measured at room temperature using Gel Permeation Chromatography (GPC) equipped with a Waters Model 510 pump, a Waters Model 410 absorbance detector, a Model 410 differential refractometer, a multi-angle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), a Waters Model 712 sample processor, and five ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, $10^5$and 100 Å. THF was used as the eluent at a flow rate of 1 mL/min. Refractive index increment (dn/dc) of poly(αMeSt-*b*-IB) diblock copolymer was calculated from the individual dn/dc values of PαMeSt and PIB using the additive rule.

^{1}H NMR spectra were measured by using a Bruker 250 MHz instrument in $CDCl_3$ for poly(αMeSt-*b*-IB) diblock macroinitiators and in a $CDCl_3$/trifluoroacetic acid (95/5 v/v) mixture for poly(αMeSt-*b*-IB-*b*-PVL) triblock copolymers (34). The number average molecular weight ($\overline{M}_n$) of the PPVL segment in block copolymers was estimated by ^{1}H NMR spectroscopy from the intensity ratio of the PαMeSt aromatic group signal at $\delta = 6.75 \sim 7.25$ ppm, and the signal of the PPVL methylene group at $\delta = 4.10$ ppm.

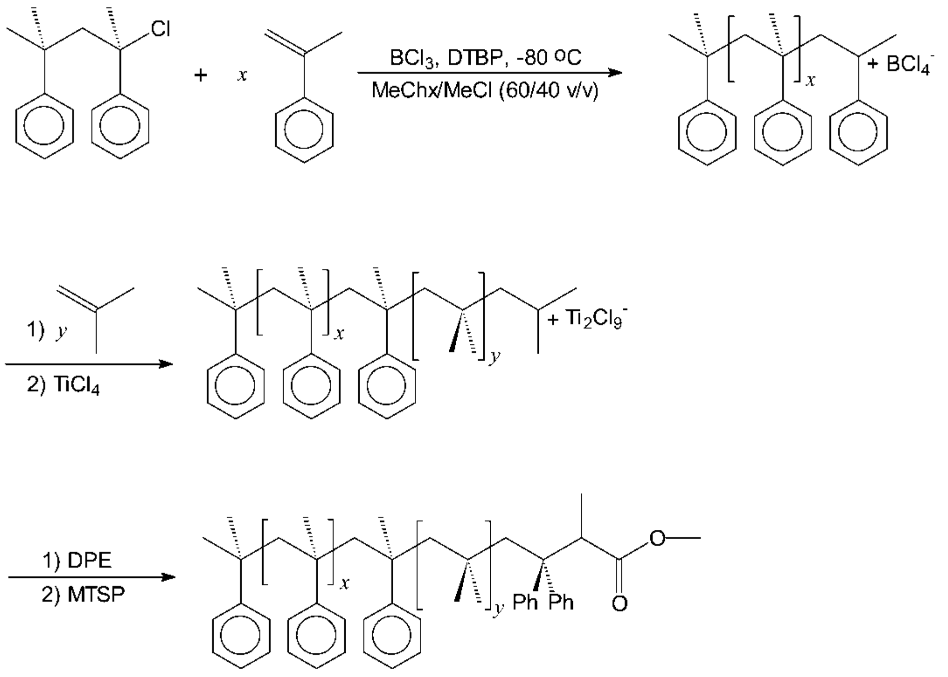
Differential scanning calorimetry (DSC) was performed with a 2910 Modulated DSC (TA Instruments) using a heating/cooling scan rate of 10°C/min in the temperature range −100°C to 250°C. Each sample was first scanned from −100°C to 250°C, maintained at that temperature for 1 min, and cooled down until −100°C. The melting temperature (T_m) of PPVL block and the glass transition temperature (T_g) of PIB segment were taken as the peak temperature of the melting endotherm and as the onset point of the specific heat jumps, respectively, in the heating scan, while crystallization temperature (T_c) of PPVL block was taken as the peak temperature of the exotherm in the cooling scan.

Optical characterization of the block copolymers were performed on a Leica DMRXP polarizing microscope equipped with a Wild Leitz MPS46 Photoautomat along with a Linkam LTS 350 hot stage and a Linkam TP92 controller. Films were prepared from an isotropic melt of the bulk samples between two microscope cover slips. The heating rate was 20°C/min and the temperature was held at 255°C for 5 min before cooling started at the rate of 10°C/min.

Results and Discussion

Synthesis of Poly(αMeSt-b-IB) Diblock Macroinitiator

Simple sequential monomer addition was attempted to obtain well-defined poly(αMeSt-*b*-IB) copolymers carrying ω-methoxycarbonyl group. As shown in Scheme 1, living PαMeSt ($\overline{M}_n = 9{,}530$ and $\overline{M}_w/\overline{M}_n = 1.13$) was first polymerized using the DiαMeSt◆(HCl/BCl_3 initiating system in the presence of DTBP as a proton trap in MeChx/MeCl (60/40 v/v) solvent mixture at −80°C, followed by the addition of IB. The polymerization of IB was further propagated by the addition of $TiCl_4$. After complete conversion of IB, *in-situ* chain-end functionalization was carried out by capping with DPE, followed by quenching with MTSP. Figure 1 demonstrates GPC chromatograms of the



Scheme 1. Synthetic route to poly(αMeSt-*b*-IB) diblock macroinitiator via sequential monomer addition of αMeSt and IB.

poly(αMeSt-*b*-IB) copolymers measured using both refractive index (RI) and ultraviolet (UV at $\lambda = 254\,\text{nm}$) detectors. Similar to the previous report (30), the GPC traces exhibit bimodal distribution in both RI and UV traces, and the smaller peak at higher elution volume was attributed to the PαMeSt homopolymer, indicating significant amount of PαMeSt homopolymer contaminant in final product. From the UV trace using a peak analysis software (PeakFit, Jandel Scientific), the blocking efficiency was calculated to be ~50%. We have previously reported (30) that upon addition of $TiCl_4$ to PαMeSt-IB_1-Cl intramolecular alkylation competes with initiation. Due to this side reaction only ~50% of the chains actually participate in initiation and the $\overline{M}_n$ of the PIB segment is much higher than theoretical (see Table 1). The PαMeSt homopolymer however could be easily removed from the product obtained after capping and functionalization by repeated fractionation using Hex/ethyl acetate mixture.

In order to avoid chain end decomposition and homoPαMeSt contamination, the living PαMeSt chain end was modified with *p*ClαMeSt after complete conversion of αMeSt (Scheme 2). It was based on our recent finding that poly(αMeSt-*b*-IB) copolymer can be prepared via capping the living PαMeSt chain ends with a few units of *p*ClαMeSt just before the addition of IB (35). The absence of chain end decomposition upon addition of $TiCl_4$ can be attributed to the reduced tendency of intramolecular alkylation due to deactivation of the aromatic ring by the *p*-chloro substituent. As presented in Figure 2, GPC traces of the block copolymer exhibited narrow molecular weight distribution in both RI and UV detection, confirming the synthesis of well-defined diblock copolymers. We assume that the oligomeric *p*ClαMeSt block segment is miscible with

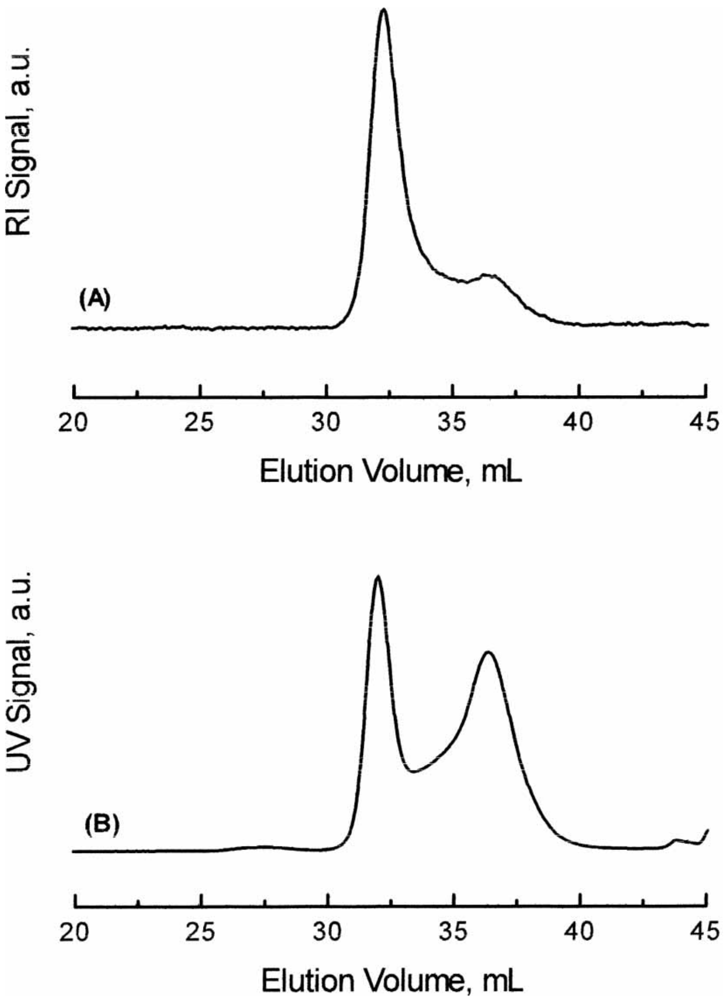


Figure 1. GPC traces of poly(αMeSt-*b*-IB) copolymer obtained via sequential monomer addition of αMeSt and IB.

the PαMeSt block and will yield one glassy microphase. Therefore for simplicity *p*ClαMeSt is omitted in the structure representation of the block copolymers.

Synthesis of Ternary Semicrystalline Poly(αMeSt-b-IB-b-PVL) Copolymers

For the synthesis of semicrystalline ABC triblock copolymers (Scheme 3), the ω-carboxylate poly(αMeSt-*b*-IB) macroinitiator obtained by hydrolysis of the ω-methoxycarbonyl end was used to initiate AROP of PVL in conjunction with 18-crown-6 in THF at 60°C. By comparison of the ^{1}H NMR spectra of the poly(αMeSt-*b*-IB-*b*-PVL) copolymer and poly(αMeSt-*b*-IB) diblock macroinitiator, it can be seen clearly that the corresponding signals attributed to the respective characteristic resonance peaks of PαMeSt, PIB, and PPVL segments are incorporated in the block copolymers, as assigned in Figure 3. To

Table 1

Results on the molecular weights and molecular weight distributions of PαMeSt homopolymers, poly(αMeSt-*b*-IB) diblock and poly(αMeSt-*b*-IB-*b*-PVL) copolymers

	P(αMeSt)		P(αMeSt-*b*-IB)		P(αMeSt-*b*-IB-*b*-PVL)	
Sample	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n^b$	wt.% ratio of each blocks[b]
ABC-1[c]	9,530	1.13	116,200[a]	1.38[a]	148,000	6.7–55.2–38.1
ABC-2[c]	9,530	1.13	69,600[a]	1.31[a]	132,000	7.5–46.8–45.7
ABC-3[d]	10,390	1.09	58,000	1.14	76,000	13.3–58.0–28.7
ABC-4[d]	10,390	1.09	58,000	1.14	91,000	11.0–54.7–34.3

[a] Measured after fractionation of unreacted PαMeSt homopolymer in P(αMeSt-*b*-IB) copolymer.

[b] Determined by ^{1}H NMR.

[c] P(αMeSt-*b*-IB) macroinitiator prepared by simple sequential monomer addition of αMeSt and IB.

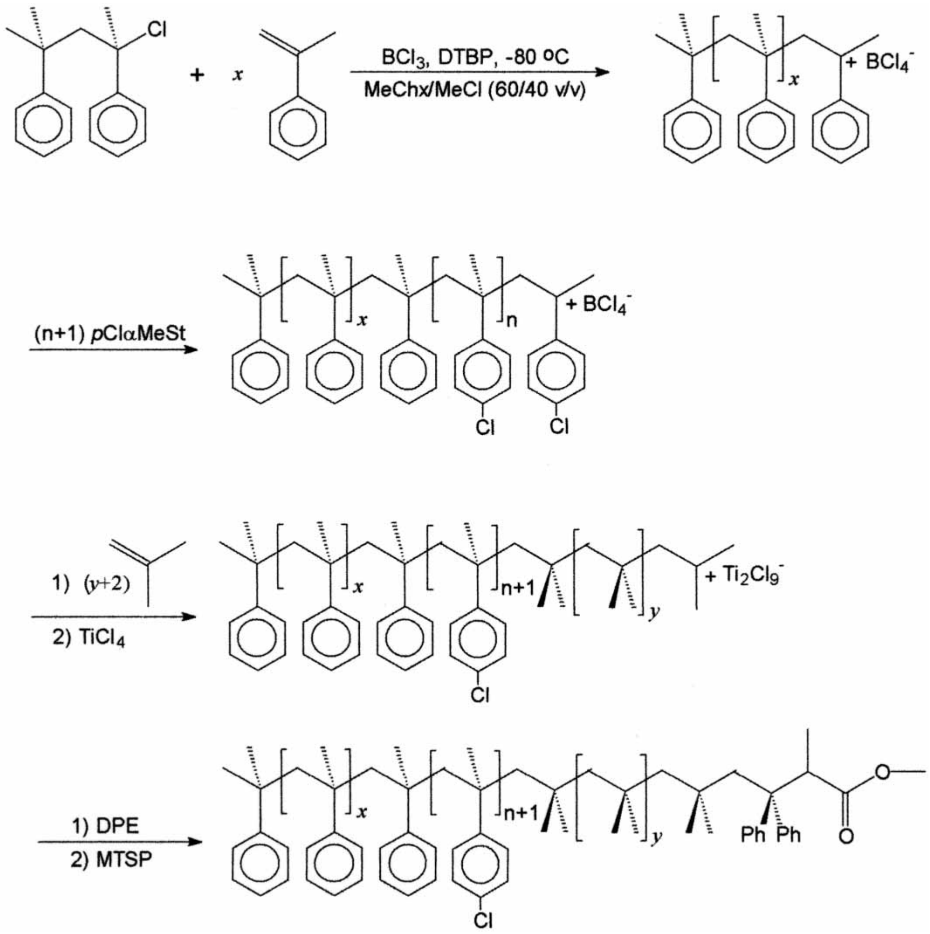
[d] P(αMeSt-*b*-IB) macroinitiator prepared by sequential monomer addition from modified PαMeSt chain ends with *p*ClαMeSt to IB.

further examine the structural integrity of the poly(αMeSt-*b*-IB-*b*-PVL) copolymers, selective solvent extraction with Hex was carried out to eliminate unreacted poly(αMeSt-*b*-IB) macroinitiator. The extracted solution was collected, dried in vacuum at 50°C for 24 h, and weighed to determine the blocking efficiency. Based on the weight of the soluble and insoluble fractions the blocking efficiency was calculated to be around 65% for all compositions. This value is much lower than the 90–96% reported for poly(IB-*b*-PVL) diblock copolymers and may be attributed to incomplete hydrolysis of the ω-methoxycarbonyl groups due to the limited solubility of high molecular weight poly(αMeSt-*b*-IB) diblock copolymer in the solvent mixture used for hydrolysis.

Molecular weights, molecular weight distributions and compositions of the pure poly(αMeSt-*b*-IB-*b*-PVL) copolymers are summarized in Table 1. The molecular weights and molecular weight distributions of PαMeSt homopolymer and poly(αMeSt-*b*-IB) copolymers were determined by GPC. Since the obtained triblock copolymers were insoluble in common organic solvents even at high temperature due to high content of PPVL segment, however, the molecular weights of PPVL segment in the block copolymers was calculated from the overall composition determined from the ^{1}H NMR spectrum (Figure 3) using the integration values of the methylene signals ($\delta = 4.10$ ppm) of PPVL blocks and the aromatic signals ($\delta = 6.75$–7.25 ppm) of PαMeSt segments.

Thermal Characterization

DSC thermograms of PαMeSt homopolymer, poly(αMeSt-*b*-IB) copolymer with 20 wt% of PαMeSt segment, and 4 different compositions of poly(αMeSt-*b*-IB-*b*-PVL) copolymers are presented in Figure 4. In Figure 4, the T_g of the PIB segment in ternary ABC triblock copolymers is observed around −70°C, which is in accordance with the value



Scheme 2. Synthetic route to poly(αMeSt-*b*-IB) diblock macroinitiator via sequential monomer addition from modified PαMeSt chain ends with *p*ClαMeSt to IB.

reported previously (32). However, although the PαMeSt homopolymer exhibited a T_g around 180°C, the T_g of PαMeSt segment in the triblock copolymers could not be detected. Even in the case of poly(αMeSt-*b*-IB) diblock copolymers with 20 wt% content of PαMeSt, we were unable to detect the T_g of PαMeSt segment. This was attributed to the limited sensitivity of DSC instrument used. The T_ms of PPVL segment in the block copolymers were clearly seen in the range of 200 ~ 240°C. From the melting enthalpy normalized for the content of PPVL segment, the degree of crystallinity (X_{PPVL}) of PPVL segment in ternary ABC block copolymers are calculated to be in the range of 72 ~ 92% (Table 2). For the calculation of the X_{PPVL}, the value of $\Delta H_m^0 = 148.4\,J/g$ was taken for 100% crystalline PPVL from the literature (36).

The crystallization behavior of the PPVL segment in ternary ABC triblock copolymers was further investigated with DSC cooling scans, as shown in Figure 5. Regardless of the content of PPVL segments in ABC block copolymers, the T_c was observed at the same temperature around 165 ~ 167°C. We have reported previously

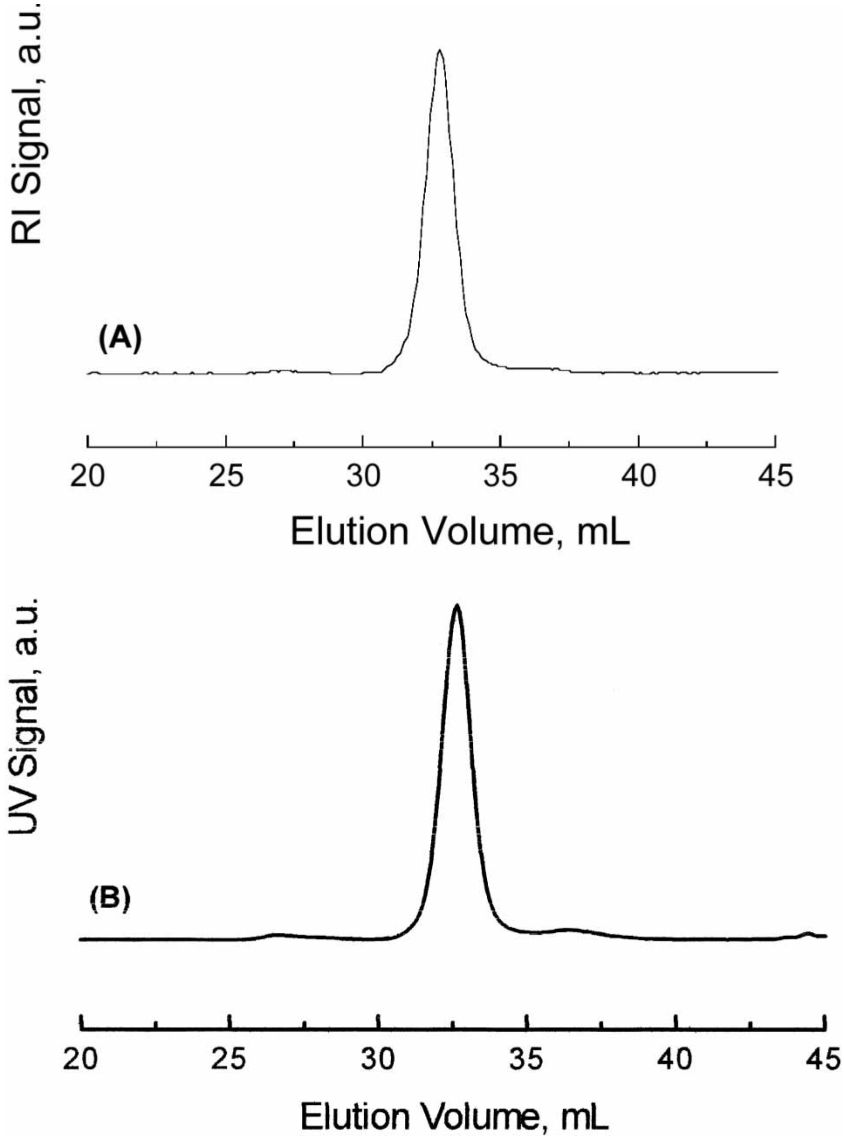
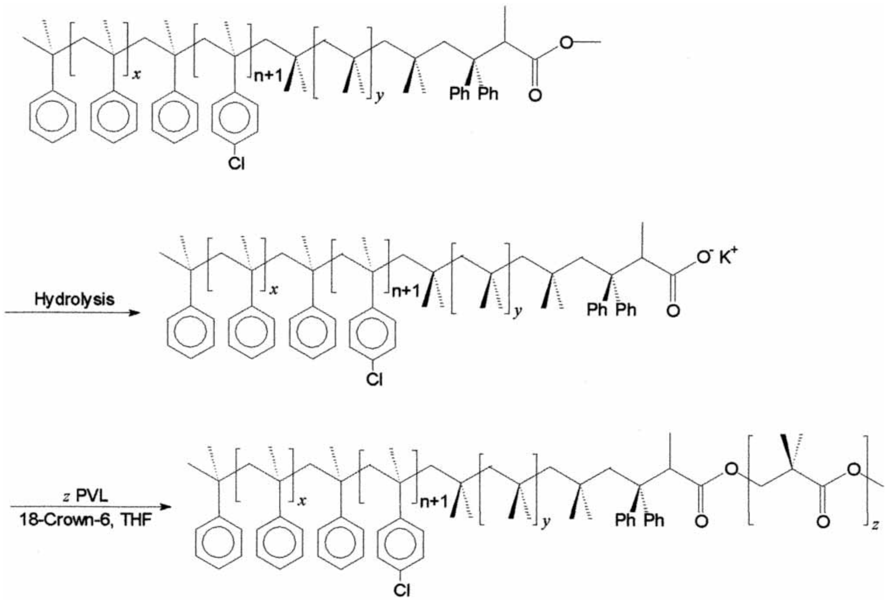


Figure 2. GPC traces of poly(αMeSt-*b*-IB) copolymer obtained via sequential monomer addition from modified PαMeSt chain ends with *p*ClαMeSt to IB.

(32) the confined crystallization of PPVL microphase in poly(IB-*b*-PVL) and poly(PVL-*b*-IB-*b*-PVL) when PPVL forms spherical or cylindrical microdomains in the melt. This also resulted in a large decrease in T_c. However, compositions that resulted in lamellar morphology showed no change in T_c and yielded large spherulitic superstructures, which is likely the case for all four ABC block copolymers. Polarized optical micrographs of semicrystalline ternary ABC copolymers are shown in Figure 6. Spherulitic superstructures of PPVL segment upon crystallization are clearly visible for all four samples, indicating the replacement of the melt microstructure by a crystallization-driven spherulitic lamellar



Scheme 3. Synthetic route to poly(αMeSt-*b*-IB-*b*-PVL) copolymer.

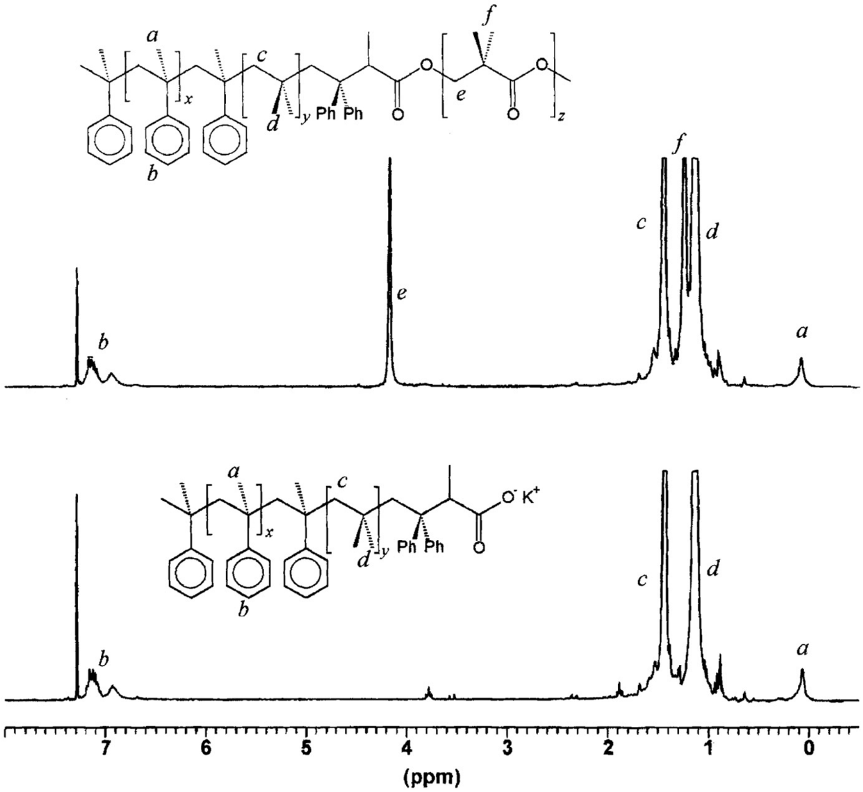


Figure 3. ^{1}H NMR spectra of poly(αMeSt-*b*-PVL) copolymer and poly(αMeSt-*b*-IB) macroinitiator.

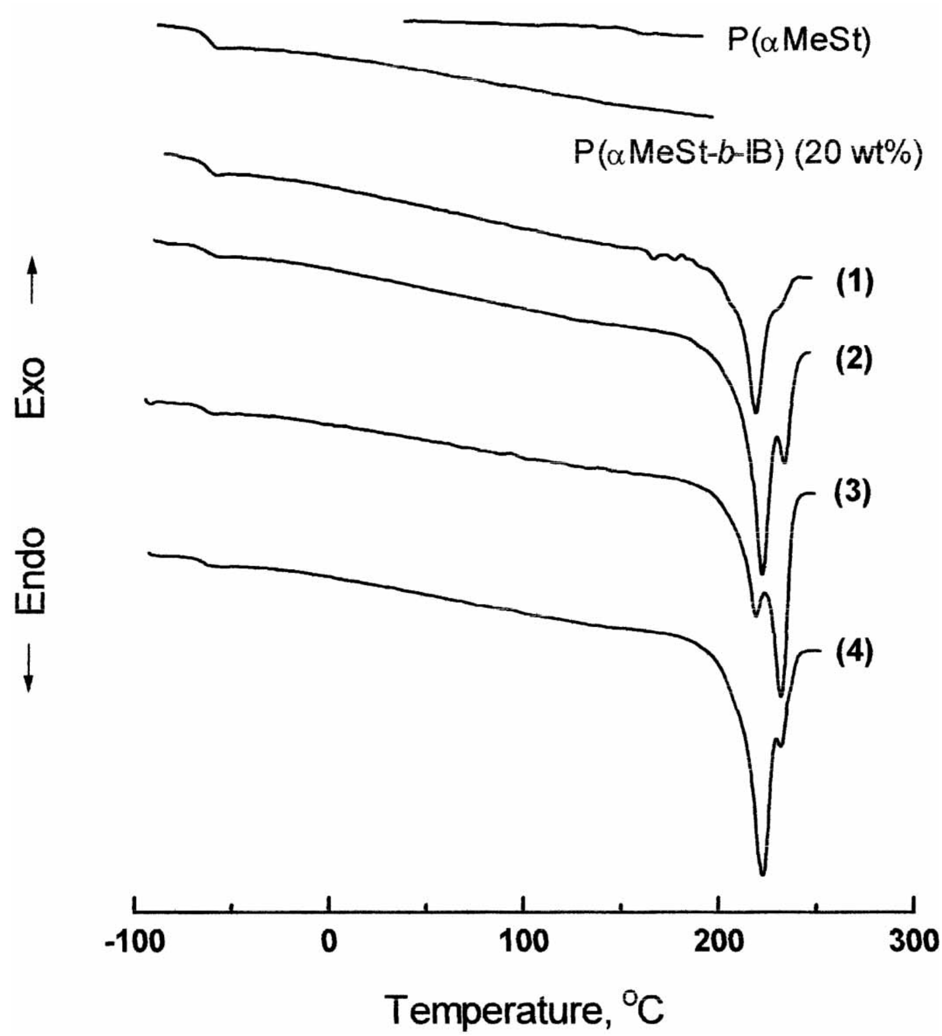


Figure 4. DSC heating traces of PαMeSt homopolymer, poly(αMeSt-*b*-IB) copolymer with 20 wt% of PαMeSt segment, and poly(αMeSt-*b*-IB-*b*-PVL) copolymers, (1) ABC-1, (2) ABC-2, (3) ABC-3, (4) ABC-4.

Table 2
Glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c) for block copolyemrs determined from DSC

Sample	T_g of PIB (°C)	T_m of PPVL (°C)	T_c of PPVL (°C)	% Crystallinity ($\Delta H_m/\Delta H_m^o$)
ABC-1	−66	232	167	71.7
ABC-2	−66	235	166	81.4
ABC-3	−67	234	165	73.8
ABC-4	−65	235	167	92.0

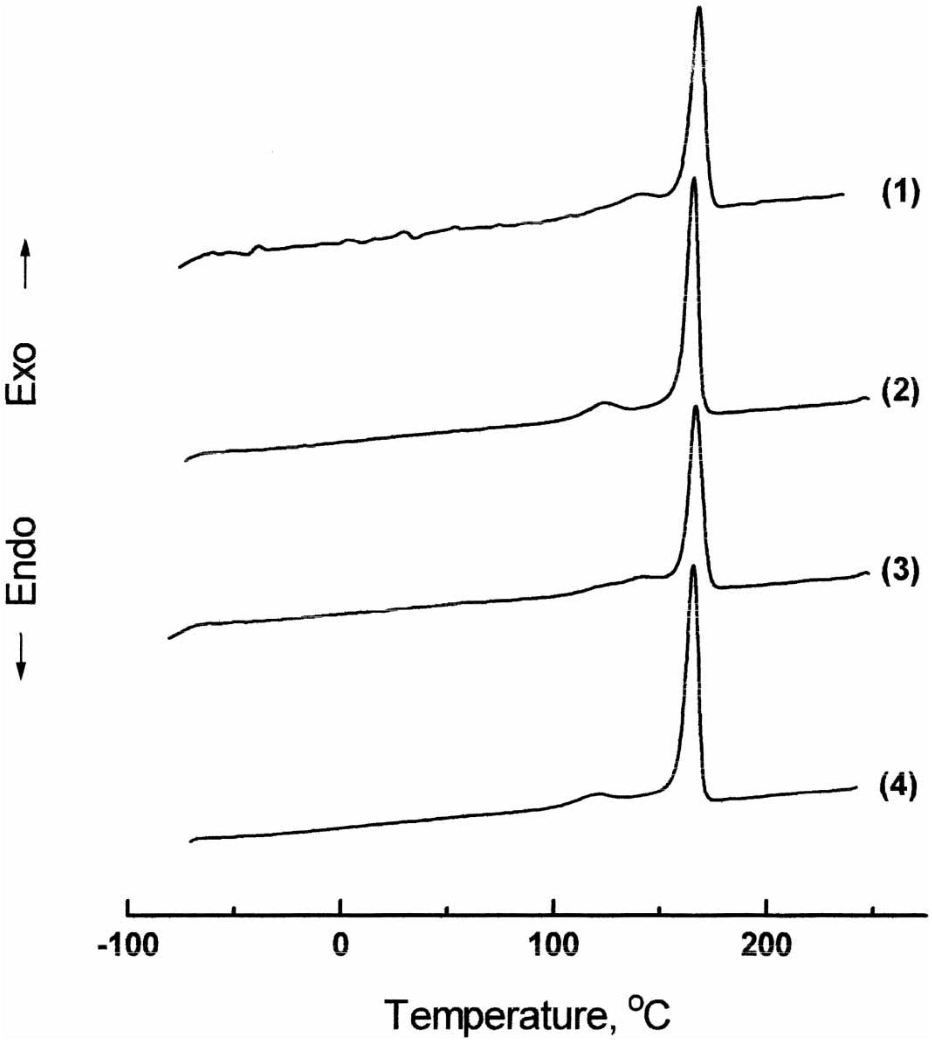


Figure 5. DSC cooling traces of poly(*α*MeSt-*b*-IB-*b*-PVL) copolymers, (1) ABC-1, (2) ABC-2, (3) ABC-3, (4) ABC-4.

morphology radiating from the nucleation center. It is similar to previously reported result on semicrystalline ternary PS-PB-PCL (37). Considering the composition of ABC-3 containing 28.7 wt% PPVL, however, it is somewhat surprising to observe the spherulitic morphology for ABC-3, which is expected to form cylinders. Morphology of compression-molded ABC triblock copolymers was studied using transmission electron microscopy (TEM), along with RuO_4 staining of ultrathin section of samples. The morphology of ABC triblock copolymers could not be identified clearly, since the staining selectivity of the RuO_4 was inefficient for distinguishing three different phases of triblock copolymers (38). It is clear from Figure 6, however, that ABC-3 shows much less defined spherulites compared to the other three samples. Due to the small sample size a detailed study of the mechanical properties could not be undertaken. A limited study revealed that ABC-2

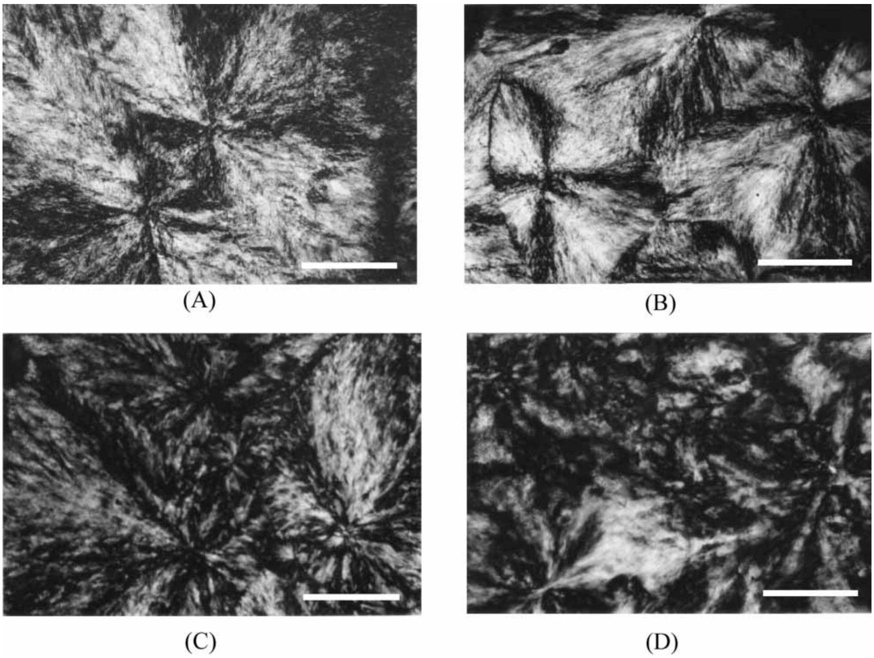


Figure 6. Polarized optical micrographs taken at T_c of each sample by 10°C/min of cooling rate from the melt, (1) ABC-1, (2) ABC-2, (3) ABC-3, (4) ABC-4. (Scale bar = 250 μm)

(αMeSt/IB/PVL = 7.5/46.8/45.7 wt%) exhibited 38.5 MPa tensile strength, 10.7 MPa modulus, and 53% ultimate elongation.

Conclusions

The synthesis of ternary semicrystalline poly(αMeSt-*b*-IB-*b*-PVL) linear triblock copolymers was successfully achieved via combination of sequential living cationic polymerization and site-transformation from living cationic to AROP. First, sequential living cationic polymerization from living PαMeSt chain ends to IB was carried out to obtain the precursor of poly(αMeSt-*b*-IB) diblock macroinitiator. However, this method resulted in significant PαMeSt homopolymer contamination due to low crossover efficiency.

By employing the modified sequential monomer addition, poly(αMeSt-*b*-IB) diblock macroinitiator carrying ω-carboxylate potassium salt was successfully prepared, in which sequential monomer addition from living PαMeSt chain ends modified with *p*ClαMeSt to IB was utilized to achieve quantitative crossover efficiency. After complete conversion of IB, capping with DPE, followed by *in-situ* quenching with MTSP resulted in poly(αMeSt-*b*-IB) copolymer having methoxycarbonyl end group at chain ends. Poly(αMeSt-*b*-IB) diblock macroinitiator, prepared by subsequent hydrolysis of ω-methoxycarbonyl group, initiated AROP of PVL in conjunction with 18-crown-6 in THF at 60°C. Characterization by ^{1}H NMR spectroscopy, and DSC confirmed that poly(αMeSt-*b*-IB-*b*-PVL) copolymers were obtained with low glass transition ($T_g = -66$°C) rubbery PIB, amorphous glassy PαMeSt, and high melting ($T_m = 232 \sim 235$°C) PPVL with $72 \sim 92$% of crystallinity.

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