Preparation of periodic copolymers by living anionic polymerization mechanism assisted with a versatile programmed monomer addition mode

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ABSTRACT

Assisted by a versatile programmed monomer addition mode, the well-defined periodic Poly(styrene-*per*-isoprene) [Poly(St-*per*-Is)] copolymers are innovatively prepared by living anionic polymerization (LAP) of a general monomer pair of styrene and isoprene. For comparison, the random Poly(St-*ran*-Is) and diblock PS-*b*-PI copolymers are also synthesized. The Differential Scanning Calorimetry (DSC) analysis shows that the periodic Poly(St-*per*-Is) copolymers always have relatively higher glass transition temperature (T_gs) than the corresponding random Poly(St-*ran*-Is) analogues with the same molar ratio [St]/[Is] and close molecular weight (MW). The T_gs of copolymers follow a general tendency of $T_{g,\text{Poly(St-}per\text{-Is)}} > T_{g,\text{PS-}b\text{-PI}} > T_{g,\text{Poly(St-}ran\text{-Is)}}$. The reason is rationalized to the different sequence of styrene and isoprene units arranged along the copolymers.

1. Introduction

Enlightened by the unique functions of natural bio-macromolecules with well-defined sequence, the sequence copolymers are attracting more and more attentions in recent years [1–11]. However, the efficient synthesis of these copolymers remains an outstanding challenge. Among all the attempts, the solid-phase synthesis [12,13], template synthesis [14–16] and iterative exponential growth [17,18] represented the mostly promising and, however, were largely limited with their complicated operation procedure and low producing yield. The conventional free radical polymerization showed limited possibility in synthesis of sequence copolymers due to the low selectivity of growing species to monomers in a copolymerization system. Up to now, the copolymerization of monomer pair of maleimide and styrene was found as the only successful example for the synthesis of alternative copolymers. In such case, once the electron-rich styrene or electron-deficient maleimide was added onto copolymer, the formed radical at copolymer end could alter the activity of growing species, which showed less homopolymerization tendency and favored copolymerization by adding a different monomer. Later, assisted with the well developed controlled radical polymerization (CRP) techniques, such as atom transfer radical polymerization (ATRP), nitroxide controlled radical polymerization (NMRP), and reversible addition-fracture chain transfer polymerization (RAFT), the sequence copolymer further gained improved control [19–27]. For example, Lutz *et al* contributed the excellent works and synthesized a series of encoding copolymers by a periodic addition of mailmide into the ATRP of styrene [28,29].

Aiming to enrich the kinds of sequence copolymers and synthesize sequence copolymers from other monomer pairs with less selectivity on growing species, the monomer addition procedure was also improved to increase the possibility to sequence copolymers. For example, by simulating the polymerization kinetics, Luo *et al* prepared a series of sequence copolymers by either RAFT or ATRP technique using a programmed monomer addition procedure [30,31]. Similarly, Broadbelt *et al* succeeded the synthesis of sequence copolymer by NMRP technique [32]. However, due to the readily happened side reactions (such as the combination termination, disproportionation termination, and chain transfer) on growing macro-radicals in the monomer-starvation state, the

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copolymerization system should always keep at a low monomer conversion. Thus, the remained monomers would complicate the monitoring on polymerization process and the addition rate of monomers was always challenged. In most cases, the copolymers were still obtained with defective sequence.

Alternatively, the living anionic polymerization (LAP) was always employed to target model polymers with controlled structure, compositions, molecular weight (MW) and narrow molecular weight distribution (M_w/M_n). Unlike the controlled radical copolymerization, the species in LAP are very stable in a monomer-starvation state. The monomer conversion in LAP can also be readily modulated due to the predictable polymerization kinetics. These advantages would facilitate the synthesis of sequence copolymers by a LAP technique [33–36]. However, up to now, only limited alternating copolymers have been produced by LAP using the monomer pairs containing a non-hompolymerizable monomer [37–39], such as the combination of diphenylethylene (DPE) and styrene (St) or isoprene (Is). Obviously, the control on monomer sequence in LAP system also majorly depended on the reactivity ratios of monomers. The available monomer pairs to sequence copolymers were still limited, and the general monomers were mostly excluded [40–42].

In this contribution, assisted by a versatile programmed monomer addition mode, the well-defined sequence copolymers was synthesized. In detail, the periodic Poly(styrene-*per*-isoprene) [Poly(St-*per*-Is)] copolymers were firstly prepared by LAP mechanism by using a general monomer pair of styrene and isoprene (Scheme 1). The random Poly(St-*ran*-Is) and diblock PS-*b*-PI copolymers with different monomer sequence were also synthesized and used for comparison on their thermal property. The results led to a conclusion that the thermal property had much dependence on monomer sequence arranged along the copolymers.
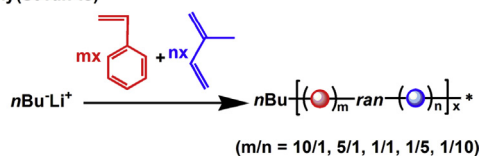
2. Materials and methods

2.1. Materials

Styrene (St, 99%, Sinopharm Chemical Reagent Co. (SCR)) was dried over CaH_2 and distilled under reduced pressure before use.
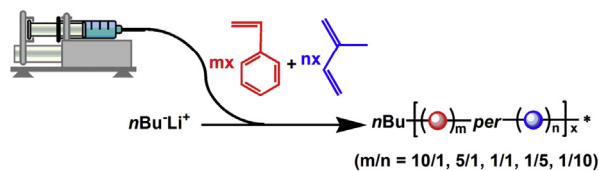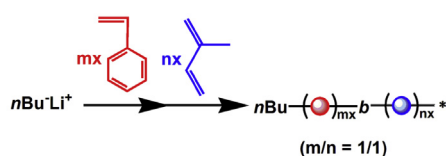

Scheme 1. The illustrated synthetic procedure for periodic Poly(St-*per*-Is) (A), random Poly(St-*per*-Is) (B) and diblock copolymer PS-*b*-PI (C).

Isoprene (Is, 99%, SCR) and cyclohexane (99%, SCR) were dried over CaH_2 and distilled before use. Tetrahydrofuran (THF, 99%, SCR) was refluxed and distilled from potassium naphthalenide solution. *n*-Butyllithium (*n*Bu$^-$Li$^+$, 1.6 M in hexane, J&K) was used as received. All other reagents were purchased from SCR and used as received except for additional declaration.

2.2. Synthesis of periodic copolymer Poly(St-per-Is)

In a typical example for copolymerization with feed molar ratio [St]/[Is] = 1/1, the mixture of solvents cyclohexane (150 mL) and THF (10 mL), metered *n*Bu$^-$Li$^+$ (5.5 mL, 8.0 mmol) were sequentially introduced into a 500 mL ampoule. Subsequently, the mixture of monomers styrene (26.6 mL, 0.23 mol) and isoprene (23.2 mL, 0.23 mol) was injected into the above ampoule in 8.0 h with a constant addition rate controlled by a programmed syringe pump (KDScientific Legato 100). The polymerization was finally terminated by addition of 4.0 mL acidic methanol (0.1 M HCl). The mixture was concentrated and precipitated into methanol for three times. The product was collected as periodic Poly(St-*per*-Is) and further dried under vacuum to a constant weight. ^{1}H NMR (CDCl$_3$, δ, ppm, TMS): 0.80 (C**H**$_3$CH$_2$-), 1.26–2.25 (m, -C(C**H**$_3$)- on PI, aliphatic main chain -C**H**$_2$C**H**- on PI and PS), 1.86 (m, -C(C**H**$_3$)=CH- of 1,4-addition, -C(C**H**$_3$)=CH$_2$ of 3,4-addition), 4.63–4.69 (-(CH$_3$)C=C**H**$_2$ of 3,4-addition), 4.95 (-CH=C**H**$_2$ of 1,2-addition), 5.08 (-C**H**=C(CH$_3$)- of 1,4-addition), 5.70 (-C**H**=CH$_2$ of 1,2-addition), 6.30–7.30 (m, 5H, aromatic -C$_6$**H**$_5$ on PS). SEC: $M_{n,SEC} = 4670$ g/mol, $M_w/M_n = 1.07$.

2.3. Synthesis of random copolymer Poly(St-ran-Is)

In a typical example for copolymerization with feed molar ratio [St]/[Is] = 1/1, the mixture of solvents cyclohexane (150 mL) and THF (10 mL), mixture of monomers styrene (26.6 mL, 0.23 mol) and isoprene (23.2 mL, 0.23 mol) were sequentially introduced into a 500 mL ampoule. Subsequently, the metered *n*Bu$^-$Li$^+$ (5.5 mL, 8.0 mmol) was rapidly injected into the ampoule to start the polymerization. The termination and purification procedure were similar to that for the above periodic Poly(St-*per*-Is). The product was collected as random Poly(St-*ran*-Is) and further dried under vacuum to a constant weight. ^{1}H NMR (CDCl$_3$, δ, ppm, TMS): 0.80 (C**H**$_3$CH$_2$-), 1.26–2.25 (m, -C(C**H**$_3$)- on PI, aliphatic main chain -C**H**$_2$C**H**- on PI and PS), 1.86 (m, -C(C**H**$_3$)=CH- of 1,4-addition, -C(C**H**$_3$)=CH$_2$ of 3,4-addition), 4.63–4.69 (-(CH$_3$)C=C**H**$_2$ of 3,4-addition), 4.95 (-CH=C**H**$_2$ of 1,2-addition), 5.08 (-C**H**=C(CH$_3$)- of 1,4-addition), 5.70 (-C**H**=CH$_2$ of 1,2-addition), 6.30–7.30 (m, 5H, aromatic -C$_6$**H**$_5$ on PS). SEC: $M_{n,SEC} = 4810$ g/mol, $M_w/M_n = 1.06$.

2.4. Synthesis of homopolymer PS and PI, and diblock copolymer PS-b-PI

The synthetic procedure for PS and PI, and diblock copolymer PS-*b*-PI was similar to that for random Poly(St-*ran*-Is). For the homopolymer PS and PI, the above mixture of monomers was replaced by pure styrene or isoprene, respectively. For diblock copolymer, the sequential addition technology of styrene and isoprene was adopted. SEC: PS, $M_{n,SEC} = 4590$ g/mol, $M_w/M_n = 1.06$; PI, $M_{n,SEC} = 5410$ g/mol, $M_w/M_n = 1.05$; PS-*b*-PI, $M_{n,SEC} = 5850$ g/mol, $M_w/M_n = 1.07$.

2.5. Characterization

The molecular weight (MW) and molecular weight distribution (M_w/M_n) of polymers were analyzed by size exclusion chromatography (SEC) measurement, which was performed in THF at 35 °C