

SYNTHESIS OF TRIBLOCK COPOLYMERS OF STYRENE AND ISOPRENE BY A NITROXIDE-MEDIATED LIVING FREE RADICAL POLYMERIZATION

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Abstract The controlled free radical polymerization of styrene and isoprene initiated with benzoyl peroxide (BPO) in the presence of 2,2,6,6-tetramethyl piperidine-*N*-oxyl (TEMPO) at 125 °C were performed. The obtained polyisoprene and polystyrene homopolymers served as macroinitiators for block copolymerization of isoprene and styrene to synthesize poly(styrene-*b*-isoprene) and poly(isoprene-*b*-styrene) diblock copolymers. Diblock copolymers with well-defined structures as well as controlled and narrow molecular weight distribution were obtained from the lower-mass polystyrene and polyisoprene homopolymers. These copolymers were found to be active as macroinitiators in the synthesis of the poly(styrene-*b*-isoprene-*b*-styrene) and poly(isoprene-*b*-styrene-*b*-isoprene) triblock copolymers. ¹H-NMR spectroscopy and gel permeation chromatography (GPC) were used for the investigation of polymer structure, molecular weight and polydispersity (PD).

Keywords Diblock and triblock copolymer, Controlled radical polymerization, TEMPO, Polystyrene, Polyisoprene

INTRODUCTION

The control of molar mass characteristics and monomer sequence in block copolymers is becoming increasingly important in macromolecular science. Radical polymerization initiated by alkoxyamines has attracted much attention because it exhibits the characteristics of living polymerizations^[1–6].

Living free radical polymerization strategy initially introduced by Rizzardo and coworkers was originally used to advantage in the control of polydispersities by Georges *et al.* Georges and coworkers employed a bimolecular initiating system consisting of benzoyl peroxide (BPO) and excess 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO)^[7–10]. The resulting polymers have been shown to have narrow molecular weight distributions, well-defined chain lengths and complex architecture.

Recently living free radical polymerization has been used for preparing block copolymers of styrene with acrylate, vinylpyridine, acrylonitrile, butadiene and isoprene^[11–14]. Georges *et al.*^[13] studied this reaction using a TEMPO-functionalized polystyrene. On heating, polystyryl radical initiated the polymerization of 1,3-butadiene, controlled by TEMPO, hence leading to poly(styrene-*b*-butadiene) block copolymers. Another method was suggested by Kobatake *et al.*^[15] who reported the synthesis and characterization of benzyloxyamine functionalized with an epoxide end-group that acts as a terminator in the anionic polymerization of 1,3-butadiene, leading to a nitroxy-functionalized polybutadiene. This polybutadiene was used as original macroinitiator for the radical controlled polymerization of styrene, leading to poly(butadiene-*b*-styrene) block copolymer^[16].

Interestingly, Benoit *et al.*^[17] investigated the use of α -hydridoalkoxyamines as counter radicals in the radical controlled homopolymerization of 1,3-dienes and copolymerization of 1,3-dienes, with various functionalized vinyl monomers leading to random and block copolymers.

Although the versatile use of controlled free radical polymerization is actually restricted by a limited number

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of applicable monomers and elevated temperatures (higher than 100 °C), it offers great potential for the preparation of well defined block copolymers and represents distinct advantages over other living systems presently used for block copolymer synthesis^[18–22]. First, the polymerization process does not require high purity monomers and does not need special precautions to ensure anhydrous conditions. Secondly, since the initial *N*-oxyl-capped polymers are stable in air and at room temperature, they can be isolated, purified and stored. Therefore in block copolymer preparation the first block can be synthesized, stored and used as macroinitiator as it is needed^[21].

Therefore, in the present work we employed living radical polymerization as described above for the synthesis of poly(styrene-*b*-isoprene-*b*-styrene) (SIS) and poly(isoprene-*b*-styrene-*b*-isoprene) (ISI). When the coupling technique is used problems associated with producing pure end functional polymers and difficulties associated with conducting reactions between polymers may be encountered. Proton H-NMR spectroscopy and GPC were used to investigate the structure of all polymers.

EXPERIMENTAL

Materials and Analysis

The styrene (Fluka) was distilled under reduced pressure. Isoprene (Merck) was distilled prior to use. BPO was obtained from Merck and purified by reprecipitation from chloroform into methanol. TEMPO was prepared according to the literature procedure^[23–25]. Acetone, calcium chloride, ammonium chloride, *para*-nitrotoluene, hydrazine hydrate ($\text{NH}_2\text{NH}_2 \cdot x\text{H}_2\text{O}$, $x \approx 1.5$, $d = 1.024 \text{ g/mL}$) and solvents were purchased from Merck and used without further purification.

¹H-NMR spectra were recorded on FT-NMR 500 MHz. The molecular weight of the resulting polymers was obtained with a Maxima 820 GPC analysis instrument using polystyrene (10^5 , 10^4 , 10^3 nm) calibration standards with tetrahydrofuran (THF) as the mobile phase.

Preparation of Polystyrene-TEMPO (PS-TEMPO)

PS-TEMPO adducts were prepared as described previously^[26]. In a typical run, a mixture of styrene, BPO ($6.09 \times 10^{-2} \text{ mol L}^{-1}$) and TEMPO ($8 \times 10^{-2} \text{ mol L}^{-1}$) was transferred to a glass tube, degassed with several freeze-thaw cycles, and sealed under vacuum. Then the mixture was heated at 95 °C for 3.5 h and at 125 °C for 6 h to yield a polymer. The polymer was recovered by precipitation from a large excess of methanol purified by reprecipitation with a chloroform (solvent)/methanol (nonsolvent) system and thoroughly dried (yield 31%), which according to the PS-calibrated GPC, had a number-average molecular weight M_n of 4270 and $PD = 1.11$.

Preparation of Polyisoprene-TEMPO (PI-TEMPO)

A mixture of isoprene, BPO ($9 \times 10^{-2} \text{ mol L}^{-1}$) and TEMPO ($11.8 \times 10^{-2} \text{ mol L}^{-1}$) was transferred to a glass tube degassed with several freeze-thaw cycles, and sealed under vacuum. The tube was heated at 95 °C for 6 h and at 125 °C for 70 h to yield a polymer. The polymer was recovered by precipitation from a large excess of methanol and was dried under vacuum to constant weight (yield 40%). M_n of the polymer was 4500 and $PD = 1.31$.

Preparation of Poly(styrene-*b*-isoprene)

In a polymerization ampoule were placed 0.20 g of the PS-TEMPO sample (prepared as described above) and 2.0 g of isoprene. After dissolving the PS-TEMPO in isoprene, the solution was degassed and sealed under vacuum. The copolymerization reaction was allowed to proceed at 125 °C. The copolymer was precipitated from methanol and isolated by filtration and finally dried (yield 20%). The characteristics of the block copolymer are summarized in Table 1.

Preparation of Poly(isoprene-*b*-styrene)

To a polymerization ampoule were added 0.20 g of PS-TEMPO and 2.0 g of styrene. The mixture was degassed and sealed under vacuum. The polymerization reaction was allowed to proceed at 125 °C. The copolymer was then precipitated from methanol and isolated by filtration and finally dried (yield 60%). The reaction time and characteristics of the block copolymer are shown in Table 2.

Preparation of Poly(styrene-*b*-isoprene-*b*-styrene)

To a polymerization ampoule were added 0.2 g of a poly(styrene-*b*-isoprene) diblock copolymer (prepared as described above), 2.0 g of styrene and a small amount of acetic anhydride. The mixture was degassed and sealed under nitrogen. The polymerization reaction was allowed to proceed at 125°C. The triblock copolymer was then precipitated from methanol and isolated by filtration and finally dried (yield 40%). Table 1 summarizes the results.

Preparation of Poly(isoprene-*b*-styrene-*b*-isoprene)

Into a polymerization ampoule were placed 0.2 g of the poly(isoprene-*b*-styrene) sample and 2.0 g of isoprene. The solution was degassed and sealed under vacuum. The polymerization reaction was allowed to proceed at 125°C for 70 h. The triblock copolymer was precipitated from methanol, isolated by filtration and finally dried (yield 25%). The results were collected in Table 2.

Table 1. Molecular weight and polydispersity for PS-T, PS-*b*-PI-T and PS-*b*-PI-*b*-PS-T

Sample	Initiator	Time (h)	Yield (%)	M_n	M_w	PD
PS-T	BPO-T	6	31	4270	4730	1.11
PS- <i>b</i> -PI-T	PS-T	60	20	9760	11390	1.17
PS- <i>b</i> -PI- <i>b</i> -PS-T	PS- <i>b</i> -IP-T	3	40	30570	49020	1.60

Table 2. Molecular weight and polydispersity for PI-T, PI-*b*-PS-T and PI-*b*-PS-*b*-PI-T

Sample	Initiator	Time (h)	Yield (%)	M_n	M_w	PD
PI-T	BPO-T	70	40	4500	5900	1.31
PI- <i>b</i> -PS-T	PI-T	6	60	15150	19630	1.30
PI- <i>b</i> -PS- <i>b</i> -PI-T	PI- <i>b</i> -PT-T	70	25	25190	35990	1.43

RESULTS AND DISCUSSION

Since TEMPO is most widely employed as nitroxyl mediator, we initially attempted to study the polymerization of styrene and isoprene with TEMPO at 125°C. Living radical polymerization of styrene was performed in bulk by using BPO as an initiator in the presence of TEMPO at 125°C for 6 h, after being held at 95°C for 3.5–4 h according to the method described in the literature^[26, 27]. Reaction of TEMPO-terminated polystyrene with isoprene resulted in the formation of PS-*b*-PI-T, and reaction of PS-*b*-PI-T with styrene resulted in the formation of PS-*b*-PI-*b*-PS triblock copolymer, whose GPC chromatogram showed a distinct shift to higher molecular weight. The polydispersity remained respectively low and the absence new or residual peaks in the GPC indicates that the product is free of polyisoprene and polystyrene homopolymer (Fig. 1). We also performed a blank polymerization of styrene and isoprene under the same conditions similar to original experiments and observed that in the case of isoprene no thermal homopolymer occurred and in the case of styrene no collectable amount of polystyrene was obtained. The molecular weight and molecular weight distribution of PS-T, PS-*b*-PI-T and PS-*b*-PI-*b*-PS obtained from the above living radical polymerization are summarized in Table 1.

Diblock copolymers of styrene and isoprene were synthesized using the nitroxide-mediated free radical polymerization process for the purpose of showing that the chain-terminating nitroxyl group from the end of the first block to the end of the second block is unequivocally demonstrated by ¹H-NMR spectroscopy. To demonstrate the transfer of chain-capping nitroxyl group from the first to the second block, low molecular weight block copolymers were prepared so that the end group of the polymer chain could be easily monitored by ¹H-NMR spectroscopy. Attention was focused on the resonance of the methyl groups of the nitroxyl (piperidinyloxy) unit, the chemical shifts of which were expected to be different, depending on whether the nitroxyl group was attached to a styrene or to an isoprene monomer unit.

The resonance of the benzylic methine and allylic methylene protons of the styrene and isoprene monomer units bonded to the piperidinyloxy group was also monitored (b and c, respectively, in structures 1 and 2).

Figure 2 shows the ¹H-NMR spectrum of polystyrene-TEMPO (PS-T: M_n = 4270, PD = 1.11) obtained from

living radical polymerization of styrene initiated by TEMPO/BPO. It is obvious that the signals at both $\delta = 1.49\text{--}1.91$ and $\delta = 6.65\text{--}7.28$ could be attributed to methylene, methine and aromatic protons of styrene respectively. The signals of proton derived from the piperidinyloxy methyl resonance of TEMPO ($\delta = 0.19\text{--}1.07$) are also observed. Three broad resonances (b; inset of Fig. 2) centered at $\delta = 4.03$, 4.45 and 4.60 were assigned to the benzylic proton of the styrene unit bonded to the piperidinyloxy group. Polystyrene tacticity effects cause this methine resonance to split into three resonances. Between these peaks is a broad, complex resonance ($\delta = 4.14\text{--}4.39$) similarly assigned to the methylene protons of the styrene unit attached to the benzoate group at the initiating chain end (a; structure 1).

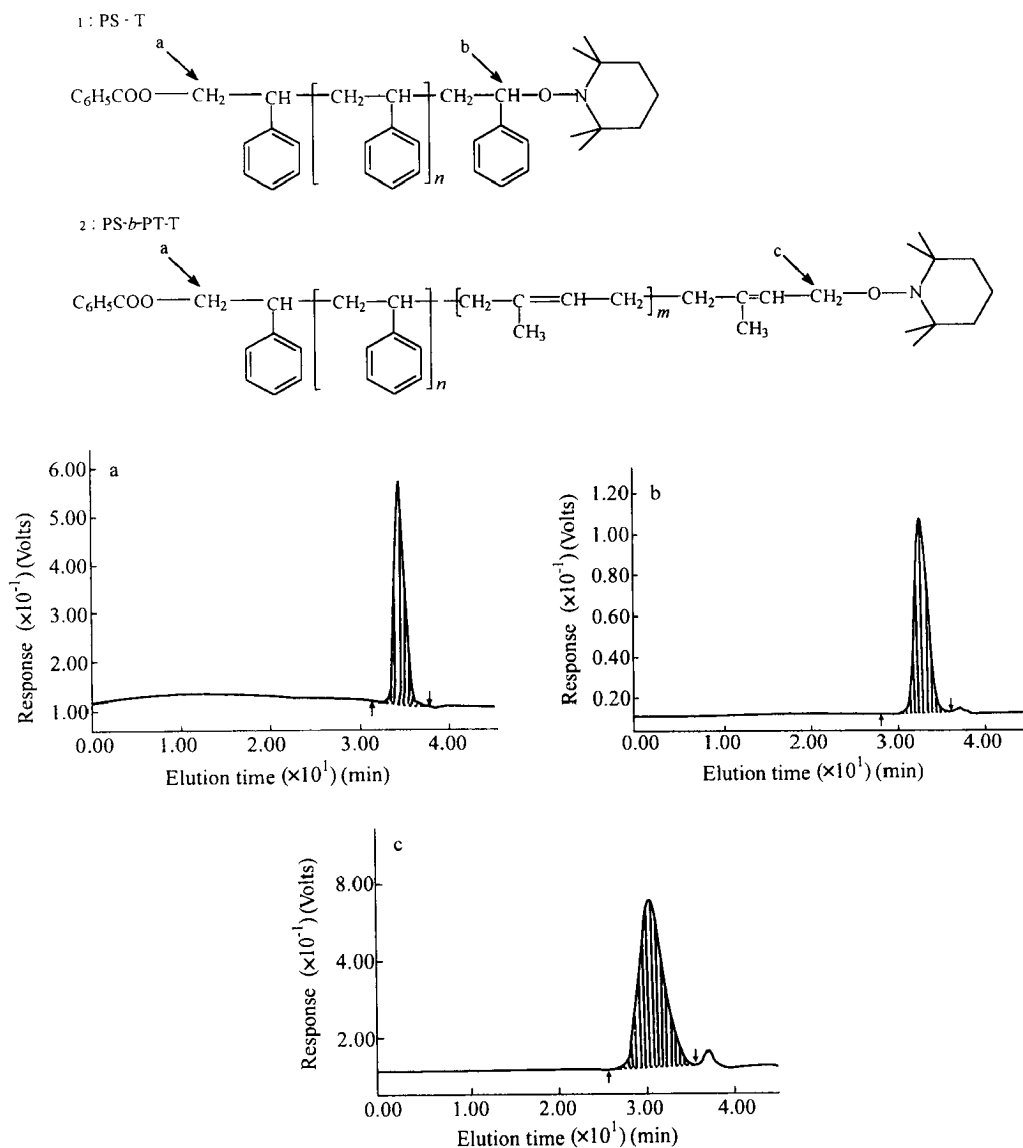


Fig. 1 The GPC diagrams of (a) PS-TEMPO $M_n = 4270$, $PD = 1.1$, (b) PS-b-PI-TEMPO, $M_n = 9760$, $PD = 1.1$ and (c) PS-b-PI-b-PS $M_n = 30570$, $PD = 1.6$

Reaction of the TEMPO-terminated polystyrene with isoprene resulted in the formation of poly(styrene-*b*-isoprene), as shown in Fig. 3. The methyl resonances of the piperidinyloxy group attached to polystyrene were

absent from the ^1H -NMR spectrum of the diblock copolymer, being replaced by new methyl resonances at $\delta = 0.95$ – 1.22 of the piperidinyloxy group attached to polyisoprene block. The three resonances for the benzylic protons bonded to the oxygen of the piperidinyloxy fragment were also absent and being replaced by resonances centered at $\delta = 4.19$ and 4.33 (c; inset of Fig. 3). These peaks are attributed to terminal *trans* and *cis* isomer unit, respectively, of the isoprene 1,4-addition product (c, structure 2). Since chain extension to form the diblock occurs only at TEMPO-terminated end of the polymer chain, the methylene resonances attributed to the benzoate attachment to styrene remain unaffected. This results are similar to those which was obtained by Georges *et al.*^[13].

A number of additives such as camphorsulfonic acid or acetic anhydride have been shown to accelerate TEMPO-based polymerization with a concomitant increase in the degree of control over the polymerization^[5]. In the case of preparation of PS-*b*-PI-*b*-PS-T from PS-*b*-PI-T we used a small amount of acetic anhydride to accelerate the rate of polymerization.

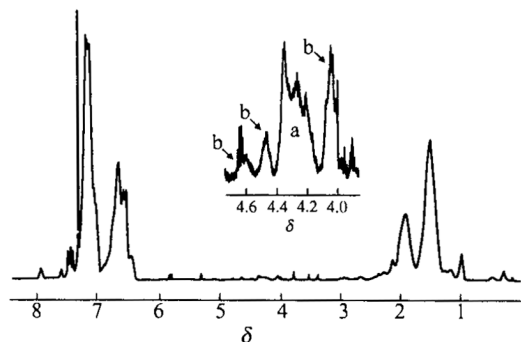


Fig. 2 ^1H -NMR spectra of PS-TEMPO, $M_n = 4270$

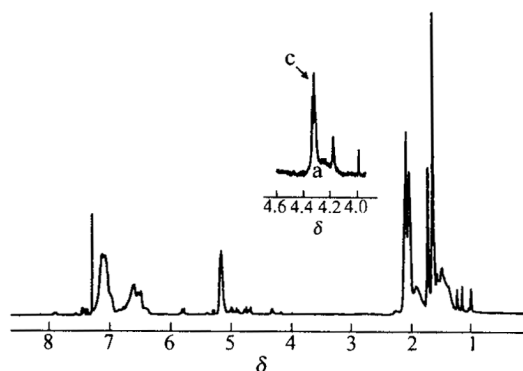


Fig. 3 ^1H -NMR spectra of PS-*b*-PI-TEMPO, $M_n = 9760$

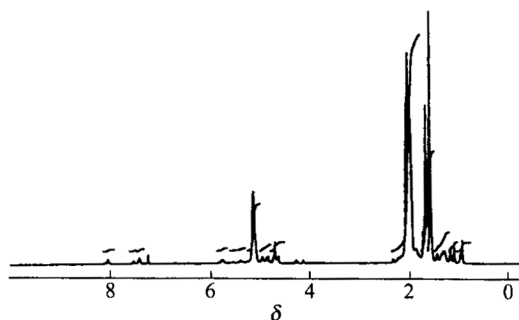


Fig. 4 ^1H -NMR spectra of PI-TEMPO, $M_n = 4500$

Living radical polymerization of isoprene was also performed in bulk with BPO as an initiator in the presence of TEMPO at 125°C for 70 h after being held at 95°C for 6 h. Polyisoprene was isolated in 40% yield and found to have molecular weight, $M_n = 4500$ and $PD = 1.3$. The ^1H -NMR spectra of low molecular weight polyisoprene prepared by the above procedure show the expected signals for both the aliphatic and olefinic protons of the isoprene backbone ($\delta = 5.74$ – 5.77 , 5.13 – 5.26 and 4.88 – 4.96 for olefinic H, $\delta = 1.90$ – 2.05 and $\delta = 1.46$ – 1.75 for aliphatic H) as well as resonances for the chain ends resulting from the BPO and TEMPO fragments at ($\delta = 0.95$ – 1.20 for TEMPO and $\delta = 7.43$ – 7.56 for BPO) (Fig. 4). This allows the molecular weight, $M_n = 4500$, to be determined from the end group analysis. The chemical shifts and peak intensities of the vinyl hydrogens in the ^1H -NMR spectrum (*ca.* $\delta = 5.13$) showed a microstructure of predominately 1,4-*cis* and *trans* repeat units that is essentially the same as that obtained in a conventional free radical isoprene polymerization^[28]. The polyisoprene prepared by the above procedure was found to be active as macroinitiator in the synthesis of diblock copolymer. A similar strategy was examined for the preparation of isoprene/styrene

block copolymer. In this case the polyisoprene terminated TEMPO was first prepared and then it was used to polymerize styrene at 125°C under vacuum for 6 h. This resulted in 60% conversion and yielded the block, PI-*b*-PS-T copolymer. In the case of PI-*b*-PS-T, the initiation of the second styrene block from the starting polyisoprene blocks proceeded smoothly to give well-defined block copolymers with no detectable amounts of unreacted homopolystyrene. Reaction of PI-*b*-PS-T with isoprene resulted in the formation of PI-*b*-PS-*b*-PI triblock copolymer whose GPC chromatogram showed a distinct shift to higher molecular weight (Fig. 5). The obtained molecular weight and molecular weight distribution of PI-T, PI-*b*-PS-T and PI-*b*-PS-*b*-PI are summarized in Table 2.

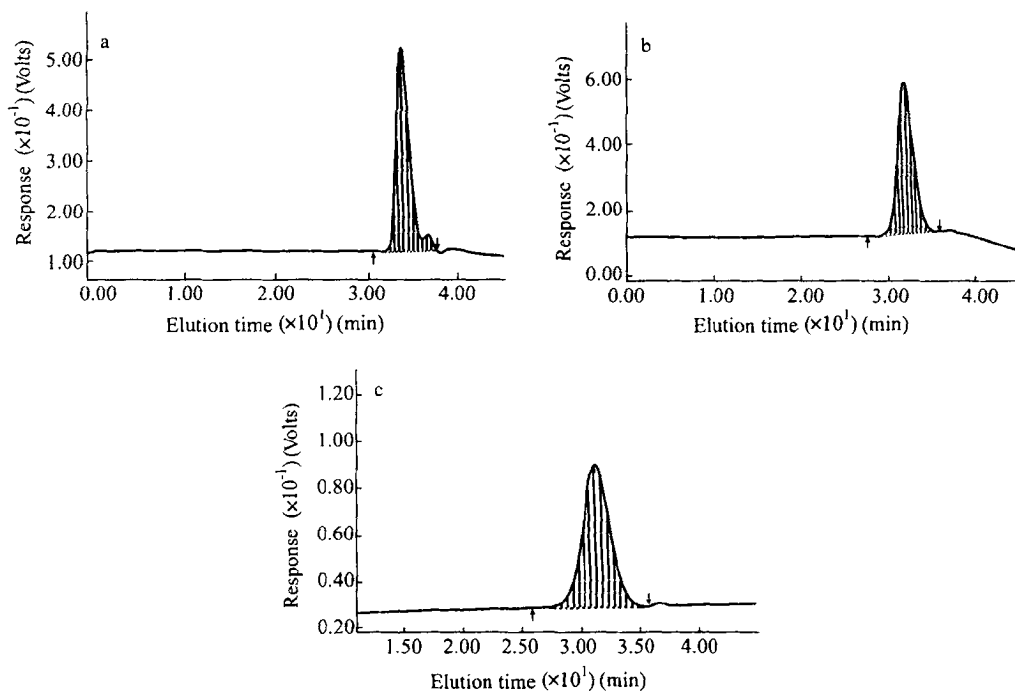


Fig. 5 The GPC diagrams of (a) PI-TEMPO, $M_n = 4500$, $PD = 1.3$
(b) PI-PS-TEMPO, $M_n = 15150$, $PD = 1.29$ (c) PI-PS-PI, $M_n = 25186$, $PD = 1.42$

CONCLUSION

We synthesized 2,2,6,6-tetramethylpiperidine-*N*-oxyl as the capping agent in three steps from acetone and ammonia in our laboratory and used for the preparation of living polymers. The controlled radical polymerization technique was applied to the preparation of polystyrene and polyisoprene homopolymers as well as diblock and triblock copolymers. The molar mass of the macroinitiator played a fundamental role in the efficiency of starting the block copolymerization reactions. In particular, block copolymers with well defined structures and narrow molar mass distributions can be obtained only by starting the block copolymerization reaction with a low molar mass macroinitiator.

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