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Synthesis of Poly(isobutylene-*block*-methyl methacrylate) by a Novel Coupling Approach

Tomoya Higashihara, Dingsong Feng, and Rudolf Faust*

Department of Chemistry, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854

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ABSTRACT: The synthesis of poly(isobutylene-*b*-methyl methacrylate) has been accomplished by a novel coupling approach combining living cationic and anionic polymerization techniques. By capping living polyisobutylene (PIB) with 1,3-butadiene, a chloroallyl chain-end-functionalized PIB (PIB−AllylCl) was prepared. Coupling of the purified and isolated product and living poly(methyl methacrylate) (PMMALi) was then attempted in tetrahydrofuran at −78 °C. However, coupling was absent, and the addition of cesium iodide as a catalyst to increase the coupling rate was also unsuccessful. Halogen exchange reaction of PIB−AllylCl using an excess of lithium bromide proceeded quantitatively to yield the bromoallyl counterpart (PIB−AllylBr). The PIB−AllylBr was coupled with PMMALi in THF at −78 °C with high efficiency (>95%) and yielded the expected diblock copolymer.

Introduction

Block copolymers containing hard and soft segments are of great interest since they may induce nanodomain arrangements so as to minimize interfacial energies between different polymer segments yielding phase-separated morphologies. Recently, much attention has been paid to applications of ABA triblock copolymers in drug eluting coronary stent systems. For example, poly(styrene-*b*-isobutylene-*b*-styrene) triblock copolymer has recently been employed as a drug carrier coating material for the TAXUS Express2 Paclitaxel-Eluting Coronary Stent system by Boston Scientific Corp.[1]

Living polymerization, where neither chain transfer nor termination takes place during polymerization, is the most effective method for the preparation of such block copolymers. Living polymerization yields polymers with the molecular weight determined by the [monomer]/[initiator] ratio and narrow molecular weight distribution. Although each living polymerization system provides a limited range of polymers, unique polymers not available by a single method can be synthesized by the combination of various polymerization techniques.

Recently, Müller et al. reported the synthesis of poly(isobutylene-*b*-alkyl methacrylate) and poly(alkyl methacrylate-*b*-isobutylene-*b*-alkyl methacrylate) by combining cationic and anionic polymerizations.[2,3] First, 1,1-diphenyl-1-methoxy or 2,2-diphenylvinyl end-functionalized polyisobutylene (PIB) was prepared by the reaction of 1,1-diphenylethylene (DPE) and living PIB. The chain end of the resulting polymer was metalated with alkali metals in tetrahydrofuran at room temperature, and the macroanion could initiate the polymerization of methyl methacrylate (MMA). This method seems inconvenient due to the need of alkali metal since lithiation with alkyllithium (e.g., butyllithium) does not proceed quantitatively.[4] A more recent attempt has been demonstrated by Müller et al. for the preparation of thiophene end-functionalized PIB and subsequent metalation of the polymer chain end with an alkyllithium compound, followed by polymerization of *tert*-butyl methacrylate with the generated macroanion.[5] The advantage of this process is simple and complete metalation. However, a large excess of thiophene must be used in the functionalization of PIB cation to prevent the coupling reaction between thiophene-functionalized PIB and living PIB. Moreover, the blocking efficiency is only about 80% even when low molecular weight is targeted. Very recently, our group has developed a new and efficient method involving the synthesis of DPE end-functionalized PIB by monoaddition of 1,4-bis(1-phenylethenyl)benzene (para-double diphenylethylene, PDDPE) to living PIB.[6−8] The resulting macromonomer is metalated with *n*-butyllithium followed by initiating the polymerization of methacrylates with the generated macrocarbanion. The blocking efficiency is high (>90%); however, the method requires multiple stages that involve the syntheses of PDDPE and DPE end-functionalized PIB, lithiation of the terminus, and polymerization of methacrylates.

Herein, we report on the development of a novel methodology in which a coupling reaction is performed between haloallyl chain-end-functionalized PIB and living poly(methyl methacrylate) (PMMALi) for the synthesis of poly(isobutylene-*b*-methyl methacrylate).

Experimental Section

Materials. Hexanes and methanol (Doe & Ingals, Technical grade) were purified by simple distillation. Toluene (Aldrich, 99+%) and acetone (Doe & Ingals, Technical grade) were refluxed with calcium hydride (CaH_2) and potassium carbonate, respectively, for 12 h and then distilled. Toluene and tetrahydrofuran (THF) for anionic polymerizations were finally dried by the distillation over 1,1-diphenylhexyllithium (DPH-Li) on a vacuum line (10^{-6} Torr). *n*-Butyllithium (^{n}BuLi, FMC Lithium, 15 wt % solution in hexanes) and 1,1-diphenylethylene (DPE, Aldrich, 97%) were used as received. The active concentration of a ^{n}BuLi solution was determined by the polymerization of styrene. Methyl methacrylate (MMA) was distilled over CaH_2 and then distilled over triethylaluminum (Aldrich, 1.9 M solution in toluene) on the vacuum line. Cesium iodide (CsI, Aldrich, 99.9%) was purified by drying under high vacuum ($<10^{-6}$ Torr) for 24 h followed by the titration with DPH-Li in THF. Benzyl bromide (Aldrich, 98%) was stirred with CaH_2 at 25 °C for 48 h and then distilled under high vacuum ($<10^{-6}$ Torr). Chloroallyl chain-end-functionalized polyisobutylene (PIB−AllylCl) was synthesized as described elsewhere[9] and purified by

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* Corresponding author: Tel 1-978-934-3675; Fax 1-978-934-3013; e-mail Rudolf_Faust@uml.edu.

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Table 1. Coupling Reaction of PIB−AllylCl (M_n = 4610, PDI = 1.10) with PMMALi in THF at −78 °C for 12 h

	homo-PMMA			after reaction		
	M_n (g/mol)		PDI[b]		M_n (g/mol)[c]	molar mass[c]
run	calcd[a]	GPC		high M_n/low M_n	high M_n/low M_n	ce[d]
1	20 300	26 800	1.06	27 100/5100	92.2/7.8	0
2[e]	20 300	26 200	1.18	27 000/4890	93.8/6.2	0

[a] Calculated from the equation: M_n(calcd) = 57.1 (C_4H_9) + 180 (DPE) + 100.12 (MMA) × [MMA]/[DPE] + 1 (H). [b] Polydispersity. [c] Determined from GPC. [d] Coupling efficiency determined by ^{1}H NMR. [e] Coupling reaction was carried out in the presence of CsI.

the precipitation with hexanes/methanol twice, followed by the azeotropic distillation of a trace amount of water with dry toluene thrice. Lithium bromide (LiBr, Aldrich, >99%) was used as received.

Coupling Reaction of PIB−AllylCl with PMMALi. The polymerization of methyl methacrylate and subsequent coupling reaction with PIB−AllyCl were carried out in THF at −78 °C under a high vacuum (<10^{-6} Torr) in a sealed glass reactor with break-seals. The reagents were added in the following order: ^{n}BuLi (0.0064 M), DPE (0.002 M), MMA (0.4 M), and PIB−AllylCl (0.000 67 M).

In a typical experiment (run 1), to a 500 mL round-bottom flask equipped with break-seals were added DPE (0.054 g, 0.3 mmol) and ^{n}BuLi (1.6 M × 0.6 mL = 0.96 mmol) in hexanes using dried gastight syringe under argon. After evaporating hexanes completely under a high vacuum, THF (140 mL) was added at −78 °C by trap-to-trap distillation over DPH-Li. The solution was allowed to stand at −78 °C for 20 min and then at 25 °C for 2 h to decompose ^{n}BuLi used in excess. After degassing the solution at −78 °C for 20 min and heat-sealing the apparatus off the line, MMA (6 g, 60 mmol) was added by the distillation with vigorous stirring to start the polymerization. After 30 min, a small portion of living poly(methyl methacrylate) (PMMALi) was taken out by the heat-sealing procedure and quenched with methanol (1 mL) for characterizations. Finally, a THF solution (5 mL) of PIB−AllylCl (M_n(GPC) = 4610, PDI = 1.10, 0.46 g, 0.1 mmol) was added to the remainder and stirred. After 12 h, the system was quenched with an excess of benzyl bromide (0.71 mL, 6 mmol). The solution was poured into methanol (500 mL) to precipitate the polymer.

Halogen Exchange Reaction of PIB−AllylCl to PIB−AllylBr. The titled reaction was carried out in a toluene/acetone mixture (65/35, v/v) using a large excess ([LiBr]/[PIB−AllylCl] = 108 or 201) of anhydrous LiBr under a dry nitrogen atmosphere.

A typical experiment is as follows: In a two-necked round-bottomed flask, PIB−AllylCl (M_n(GPC) = 4610, PDI = 1.10, 1.50 g, 0.326 mmol, 0.5 wt %), LiBr (5.72 g, 65.5 mmol), toluene (195 mL), and acetone (105 mL) were placed and refluxed with stirring. After 12 h, the solution was cooled to room temperature. Then, the solvent was evaporated under the reduced pressure. Excess LiBr was removed by washing with distilled water trice. The polymer was finally purified by the precipitation using a hexanes/methanol system twice, followed by the azeotropic distillation with dry toluene thrice.

Coupling Reaction of PIB−AllylBr with PMMALi. The polymerization of methyl methacrylate and subsequent coupling reaction with PIB−AllyBr were carried out in THF at −78 °C under a high vacuum (<10^{-6} Torr) in a sealed glass reactor with break-seals. The active concentration of PMMALi was calculated from the molecular weight determined by GPC and the weight of MMA consumed. [PMMALi]/[PIB−AllylCl] was adjusted by changing each concentration in the range as follows; [PMMALi] = 0.001 65−0.002 99 M, [PIB−AllylBr] = 0.000 67−0.002 65 M.

In a typical experiment (run 7), to a 250 mL round-bottom flask equipped with break-seals were added DPE (0.017 g, 0.0944 mmol) and ^{n}BuLi (1.6 M × 0.2 mL = 0.32 mmol) in hexanes using a dried gastight syringe under argon. After evaporating hexanes completely under a high vacuum, THF (23 mL) was added at −78 °C by the trap-to-trap distillation over DPH-Li. The solution was allowed to stand at −78 °C for 20 min and then at 25 °C for 2 h to decompose ^{n}BuLi used in excess. After degassing the solution at −78 °C for 20 min and heat-sealing the apparatus off the line, MMA (2.2 g, 22 mmol) was added by the distillation with vigorous stirring to start the polymerization. After 30 min, a small portion of PMMALi was taken out and quenched with methanol (1 mL) for characterizations. Finally, a THF solution (5 mL) of PIB−AllylBr (M_n(GPC) = 4630, PDI = 1.12, 0.350 g, 0.0745 mmol) was added to the remainder and stirred. After 40 h, the system was quenched with an excess of benzyl bromide (0.36 mL, 3.0 mmol). The solution was poured into methanol (300 mL) to precipitate the polymer.

Measurements. Molecular weights and molecular weight distributions were measured with a Waters HPLC system equipped with a model 510 HPLC pump, model 410 differential refractometer, model 441 absorbance detector (254 nm), online multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), 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 a carrier solvent at a flow rate of 1.0 mL/min at room temperature. Nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker 500 MHz spectrometer using $CDCl_3$ as a solvent. ^{1}H NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane (TMS) as internal standard (δ_H 0.00).

Results and Discussion

Coupling Reaction of PIB−AllylCl with PMMALi. Recently, our group has developed a simple and powerful method to prepare chloroallyl chain-end-functionalized PIB (PIB−AllylCl) by the capping reaction of living PIB cation with 1,3-butadiene in hexanes/MeCl (60/40, v/v) at −80 °C followed by instantaneous ion collapse, as described elsewhere.[9] The allyl halide functionality is well-known in organic chemistry to be reactive toward nucleophilic compounds such as alkoxide, carboxide, amine, Grignard reagents, and so on. Indeed, allyl bromide reacted efficiently with living poly(methyl methacrylate) anion (PMMALi) in THF at −78 °C to form vinyl chain-end-functionalized PMMA reported by Andrews, Melby, and co-workers.[10] We intended to exploit the reactivity of PIB−AllylCl for synthesizing AB diblock copolymers by coupling with PMMALi.

Methyl methacrylate (MMA) was polymerized by 1,1-diphenylhexyllithium (DPH−Li) in THF at −78 °C for 20 min, and then a THF solution of PIB−AllylCl (M_n(GPC) = 4610, PDI = 1.10) was added into the polymerization system. The coupling reaction was allowed to proceed for 12 h. The concentrations of reagents were as follows: ^{n}BuLi (0.0064 M), DPE (0.002 M), MMA (0.4 M), and PIB−AllylCl (0.000 67 M). The active concentration of PMMALi was calculated from the M_n value determined by GPC and the amount of monomer consumed. On the basis of this determination, a 2.2-fold excess of PMMALi was used toward PIB−AllylCl.

The GPC RI traces of the polymer mixture after the coupling reaction showed two peaks corresponding to homo-PMMA (M_n = 26 800, PDI = 1.06) and the unreacted PIB−AllylCl (M_n = 4610, PDI = 1.10). In addition, the mass ratio of PMMA and PIB−AllylCl determined from GPC (92/8) is almost identical

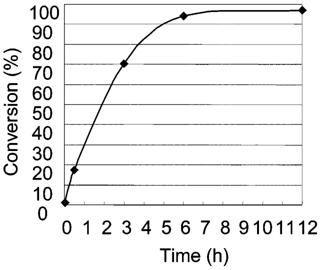
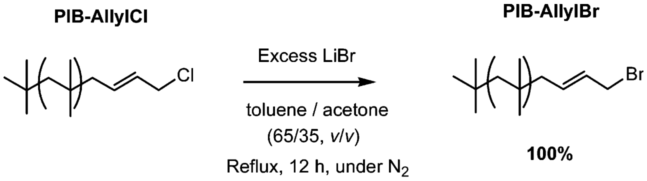


Figure 1. Time−conversion plots of halogen exchange reaction, [LiBr]/[PIB−AllylCl] = 108.

Scheme 1. Halogen Exchange Reaction of PIB−AllylCl into PIB−AllylBr



with the calculated ratio (93/7) based on gravimetry in the absence of coupling reaction. The results are summarized in Table 1.

The ^{1}H NMR spectrum of the polymer mixture still showed the signals assignable to chloroallyl methine protons ($\delta = 5.58$, 5.80 ppm) and methylene protons next to the chlorine atom ($\delta = 4.05$ ppm). By comparing these signals and the signal corresponding to methylene protons of the PIB main chain, coupling is absent. It can be concluded that the reactivity of terminal allyl chloride functionality is not high enough toward the enolate anion of PMMALi in THF at −78 °C.

Hadjichristidis and co-workers have successfully employed CsI as a catalyst in the coupling reaction between living poly(*tert*-butyl methacrylate) and chlorobenzyl end-functionalized poly(dimethylsiloxane).[11] Following this example CsI was added as a catalyst to increase the rate of the coupling reaction. The allyl chloride functionality is expected to be transformed into the more reactive allyl iodide via in-situ halogen exchange resulting in a faster coupling reaction with PMMALi. However, both GPC and ^{1}H NMR measurements showed the absence of coupling. We have no clear explanation at the present time, but halogen exchange might be too slow in THF at −78 °C.

Halogen Exchange Reaction of PIB−AllylCl to PIB−AllylBr. Halogen exchange reactions with alkali metal halide compounds are often utilized in organic synthesis; however, there has been few examples for the extension to chain-end-functionalized polymers. According to a recent report, when a mixture of ω-chlorobenzyl (10%)- and ω-bromobenzyl (90%)-functionalized PMMA was treated with a large excess of anhydrous LiBr in acetone at reflux temperature, the chain ends were completely transformed into ω-bromobenzyl functionality.[12] We expected that such a reaction would be also applicable to PIB−AllylCl, which bears a chemically similar chain-end functionality, transforming into bromoallyl chain-end-functionalized PIB (PIB−AllylBr), as shown in Scheme 1.

The first trial experiment was carried out with PIB−AllylCl (M_n(GPC) = 4610, PDI = 1.10) in the presence of 108-fold excess of LiBr in a mixture of toluene/acetone (65/35, v/v) at reflux temperature. Figure 1 shows the time−conversion plot of polymers during the transformation reaction. The reaction yield was increased to 97% after 12 h. The results are summarized in Table 2.

To realize 100% conversion, the amount of LiBr was increased to 201-fold excess toward the chain end without any other changes in the reaction conditions. In the ^{1}H NMR spectrum (Figure 2) of the resulting polymer, resonances at 4.05 and 5.60 ppm assigned to the chloromethylene and chloroallyl methine protons at the chain end completely disappear; instead, new resonances at 3.97 and 5.68 ppm assigned to bromomethylene and bromoallyl methine protons appear. This observation indicates 100% conversion. The GPC RI traces are almost identical in their shape and elution volume, revealing that the PIB chain remained intact during the transformation reaction (see Figure 3). The results are also summarized in Table 2. Although we successfully transformed PIB−AllylCl into the activated PIB−AllylBr by halogen exchange reaction with an excess amount of LiBr, direct cationic synthesis of PIB−AllylBr is also possible using methylaluminum bromide as a co-initiator for the polymerization of IB followed by capping with 1,3-butadiene.[13]

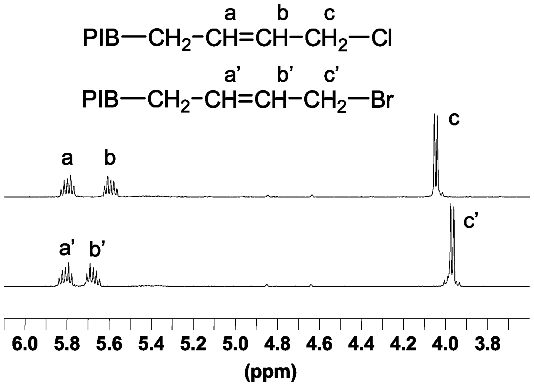


Figure 2. ^{1}H NMR spectra of polymers (A) before and (B) after halogen exchange reaction, [LiBr]/[PIB−AllylCl] = 201, 12 h.

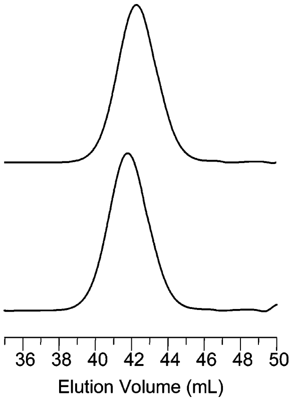


Figure 3. GPC RI traces of polymers (A) before and (B) after halogen exchange reaction of PIB−AllylCl into PIB−AllylBr, [LiBr]/[PIB−AllylCl] = 201, 12 h.

Table 2. Halogen Exchange Reaction of PIB−AllylCl into PIB−AllylBr in Toluene/Acetone (65/35, v/v)

			M_n (g/mol)		
t	[LiBr]/[PIB−AllylCl]	conv	calcd[a]	GPC	PDI
0.5	108	17.5			
3	108	70.3			
6	108	94.1			
12	108	97.2	4660	4970	1.15
12	201	100	4660	4630	1.12

[a] Calculated based on the molecular weight of PIB−AllylCl determined by GPC: 4610 (PIB−AllylCl) − 35.5 (chlorine) + 79.9 (bromine).

Coupling Reaction of PIB−AllylBr with PMMALi. The more reactive PIB−AllylBr thus prepared has subsequently been employed in the coupling reaction with PMMALi. The synthetic route is illustrated in Scheme 2.

Table 3. Coupling Reaction of PIB−AllylBr (M_n = 4630, PDI = 1.12) with PMMALi in THF at −78 °C for 16 h

	homo-PMMA			after reaction			
	M_n (g/mol)			M_n (g/mol)[b]	mass (wt %)[b]	ce (%)[c]	
run	GPC	PDI[a]	[PMMALi]/[PIB−AllylBr]	high M_n/low M_n	high M_n/low M_n	^{1}H NMR	extraction[d]
3	22 800	1.05	2.35	23 400/−	100/0	97	96
4	22 600	1.09	1.02	26 200/4450	95.0/5.0	75	76
5	19 400	1.12	1.10	23 600/4700	96.6/3.4	90	88
6	19 600	1.09	1.25	22 800/4380	97.4/2.6	95	95
7[e]	26 800	1.08	1.10	29 900/−	100/0	96	

[a] Polydispersity. [b] Determined from GPC. [c] Coupling efficiency. [d] Determined by weight ratio of PIB−AllyBr used in the reaction and extracted with hexanes from the reaction mixture. [e] Reaction time was 40 h.

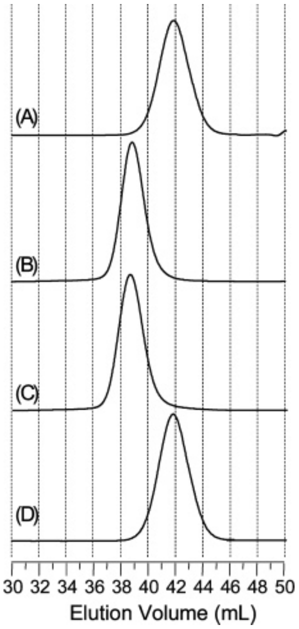
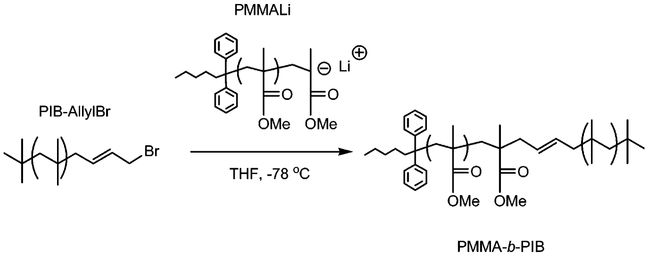


Figure 4. GPC RI traces of (A) precursory PIB−AllylBr, (B) homo-PMMA, (C) polymer mixture obtained by the coupling reaction in THF at −78 °C for 16 h, and (D) hexanes extracted product from the polymer mixture, [PMMALi]/[PIB−AllylBr] = 2.35 (run 3).

Scheme 2. Coupling Reaction of PIB−AllylBr with PMMALi



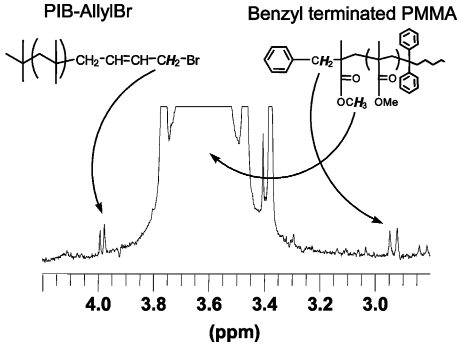


Figure 5. ^{1}H NMR spectra of polymers obtained after termination of the coupling reaction with benzyl bromide, [PMMALi]/[PIB−AllylBr] = 1.10, reaction time = 16 h (run 5).

First, a 2.35-fold excess of PMMALi initiated with DPH-Li was used in the coupling reaction of PIB−AllylBr (M_n(GPC) = 4630, PDI = 1.12) in THF at −78 °C for 16 h. Figure 4A−C shows the GPC RI traces of PIB−AllylBr, homo-PMMA, and polymer mixture after the coupling reaction. The residual PIB−AllylBr peak cannot be found at all at the lower molecular weight region after the reaction (see Figure 4C), strongly suggesting effective coupling reaction. To determine the coupling efficiency more accurately, ^{1}H NMR spectroscopy was performed. The resonances assigned to the bromoallyl methine protons at 5.68 and 5.80 ppm almost disappeared; instead, new resonances appear at 5.43 and 5.14 ppm assigned to the olefin protons at the junction of AB diblock copolymer. A very small signal at 3.97 ppm, however, still remains assignable to bromoallyl methylene protons of the original PIB−AllylBr. By comparing this signal with the new signal at 5.43 ppm corresponding to the olefin proton, 97% coupling efficiency was determined. The results are summarized in Table 3.

To further corroborate the coupling efficiency, solvent extraction from the polymer mixture was carried out with hexanes for 48 h. The extracted hexanes soluble part corresponded to the unreacted original PIB−AllylBr, as shown in Figure 4D. By gravimetry 96% coupling efficiency was calculated, which agrees well with the value obtained by ^{1}H NMR spectroscopy. It is thus evident that the use of PIB−AllylBr in place of PIB−AllylCl is necessary to achieve high coupling efficiency.

Although high coupling efficiency (>96%) was achieved, the resulting polymer still contains a large amount of homo-PMMA since PMMALi was used in large excess. Therefore, the challenge is to demonstrate efficient coupling reaction with stoichiometric reactants. Thus, three experiments were carried out where the ratio of [PMMALi]/[PIB−AllylBr] was varied from 1.02, 1.10, to 1.25 in the coupling reaction in THF at −78 °C for 16 h.

The residual peak corresponding to the unreacted PIB−AllylBr decreases with increasing [PMMALi]/[PIB−AllylBr] ratio. The ^{1}H NMR spectra also show the decrease of unreacted PIB−AllylBr with the increase of the ratio for 1.02, 1.10, and 1.25 to give 75, 90, and 95% of coupling efficiency, respectively. Similar results were also obtained by solvent extraction of unreacted PIB−AllylBr with hexanes. The results are summarized in Table 3. The highest content of diblock copolymer in the resulting polymer mixture being 82 mol % based on PIB−AllylBr (together with 18 mol % homo-PMMA contamination) was observed when the ratio of 1.10 was used.

To investigate whether the unreacted PMMALi (20 mol % of the original PIB−AllylBr) is still active in THF at −78 °C after 16 h in the presence of 10% unreacted PIB−AllylBr, the reaction was quenched with benzyl bromide. Figure 5 displays the ^{1}H NMR spectrum showing a signal assignable to benzyl methylene protons at the PMMA termini.

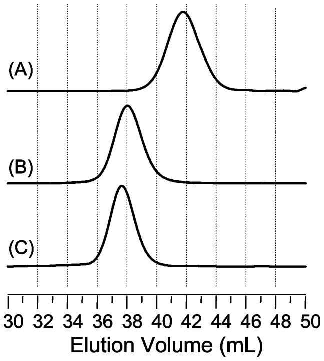


Figure 6. GPC RI traces of (A) precursor PIB−AllylBr, (B) homo-PMMA, and (C) polymers obtained by the coupling reaction in THF at −78 °C for 40 h, [PMMALi]/[PIB−AllylBr] = 1.10 (run 7).

By comparing the intensities of benzyl methylene protons and bromoallyl methylene protons coming from the unreacted PIB−AllylBr ~12% of PMMA toward the original PIB−AllylBr, that is, 60% of the whole unreacted PMMALi, was found to be still active. This suggests that the reaction is somewhat sluggish under the conditions employed here and may possibly take longer to go to completion. A simple extension of the reaction time to 40 h worked well, resulting in the improvement of the coupling efficiency at the ratio of [PMMALi]/[PIB−AllylBr] = 1.10. The GPC RI traces are shown in Figure 6. Significantly, unreacted PIB−AllylBr was not observed at the lower molecular weight side. The ^{1}H NMR spectrum confirmed very high coupling efficiency (96%). Accordingly, we have accomplished the synthesis of poly(isobutylene-*b*-methyl methacrylate) (M_n(GPC) = 29 900, PDI = 1.09, PMMA/PIB (^{1}H NMR) = 85/15, w/w, 87 mol %) with insignificant homo-PMMA contamination.

Conclusions

We have proposed a new coupling approach in which living cationic and anionic polymerizations could be combined to synthesize poly(isobutylene-*b*-methyl methacrylate). Unexpectedly, PIB−AllylCl was unreactive toward PMMALi in THF at −78 °C in the absence or presence of CsI. PIB−AllylCl, however, can be quantitatively converted into PIB−AllylBr by halogen exchange reaction using an excess of LiBr. Coupling proceeds readily with the more reactive PIB−AllylBr to afford the expected poly(isobutylene-*b*-methyl methacrylate) with high coupling efficiency (>95%). Although we demonstrated the coupling reaction using only PMMALi in this article, other (meth)acrylic monomers as well as dienes and styrenic monomers could potentially be used to produce new materials. In addition, it could be possible to synthesize not only AB diblock but also ABA triblock or (AB)$_n$ type star-block copolymers. The more reactive PIB−AllylBr may possibly be effective not only in coupling the reaction with living anionic polymers but also as a macroinitiator in atom transfer radical polymerization (ATRP).[14,15] These are now under investigation.

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