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Articles

Allyl Halide (Macro)initiators in ATRP: Synthesis of Block Copolymers with Polyisobutylene Segments

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ABSTRACT: Allyl halides (allyl-X) and polyisobutylene with allyl halide end group (PIB-allyl-X where X = Cl, Br) were investigated as (macro)initiators in atom transfer radical polymerization (ATRP). Studies with low molecular weight allyl halide initiators that model the PIB-allyl-X macroinitiator were performed first. Polymerization of styrene (St) using allyl halides in the presence of CuX/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) catalyst was controlled, but polystyrene with lower polydispersity was obtained with the Br-based initiator−catalyst system. ATRP of methyl methacrylate (MMA) initiated by allyl halides was not as successful. Polymerization of MMA with allyl-Cl and CuCl/dNbpy catalyst resulted in polymer with molecular weight 4 times higher than the predicted value. The polymerization initiated by allyl-Br in the presence of CuCl/dNbpy catalyst was better controlled but still resulted in polymers with molecular weights 2 times higher than the theoretical values. The addition of 10 mol % St to MMA significantly improved the polymerization control. The values of the ATRP equilibrium constants (K_{ATRP}) of allyl halides were determined and were close to these of 2-haloisobutyrates. Therefore, the low initiation efficiency from allyl-Br during ATRP of MMA is predominantly caused by the slow addition of allyl radical to monomer rather than low K_{ATRP}. Extension from PIB-allyl-Br was then conducted to obtain well-defined block copolymers. For example, starting from PIB-allyl-Br macroinitiator (M_n = 4600 g/mol, M_w/M_n = 1.12), a polyisobutylene-*b*-polystyrene (PIB-*b*-PSt, M_n = 21 400 g/mol, M_w/M_n = 1.14), and polyisobutylene-*b*-poly(methyl methacrylate-*co*-styrene) (PIB-*b*-P(MMA-*co*-St), M_n = 26 000 g/mol, M_w/M_n = 1.32) were obtained. Extension of PIB-allyl-Br with MMA without styrene resulted in a block copolymer with a bimodal molecular weight distribution.

Introduction

As new polymeric materials are in demand, block copolymers are becoming more and more important. Block copolymers, defined as macromolecules composed of two or more continuous sequences of chemically different repeat units, continue to remain a subject of intense research and technological interest due to their unusual and useful properties.[1,2] Current and potential high-technology applications of block copolymers are based on their ability to self-assemble, in bulk as well as in selective solvents, into ordered nanostructures.[3,4] Domain size and shape as well as the interdomain distance in these nanostructures can be manipulated by changing the molecular weight, chemical structures, molecular architecture, and composition of block copolymers. Therefore, synthetic procedures that allow for the efficient synthesis of well-defined segmented copolymers are becoming increasingly important.

High-performance applications require well-defined and properly designed block copolymers. The access to well-defined block copolymers was opened by Szwarc in the early 1950s by developing the living anionic polymerization.[5] Subsequently, other mechanisms were employed to prepare well-defined block copolymers.[6] An interesting possibility is to prepare block copolymers by the combination of two different mechanisms.[7] This way it is possible to expand the range of accessible block copolymers. For example, polyisobutylene (PIB),[8–11] a very important commercial material, can be prepared only via cationic polymerization. PIB-based block copolymers have attracted significant interest because of their unique properties such as UV and thermo-oxidative stability resulting from the saturated backbone structure. Additional important features of these materials include high mechanical damping, high gas barrier properties, biocompatibility, and biostability. Their commercial potential as thermoplastic elastomers and biomaterials has been the subject of a number of research papers and reviews.[12–19] However, cationic polymerization cannot be used for the synthesis of other interesting segments such as poly(meth)acrylates. They can be readily prepared by radical or anionic polymerization. Thus, the synthesis of the polyisobutylene−poly(meth)acrylate block copolymers requires some type of mechanistic transformation. Since alkyl halides are at the chain end of “living” polyisobutylene, the simplest approach may be based on employing them for atom transfer radical polymerization (ATRP).[20–25] However, tertiary alkyl halides are poor ATRP initiators. Difunctional PIB, capped with several units of styrene, Cl-St-*b*-PIB-*b*-St-Cl, prepared cationically was used as an efficient difunctional macroinitiator for homogeneous ATRP. It was extended via ATRP with well-defined segments built from styrene (St), methyl acrylate (MA),

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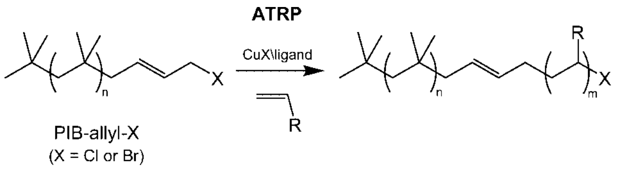
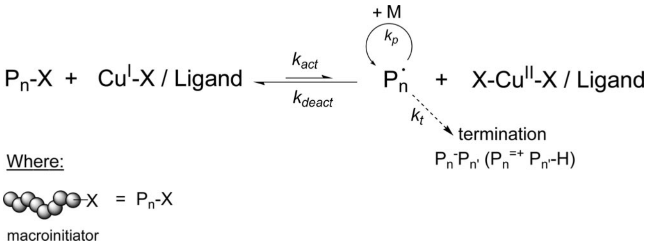
Scheme 1. Preparation of PIB-Based Block Copolymers via ATRP Using Allyl Halide-Terminated PIB as Macroinitiator



Scheme 2. Preparation of Block Copolymers via ATRP[a]



[a] $P_n{-}X$ = dormant species (macroinitiator), $P_n^\bullet$ = propagating species, M = monomer, $Cu^I{-}X$/ligand = transition metal complex (activator), $X{-}Cu^{II}{-}X$/ligand = oxidized metal complex (deactivator), k_{act} = rate constants of activation, k_{deact} = rate constant of deactivation, k_p = rate constant of propagation, and k_t = rate constant of termination.

methyl methacrylate (MMA), and isobornyl acrylate (IBA).[26–29] Recently, Faust et al. reported a straightforward synthesis of PIB terminated with an allyl halide group (PIB-allyl-X, where X = Br or Cl) using cationic polymerization.[30,31] It was achieved by the addition of 1,3-butadiene (BD) in the presence of $Me_{1.5}AlBr_{1.5}$ or $TiCl_4$ co-initiator to living PIB.

Thus, the main aim of this work is to test allyl halide model species and chain termini as ATRP initiators for the ultimate preparation of PIB-based block copolymers via the combination of cationic and ATRP mechanisms (Scheme 1).

The efficiency of initiation and cross-propagation in ATRP depends strongly on the structure of involved dormant species. ATRP, shown schematically in Scheme 2,[20] relies on establishing a dynamic equilibrium between a low concentration of active propagating chains, $P_n^\bullet$, and a large amount of dormant chains, $P_n{-}X$, which are unable to propagate or terminate but can be reactivated in a reaction with a low oxidation state transition metal complex such as $Cu^I{-}X$/ligand. Thus, the probability of bimolecular termination reactions is decreased, and the radical polymerization behaves as a living system. To form a block copolymer by ATRP, a macroinitiator chain capped with a halogen ($P_n{-}X$) is activated by a Cu^I-based catalyst and extended with a monomer (M). In order to obtain a well-defined block copolymer via ATRP, the following condition should be fulfilled:[32,33] $K_{\mathrm{ATRP}}^{\mathrm{initiator}}k_i > K_{\mathrm{ATRP}}^{\mathrm{polymer}}k_p$, where k_i and k_p are the rate constants for initiation (or cross-propagation) and propagation of the monomer M, respectively, and $K_{\mathrm{ATRP}} = k_{act}/k_{deact}$, where k_{act} and k_{deact} are the rate constants for activation and deactivation, respectively, and “polymer” represents the alkyl halide derived from M.[25,34] Thus, only when the apparent rate of initiation is greater than that of propagation, will all chains begin growth within a narrow time frame, and a product with a narrow molecular weight distribution will be obtained. The dependence of k_{act} and K_{ATRP}[35] on structure of initiators,[36,37] ligands,[38] and solvents[39] was reported.[23,40–42] However, the reactivity of allyl halides as ATRP (macro)initiators has not yet been studied.

This article focuses on the preparation of block copolymers using PIB-allyl-X as macroinitiators in ATRP. To determine the optimal reaction conditions for efficient chain extension, studies with low molecular weight allyl halide initiators that model the PIB-allyl-X macroinitiators were performed. The allyl-Cl and allyl-Br were used as initiators in ATRP of St and MMA. Next, K_{ATRP} was measured for allyl halide initiators in order to evaluate their reactivity. Extension from the PIB-allyl-X macroinitiator was then conducted using optimized reaction conditions to obtain well-defined block copolymers.

Experimental Section

Chemicals. Styrene (St) (Aldrich, 99%) and methyl methacrylate (MMA) (Acros, 99%) were passed through a column filled with basic alumina prior to the experiments in order to remove the polymerization inhibitor. 4,4′-Dinonyl-2,2′-bypyridine[43](dNbpy) (Aldrich), 2,2′-bipyridine (bpy) (Aldrich), copper(II) chloride (Acros, 99%), copper(II) bromide (Acros, 99%), allyl chloride (allyl-Cl) (Aldrich, 99%), and allyl bromide (allyl-Br) (Aldrich, 99%) were used as received. Tris(2-pyridylmethyl)amine (TPMA) was synthesized according to a literature procedure.[44,45] Toluene (Fisher Scientific, 99.9%) was distilled over sodium and stored over molecular sieves. Acetonitrile (MeCN) (Aldrich, 99.9%) used in model reactions and the other liquid reagents and solvents were deoxygenated by purging with nitrogen for several hours prior to use. Copper(I) bromide (Acros, 98%) and copper(I) chloride (Acros, 95%) were washed with glacial acetic acid in order to remove any soluble oxidized species, filtered, washed with ethanol, and dried. PIB-allyl-Br ($M_{\mathrm{n,NMR}}$ = 4600 g/mol, M_w/M_n = 1.12) was synthesized using previously reported procedures.[30]

Procedure for ATRP of Styrene Using Allyl-Br as Initiator. CuBr (15.6 mg, 0.11 mmol), dNbpy (89.1 mg, 0.22 mmol), and a magnetic stir bar were placed in a Schlenk flask, and the flask was closed and thoroughly flushed with nitrogen. Deoxygenated St (5.0 mL, 44 mmol) and allyl-Br (9.4 μL, 0.11 mmol) in deoxygenated toluene (2.5 mL) were transferred via N_2-purged syringes to the Schlenk flask. An initial sample was taken, and the sealed flask was placed in thermostated oil bath at 110 °C. Samples were taken at timed intervals and analyzed by gel permeation chromatography (GPC) and gas chromatography (GC) to follow the progress of the reaction.

Procedure for ATRP of Styrene Using PIB-allyl-Br as Macroinitiator. PIB-allyl-Br ($M_{\mathrm{n,NMR}}$ = 4600 g/mol, M_w/M_n = 1.12) (0.26 g, 5.65×10^{-2} mmol) was placed in Schlenk flask and dissolved in toluene (1.3 mL). The flask was closed, and the polymer solution was purged with nitrogen for 15 min. A deoxygenated solution of CuCl (11.2 mg, 11.3×10^{-2} mmol) and dNbpy (92.3 mg, 22.6×10^{-2} mmol) in St (2.60 mL, 22.6 mmol) was transferred via a N_2-purged syringe to the Schlenk flask. An initial sample was taken, and the sealed flask was placed in thermostated oil bath at 110 °C. Samples were taken at timed intervals and analyzed by GPC and GC to follow the progress of the reaction.

Characterization. Molecular weights and polydispersities were determined by GPC, conducted with a Waters 515 pump and a Waters 2414 differential refractometer using a series of three PSS columns (Styragel 10^5, 10^3, 10^2 Å) in THF as the eluent at 35 °C, at a flow rate of 1 mL/min. Linear polystyrene and poly(methyl methacrylate) standards were used for calibration in the analysis of block copolymers with polystyrene and poly(methyl methacrylate) segments, respectively. Conversion of monomers was determined using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector using a J&W Scientific 30 m DB WAX Megabore column using toluene in the reaction mixture as the internal standard. Conversions were calculated by detecting the decrease of the monomer peak area relative to the peak area of toluene. The spectroscopic measurements were performed on a Cary 5000 (Varian) UV/vis spectrometer.

Determination of K_{ATRP}. CuX (X = Br or Cl, 0.05 mmol) and the ligand, TPMA (0.0145 g, 0.05 mmol) or bpy (0.0156 g, 0.1 mmol), were added to a Schlenk flask. The flask was closed with a ground glass joint fused to a quartz cuvette and was then evacuated and back-filled with nitrogen five times. Deoxygenated MeCN (10 mL) was added into the flask via a nitrogen-purged syringe through the side arm of the flask. The contents were

Table 1. Experimental Conditions and Properties of PSt and PMMA Prepared by Normal ATRP Using Allyl-Cl and Allyl-Br as Initiators[a]

entry	$[M]_0$	$[CuX]_0$	T [°C]	[allyl-X]$_0$	time [min]	conv [%]	$M_{n,theo}$[c]	$M_{n,GPC}$	M_w/M_n
1	400 St	1.0 CuCl	110	1.0 ally-Cl	1230	46	19 200	24 200	1.31
2	400 MMA	1.0 CuCl	70	1.0 allyl-Cl	1500	70	28 200	120 000	1.57
3	400 St	1.0 CuBr	110	1.0 allyl-Br	4940	39	16 500	19 400	1.19
4	400 St	1.0 CuCl	110	1.0 allyl-Br	6000	38	16 000	12 700	1.25
5	400 MMA	1.0 CuBr	90	1.0 allyl-Br	90	43	17 200	46 100	1.27
6[b]	400 MMA	0.3/0.03 CuBr/$CuBr_2$	70	1.0 allyl-Br	510	37	14 500	40 600	1.35
7	400 MMA	1.0 CuCl	90	1.0 allyl-Br	360	60	24 200	38 900	1.13
8	360/40 MMA/St	1.0 CuCl	90	1.0 allyl-Br	2655	53/72	22 000	26 800	1.26

[a] [Allyl-X]$_0$/[dNbipy]$_0$ = 1/2; in toluene (0.5 vol equivalent vs monomer M). [b] [Allyl-Br]$_0$/[dNbpy]$_0$ = 1/0.63. [c] $M_{n,theo} = ([M]_0/[allyl\text{-}X]_0) \times \text{conversion} \times M_{monomer}$.

stirred until a solution (orange in the case of TPMA or dark brown in the case of bpy) was formed. The corresponding allyl halide (1 mmol, deoxygenated by purging with nitrogen) was then injected to the Schlenk flask via a N_2-purged microsyringe. The absorbance at a wavelength corresponding to the λ_{max} of the generated Cu^{II} halide complex was monitored at timed intervals. The concentration of the deactivator in the system was calculated using values of the extinction coefficients for the Cu^{II} halide complexes determined separately in MeCN: $\epsilon_{955} = 198.7$ M^{-1} cm^{-1} for $CuBr_2$/TPMA, $\epsilon_{745} = 336.5$ M^{-1} cm^{-1} for $CuBr_2$/bpy, and $\epsilon_{955} = 178.3$ M^{-1} cm^{-1} for $CuCl_2$/TPMA. The values of K_{ATRP} were obtained from the time dependence of accumulation of deactivator in the reaction system, as described in the literature.[35] Each experiment was repeated twice, and an average value of K_{ATRP} was calculated. In all cases, the two individual values of K_{ATRP} for each allyl halide−catalyst system were very close and did not differ by more than 15%. The temperature inside the spectrometer was measured as 22 ± 2 °C.

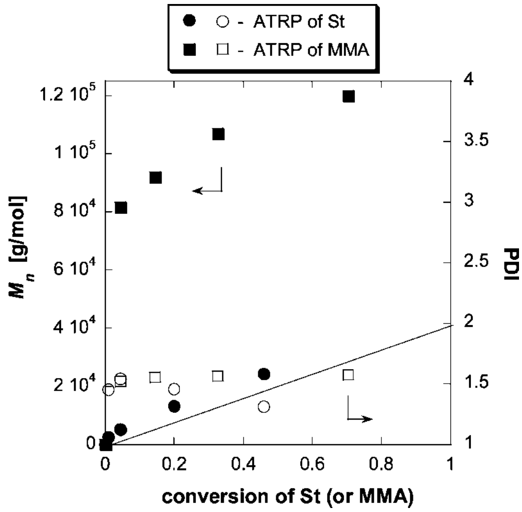


Figure 1. Molecular weight (M_n) and polydispersity (PDI) as a function of conversion in ATRP of styrene (St) (●, ○) and methyl methacrylate (MMA) (■, □) in the presence of allyl-Cl initiator. Experimental conditions: $[M]_0/[allyl\text{-}Cl]_0/[CuCl]_0/[dNbipy]_0 = 400/1/1/2$, in toluene (0.5 volume equivalent vs monomer), $T = 110$ °C for polymerization of St and $T = 70$ °C for polymerization of MMA (Table 1, entries 1 and 2).

Results and Discussion

Polymerization of St and MMA via ATRP with Allyl-Cl as Model Initiator. Low molecular weight allyl-Cl that models the PIB-allyl-Cl chain end was used to initiate the ATRP of St and MMA. The polymerization of St was carried out in the presence of CuCl/dNbpy as active complex at 110 °C, targeting a final number-average degree of polymerization (DP_n) of 400. The polymerization of MMA was carried out under similar conditions but at lower temperature (70 °C). Entries 1 and 2 in Table 1 summarize the conditions and results of the performed polymerizations using allyl-Cl as ATRP initiator. Figure 1 shows the increase of molecular weight with conversion during the ATRP of St and MMA. It can be seen that in the polymerization of St molecular weights were well controlled, but polymers with relatively high polydispersities (PDI = M_w/M_n) were obtained. The polymerization of MMA resulted in polymers with broad molecular weight distributions and molecular weights markedly higher than theoretical values predicted from quantitative initiation. The initiation efficiency from allyl-Cl during the polymerization of MMA was only 24%. These results indicate that allyl-Cl initiator is not reactive enough for a well-controlled ATRP process, especially for the polymerization of MMA which forms rather active dormant species (compared to these formed in the polymerization of St).

Polymerization of St and MMA via ATRP with Allyl-Br as Model Initiator. Commonly used ATRP initiators such as alkyl bromides are more active (~10 times) than alkyl chlorides because the C−Br bond is much weaker than the C−Cl bond.[36,37] Therefore, it was expected that allyl-Br initiator will be more reactive than allyl-Cl in the ATRP process and better control over the polymerization will be achieved. Entries 3–8 in Table 1 summarize all the conditions and results of performed polymerizations using allyl-Br as ATRP initiator. When using bromine-based initiators, a technique called "halogen exchange" may be used in order to further improve the efficiency of initiation.[34,46] This technique employs CuCl- instead of CuBr-based catalyst in the presence of bromide-terminated initiators and has been successfully applied to many systems including the synthesis of block copolymers.[47–55]

Figure 2a depicts the increase of molecular weight with conversion for ATRP of St initiated with allyl-Br using CuBr/dNbpy or CuCl/dNbpy as the catalyst. Both polymerizations were well controlled resulting in polymers with molecular weights close to the theoretical values and low PDIs. ATRP of MMA using allyl-Br initiator was not as successful. It can be observed in Figure 2b that the initiation efficiency during ATRP of MMA was poor, and the molecular weights as determined by GPC were about twice higher than the predicted values. The molecular weight distribution was narrowest when the halogen exchange technique was used, but the initiation efficiency from allyl-Br was still only 62%. In the last experiment (Table 1, entry 8) a small amount of St was used as a comonomer in ATRP of MMA. It was reported that addition of 10 mol % of St can significantly improve the initiation efficiency form less active initiators such as methyl 2-bromopropionate and 1-phenylethyl bromide during the polymerization of MMA.[56] The results in Table 1 (entry 8) and Figure 2b show that upon addition of 10 mol % St the control over the ATRP of MMA in the presence of allyl-Br was improved, molecular weights were close to the theoretical values, and low PDIs were observed. A styryl halide end group is less reactive than a methacrylate end group; therefore, the activity of the polystyrene dormant species becomes more comparable to that of the

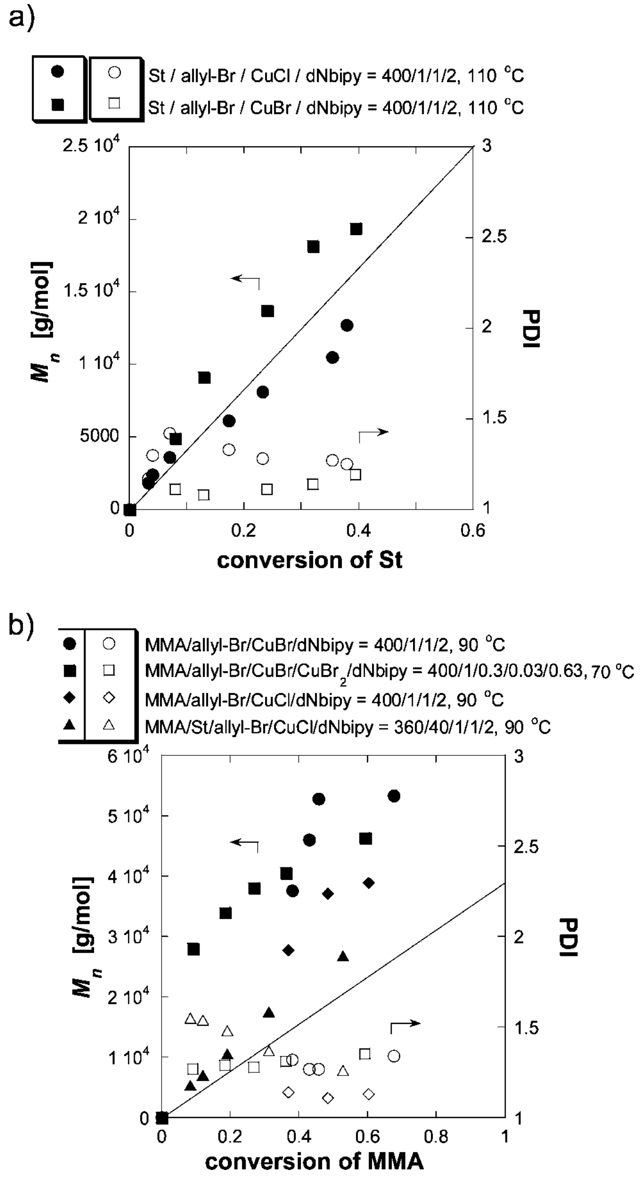


Figure 2. Molecular weight (M_n) and polydispersity (PDI) as a function of conversion in ATRP of (a) styrene (St) and (b) methyl methacrylate (MMA) in the presence of allyl-Br initiator. Experimental conditions: $[M]_0/[\text{allyl-Br}]_0/[\text{CuX}]_0/[\text{dNbipy}]_0 = 400/1/1/2$, in toluene (0.5 volume equivalent vs monomer), $T = 110$ °C for polymerization of St and $T = 70$ or 90 °C for polymerization of MMA (Table 1, entries 3–8).

Table 2. Values of K_{ATRP} for the Reaction of Allyl Halides with Cu(I) Complexes in MeCN at 22 ± 2 °C

allyl halide	catalyst	K_{ATRP}[a]
allyl bromide	CuBr/TPMA	1.72×10^{-5} (1.58×10^{-5}, 1.85×10^{-5})
allyl bromide	CuBr/bpy	3.00×10^{-9} (3.06×10^{-9}, 2.94×10^{-9})
allyl chloride	CuCl/TPMA	2.34×10^{-6} (2.31×10^{-6}, 2.37×10^{-6})

[a] The average K_{ATRP} value is shown, followed, in parentheses, by the two values determined from separate experiments.

unreacted initiator, and the problem of poor initiation efficiency is minimized.[56]

Determination of K_{ATRP} for Allyl Halide ATRP Initiators. The precise values of ATRP equilibrium constants for both allyl bromide and allyl chloride are necessary to optimize the reaction conditions for polymerizations initiated with these halides or in the aforementioned chain extension reactions. The ATRP equilibrium constants for the reaction of allyl bromide with CuBr/TPMA and CuBr/bpy and of allyl chloride with CuCl/TPMA were determined. There is no literature data on the values of K_{ATRP} with allyl halides, and it is of general interest to compare the activity of allyl halides as ATRP initiators to other alkyl halides that mimic the chain ends of various polymers. Allyl halides are not only models of the chain ends of allyl halide-terminated PIB but also structurally resemble the defects in poly(vinyl chloride) which have been reported[57,58] to initiate the polymerization of vinyl monomers yielding the corresponding graft copolymers.

All measured and averaged values of K_{ATRP} for all studied allyl halide−catalyst combinations are reported in Table 2.

The values of the ATRP equilibrium constant for the reactions of allyl bromide were very close to those of ethyl 2-bromoisobutyrate. For instance, the reported values of K_{ATRP} for EBiB reacting with CuBr/TPMA and CuBr/bpy in MeCN are 9.65×10^{-6} and 3.93×10^{-9}, respectively,[35] which are comparable to the values shown in the first two rows in Table 2. However, it is known that although EBiB structurally resembles the polymethacrylate chain end, its reactivity in ATRP is a few times lower than the dormant species in PMMA due to strong penultimate effects.[59–62] Moreover, the efficiency of initiation of allyl halides is a function of both K_{ATRP} and the rate constant of addition of the allyl radical to the monomer of interest (in other words, the initiation rate constant, k_i). Although the magnitude of K_{ATRP} of allyl halides matches that of 2-haloisobutyrate and should be acceptable for cross-propagation, the rate of addition of the relatively stabilized allyl radical to monomers may be low, which might result in reduced chain extension efficiency. Indeed, rate constant of cross-propagation

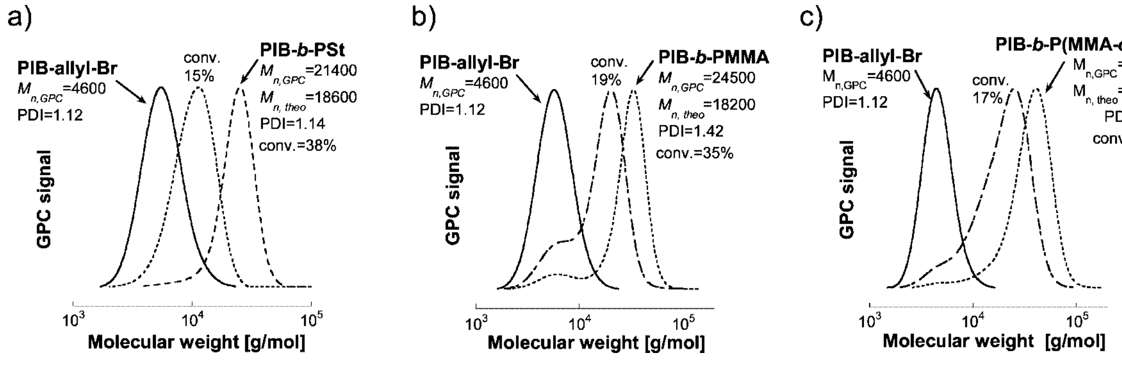


Figure 3. GPC traces of PIB-allyl-Br macroinitiator before and after chain extension with (a) St, (b) MMA, and (c) MMA/St copolymer. Experimental conditions for extension with St: $[\text{St}]_0/[\text{PIB-allyl-Br}]_0/[\text{CuCl}]_0/[\text{dNbpy}]_0 = 400/1/2/4$, $T = 110$ °C, in toluene (0.5 vol equiv vs monomer). Conditions for extension with MMA: $[\text{MMA}]_0/[\text{PIB-allyl-Br}]_0/[\text{CuCl}]_0/[\text{dNbpy}]_0 = 400/1/1/2$, $T = 70$ °C, in toluene (0.5 vol equiv vs monomer). Conditions for extension with MMA and St: $[\text{MMA}]_0/[\text{St}]_0/[\text{PIB-allyl-Br}]_0/[\text{CuCl}]_0/[\text{dNbpy}]_0 = 360/40/1/1/2$; $T = 70$ °C, in toluene (0.5 vol equiv vs monomer).

from polybutadiene radical to MMA is ~4 times smaller than the rate constant of MMA homopropagation.[63]

Synthesis of Polyisobutylene-*b*-polystyrene (PIB-*b*-PSt) and Polyisobutylene-*b*-poly(methyl methacrylate) (PIB-*b*-PMMA) Block Copolymers Using PIB-allyl-Br as ATRP Macroinitiator. PIB-allyl-Br macroinitiator was synthesized via cationic polymerization ($M_{\mathrm{n,NMR}} = 4600$ g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.12$) as described in the literature.[30] Then, it was extended with St, MMA, and the mixture of 90 mol % MMA with 10 mol % St. Figure 3a presents GPC traces before and after extension of PIB-allyl-Br with St using ATRP. The extension was well controlled, as evidenced by the monomodal and symmetrical GPC traces, and a final block copolymer was formed with a low polydispersity (PDI = 1.14). The extension of PIB-allyl-Br with MMA was less successful even for systems with halogen exchange. Figure 3b presents GPC traces before and after extension of PIB-allyl-Br with pure MMA using ATRP. A bimodal distribution of molecular weights was clearly observed even after 35% monomer conversion was reached, and PDI increased from 1.12 to 1.42. This is a clear indication of poor initiation efficiency of the PIB-allyl-Br macroinitiator, which can be attributed to slow addition of allyl radical to MMA as discussed in the previous paragraph. Slow addition may be also accompanied by transformation of allyl bromide to allyl chloride chain end before reaction with MMA. With 10 mol % St present, a cleaner shift of the GPC trace was observed (Figure 3c). At 17% monomer conversion bimodal distribution was still observed, but PIB-allyl-Br was almost fully consumed when the conversion reached 42% (only small tailing of GPC trace was present). Under such conditions, PIB-*b*-P(MMA-*co*-St) block copolymer with controlled molecular weight and relatively low PDI (1.32) was obtained. These results prove that in the presence of a small amount of St the initiation efficiency can be increased, and more efficient extensions from PIB-allyl-Br with MMA can be achieved.

Conclusions

Allyl halides and polyisobutylene with allyl halide end groups were evaluated as ATRP initiators. Polymerization of St initiated with allyl-Cl initiator resulted in a polymer with controlled molecular weight but relatively broad molecular weigh distribution. Polymerization of MMA with the same initiator resulted in polymer with molecular weight 4 times higher than the predicted value. These results indicate that allyl-Cl was not reactive enough for well-controlled ATRP. Polymerization of St initiated with allyl-Br initiator resulted in well-controlled polymerization, but ATRP of MMA with the same initiator resulted in polymer with molecular weight about 2 times higher than the predicted value. The control over the polymerization of MMA was slightly improved by using the halogen exchange technique, and it was successful upon addition of 10 mol % St. Poly(methyl methacrylate-*co*-styrene) was obtained with controlled molecular weight and relatively low PDI. The measurements of K_{ATRP} for allyl-Br revealed that this initiator has ATRP activity similar to ethyl 2-bromoisobutyrate, commonly used ATRP initiator for polymerization of MMA. Therefore, the slow rate of addition of allyl radical to MMA monomer could be responsible for poor initiation efficiency from allyl-Br initiator. Successful extension from PIB-allyl-Br was then conducted to obtain well-defined block copolymers: PIB-*b*-PSt and PIB-*b*-P(MMA-*co*-St). Extension of PIB-allyl-Br with MMA without St resulted in a block copolymer with a bimodal molecular weight distribution. Therefore, allyl-Br and polyisobutylene with allyl-Br end group can be successfully used as ATRP (macro)-initiators under appropriate conditions. Because of the straightforward synthesis of PIB-allyl-Br, the preparation of a wide range of PIB-based block copolymers modified by ATRP is now more feasible.

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