End-Functional Poly(*tert*-butyl acrylate) Star Polymers by Controlled Radical Polymerization

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Received July 6, 1999; Revised Manuscript Received February 14, 2000

ABSTRACT: Star-shaped poly(*tert*-butyl acrylate) (P*t*BA) was prepared by an “arm first” method using copper-mediated atom transfer radical polymerization (ATRP). Divinylbenzene, 1,4-butanediol diacrylate, and ethylene glycol dimethacrylate were employed as the coupling reagents. P*t*BA star polymers were successfully prepared using preformed P*t*BA macroinitiators. Several factors pertinent to star polymer formation, including the choice of exchange halogen and solvent, the addition of copper(II) species, the ratio of coupling reagent to macroinitiator, and the reaction time for the star formation, were addressed. Functional initiators were introduced to directly prepare arms with α-functionalities since ATRP is highly tolerant to functional groups. End-functional star polymers with various functionalities, such as hydroxy, epoxy, amino, cyano, and bromine, on the outer layers were successfully synthesized.

Introduction

The synthesis of materials with controlled compositions and architectures continues to be a focus of considerable current research. The interest in star-shaped polymers stems from their unique shape and possible processing advantages due to their compact structure.[1] Well-defined star polymers are typically prepared by various living polymerization techniques. There are three basic synthetic routes for star polymers. The core-first technique involves the use of a multifunctional initiator, and the number of arms in the star polymer can be determined by the number of initiating sites on the initiator.[1−3] The arm-first technique involves the synthesis of preformed arms, usually through living polymerization, followed by reaction with a multifunctional linking agent.[4−6] The third method is a slight variation of the arm-first technique, which sometimes is also termed the “nodule” method.[7−9] In this method, the reactive macroinitiators (arms) produced by a living polymerization technique are cross-linked by a divinyl reagent to form star polymers. The mechanism of the “nodule” method is shown in Scheme 1. First, a few units of divinyl reagents add to the reactive macroinitiators (arms) to form short block copolymers with dangling vinyl groups. Then, the reactive macroinitiator chain ends react with the dangling vinyl groups to form a microgel core or add to a sterically accessible star core. Finally, core−core coupling reaction can occur to form a higher-order star polymer.

Controlled/“living” radical polymerization processes have proven to be versatile for the synthesis of polymers with well-defined structures and complex architectures.[10−13] Star polymers have been prepared by various controlled radical polymerization approaches, including nitroxide-mediated stable free radical polymerization (SFRP),[14] atom transfer radical polymerization (ATRP),[15−20] and, more recently, reversible addition−fragmentation chain transfer polymerization (RAFT).[21] Most of the star polymers were prepared by the core-first technique. For example, modified calixarenes have been used as initiators to produce well-defined methacrylic[17] and styrenic[18] star polymers. Hybrid inorganic−organic multifunctional initiators derived from cyclotriphosphazenes and cyclosiloxanes have also been employed.[19,20] Recently, Hedrick and co-workers combined various living polymerization techniques and prepared dendrimer-like star polymers.[22,23]

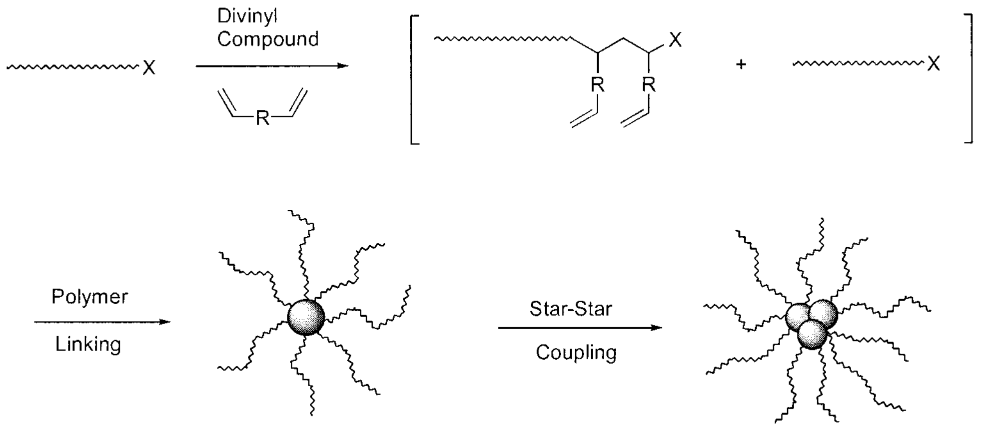
Previously, we reported the synthesis of polystyrene (PSt) star polymers by the “nodule” method using copper-mediated ATRP.[24] However, the yield of the PSt star polymer was ca. 85%, and a significant amount of PSt macroinitiator remained in the final product, partially due to the relatively high radical concentration during the PSt macroinitiator synthesis. In this paper, we report the synthesis of poly(*tert*-butyl acrylate) (P*t*BA) star polymers with high yields (up to 95%) by the same approach. Several factors pertinent to the star polymer formation, such as the choice of the divinyl reagent, exchange halogen and solvent, the ratio of coupling reagent to macroinitiator, and the reaction time for the star formation, are addressed. The syntheses of end-functional star polymers with various functional groups, such as hydroxy, epoxy, amino, bromine, and cyano groups, are also reported.

Results and Discussion

ATRP of *tert*-Butyl Acrylate. *tert*-Butyl acrylate (*t*BA) was polymerized using CuBr complexed by *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the catalyst and methyl 2-bromopropionate (MBP) as the initiator.[25] Under typical reaction conditions, a linear semilogarithmic plot of monomer conversion vs time was observed, indicating a constant number of propagating chains (Figure 1). The molecular weights (M_n) of P*t*BA increased linearly with monomer conversion and agreed well with the predicted values assuming that each initiator molecular produced one polymer chain (Figure 2). Size exclusion chromatography (SEC) traces of the obtained polymers displayed narrow and monomodal molecular weight distribution (M_w/M_n) which decreased with monomer conversion. These observations suggested that the polymerization was a controlled process. The Br ω-functionality of thus-prepared P*t*BA as an isolated macroinitiator was assessed by chain extension using a fresh batch of *t*BA monomer or cross-propagation to styrene (St) to form a block copolymer. Figure 3 displays the overlaid SEC traces of the P*t*BA

10.1021/ma991076m CCC: $19.00 © 2000 American Chemical Society
Published on Web 03/15/2000

Scheme 1



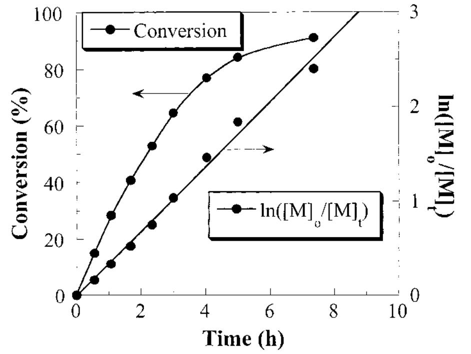


Figure 1. Semilogarithmic kinetic plot for the ATRP of *t*BA in 20 vol % anisole. $[CuBr]_0 = [PMDETA]_0 = [\text{methyl 2-bromopropionate}]_0/2 = 0.055$ M, $[t\text{BA}]_0 = 5.5$ M, and $T = 60$ °C.

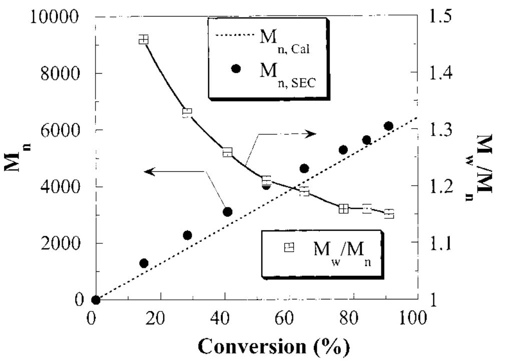


Figure 2. Evolution of experimental molecular weights and polydispersities with monomer conversion for the ATRP of *t*BA in 20 vol % anisole. See Figure 1 for reaction conditions.

macroinitiator, the resulting polymer after chain extension to a new batch of *t*BA, and the P*t*BA-*b*-PSt block copolymer. The relatively clean shift of the SEC traces toward higher molecular weights indicated that most of the P*t*BA macroinitiator chain ends had reactive Br functional groups.

Effect of the Coupling Reagent. Three commercially available divinyl reagents, divinylbenzene (DVB), 1,4-butanediol diacrylate (BDDA), and ethylene glycol dimethacrylate (EGDMA), were reacted with the P*t*BA macroinitiator ($M_{n,SEC} = 6900$, $M_w/M_n = 1.18$) using CuBr/PMDETA as the catalyst in anisole at 110 °C. DVB, BDDA, and EGDMA were chosen as the coupling reagents due to their structural resemblance to styrene, acrylate, and methacrylate, the three common monomers used in ATRP. Under the reaction conditions, EGDMA led to a complete gelation of reaction mixture within 1.5 h, while BDDA and DVB led to no significant gelation after 20 h. When BDDA was used as the coupling reagent, the reaction medium turned viscous quickly but remained fluid. The SEC trace showed that BDDA led to significant star–star coupling and afforded star polymers with high molecular weights and broad molecular weight distributions. In contrast, DVB led to the formation of star polymers with relatively narrow molecular weight distributions (Figure 4). These results were consistent with our previous studies on the PSt star polymer formation under similar conditions.[24]

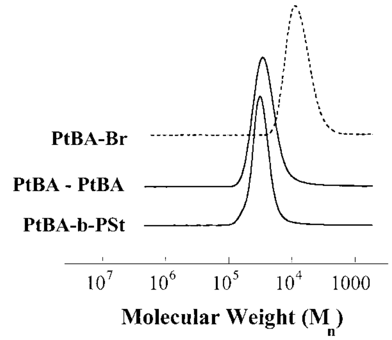


Figure 3. Synthesis of block copolymers with styrene and chain extension to *t*BA using preformed P*t*BA macroinitiator. $[CuBr]_0 = [PMDETA]_0 = [Pt\text{BA}]_0 = 0.029$ M; For styrene: $[\text{styrene}]_0 = 8.7$ M, $T = 110$ °C, reaction time = 2.1 h. For *t*BA: $[t\text{BA}]_0 = 6.8$ M, $T = 90$ °C, reaction time = 1.5 h.

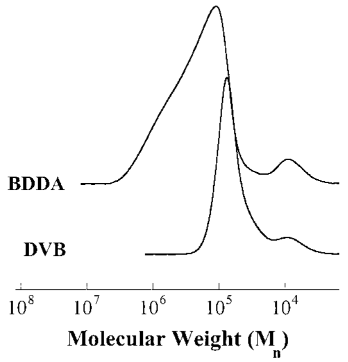


Figure 4. Synthesis of P*t*BA star polymers using divinylbenzene (DVB) or 1,4-butanediol diacrylate (BDDA) as the coupling reagent. $[CuBr]_0 = [PMDETA]_0 = [Pt\text{BA}]_0 = [\text{DVB}]_0/15 = [\text{BDDA}]_0/15 = 0.051$ M in anisole, $T = 110$ °C, reaction time = 5 h.

Effect of DVB to Macroinitiator Ratio. The formation of star P*t*BA using DVB as the coupling reagent was studied in more detail with varying ratios of DVB to P*t*BA macroinitiator. The molecular weights of star polymers increased with an increasing ratio of DVB to

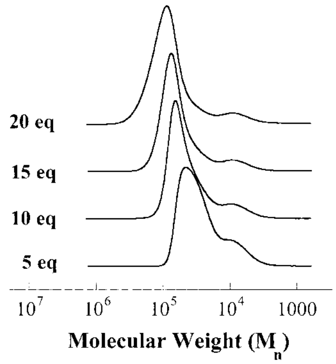


Figure 5. Effect of the divinylbenzene to P*t*BA macroinitiator ratio on the synthesis of P*t*BA star polymers. $[CuBr]_0 = [PMDETA]_0 = [PtBA]_0 = [DVB]_0/x = 0.051$ M in anisole (x = 5, 10, 15, or 20), $T = 110$ °C, reaction time = 5 h.

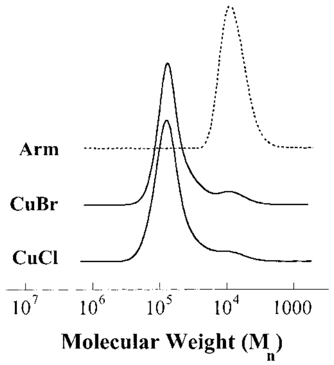


Figure 6. Effect of halogen exchange on the synthesis of P*t*BA star polymers. $[CuCl]_0 = [CuBr]_0 = [PMDETA]_0 = [PtBA]_0 = [DVB]_0/15 = 0.051$ M in anisole, $T = 110$ °C, reaction time = 5 h.

P*t*BA. The ratio of DVB/P*t*BA of 15 was found to be optimal, leading to a high yield (i.e., high conversion of the macroinitiator) of star polymer without significantly broadening the molecular weight distribution ($M_w/M_n \sim 1.4$) (Figure 5). The yield of star polymer was estimated from the ratio of SEC peak integration of the star polymer and the macroinitiator using the function provided by the SEC analysis software. Lower ratios of DVB to P*t*BA afforded star polymers with lower yields. For example, DVB/P*t*BA ratios of 5 and 10 resulted in yields of 82% and 86%, respectively. A higher DVB/P*t*BA ratio of 20 led to significantly broader molecular weight distributions of star polymers without significant improvement of the yield. The molecular weights of the star polymer ($M_{n,SEC}$) were estimated from linear polystyrene-calibrated SEC with a differential refractometer detector. These were apparent molecular weights since the hydrodynamic volumes of P*t*BA star polymers were obviously different from those of linear polystyrenes. For example, molecular weights measured by a triple detection SEC system ($M_{n,3D-SEC}$) with on-line differential refractometer, viscometer, and light scattering were approximately 1.5 times larger than those based on linear polystyrene standards ($M_{n,SEC} = 53\,600$, $M_{n,3D-SEC} = 86\,500$).

Effect of $CuBr_2$ and Halogen Exchange. Other factors pertinent to the polymerization were adjusted in an attempt to further improve the yield of star polymer formation. Additional $CuBr_2$ (20% of total copper) was added in the hope that radical coupling reaction would be further suppressed in the presence of excess copper(II) deactivator. However, SEC analysis of the resulting polymer showed that the yield was not improved (Supporting Information, Figure 1S). The use of CuCl/PMDETA as the catalyst was also studied. It was reported previously that halide-exchange reaction using macroinitiators with Br end groups in the presence CuCl/ligand led to an improved macroinitiator initiation in comparison with the propagation of the second monomer during the block copolymer formation.[26] Thus, employing halide exchange in star polymer formation would favor cross-propagation to form the short DVB block and disfavor cross-linking to form the microgel star core, since C−Br bonds were broken during the cross-propagation and mainly C−Cl bonds were cleaved during the cross-linking. Indeed, the yield of the P*t*BA star polymer formation was improved from 90% to 95% when CuCl was used in place of CuBr, and polymers with similar molecular weights and molecular weight distributions were obtained (Figure 6).

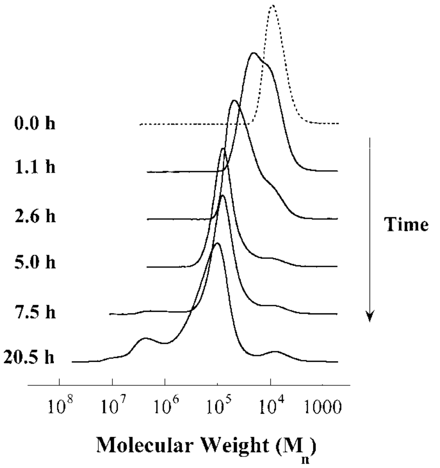


Figure 7. Formation of P*t*BA star polymers in the presence of DVB at various reaction time. $[CuCl]_0 = [PMDETA]_0 = [PtBA]_0 = [DVB]_0/15 = 0.051$ M in anisole, $T = 110$ °C.

Effect of Reaction Time. Using a ratio of DVB/P*t*BA/CuCl/PMDETA = 15/1/1/1, the kinetics of star formation was studied. The conversion of DVB was followed using gas chromatography (GC). A reaction time of 5 h seemed to be optimal for the star formation. Longer reaction times led to star−star coupling which was evident from the presence of a high molecular weight shoulder in the SEC traces for the reaction time of 7.5 and 20 h (Figure 7). The semilogarithmic plot of DVB conversion vs time displayed first-order kinetics with respect to DVB until the reaction time of 5 h, and then the conversion leveled off, which was consistent with the SEC data (Figure 8). This suggested that during the first 5 h of the reaction there were active macroinitiator chain ends and sterically accessible star cores in the reaction solution. The macroinitiator chains continued to add to the DVB molecules in solution and to the dangling vinyl groups on the DVB block on other polymer chains. After 5 h, un-cross-linked macroinitiator chains were nearly depleted, and the star core became sterically congested. As a result, the consumption of DVB and the addition of polymeric radical to star core progressively slowed down. The star formation process was also followed by ^1H NMR as shown in Figure 9. Figure 9A displays the ^1H NMR of the P*t*BA macroinitiator. The methoxy protons (H_a) and the proton (H_b) adjacent to the Br group on the last *t*BA unit were clearly visible. During the star formation, the signal from H_b decreased with the reaction time and eventually disappeared, indicating that all the macroinitiator chain

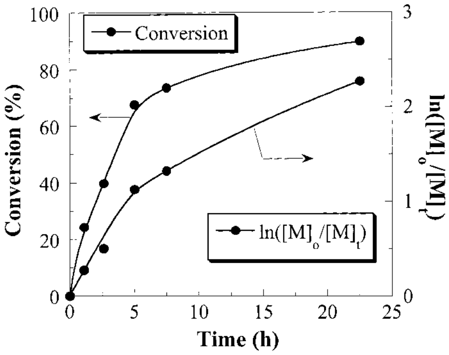


Figure 8. Semilogarithmic kinetic plot of DVB conversion vs time during the P*t*BA star polymer formation. $[\mathrm{CuCl}]_0 = [\mathrm{PMDETA}]_0 = [\mathrm{P}t\mathrm{BA}]_0 = [\mathrm{DVB}]_0/15 = 0.051$ M in anisole, $T = 110$ °C.

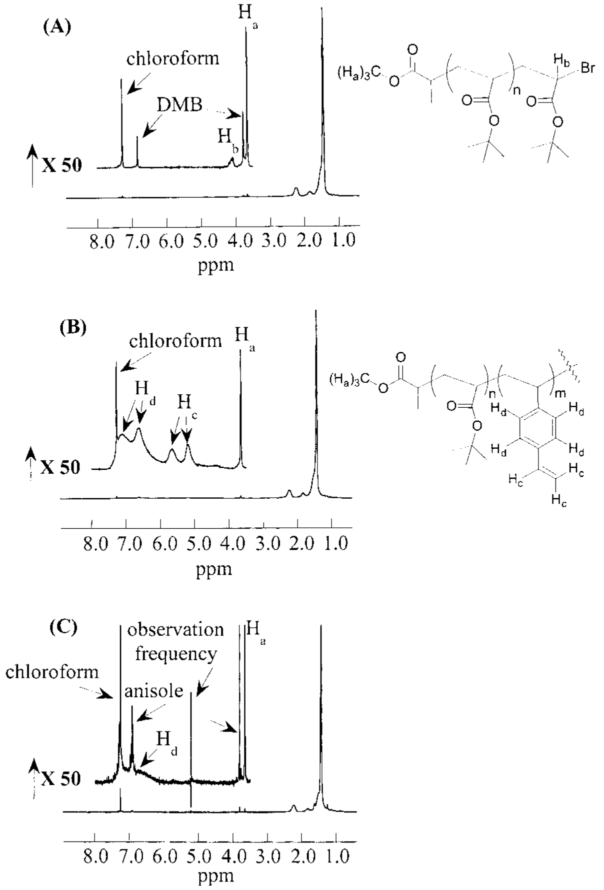


Figure 9. (A) ^{1}H NMR spectrum of P*t*BA macroinitiator prepared in *p*-dimethoxybenzene (DMB). **(B)** ^{1}H NMR spectrum of P*t*BA star polymer after reacting with DVB for 1 h. **(C)** ^{1}H NMR spectrum of P*t*BA star polymer after reacting with DVB for 20 h. $[\mathrm{CuCl}]_0 = [\mathrm{PMDETA}]_0 = [\mathrm{P}t\mathrm{BA}]_0 = [\mathrm{DVB}]_0/15 = 0.051$ M in anisole, $T = 110$ °C.

extended to form block copolymers with DVB. The dangling vinyl protons (H_c) and phenyl protons (H_d) on the DVB units showed an initial increase in intensities but decreased with the reaction time and had significantly lower intensities than those estimated from DVB conversion (Figure 9B,C). These results were consistent with the formation of a star-shaped polymer with mobile P*t*BA arms and a DVB microgel core. The initially formed star core was loose and had some degree of intramolecular mobility. The star core hardened as cross-linking progressed. The loss of intramolecular mobility eventually caused the ^{1}H NMR signals of the microgel core to be too broad to be detected. Similar observations were reported on the synthesis of star polymers by other living polymerization techniques.[27,28]

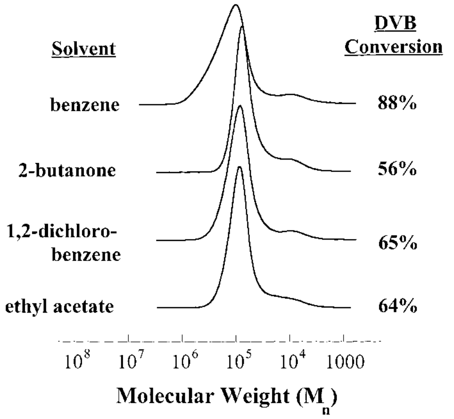
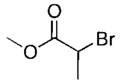
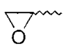
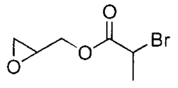
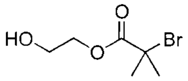
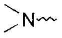
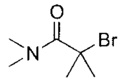
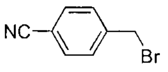
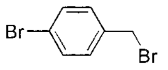


Figure 10. Synthesis of P*t*BA star polymers in the presence of DVB in various solvents. $[\mathrm{CuCl}]_0 = [\mathrm{PMDETA}]_0 = [\mathrm{P}t\mathrm{BA}]_0 = [\mathrm{DVB}]_0/15 = 0.051$ M, $T = 110$ °C, reaction time = 5 h.

Effect of Solvent. Reactions were carried out in various solvents to study the effect of the solvent on the star formation process. After the same amount of reaction time (5 h), star polymers formed in benzene showed significantly higher molecular weights and broader molecular weight distributions than those obtained in polar solvents (Figure 10). In addition, benzene led to higher conversions of DVB and higher degrees of cross-linking indicated by the formation of some insoluble star polymers (gels). These observations were attributed to the relatively poor solubility of copper(II) complex in a nonpolar solvent such as benzene, since a lower concentration of copper(II) complex could result in a higher concentration of radicals and hence more radical determination reactions. Polar solvents, such as 1,2-dichlorobenzene and ethyl acetate, provided star polymers with similar molecular weights distributions and DVB conversions as in the case of anisole. 2-Butanone as a solvent afforded star polymers with slightly lower molecular weight and DVB conversion, probably due to the better solubility of copper(II) complexes and/or relatively lower solubility of polystyrene units in this solvent.

End-Functional P*t*BA Star Polymers. A variety of functional initiators were used during the macroinitiator synthesis due to the tolerance of ATRP process to different functional groups.[29] For example, 1,2-epoxypropyl 2-bromopropionate was used to prepare P*t*BA macroinitiator with an epoxy α-functional and a bromine ω-functional end. The isolated macroinitiator had $M_{n,\mathrm{SEC}} = 5600$ and $M_w/M_n = 1.22$ by SEC. Alternatively, the molecular weight was determined using ^{1}H NMR by comparing the integration of the protons on the side chains with that of protons adjacent to the α- or ω-functional group (Figure 11A). The consistency of molecular weight obtained by NMR ($M_{n,\mathrm{NMR}} = 6300$) with that by SEC suggested high functionality of the P*t*BA macroinitiator on both polymer chain ends. When this functional macroinitiator was reacted with DVB, star polymers with epoxy end-functional groups were obtained (Figure 12). The yield of the star polymer using the epoxy functional macroinitiator was similar to that of nonfunctional P*t*BA, which suggested that star formation under ATRP conditions was not effected by the presence of functional groups. The ^{1}H NMR spectrum of epoxy functional star polymer showed the presence

Table 1. Synthesis of Telechelic P*t*BA Star Polymers with Different End-Functional Groups Using α-Functional Macroinitiators[a]

Functional Group	Initiator	$M_{n,sec}$ of Arm	M_w/M_n of Arm	$M_{n,sec}$ of Star[b]	M_w/M_n of Star[c]	Star Polymer Yield
HS∼		6900[d]	1.18	37800	1.39	95%
		5600[d]	1.22	34100	1.56	90%
HO∼		6700[d]	1.19	72700	1.91	88%
		9900[e]	1.19	103000	1.45	89%
NC∼		8200[e]	1.13	82900	1.41	92%
Br∼		11820[e]	1.17	129000	1.49	91%

[a] $[CuCl]_0 = [PMDETA]_0 = [PtBA]_0 = [DVB]_0/15 = 0.051$ M in anisole, $T = 110$ °C, reaction time = 5 h. [b] Based on linear polystyrene standards. [c] Macroinitiator peak was excluded. [d] $[CuBr]_0 = [PMDETA]_0 = [initiator]_0/2 = 0.055$ M, $[tBA]_0 = 5.5$ M in acetone, $T = 60$ °C. [e] $[CuBr]_0 = [PMDETA]_0 = [initiator]_0/2 = 0.055$ M, $[tBA]_0 = 5.5$ M in acetone, $T = 90$ °C.

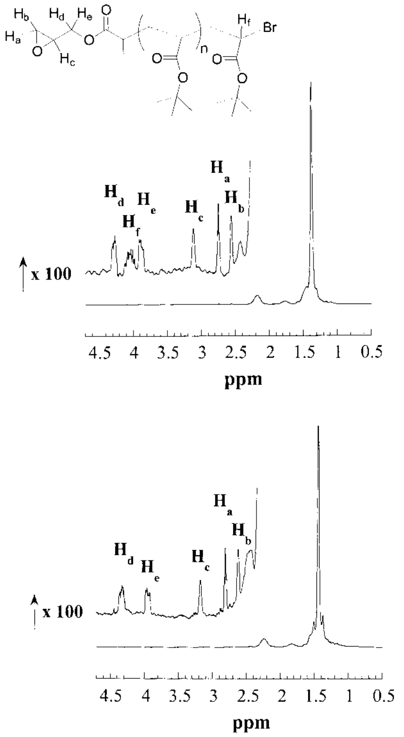


Figure 11. (A) ^{1}H NMR spectrum of the P*t*BA macroinitiator with epoxy α-functional and bromine ω-functional chain ends. **(B)** ^{1}H NMR spectrum of P*t*BA star polymer after reacting epoxy end-functional PtBA macroinitiator with DVB in 1,2-dichlorobenzene, $[CuCl]_0 = [PMDETA]_0 = [PtBA]_0 = [DVB]_0/15 = 0.051$ M, $T = 110$ °C, reaction time = 5 h.

of the epoxy group as well as the disappearance of signals from the proton adjacent to Br group on the last *t*BA unit (H_f) (Figure 11B). Again, signals from DVB microgel core and the dangling vinyl bonds had lower intensities than the values estimated from DVB conversion as discussed previously. These data were consistent with the proposed star formation mechanism. Similarly, star polymers with hydroxy, amino, cyano, and bromine end-functional groups on the outer layers were prepared in good yields (Table 1). The conservation of the functional groups was confirmed by ^{1}H NMR measurement. In addition, the molecular weight distributions of end-functional P*t*BA star polymers were similar to those of star polymers without any end-functionalities (Supporting Information, Figures 2S, 3S, 4S, and 5S).

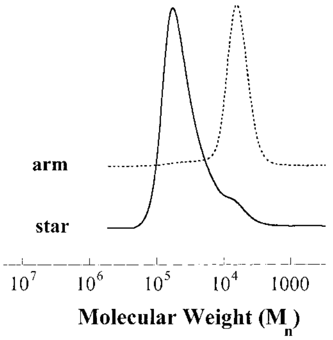


Figure 12. SEC traces of epoxy end-functional P*t*BA star polymer and epoxy end-functional P*t*BA macroinitiator before reaction with DVB. $[CuCl]_0 = [PMDETA]_0 = [PtBA]_0 = [DVB]_0/15 = 0.051$ M in anisole, $T = 110$ °C, reaction time = 5 h.

Conclusion

P*t*BA star polymers have been successfully prepared by the “arm first” method using copper-mediated ATRP. Among different divinyl coupling reagents used, DVB provided P*t*BA star polymers with highest yield (ca. 95%) and narrowest molecular weight distribution ($M_w/M_n \sim 1.4$). Several factors pertinent to star polymer formation, including the choice of the exchange halogen, the addition of copper(II) species, the ratio of DVB to PSt, and the star formation time, were addressed. End-functional stars have been successfully synthesized by introducing α-functional groups directly onto the P*t*BA macroinitiators. Star polymers with various end-functionalities, such as hydroxy, epoxy, amino, cyano, and bromine groups, were prepared.

Experimental Section

Materials. *tert*-Butyl acrylate (*t*BA) was washed with 5% NaOH aqueous solution to remove any acid impurities and then washed with H_2O until the aqueous phase was neutral. The solution was dried over $CaCl_2$, filtered, and then distilled under reduced pressure. The monomer was stored at −20 °C under argon prior to use. CuBr was purified according to the published procedure.[30] Divinylbenzene (tech., 80%, mixture of isomers, Aldrich), 1,4-butanediol diacrylate (tech., 90%, Aldrich), and ethylene glycol dimethacrylate (98%, Aldrich) were distilled under reduced pressure and stored at −20 °C. Other reagents were all commercial products and used without further purification.

Kinetic Studies of the ATRP of *t*BA. A dry round-bottom flask with a magnetic stir bar was charged with CuBr (19.6 mg, 0.137 mmol), *t*BA (2 mL, 13.7 mmol), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) (28.5 μL, 0.137 mmol), and anisole (0.5 mL). The flask was sealed with a rubber septum and degassed by three freeze−pump−thaw cycles. The flask was then immersed in an oil bath thermostated at 60 °C, and methyl 2-bromopropionate (MBP) (30.4 mL, 0.272 mmol) was added slowly. At timed intervals, aliquots of the reaction solution were withdrawn via syringes fitted with stainless steel needles and were dissolved in THF to measure conversion (GC) and molecular weight (SEC).

Synthesis of *t*BA Macroinitiators. P*t*BA macroinitiators were prepared in 25 vol % *p*-dimethoxybenzene (DMB) solution at 60 °C using the above-mentioned procedure. The reaction mixture was dissolved in acetone after the polymerization and was precipitated in 50 vol % methanol/H_2O after passing through an alumina column to remove the copper complexes. The samples were redissolved in ethyl ether and then concentrated using a rotary evaporator, followed by drying under vacuum at room temperature for 2 days.

Synthesis of Star Polymers Using Macroinitiators. In a typical experiment, a dry glass tube with a magnetic stir bar was charged with CuBr (4.2 mg, 29.3 μmol), P*t*BA macroinitiator (0.2 g, 29.0 μmol), DVB (62.0 μL, 0.435 mmol), PMDETA (6.1 μL, 29.2 μmol), and anisole (0.5 mL). The glass tube was degassed by three freeze−pump−thaw cycles, sealed under vacuum, and then immersed in an oil bath thermostated at 110 °C. After 5 h, the glass tube was taken out and broken. The sample was dissolved in THF to measure monomer conversion (GC) and molecular weight (SEC).

Characterization. Monomer conversions were determined from the concentration of the residual monomer on a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column and a flame ionization detector with helium as the carrier gas. Molecular weights and molecular weight distributions were measured using Polymer Standards Service (PSS) columns (Guard, 10^5, 10^3, and 10^2 Å) coupled with a Waters 410 differential refractometer using THF as the eluent. Triple detection SEC (3D-SEC) was measured in THF using a Spectrasystem P1000 chromatograph pump equipped with PSS (1000, 10^5, and 10^6 Å) and Phenomenex (guard) columns in series with a Wyatt Minidawn light-scattering detector operating at 90° then in parallel with a Waters 410 differential refractometer and a Viscotek T50 intrinsic viscometer. Polystyrene and poly(methyl methacrylate) standards were used to calibrate the columns. PSS SEC scientific software version 4.02 was used to analyze the data. ^{1}H NMR was performed on a Brucker WP300 instrument using $CDCl_3$ as the solvent.

Acknowledgment. This work was financially supported by the industrial members of ATRP consortium at Carnegie Mellon University. We thank Kelly Davis for helpful suggestions on the ATRP of *t*BA and providing some of the P*t*BA macroinitiators. We are grateful to Jeff Pyun and Mathew Peterson for their help with triple detection SEC and ^{1}H NMR, respectively.

Supporting Information Available: SEC traces showing effect of added copper(II) and the formation of end-functional star polymers with hydroxy, amino, cyano, and bromine groups. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA991076M