DOI: 10.1021/ma900459g

Macromolecules
ARTICLE

Development of Branching in Atom Transfer Radical Copolymerization of Styrene with Triethylene Glycol Dimethacrylate

Hong-Jun Yang, Bi-Biao Jiang,* Wen-Yan Huang, Dong-Liang Zhang, Li-Zhi Kong, Jian-Hai Chen, Chun-Lin Liu, Fang-Hong Gong, Qiang Yu, and Yang Yang

School of Materials Science and Engineering, Jiangsu Polytechnic University, Changzhou 213164, China

Received March 4, 2009; Revised Manuscript Received June 16, 2009

ABSTRACT: The branching copolymerization of styrene with triethylene glycol dimethacrylate (*tri*-EGDMA) as the branching agent was carried out using atom transfer radical polymerization (ATRP) in anisole at 90 °C. The resulting copolymers were analyzed using ^{1}H NMR and triple detection size exclusion chromatography (TD-SEC). The NMR analysis shows that the pendent vinyl groups react even in the early stages of the polymerization. Analysis of the changes in the molecular weight and polydispersity of the copolymers suggests that the reaction system contains three components: the primary chains, the slightly branched chains comprising of two primary chains, and the highly branched chains consisting of more than three primary chains. The coupling reaction mainly takes place between the primary chains, resulting in the slightly branched chains in the early stages of the reaction, the weight fraction of the branched chains and the degree of branching increase gradually with monomer conversion, highly branched chains mainly form at relatively high monomer conversions.

Introduction

Branched polymers have recently received much attention as materials with novel physical properties.[1] These polymers have lower viscosity compared to their linear counterparts of the same molecular weight. In 1995, Fréchet et al. reported an important synthetic method for the preparation of branched vinyl polymer through self-condensing vinyl polymerization (SCVP).[2] Shortly afterward, SCVP was expanded to controlled/"living" radical polymerization and vinyl branched polymers were prepared by nitroxide-mediated radical polymerization,[3−5] atom transfer radical polymerization (ATRP),[6−16] reversible addition−fragmentation chain transfer (RAFT) polymerization,[17−20] oxyanionic polymerization,[21,22] and group transfer polymerization (GTP).[23−27] However, SCVP usually requires the prior synthesis of the monomer−initiator precursor, which is quite tedious. Consequently, Baskaran reported the synthesis of branched polystyrene *via* anionic SCVP of divinylbenzene.[28] Since controlled/"living" radical polymerization is not only highly controlled but also experimentally forgiving, Sherrington's group prepared branched poly(methyl methacrylate)s through ATRP with ethylene glycol dimethacrylate (EGDMA) as the branching agent.[29] By now, several research groups have reported the synthesis of branched polymers using divinyl monomers by ATRP,[30−40] RAFT,[41−44] and GTP.[29,45] In particular, Armes et al. focused on the evolution of branching with monomer conversion in the ATRP of 2-hydroxypropyl methacrylate and EGDMA, they found that the formation of highly branched chains occurred only at high monomer conversion, and it was essential to keep the molar ratio of divinyl monomer to initiator less than 1 to suppress gelation.[33] Zhu and our group also obtained similar experimental results.[31,39]

Zhu et al. studied the homopolymerization of dimethacrylate and the copolymerization of methyl methacrylate with dimethacrylate *via* ATRP.[31] They found most of the pendent vinyl groups consumed and the gels had more homogeneous network structures than those from conventional radical polymerization. Recently, Matyjaszewski et al. focused their attention on determining the gel point during ATRP in the presence of divinyl monomers.[36,38] They found all vinyl groups, including the pendent one, had similar reactivity during the copolymerization, and the reaction under ATRP condition was essentially statistical, closely following the prediction of Flory and Stockermayer.

Although a few studies conclude that the significant branching mainly occurs at high monomer conversion, there are no quantitative studies on the variation in weight fraction of components having different molecular weight and degree of branching with monomer conversion. Also, they do not discuss the development of branching throughout the polymerization, especial in the early stages in any detail. Understanding the branching formation mechanism throughout the reaction is beneficial to preparation of a branched polymer, or gel with controlled structures such as the distribution of the branching or the cross-linking points. Herein, we focused on the development of branching and the variation of different components throughout the reaction in the ATRP of styrene with triethylene glycol dimethacrylate (*tri*-EGDMA) using ^{1}H NMR and triple detection size exclusion chromatography (TD-SEC).

Experimental Section

Materials. Triethylene glycol dimethacrylate (*tri*-EGDMA, Aldrich Chemical Co.), 2,2′-bipyridine (Bpy, Shanghai Chemical Co.), and *tert*-butyl-2-bromoisobutyrate (*t*-BB*i*B, Shanghai Chemical Co.) were of analytical grade and used as received. Styrene (analytical grade, Shanghai Chemical Co.) was distilled under reduced pressure. Cu^{I}Br (analytical grade, Shanghai Chemical Co.) was purified by stirring in glacial acetic acid, washing with methanol, and then drying under vacuum at 70 °C. Anisole, *n*-hexane, and tetrahydrofuran (THF) were of analytical grade and used without further purification.

*Corresponding author. E-mail: jiangbibiao@jpu.edu.cn. Telephone: (86)519-8633-0006. Fax: (86)519-8633-0047.

 Published on Web 07/24/2009

Kinetic Studies of the ATRP of Styrene and Formation of Branched Copolymer. *Linear Polystyrene*. In a typical synthesis, styrene (5.20 g, 50 mmol), *t*-BB*i*B (0.56 g, 2.5 mmol), $Cu^{I}Br$ (0.36 g, 2.5 mmol), and Bpy (0.98 g, 6.25 mmol) were added to a 100 mL round-bottomed flask equipped with a stir bar; anisole (2.6 g) was added as the internal standard. The flask was cycled between vacuum and argon (×6 times), and then the flask was immersed in a preheated (90 °C) oil bath. Aliquots (~0.5 mL) of the reaction mixture were taken *via* a syringe through a septum at predetermined intervals and the polymerization was stopped by exposing to the air. After the conversion of the reactants was measured by gas chromatography (GC) analysis, the reaction mixture was diluted into 1 mL of THF and filtered by PTFE film (×4 times). Molecular weight, polydispersity, and intrinsic viscosity were obtained from triple detection size exclusion chromatography (TD-SEC).

Branched Poly(styrene-co-tri-EGDMA). In a typical experiment, styrene (20.8 g, 200 mmol), *tri*-EGDMA (2.56 g, 9 mmol), *t*-BB*i*B (2.24 g, 10 mmol), $Cu^{I}Br$ (1.43 g, 10 mmol), and Bpy (3.90 g, 25 mmol) were placed into a 100 mL round-bottomed flask equipped with a stir bar; anisole (10.4 g) was added as the internal standard. The flask was cycled between vacuum and argon (× 6 times) and then the flask was immersed in a preheated (90 °C) oil bath. Samples (~1 mL) were taken *via* a syringe through a septum at predetermined intervals and the polymerization was stopped by exposing to the air. After the conversion of the reactants was measured by GC, the rest of the sample was diluted into 1 mL of THF and filtered by PTFE film (×4 times), and then the solution was analyzed by TD-SEC to obtain molecular weight, polydispersity and intrinsic viscosity. Finally, the reaction mixture was precipitated into a large excess of *n*-hexane to remove the unreacted reactants, and the purified copolymer was dried under vacuum and analyzed by NMR. ^{1}H NMR spectroscopy were used to calculate the consumption of the pendent vinyl group by comparing the integral value of the pendent vinyl resonances at δ 5.6 ppm (Peak *i* in Figure 2) and 6.2 ppm (Peak *h* in Figure 2) with that of the ether methylene protons in the incorporated *tri*-EGDMA units at δ 2.8 to 3.8 ppm (Peak *g* in Figure 2).

Proton Nuclear Magnetic Resonance Spectroscopy. ^{1}H NMR (500 MHz) spectra were recorded on a Bruker ARX-500 type NMR spectrometer at 25 °C with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. The consumption of the pendent vinyl groups in the polymer chain can be quantitatively determined by its ^{1}H NMR data.[36] In order to reduce the inaccuracy derived from too low weight fraction of the pendent vinyl group, the experiment with *t*-BB*i*$B_{1.0}$-*tri*-$EGDMA_{0.9}$-$styrene_{20}$ was carried out in the following studies unless stated otherwise.

Analysis of Reactants Consumption. Conversion of the reactants was determined using a HP-689 gas chromatography instrument equipped with a HP-5 column (30 m × 0.54 mm × 0.5 μm); anisole was used as the internal standard. The carrier gas was hydrogen at 1 mL/min, and the column temperature was increased from a starting value of 90 °C at sample injection to a maximum of 300 at 10 °C/min. The peaks were identified by the corresponding pure reactants.

Triple Detection Size Exclusion Chromatography. Molecular weight, polydispersity and intrinsic viscosity were obtained by TD-SEC detection at 25 °C. The instrumentation consisted of the following: a Waters 1515 isotratic HPLC pump with 5 μm Waters styragel columns (guard, 0.5 HR, 4 HR and 1 HR, the molecular weight ranges of the three HR columns are 0−1000, 100−5000, and 5000−500000 g/mol, respectively); a Waters 717 PLUS autosamples; a Waters 2414 differential refractive index (DRI) detector, the wavelength is 880 nm; a multi angle laser light scattering (MALLS) detector (Wyatt mini Dawn TRISTRA light scattering, three detection angles are 45°, 90° and 135°, the wavelength and power are 690 nm and 220 w); a Wyatt Visco Star viscometer detector; a Waters Breeze data manager. The eluent was HPLC grade THF delivered at 1.0 mL/min.

Results and Discussion

The preparation of branched polymers *via* atom transfer radical polymerization (ATRP) of vinyl and divinyl monomers has been reported.[30−40] Analysis of the changes in the molecular weight and polydispersity of the polymers shows that the formation of highly branched chains occurs mainly at high monomer conversions.[31,33,39] Kinetic studies also demonstrate that the divinyl monomer is consumed some faster than the monovinyl monomer.[33,39] Furthermore, all vinyl groups, including the pendent one, are equally reactive during the copolymerization.[33,36] Inspired by these works, we focused on the branching formation mechanism in the ATRP of styrene with triethylene glycol dimethacrylate (*tri*-EGDMA), and the components and their variation with monomer conversion using NMR and triple detection size exclusion chromatography (TD-SEC) in the present study.

Kinetic Behavior. In order to understand the development of branching throughout the copolymerization, we carried out a more detailed analysis by taking samples at regular intervals during the reaction. Figure 1 illustrates the ATRP kinetic data. The conversion of *tri*-EGDMA is increased much faster in the early stages compared to that of ethylene glycol dimethacrylate (EGDMA) as reported by Armes et al.;[33] this may lead to some early branching. The rapid conversion of *tri*-EGDMA at this stage may be attributed to the interaction of the donor and the acceptor, because styrene and *tri*-EGDMA are electron-rich and electron-poor monomers respectively. The linear semilogarithmic plot of monomer conversion vs. time proves its consumption is first-order and implies a constant radical concentration during the reaction. These results are quite different from those reported by Zhu in the copolymerization of methyl methacrylate and EGDMA in bulk,[31,32] and our own group,[39] where autoacceleration occurs at high monomer conversion due to diffusion-controlled radical deactivation.[31,46] These results suggest that the presence of anisole in our reactions is enough to maintain excellent control even at high monomer conversion.

We used NMR spectroscopy to analyze the consumption of the pendent vinyl groups with monomer conversion. Figure 2 shows a typical ^{1}H NMR spectrum with all of the resonances assigned. The consumption of free *tri*-EGDMA introduces potential branching points (pendent vinyl groups) into the primary chain. Branching occurs when the pendent vinyl groups react. We calculated the conversion of the pendent vinyl groups (C_p) according to eq 1. Since the amount of the incorporated *tri*-EGDMA unit ($N_{tri\text{-EGDMA}}$) varies as the reaction proceeds, we calculated the absolute

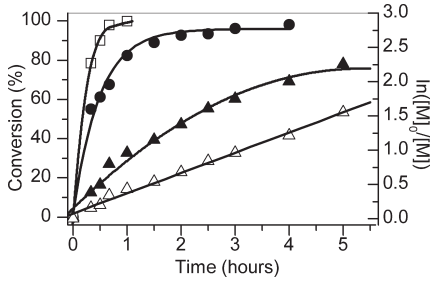


Figure 1. Kinetics for the copolymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) initiated by *tert*-butyl-2-bromo-isobutyrate (*t*-BB*i*B) in anisole at 90 °C. *t*-BB*i*$B_{1.0}$-*tri*-$EGDMA_{0.9}$-$styrene_{20}$: styrene (▲), *tri*-EGDMA (●), *t*-BB*i*B (□) and ln([M]$_0$/[M]) (△).

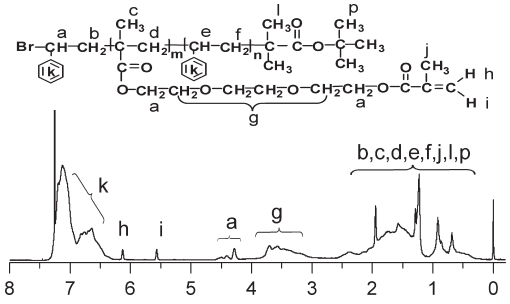


Figure 2. Typical ^{1}H NMR spectrum of the copolymers from the copolymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) initiated by *tert*-butyl-2-bromoisobutyrate (*t*-BB*i*B) in anisole at 90 °C. *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_{20}$. The absolute weight average molecular weight of the sample is 2800 g/mol. ^{1}H NMR conditions: 25 °C, $CDCl_3$ as the solvent.

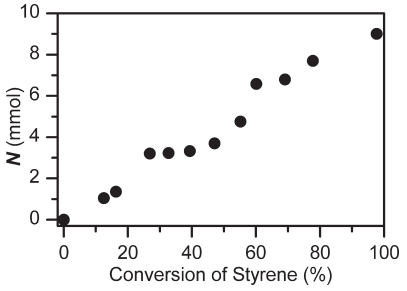


Figure 3. Consumption of the pendent vinyl groups during the copolymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) initiated by *tert*-butyl-2-bromoisobutyrate (*t*-BB*i*B) in anisole at 90 °C. *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_{20}$.

consumption of the pendent vinyl groups (N in mmol) using eq 2. N_p is the number of pendent vinyl groups, S_i, S_h, and S_g are the peak areas of the related signal (see Figure 2), 9.0 is the initial concentration of *tri*-EGDMA in mmol, and $convn_{tri\text{-EGDMA}}$ is the conversion of *tri*-EGDMA obtained from gas chromatography (GC) measurement. Figure 3 shows the results and the pendent vinyl groups do react even at very low monomer conversions.

$$C_p = \frac{N_{tri-\mathrm{EGDMA}} - N_p}{N_{tri-\mathrm{EGDMA}}} = 1 - \frac{(S_i + S_h)/2}{S_g/8} \quad (1)$$

$$N = 9.0 \times convn_{tri-\mathrm{EGDMA}} \times C_p \quad (2)$$

Triple Detection Size Exclusion Chromatography Analysis. Figure 4 shows the changes of the number average molecular weight and polydispersity with monomer conversion. The results are quite similar to the literature.[31−33,39] The molecular weight of the copolymer seems to increase more or less linearly up to about 60% monomer conversion, and the polydispersity also remains relatively low, suggesting that significant branching occurs and highly branched chains mainly form at high monomer conversion.

However, one of our main objectives is to study the development of branching throughout the reaction. In fact, we can get some clues to branching at low monomer conversion by carefully comparing the data of the copolymer with those of the homopolymer. The molecular weight of the copolymer is higher than that of the homopolymer at a given monomer conversion. The more important is that the polydispersity of the copolymer is not only wider than that of the homopolymer, also increases with monomer conversion even in the early stages, which is in sharp contrast to the results of linear ATRP.[47−49] These results suggest that the

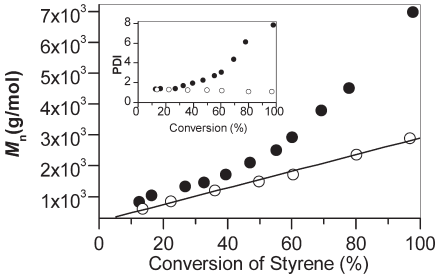


Figure 4. Changes of the number average molecular weight (M_n) and (inset) polydispersity (PDI = M_w/M_n) with styrene conversion for the copolymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) initiated by *tert*-butyl-2-bromoisobutyrate (*t*-BB*i*B) in anisole at 90 °C. *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_{20}$. Unfilled cycles are for the linear reference without *tri*-EGDMA.

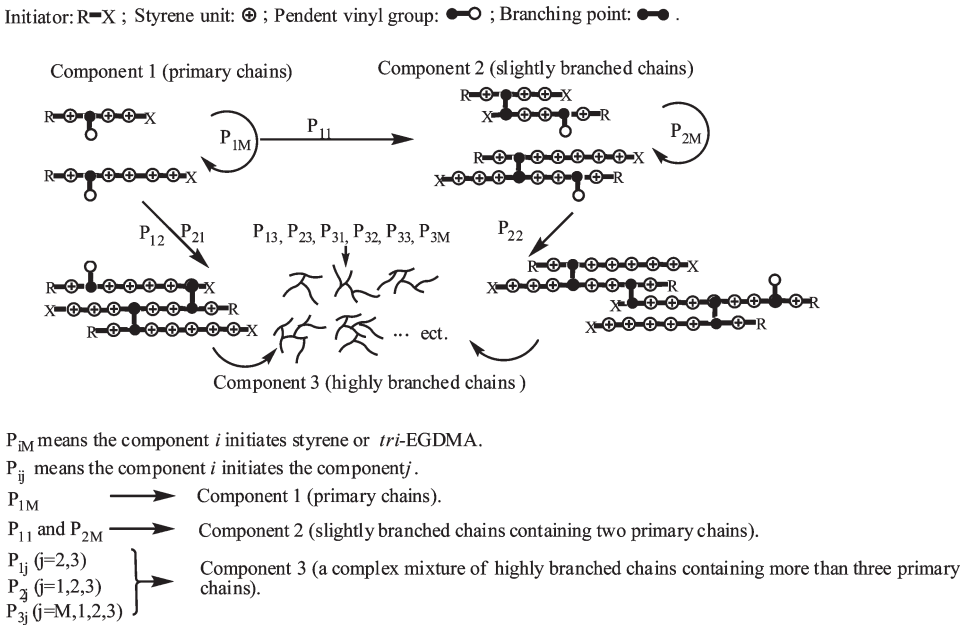
formation of branched chains occurs in the early stages of the reaction.

The smooth increase of molecular weight in the early stages, along with the approximately linear consumption of the pendent vinyl groups (N) with monomer conversion in Figure 3, suggests the coupling reaction occurs mainly between the primary chains, resulting in small and slightly branched chains. The rapid increase in molecular weight in the later stages in Figure 4 implies the coupling between branched chains becomes significant, giving rise to the formation of larger and highly branched chains (Scheme 1).

Further evidence that branching takes place in the early stages of the reaction can been seen in Figure 5, which shows the evolution of the differential molecular weight distribution with monomer conversion. For comparison, the result of the homopolymer at 35.9% monomer conversion is also listed. In contrast to the linear reference, almost all the curves of the copolymer consist of three peaks, proving the presence of three components of marked different molecular weights. We might consider that the components 1, 2, and 3 are relative to the primary chain, the slightly branched chains consisting of two primary chains and the highly branched chains containing more than three primary chains respectively. The curves at monomer conversion 12.5% and 16.3% look like monomodal, however, they are not only much wider but also asymmetrical compared to the linear reference. An overlay of SEC chromatograms from differential refractive index (DRI) detector of the copolymers at various conversions and the linear reference is shown in the Supporting Information (Figure S1).

Our big concern now is what structures the three components are of? So we integrated the peaks in SEC curves from multi angle laser light scattering (MALLS) detector to probe the dependence of the weight average molecular weight ($M_{w.MALLS}$) of the three components on monomer conversion (Figure 6). The molecular weights of components 1 and 2 increase smoothly and linearly throughout the reaction, proving that components 1 and 2 relate to the primary chains and the simple branched chains consisting of two primary chains. Component 3 is in sharp contrast to components 1 and 2, not only does its molecular weight increase rapidly but also there is marked acceleration in the increase rate of molecular weight with monomer conversion. These results suggest that component 3 is a complex mixture of molecules with different and variable numbers of primary chains. The rapid increase in molecular weight comes from the coupling between branched chains, and the acceleration in the increase rate of molecular weight is because the coupling between branched chains becomes more and more significant with evolution of polymerization.

Scheme 1. Schematic Formation of the Branched Copolymers *via* Atom Transfer Radical Polymerization of Styrene with Triethylene Glycol Dimethacrylate (*tri*-EGDMA)



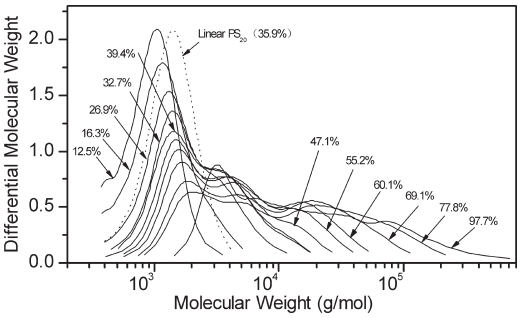


Figure 5. Evolution of the differential molecular weight distribution with conversion for the copolymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) initiated by *tert*-butyl-2-bromo-isobutyrate (*t*-BB*i*B) and the linear reference without *tri*-EGDMA at 35.9% styrene conversion. Polymerization in anisole at 90 °C, *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_{20}$.

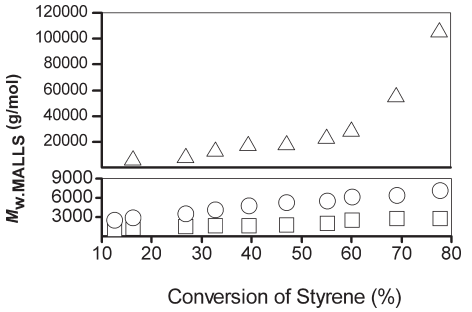


Figure 6. Variation of $M_{w,MALLS}$ of the three components with styrene conversion for the copolymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) initiated by *tert*-butyl-2-bromoisobutyrate (*t*-BB*i*B) in anisole at 90 °C. *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_{20}$: (□) component 1; (○) component 2; (△) component 3.

In order to obtain quantitative information to understand the development of branching, we determined the weight fraction (w_i) of every component by splitting the SEC-DRI curves using Gaussion function.[35,36] Figure 7 shows

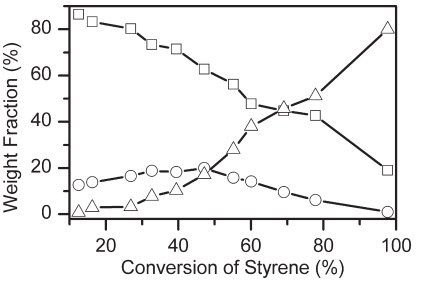


Figure 7. Variation of the weight fraction of the three components with styrene conversion for the copolymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) initiated by *tert*-butyl-2-bromo-isobutyrate (*t*-BB*i*B) in anisole at 90 °C. *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_{20}$: (□) component 1; (○) component 2; (△) component 3.

the results. As expected, the weight fraction of the component 1, w_1, decreases as the polymerization proceeds. However, at the last of the reaction, about 20% of the primary chain can not incorporate into the branched chains, which may be explained mainly by the limited content of the pendent vinyl group and the steric effect at high conversion. In fact, the pendent vinyl group is not visible in NMR spectra of the polymers obtained at high monomer conversion (≥98%). The presence of so many primary chains results in a marked polydispersity. Consequently, w_3 increases and reaches nearly to 80% finally. Surprisingly, w_2 is very small compared to w_1 and w_3, indicating the coupling of component 2 with itself and components 1 and 3 is a major reaction pathway, which makes the consumption of component 2 much faster than its formation. In addition, w_3 is not only very low (< 5%), also increases very slowly at monomer conversion less than 30%. These results prove the coupling mainly takes place between the primary chains, resulting in the slightly branched component 2 and the formation of highly branched chains is not significant at the early stages (Scheme 1).

The peak molecular weight of component 2, $M_{p.2}$, is approximately two times that of $M_{p.1}$ at the same monomer conversion as shown in Table 1, proving that the component

Table 1. Summary of Branched Copolymers from the Copolymerization of Styrene (St) and Triethylene Glycol Dimethacrylate (*tri*-EGDMA) Initiated by *tert*-Butyl-2-bromoisobutyrate (*t*-BB*i*B) in Anisole at 90 °C. *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_{20}$

$convn_{st}$ (%)	$M_{P.1}$[a] (g/mol)	$M_{P.2}$[a] (g/mol)	$M_{P.3}$[a] (g/mol)	$M_{w.MALLS}$ (g/mol)[b]	$\overline{M}_{w.MALLS}$ (g/mol)[b]	f[b]
12.5	921	2083		1243	1164	0.94
16.3	1206	2432	6042	1865	1689	0.91
26.9	1426	3252	7537	2100	2068	0.98
32.7	1643	4243	11640	2800	2980	1.06
39.4	1796	4165	13500	3674	3783	1.03
47.1	2120	5260	16600	5519	5190	0.94
55.2	2246	5520	14740	8151	8271	1.01
60.1	2418	5958	17270	11580	12823	1.11
69.1	2711	6051	22470	25210	26765	1.06
77.8	3683	6670	183000	54210	55470	1.02

[a] M_p = The peak molecular weight measured by differential refractive index (DRI) detector. [b] $M_{w.MALLS}$ = The absolute weight average molecular weight measured by multi angle laser light scattering (MALLS) detector, $\overline{M}_{w.MALLS} = \Sigma w_i \times M_{w\text{-}i.MALLS}$, $f = \overline{M}_{w.MALLS}/M_{w.MALLS}$.

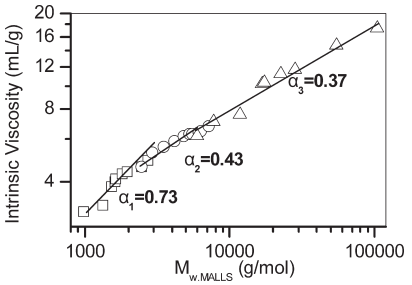


Figure 8. The Mark−Houwink plot of the three components for the copolymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) initiated by *tert*-butyl-2-bromoisobutyrate (*t*-BB*i*B) in anisole at 90 °C. *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_{20}$: (□) component 1; (○) component 2; (△) component 3.

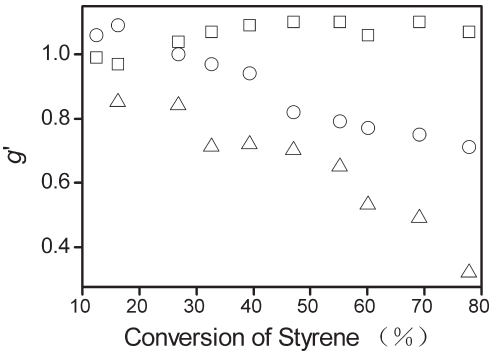


Figure 9. Variation of the Zimm branching factor of the three components with styrene conversion for the copolymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) initiated by *tert*-butyl-2-bromoisobutyrate (*t*-BB*i*B) in anisole at 90 °C. *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_{20}$: (□) component 1; (○) component 2; (△) component 3.

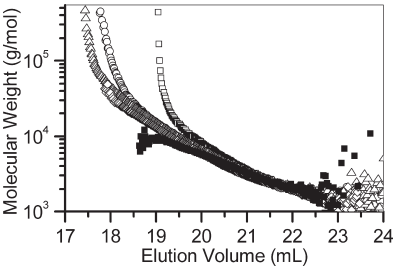


Figure 10. Relationship between molecular weight and elution volume for the polymers at about 33% styrene conversion. The polymerization of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) was initiated by *tert*-butyl-2-bromoisobutyrate (*t*-BB*i*B) in anisole at 90 °C. *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_x$, where x varies from 20 to 50: x = 20 (□), 30 (○), 40(△), 50 (◇) and the linear reference from *t*-BB*i*B$_{1.0}$-styrene$_{20}$ (■).

2 consists of two primary chains. In contrast to the relation between $M_{p.1}$ and $M_{p.2}$, $M_{p.3}$ is much bigger than $M_{p.2}$, indicating the formation of component 3 is very complex. This result suggests that component 3 consists of not only the coupling products of component 2, but also the coupling products of component 3 with any one of the three components (Scheme 1). $\overline{M}_{w.MALLS}$ coincides well with $M_{w.MALLS}$, supporting the point that the above treatment is reasonable and reliable.

Detailed Analysis of Branching. According to Fréchet's method,[2] Figure 8 shows the Mark−Houwink plot for the three components. The Mark−Houwink exponents α equal to 0.73, 0.43, and 0.37 for the components 1, 2, and 3 respectively (for the linear reference, α = 0.73), proving the component 1 is of linear structure, and the component 3 has much developed branching structure than the component 2.

The hydrodynamic volume, and hence the radius of gyration of a macromolecule in solution, is a controlling factor affecting the intrinsic viscosity (IV). So the more convenient Zimm branching factor, g' where for polymers of equal molecular weight, is usually used as a qualitative indicator to the degree of branching.[50,51]

$$g' = \mathrm{IV}_{\mathrm{Branched}}/\mathrm{IV}_{\mathrm{Linear}} \quad (3)$$

For a linear polymer, the Zimm branching factor g' equals to 1, and for a given molecular weight, the higher the branching of the polymer the smaller the g' is. Figure 9 illustrates the variation of g' with monomer conversion. The g_1' remains almost constant and equals approximately to 1.0 throughout the reaction, again proving that the component 1 relates to the primary chain. The g_2' and g_3' are less than 1 (except the first two data of g_2'), identifying that the component 2 and 3 are of branched structure. Moreover, both the g_2' and g_3' decrease gradually with increase of monomer conversion, indicating the development of branching with molecular weights. Finally, g_3' is always less than g_2' at the same monomer conversion, clearly suggesting that the component 3 has much higher degree of branching than the component 2, which proves our above deduction that the component 2 relates to the slightly branched chain.

Effects of the Dosage of Styrene on the Development of Branching. It is well-know that branched molecules have more compact structures in solution compared to linear molecules of the same molecular weight since branching results in small hydrodynamic volume. Figure 10 shows the relationship between elution volume and molecular weight for the *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_x$ copolymers at about 33% monomer conversion, where x varied from

Table 2. Summary of Branched Copolymers from the Copolymerization of Styrene (St) and Triethylene Glycol Dimethacrylate (*tri*-EGDMA) Initiated by *tert*-Butyl-2-bromoisobutyrate (*t*-BB*i*B) in Anisole at 90 °C

					component 1			component 2			component 3			
x[a]	$convn_{st}$ (%)	N[b] (mmol)	$M_{w.MALLS}$ (g/mol)[c]	g'	w_i (%)	$M_{w\text{-}i.MALLS}$ (g/mol)[c]	g_i'	w_i (%)	$M_{w\text{-}i.MALLS}$ (g/mol)[c]	g_i'	w_i (%)	$M_{w\text{-}i.MALLS}$ (g/mol)[c]	g_i'	f[e]
20	32.7	3.2	2800	0.88	73.4	1621	1.07	18.8	4147	0.97	7.8	12960	0.71	1.06
30	33.1	3.1	4563	0.91	72.0	2477	1.01	20.9	5250	0.94	7.1	17890	0.72	0.86
40	32.8	3.0	4916	0.91	70.1	2647	0.99	21.8	7215	0.91	8.1	23160	0.74	1.11
50	33.7	2.8	5252	0.92	74.3	3330	1.02	19.6	9096	0.87	6.1	22890	0.77	1.07

[a] *t*-BB*i*B$_{1.0}$-*tri*-EGDMA$_{0.9}$-styrene$_x$, x = 20, 30, 40, and 50. [b] N = The absolute consumption of the pendent vinyl groups in mmol calculated according to eq 2. [c] $M_{w.MALLS}$ = The absolute weight average molecular weight measured by multi angle laser light scattering (MALLS) detector, $\overline{M}_{w.MALLS} = \Sigma w_i \times M_{w\text{-}i.MALLS}$, $f = \overline{M}_{w.MALLS}/M_{w.MALLS}$.

20 to 50, the result of the linear reference is also illustrated. For a given elution volume less than 20.5 mL, the molecular weights of the copolymers are higher than that of the linear reference, proving the presence of branched chains regardless of the dosage of styrene. Moreover, at the same elution volume, the higher the dosage of styrene is, the lower the molecular weight of the copolymer is, proving that the polymer at higher dosage of styrene has lower degree of branching as we expected. The evolution of the differential molecular weight distribution for the four copolymers and the linear reference is shown in the Supporting Information (Figure S2).

Table 2 summarizes the quantitative results. The weight fraction of the corresponding component for the four copolymers is approximately equal, but the g' of the obtained copolymers varies from 0.88 to 0.92, indicating the degree of branching decreases with increased styrene usages.

Conclusions

We have analyzed the ATRP of styrene with *tri*-EGDMA as the branching agent using NMR and TD-SEC. This study has reached the following conclusions. First, branching can take place in the early stages of the reaction, the amount of branched chains and the degree of branching increase with monomer conversion. Second, the coupling reaction comes mainly from the primary chain in the early stages of the reaction, resulting in the small and slightly branched chains. In the later stages of the copolymerization, the coupling reaction between branched chains becomes more and more significant, giving rise to the formation of large and highly branched chains accompanied with a rapid increase in molecular weight and broad in polydispersity. Finally, the reaction system contains three components with marked different molecular weights and degrees of branching; component 1 is the primary chain, component 2 is the slightly branched chain consisting of two primary chains, and component 3 is a complex mixture of highly branched chains comprising of more than three primary chains. The much broad polydispersity of the branched polymer from ATRP should derive mainly from the coexistence of the primary chain with the highly branched chains of very high molecular weights. The degree of branching is just a value in average similar to molecular weight of polymer.

Acknowledgment. This work was supported by the Natural Science Foundation of China (20574032) and the Natural Science Foundation of Jiangsu Province (BK2007045).

Supporting Information Available: Figures showing an overlay of SEC chromatograms relating to Figure 5 and the evolution of the differential molecular weight distribution relating to Figure 10. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183–275.
(2) Fréchet, J. M. J.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080–1083.
(3) Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763–10764.
(4) Tao, Y.; He, J.; Wang, Z. M.; Pan, J. Y.; Jiang, H. J.; Chen, S. M.; Yang, Y. L. *Macromolecules* **2001**, *34*, 4742–4748.
(5) Peleshanko, S.; Gunawidjaja, R.; Petrash, S.; Tsukruk, V. V. *Macromolecules* **2006**, *39*, 4756–4766.
(6) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079–1081.
(7) Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. *Macromolecules* **1997**, *30*, 5192–5194.
(8) Matyjaszewski, K.; Gaynor, S. G.; Müller, A. H. E. *Macromolecules* **1997**, *30*, 7034–7041.
(9) Matyjaszewski, K.; Gaynor, S. G. *Macromolecules* **1997**, *30*, 7042–7049.
(10) Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym.Chem.* **1998**, *36*, 955–970.
(11) Muthukrishnan, S.; Jutz, G.; André, X.; Mori, H.; Müller, A. H. E. *Macromolecules* **2005**, *38*, 9–18.
(12) Zou, P.; Yang, L. P.; Pan, C. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 7628–7636.
(13) Muthukrishnan, S.; Erhard, D. P.; Mori, H.; Müller, A. H. E. *Macromolecules* **2006**, *39*, 2743–2750.
(14) Powell, K. T.; Cheng, C.; Wooley, K. L. *Macromolecules* **2007**, *40*, 4509–4515.
(15) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270–2299.
(16) Ren, Q.; Gong, F. H.; Jiang, B. B.; Zhang, D. L.; Fang, J. B.; Guo, F. D. *Polymer* **2006**, *47*, 3382–3389.
(17) Wang, Z. M.; He, J. P.; Tao, Y. F.; Yang, L.; Jiang, H. J.; Yang, Y. L. *Macromolecules* **2003**, *36*, 7446–7452.
(18) Cheng, K. C.; Chuang, T. H.; Chang, J. S.; Guo, W. J.; Su, W. F. *Macromolecules* **2005**, *38*, 8252–8257.
(19) Carter, S.; Hunt, B.; Rimmer, S. *Macromolecules* **2005**, *38*, 4595–4603.
(20) Carter, S.; Rimmer, S.; Sturdy, A.; Webb, M. *Macromol. Biosci.* **2005**, *5*, 373–378.
(21) Li, Y.; Armes, S. P. *Macromolecules* **2005**, *38*, 5002–5009.
(22) Li, Y.; Ryan, A. J.; Armes, S. P. *Macromolecules* **2008**, *41*, 5577–5581.
(23) Simon, P. F. W.; Radke, W.; Müller, A. H. E. *Macromol. Rapid Commun.* **1997**, *18*, 865–873.
(24) Sakamoto, K.; Aimiya, T.; Kira, M. *Chem. Lett.* **1997**, *26*, 1245–1246.
(25) Simon, P. F. W.; Müller, A. H. E.; Pakula, T. *Macromolecules* **2001**, *34*, 1677–1684.
(26) Simon, P. F. W.; Müller, A. H. E. *Macromolecules* **2001**, *34*, 6206–6213.
(27) Simon, P. F. W.; Müller, A. H. E. *Macromolecules* **2004**, *37*, 7548–7558.
(28) Baskaran, D. *Polymer* **2003**, *44*, 2213–2220.
(29) Isaure, F.; Cormack, P. A. G.; Graham, S.; Sherrington, D. C.; Armes, S. P.; Bütün, V. *Chem. Commun.* **2004**, *9*, 1138–1139.
(30) Li, Y.; Armes, S. P. *Macromolecules* **2005**, *38*, 8155–8162.
(31) Wang, A. R.; Zhu, S. *Polym. Eng. Sci.* **2005**, *45*, 720–727.
(32) Wang, A. R.; Zhu, S. P. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5710–5714.
(33) Bannister, I.; Billingham, N. C.; Armes, S. P.; Rannard, S. P.; Findlay, P. *Macromolecules* **2006**, *39*, 7483–7492.
(34) Ren, Q.; Gong, F. H.; Liu, C. L.; Zhai, G. Q.; Jiang, B. B.; Liu, C.; Chen, Y. H. *Eur. Polym. J.* **2006**, *42*, 2573–2580.
(35) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 4960–4965.

(36) Gao, H.; Min, K.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 7763–7770.
(37) Bouhier, M.; Cormack, P. A. G.; Graham, S.; Sherrington, D. C. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2375–2386.
(38) Gao, H.; Miasnikova, A.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 7843–7849.
(39) Gong, H. D.; Huang, W. Y.; Zhang, D. L.; Gong, F. H.; Liu, C. L.; Yang, Y.; Chen, J. H.; Jiang, B. B. *Polymer* **2008**, *49*, 4101–4108.
(40) París, R.; Mosquera, B.; Fuente, J. L. *Eur. Polym. J.* **2008**, *44*, 2920–2926.
(41) Liu, B.; Kazlauciunas, A.; Guthrie, J. T.; Perrier, S. *Macromolecules* **2005**, *38*, 2131–2136.
(42) Liu, B.; Kazlauciunas, A.; Guthrie, J. T.; Perrier, S. *Polymer* **2005**, *46*, 6293–6299.
(43) Vo, C. D.; Rosselgong, J.; Armes, S. P.; Billingham, N. C. *Macromolecules* **2007**, *40*, 7119–7125.
(44) Dong, Z. M.; Liu, X. H.; Lin, Y.; Li, Y. S. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6023–6034.
(45) Butun, V.; Bannister, I.; Billingham, N. C.; Sherrington, D. C.; Armes, S. P. *Macromolecules* **2005**, *38*, 4977–4982.
(46) Wang, A. R.; Zhu, S. P. *Macromolecules* **2002**, *35*, 9926–9933.
(47) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721–1723.
(48) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615.
(49) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93–146.
(50) Wang, W. J.; Kharchenko, S.; Migler, K.; Zhu, S. *Polymer* **2004**, *45*, 6495–6505.
(51) Saunders, G.; Cormack, P. A. G.; Graham, S.; Sherrington, D. C. *Macromolecules* **2005**, *38*, 6418–6422.