



## Branching Copolymerization of Styrene and Methyl Methacrylate with Divinylbenzene

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Received 19 October 2009; accepted 25 May 2010

### ABSTRACT

The branching copolymerization of styrene (St) and methyl methacrylate (MMA) with divinylbenzene (DVB) as branching agent was conducted using atom transfer radical polymerization (ATRP). The kinetics and extent of branching with respect to monomer conversion were studied in details. Gas chromatography (GC), proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectroscopy and dual detection size exclusion chromatography (DD-SEC) were used to monitor the reactions and analyze the resulting copolymers. The analysis of reactants conversion revealed that the conversion rate of DVB, having two double bonds, is only slightly faster than those of the monomers, with no donor/acceptor interactions between DVB molecules and the monomers. The molecular weight increases slowly which is still somehow larger than the theoretical value in the early stages; then deviates significantly from its theoretical estimation beyond 40% conversion and increases steeply at later stages of 70% monomer conversion. These results suggest that branching takes place in the early stages of the reaction regardless of any possible donor/acceptor interactions between the monomers and DVB molecules, and the coupling reaction originates mainly from the primary chain resulting in small chain branching. Coupling reaction between the branched chains becomes significant in the later stages of the copolymerization which produces highly branched chains. The reaction system contains three components throughout the reaction: the primary chains, the slightly branched chains comprising of two primary chains, and the highly branched chains consisting of 3 or more primary chains. Although the weight fraction of the branched chains increases with monomer conversion, there is finally 20% primary chains still left in the reaction system which gives rise to limited molecular weight and high polydispersity of the branched polymers prepared through ATRP using divinyl monomer as the branching agent.

### Key Words:

branched copolymer;  
ATRP;  
DVB;  
styrene;  
MMA.

### INTRODUCTION

Over the past two decades, hyper-branched polymers have received much attention due to their unique physical and chemical properties and potential applications in various fields [1-3]. In 1995, Fréchet reported his versatile approach named self-condensing vinyl poly-

merization of an  $\text{AB}^*$  monomer [4], where A stood for the double bond and  $\text{B}^*$  represented the initiating moiety that could be activated to form an active centre to initiate the polymerization of A. Shortly afterwards, this strategy was adapted to ATRP by Hawker [5] and

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Gaynor [6].

Unfortunately, the AB\* monomer used to prepare hyperbranched polymers via self-condensing vinyl polymerization is either very expensive [6], or tedious to prepare [4,5,7,8]. As a result, Baskaran reported his strategy to prepare hyperbranched polymer from DVB through anionic polymerization [9]. ATRP has a great benefit due to its applicability to a variety of monomers and tolerance to many solvents, additives and impurities often encountered in industrial operation, and obviously has advantages over anionic polymerization in preparing hyperbranched polymers [10]. In 2004, Sherrington reported a facile, generic and cost-effective route to branched poly(methyl methacrylate) via ATRP exploiting ethylene glycol dimethacrylate as the branching agent [11]. By now, several research groups have reported the preparation of branched polymers using divinyl monomers by ATRP [12-16].

Our research group also prepared branched polystyrene and cationic polyelectrolytes using ATRP [17-21]. Wang et al. [22], Bannister et al. [23], and our group [24] investigated the development of branching in the ATRP process of vinyl and divinyl monomers, which significant branching occurs relatively late in the process. Moreover, the ATRP branching process conforms closely to classical gelation theory in that soluble branched polymers can only be obtained when the branching agent/initiator molar ratio is less than unity.

Recently, we studied the development of branching in the ATRP of styrene and triethylene glycol dimethacrylate (*tri*-EGDMA) using triple detection size exclusion chromatography to confirm branching at the early stages of the reaction [25]. Moreover, the reaction system contains three components with marked different molecular weights and degrees of branching throughout the reaction: the primary chain, the slightly branched chain consisting of two primary chains, and the highly branched chain comprising of three or more primary chains. The much broader polydispersity of the branched polymer obtained from ATRP is expected mainly from the co-existence of the primary chain with the branched chains of different molecular weights. The degree of branching is just a value in average similar to molecular weight of polymer. Also, we consider that donor/acceptor

interactions may promote branching, since styrene and *tri*-EGDMA are the respective electron-rich and electron-poor monomers.

Although there are few studies describing the syntheses of branched vinyl polymers via ATRP, the preparation of branched vinyl copolymers of two monomers with different polarities and reactivity ratios is rare [24]. Copolymers of styrene and acrylate have found wide applications in coatings and adhesives, etc. The introduction of branching is helpful for preparation of coating resins and adhesives with high solid content.

In this work, we studied the copolymerization of styrene and MMA with DVB via ATRP using dual detection size exclusion chromatography and NMR spectroscopy. Compared to our previous studies on the preparation of branched copolymer of styrene and acrylonitrile [24], we conclude that the reaction contains three components: the primary chain, the slightly branched chain comprising two primary chains, and the highly branched chain consisting of 3 or more primary chains. The primary chains are mainly involved in coupling reactions at the early stages of the whole reaction, resulting in slightly branched chains. The coupling reaction between branched chains becomes significant by formation of highly branched chains in the later stages of the copolymerization. Of utmost importance, with monomer conversion it is possible to obtain quantitative results on the weight fractions of different chains.

## EXPERIMENTAL

### Materials

Divinylbenzene (DVB, mixture of 1,3- and 1,4-isomers and 20% ethylstyrene, Fluka, USA), *tert*-butyl-2-bromoisobutyrate (*t*-BBiB, Aldrich, USA), and 2,2'-bipyridine (Bpy, analytical reagent from Shanghai Chemical Co., Shanghai, PR China) were used without further purification. Copper (I) bromide (CuBr, analytical reagent from Shanghai Chemical Co., Shanghai, PR China) was purified by stirring in glacial acetic acid, washing with methanol and then drying under vacuum at 70°C. Styrene and MMA were distilled at reduced pressure before use. All the

solvents and other reagents were used as received.

### Polymerization Procedure

A representative procedure for the branching copolymerization is as follows: *t*-BBiB (222.9 mg, 1 mmol), DVB (80% grade, 131.1 mg, 0.8 mmol), styrene (1560 mg, 15 mmol), MMA (1500 mg, 15 mmol), CuBr (71.7 mg, 0.5 mmol) and Bpy (156.2 mg, 1 mmol) were added successively to a 100 mL three-neck round-bottom flask with a magnetic stirrer. Cyclohexanone (98 mg, 1 mmol) was added as internal standard for GC measurements. The flask was back-filled with argon more than 5 times to remove oxygen, then sealed and placed in an oil bath thermostatted at  $90 \pm 1^\circ\text{C}$ . A dark brown heterogeneous system was then obtained. Samples were taken from the flask at time intervals throughout the polymerization. Each sample was diluted with tetrahydrofuran (THF) and then filtered to remove the catalyst. Part of it was used for GC and SEC measurements to determine monomer conversion and molecular weight. The rest was precipitated in ethanol and the resulting polymer was dried and then used for  $^1\text{H}$  NMR measurements.

Linear copolymerization was carried out in the absence of DVB at conditions similar to those stated above (Feed mole ratio of *t*-BBiB/styrene/MMA/DVB/CuBr/Bpy/cyclohexanone is 1/15/15/0.8/0.5/1/1 at  $90^\circ\text{C}$ ).

### Characterization

Monomer conversions were probed by an HP-6890 GC chromatography, equipped with a DB-5 column.  $F_{\text{st}}$  of the linear copolymer was calculated according to monomer conversion, assuming that the consumed monomer was incorporated into the polymer chain. Molecular weight and polydispersity were measured by DD-SEC. SEC was performed on a SEC line consisting of a Waters 1515 isocratic HPLC pump (USA) and Waters styragel HR 4e, HR 1 and HR 0.5 columns, and a Waters 2414 refractive index detector (RI detector, detecting the molecular weight distribution or the concentration of the eluted polymers) at room temperature. The eluent was THF with a flow rate of  $1 \text{ mL min}^{-1}$  and the data were obtained with linear polystyrene standards. A multi-angle laser light scattering (MALLS, detecting the absolute weight

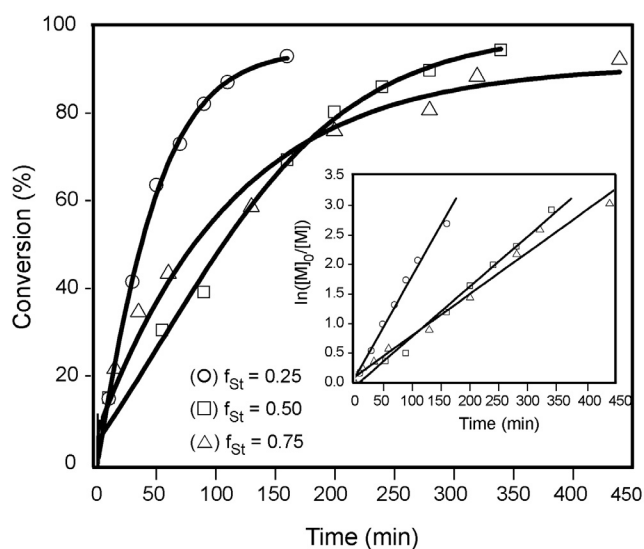
average molecular weight  $\overline{M}_{w,\text{MALLS}}$ ) was employed on a 703-T mini DAWN tristar light scattering photometer, USA. The  $\text{dn}/\text{dc}$  value of the branched copolymer was determined using an Optilab REX ( $\lambda=640 \text{ nm}$ ) interferometer refractometry (Wyatt, USA) in batch mode at  $35^\circ\text{C}$ . The  $\text{dn}/\text{dc}$  value was calculated to be  $0.1242 \pm 0.0037 \text{ mL g}^{-1}$ .

The number average molecular weight,  $\overline{M}_{n,b}$ , of the branched copolymer was calculated using the absolute weight average molecular weight,  $\overline{M}_{w,\text{MALLS}}$ , according to the literature [26]. The branched copolymer was characterized by  $^1\text{H}$  NMR using a Bruker ARX-300 type NMR spectrometer (Germany) at room temperature using  $\text{CDCl}_3$  as solvent.

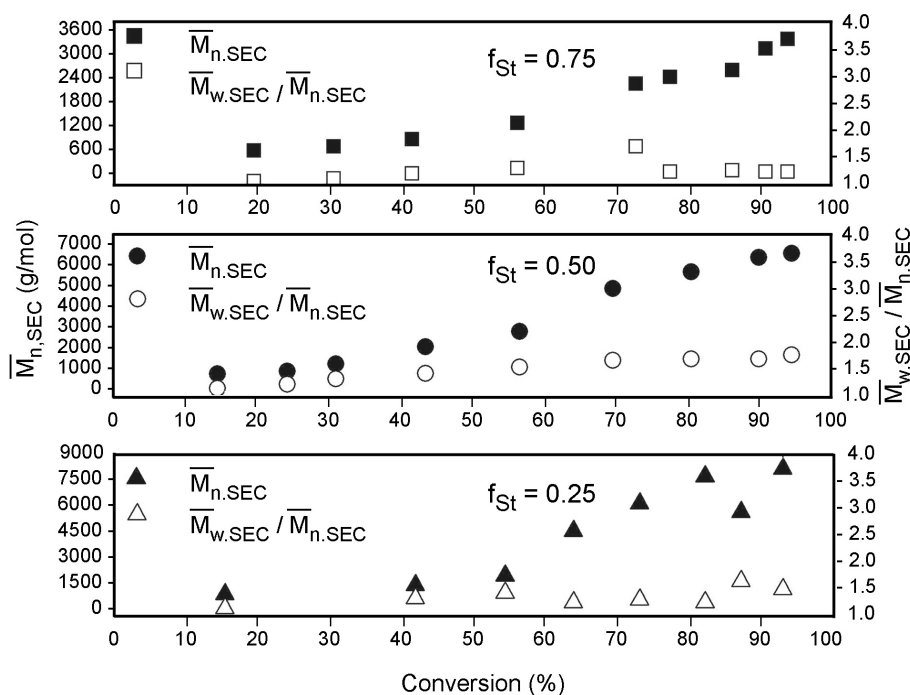
## RESULTS AND DISCUSSION

### Linear Copolymerization of Styrene and MMA

Linear copolymerization of styrene and MMA was carried out and taken as the reference for the branching copolymerization. The monomer conversion is plotted versus time as both linear (conversion) and semi-logarithmic ( $\ln([M]_0/[M])$ ) plots as shown in Figure 1. The semi-logarithmic plot of monomer concentration versus time is linear, indicating its



**Figure 1.** Kinetics for the linear ATRP of styrene and MMA. (Feed mole ratio of *t*-BBiB/styrene/MMA/DVB/CuBr/Bpy/cyclohexanone is 1/15/15/0.8/1/3/1 at  $90^\circ\text{C}$ ). The semi-logarithmic plot of monomer concentration vs. time (inset).



**Figure 2.** The molecular weight analysis results for the linear ATRP of styrene and MMA. (Feed mole ratio of *t*-BBIb/styrene/MMA/DVB/CuBr/Bpy/cyclohexanone is 1/15/15/0.8/1/3/1 at 90°C).

consumption by first-order kinetics. The results prove the successful employment of ATRP for the synthesis of styrene/MMA copolymer. It can be concluded that the polymerization rate decreases with increased initial styrene concentration due to the lower propagation rate constant, which is in agreement with the results of both conventional radical polymerization and ATRP [27,28].

Figure 2 shows the dependence of molecular weight and polydispersity on monomer conversions. Similar to reports of Braunecker et al. [10] and Kotani et al. [28] not only the molecular weight increases with monomer conversion, but also the polydispersity is maintained at relatively low values of about 1.5-1.8. In other words, chain transfer or termination has negligible effect on the polymerization and the reaction exhibits living polymerization character as observed in the homopolymerization of styrene or MMA.

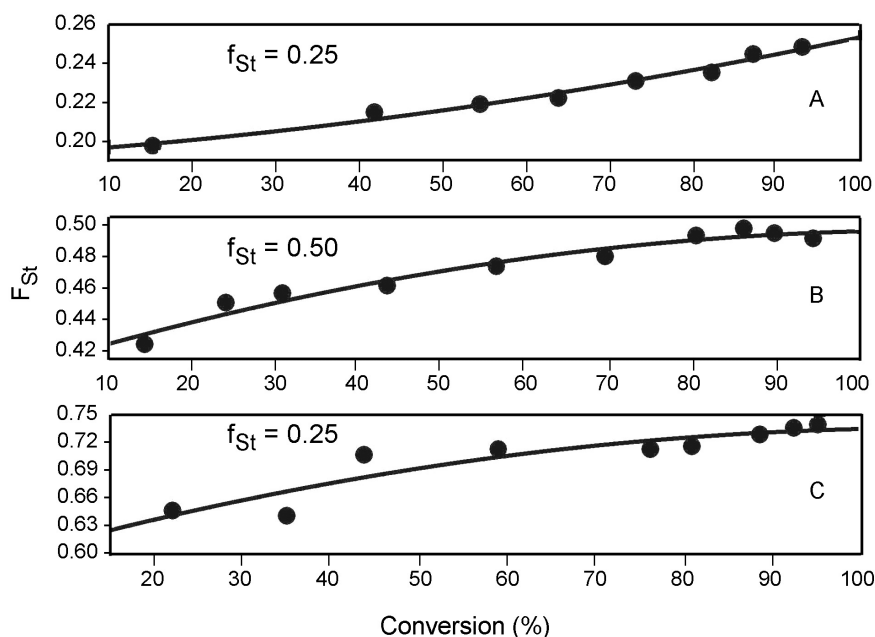
In conventional radical copolymerization, polymer is formed at different monomer conversions of quite different polymer compositions at a given initial feed composition; the instantaneous polymer composition generally is not equal to the instantaneous monomer composition. In fact, the polymer com-

position is just a statistic and average value. Figure 3 illustrates the variation of polymer composition with monomer conversion. As expected, the composition gradually approaches to and finally reaches almost the feed composition. These results indicate the existence of a gradient structure in the polymer chain due to the difference in monomer reactivity ratios, which is similar to those reported by Matyjaszewski et al. [29].

### Branching Copolymerization of Styrene and MMA

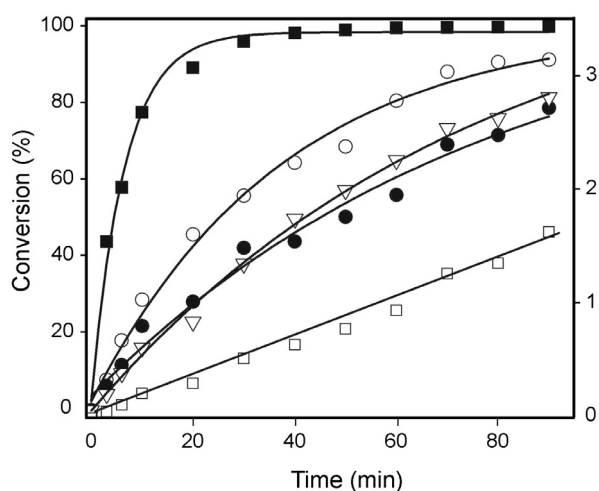
Branching copolymerization was carried out at the feed composition  $f_{St} = 0.5$ , since the reaction could give high monomer conversion in suitable polymerization rate as observed above. The conversion of the double bond was calculated based on the conversion of monomers detected by GC (styrene, MMA and DVB), assuming that the polymerization of the pendant vinyl group has negligible contribution.

Figure 4 shows the ATRP kinetics for the branching copolymerization. The linear kinetic correlation between the conversion and time is quite different from the data of Wang et al. [22] and our previous report [24] where the polymerization experienced



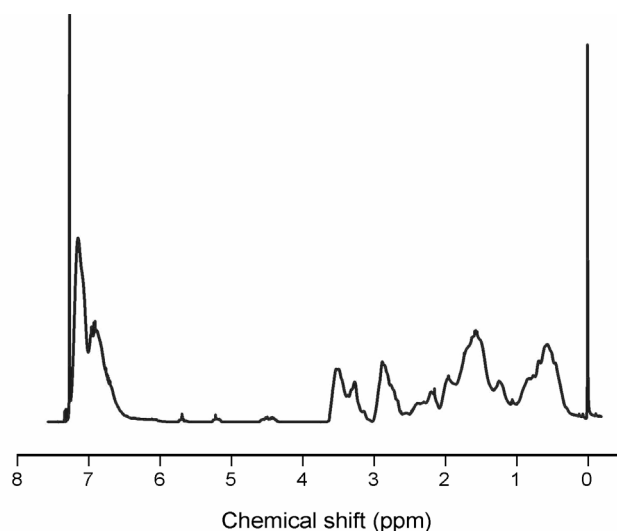
**Figure 3.** Polymer composition vs. monomer conversion for the linear ATRP of styrene and MMA. (Feed mole ratio of *t*-BBiB/styrene/MMA/DVB/CuBr/Bpy/cyclohexanone is 1/15/15/0.8/1/3/1 at 90°C).

auto-acceleration due to a diffusion-controlled radical deactivation. There is no marked difference between the conversions of MMA and styrene. The conversion of DVB molecules is somehow faster than those of the monomers, which is similar to those of ethylene glycol dimethacrylate and DVB reported by Bannister et al. [23] and our group [24]. It is also quite



**Figure 4.** ATRP kinetics for the branching ATRP of styrene and MMA. *t*-BBiB (■), DVB (○), MMA (▽), styrene (●),  $\ln([M]_0/[M])$  (□). (Feed mole ratio of *t*-BBiB/styrene/MMA/DVB/CuBr/Bpy/cyclohexanone is 1/15/15/0.8/1/3/1 at 90°C).

different from that of *tri*-EGDMA in our recent report where the conversion of *tri*-EGDMA is much faster than that of styrene [25]. We consider that the faster conversion of *tri*-EGDMA comes from the donor/acceptor interactions between styrene and *tri*-EGDMA molecules, since *tri*-EGDMA and styrene are electron-poor and electron-rich monomers, respectively.



**Figure 5.** Typical NMR spectrum of the branched copolymer. NMR conditions: 25°C in  $CDCl_3$ . (Feed mole ratio of *t*-BBiB/styrene/MMA/DVB/CuBr/Bpy/cyclohexanone is 1/15/15/0.8/1/3/1 at 90°C).

Figure 5 illustrates a typical  $^1\text{H}$  NMR spectrum of the branched copolymers. Signals at around 7.0 ppm, except the signal at 7.26 ppm related to  $\text{CDCl}_3$ , are attributed to the benzene ring. The total area of these peaks is expressed as  $S_1$ . Signals at chemical shift 5~6 ppm come from the pendant vinyl groups. Signals at 0.6~3.7 ppm related to the copolymer main chain and the total area of these peaks are expressed as  $S_2$ . The copolymer composition,  $F_{St}$ , can be calculated according to eqn (1).

$$F_{St} = [8S_1 / 5(S_1 + S_2)] \quad (1)$$

where, 5 and 8 values mean that one benzene ring has 5 protons and one MMA monomer unit contributes 8 protons to the main chain. Similar to the linear copolymerization,  $F_{St}$  value of the branched copolymers also approaches the feed composition as polymerization proceeds further.

### Development of Branching in Copolymerization Process

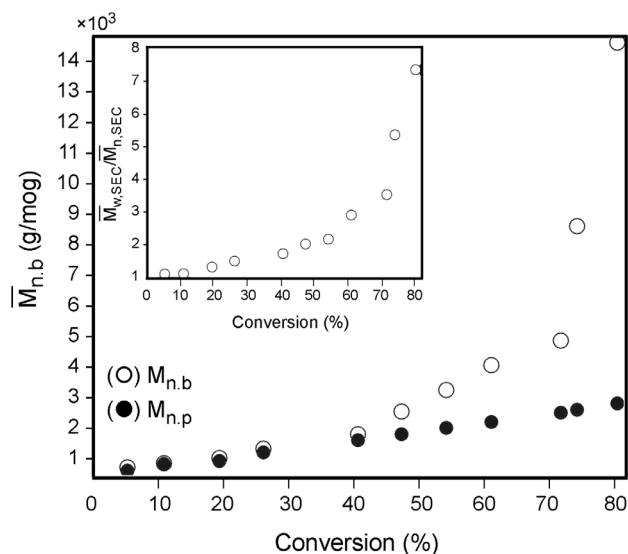
The theoretical molecular weight of the primary chain,  $\overline{M}_{n,p}$ , can be calculated from eqn (2). The number average molecular weight,  $\overline{M}_{n,b}$ , of the branched copolymer was calculated using the weight average molecular weight,  $\overline{M}_{w,MALLS}$ , according to eqn (3) [26]. Assuming no pendant vinyl group participated into polymerization and one molecule of initiator has generated one living primary chain, the value of  $\overline{M}_{n,b}$  should be equal to that of  $\overline{M}_{n,p}$ .

$$\overline{M}_{n,p} = 223 + \frac{130 \times \text{Conv}_{DVB} \times 0.8 + 104 \times \text{Conv}_{St}}{\text{Conv}_{t-BBiB}} \times \frac{15 + 100 \times \text{Conv}_{MMA} \times 15}{\text{Conv}_{t-BBiB}} \quad (2)$$

$$\overline{M}_{n,b} = \overline{M}_{w,MALLS} / (\overline{M}_{w,SEC} / \overline{M}_{n,SEC}) \quad (3)$$

where, 223, 130, 104 and 100 values are the molecular weights of  $t$ -BBiB, DVB, St and MMA, respectively.

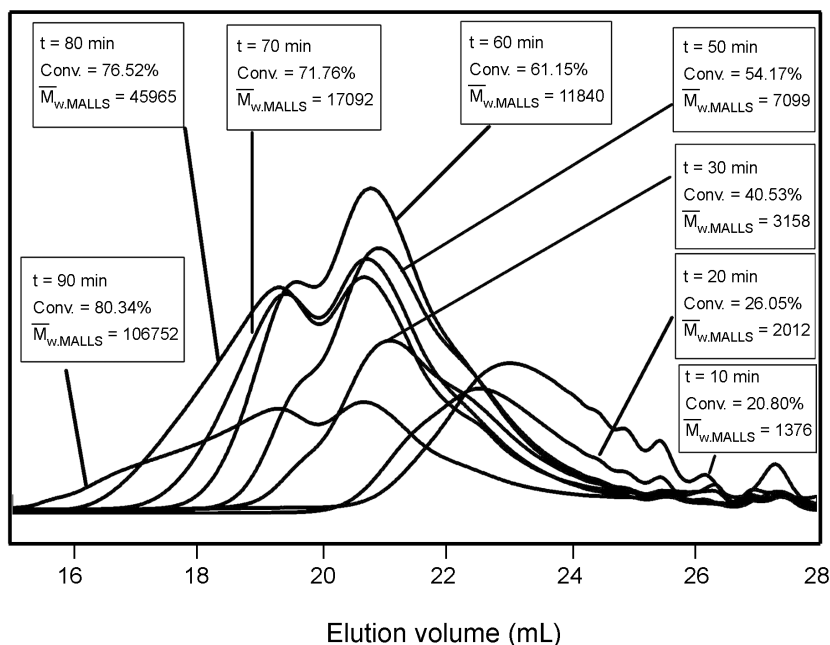
Figure 6 illustrates the changes of molecular weight and polydispersity with monomer conversion. In the early stages of the reaction (<40% monomer



**Figure 6.** Variation of molecular weight and its distribution with monomer conversion. (Feed mole ratio of  $t$ -BBiB/styrene/MMA/DVB/CuBr/Bpy/cyclohexanone is 1/15/15/0.8/1/3/1 at 90°C). Variaton of molecular weight distribution vs. monomer conversion (inset).

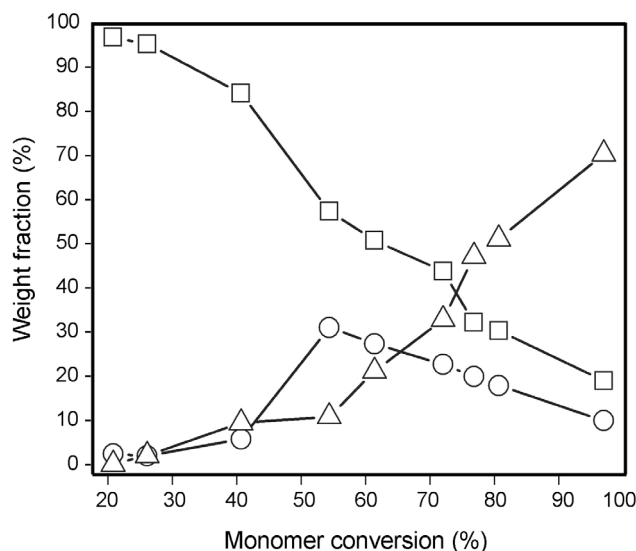
conversion),  $\overline{M}_{n,b}$  increases slowly and it is only slightly higher than  $\overline{M}_{n,p}$ . Polydispersity also increases slowly and remains relatively at low values (<1.8). These results imply that branching is negligible. Afterward,  $\overline{M}_{n,b}$  value significantly deviates from  $\overline{M}_{n,p}$  value, though there is no steep increase observed when conversion is around 40-70%. These results suggest that at this stage the coupling reaction mainly takes place by primary chain rather than the branched chain which leads chiefly to small branched chains. A steep increase in molecular weight and polydispersity occurs when monomer conversion is higher than 70%, indicating that the branching taking place between the branched chains is significant and highly branched chains are mainly formed at this stage.

Figure 7 shows the overlay of SEC chromatograms of the copolymer at different monomer conversions (from RI detector). Similar to our recent report [25], all the components consist of three peaks, suggesting the existence of three components with distinctly different molecular weights due to branching. We have proved that the three components relate to the primary chain, the slightly branched chain containing two primary chains and the mixture of much developed branched chains consisting of 3 and more



**Figure 7.** SEC Chromatograms of the copolymerization at various conversions. (Feed mole ratio of *t*-BBiB/styrene/MMA/DVB/CuBr/Bpy/cyclohexanone is 1/15/15/0.8/1/3/1 at 90°C), (From RI detector).

primary chains [25]. At 20.8% monomer conversion, the SEC sample looks like monomodal; in fact, this peak is not symmetrical and sharp as that of the linear



**Figure 8.** Variation of weight fractions of the three components with monomer conversion. Component 1: primary chain (□), component 2: slightly branched chain (○), component 3: highly branched chain (△). (Feed mole ratio of *t*-BBiB/styrene/MMA/DVB/CuBr/Bpy/cyclohexanone is 1/15/15/0.8/1/3/1 at 90°C).

copolymerization.

Figure 8 shows the changes of the weight fraction of the three components with monomer conversion according to the multi-peak splitting using Gaussian function [25]. As we expect, the weight fraction of the component 1 ( $w_1$ ) decreases with monomer conversion. However, about 20% of primary chain remains in the reaction system which should be the main reason giving rise to high polydispersity. The remaining significant amount of primary chains could be largely explained by the limited content of the pendant vinyl group and the steric effect at high conversion. In addition,  $w_3$  is not only relatively low (<10%) which also increases slowly at monomer conversion of below 40%. This result coincides well with the changes of molecular weight and reaction progress as shown in Figure 6, showing the chain coupling reaction mainly occurs by the primary chains in the early stages of the reaction.

### Effect of Dosage of DVB on Branching Copolymerization

Based on the knowledge of the branching procedure, a series of branching copolymerization were conducted at different dosages of DVB. According to

**Table 1.** Summary of branched copolymers prepared with varying concentrations of DVB\*.

Entry	[ <i>t</i> -BBiB]/[DVB]/[St]/[MMA]	<i>T</i> (h)	$\overline{M}_{n,SEC}$ (g/mol)	$\overline{M}_{w,SEC}$ (g/mol)	$\overline{M}_{w,SEC}/\overline{M}_{n,SEC}$	$\overline{M}_{w,MALLS}$ (g/mol)	$\overline{M}_{w,MALLS}/\overline{M}_{w,SEC}$
1	1/0.6/15/15	4.2	10300	40400	3.902	63000	1.5604
2	1/0.7/15/15	2.8	12200	59200	4.800	97300	1.9801
3	1/0.8/15/15	2.5	12900	82500	6.389	177600	2.1266
4	1/0.9/15/15	2.0	17500	192100	10.974	899000	4.6785
5	1/1/15/15	2.0	Gelation				
6	1/0.8/25/25	7.0	9500	15400	1.6190	19400	1.2598
7	1/0.8/20/20	4.5	10800	27700	2.6911	49800	1.7939
8	1/0.8/10/10	2.0	15200	143800	9.0400	442900	3.0806

(\* Polymerization was performed without cyclohexanone. (Feed mole ratio of *t*-BBiB/ CuBr/Bpy is 1/1/0.5 at 90°C).

Fréchet's report [4],  $\overline{M}_{w,MALLS}/\overline{M}_{w,SEC}$  ratio was used as a qualitative indicator for degree of branching. The results are summarized in Table 1.

For a given ratio of [*t*-BBiB]/[MMA]/[St]/[CuBr]/[Bpy], polymerization at higher dosage of DVB results in the formation of polymer with higher molecular weight and higher  $\overline{M}_{w,MALLS}/\overline{M}_{w,SEC}$  ratio at relatively shorter polymerization time, implying an early development of branching. It is essential that the number of divinyl monomer per primary chain should be less than one when targeting towards soluble branched polymer [22-24]. Indeed, polymerization at [*t*-BBiB]/[DVB] = 1 is very sensitive to gelation (entry 5 in Table 1).

For a given ratio of [DVB]/[*t*-BBiB] = 0.8, the increased rate of molecular weight slows down as the concentration of MMA and styrene increases, because the increased concentrations of MMA and styrene would lower the concentration of DVB and finally lower the increased rate of molecular weights. Briefly, the dosage of the branching agent has vital effect on the polymerization, especially the development of branching as with higher dosage of branching agent used, and therefore earlier branching takes place.

## CONCLUSION

The preparation of branched copolymers of styrene and MMA by ATRP using DVB as the branching agent has been studied. The reaction system contains

three components throughout the reaction: the primary chains, the slightly branched chains comprising of two primary chains, and the highly branched chains consisting of three and more primary chains. Regardless of any interaction of donor/acceptor type between the monomers and DVB molecules, the branching mechanism of the copolymerization is still similar to that of the ATRP of styrene and *tri*-EGDMA. The coupling reaction takes place mainly by the primary chains in the early stages of the reaction, resulting in the slightly branched chains. In the later stages of the copolymerization, the coupling reaction between branched chains becomes significant and forms highly branched chains.

## ACKNOWLEDGEMENT

This work was supported by the Natural Science Foundation of China and The Natural Science Foundation of Jiangsu Province.

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