



## Studies on the development of branching in ATRP of styrene and acrylonitrile in the presence of divinylbenzene

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### ABSTRACT

Branching atom transfer radical polymerization (ATRP) of styrene and acrylonitrile was attempted in the presence of divinylbenzene targeting toward soluble branched copolymer. The kinetics and the development of branching with monomer conversion were studied in detail. Gas chromatography (GC), gel permeation chromatography (GPC) coupled with multi-angle laser light scattering (MALLS), proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectroscopy and intrinsic viscosity determination were used to monitor the polymerization process and characterize the obtained copolymer. Analysis of conversion of reactants, the growth manner of molecular weight with monomer conversion and GPC traces proved that the primary chains with low polydispersity formed mainly at the early stage and then were linked in a statistical manner to start the branching at the middle or late stage. The more the branching agent was used, the earlier the branching occurred, and too much higher level of branching agent resulted in gelation. For the selected ratio of  $[t\text{-BBiB}]/[\text{DVB}]/[\text{St}]/[\text{AN}] = 1/0.9/15/15$ , with monomer conversion less than 40%, primary chains with low polydispersity formed from the polymerization of St, AN and DVB, and only a part of the primary chains contained pendent vinyl group. When monomer conversion was up to 40%, the pendent vinyl groups participated in polymerization, resulting in the linking of the primary chains statistically to start the branching. The branching became significant at monomer conversion up to 50%, giving rise to a steep increase in molecular weight and width in molecular weight distribution. As the polymerization proceeded, the polymer composition gradually approached the feed composition, identifying the obtained branched copolymer provided some gradients are in its primary chains. Finally, branched copolymer bearing about six primary chains was prepared at monomer conversion near to 80%, its absolute weight average molecular weight was about  $8.87 \times 10^4$ .

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### 1. Introduction

The synthesis of multi-component polymers remains of significant economic values due to its ability to produce materials with a great diversity of properties compared to those of homopolymers. Copolymers of styrene and acrylonitrile (SAN copolymers) are thermoplastics that have found a wide range of applications because of their chemical and thermal stabilities, and mechanical and optical properties [1]. Unfortunately, conventional free radical polymerization limited control over molecular parameters, particularly on molecular weight and its distribution.

From an academic perspective, there have been a number of interesting reports on the synthesis of controlled structure AN based copolymers over the past decade or so [2–6]. The introduction of the controlled radical polymerization techniques opened

new possibilities for the preparation of well-defined macromolecules with different compositions, macromolecular architectures, and end-functional groups. Among these methods, ATRP has a great potential due to its applicability to a variety of monomers, the possibility for synthesis of end-functionalized macromolecules, and its tolerance to many solvents, additives, and impurities often encountered in industrial operation [7,8]. Monomers with different polarities and functional groups were polymerized using ATRP, including both St and AN [9–15]. Matyjaszewski performed the linear ATRP of St and AN at azeotropic feed composition [16]. However, to date, no attempts have been made to synthesize St/AN branched copolymer by ATRP.

The physical properties of branched polymers have attracted considerable attention during the past two decades [17]. Branching in polymer can result in solution, surface, and bulk properties markedly different from those of its linear homologue.

It was proved that ATRP of divinyl monomer would result in the formation of branched polymer [18,19]. However, gelation typically occurred at low conversion. Zhu et al. studied the

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homopolymerization of ethylene glycol dimethacrylate (EGDMA) in bulk [20]. As expected, gelation occurred at very low conversion (<10%). Our group reported the homopolymerization of divinylbenzene (DVB) in bulk [19]. Unfortunately, the polymerization was also much sensitive to cross-linking at relatively low conversion (<60%).

Living radical polymerization of a small percentage of a divinyl monomer with a vinyl monomer can also lead to branching, in which cross-linking can be restrained effectively [21–24]. Li and Armes obtained water-soluble branched polymer by ATRP of 2-(dimethylamino)ethyl methacrylate (HPMA) using a dimethacrylate branching agent containing a disulfide bond [25]. They confirmed that the branched copolymer comprised statistically linked low polydispersity primary chains and also indicated that branching by chain transfer to polymer was negligible. Wang and Zhu reported a study of gelation in the ATRP of MMA and EGDMA in bulk [26]. They also used a cleavable branching agent to prove that the gel fraction was made up of primary chains with the same molecular weight and polydispersity as those produced in the absence of the branching agent. Recently, Bannister et al. have reported a study of polymerization of HPMA and EGDMA using ATRP in methanol [27]. Their study focused on the development of branching with conversion, and confirmed that the formation of branched chains occurred only at high conversion (>90%). Several groups concluded that it was essential to keep the molar ratio of divinyl monomer to initiator less than 1 in order to obtain branched polymers instead of gels [18,21,22,27].

Although there are a few studies describe the syntheses of branched polymers via ATRP of a vinyl monomer in the presence of a divinyl monomer as the branching agent, the copolymerization of two monomers with different polarity and reactivity ratios has not been attempted in detail by now. In this paper, the ATRP of St and AN was studied in the presence of DVB as the branching agent targeting toward soluble branched copolymer. In particular, the kinetics of the copolymerization and the development of branching with monomer conversion were focused. It was proved that polymerization resulted in the formation of primary chains with pendent vinyl groups at the early stage and branching only occurred when monomer conversion was higher than 40%; the development of branching was determined by the concentration of the branching agent. Branched copolymer with molecular weight as high as  $8.87 \times 10^4$  was prepared at monomer conversion near to 80%.

## 2. Experimental section

### 2.1. Materials

DVB was used as-supplied by the Fluka Chemical Co. and was of ~80% technical grade quoted as an 80% mixture of 1,3- and 1,4-DVB isomers and 20% 1,3- and 1,4-ethylstyrene isomers. *t*-BBiB (purity above 99%) was used as-supplied by the Aldrich Chemical Co. 2,2'-Bipyridine (Bpy), styrene and acrylonitrile were purchased from Shanghai Chemical Co. Styrene and acrylonitrile were purified using NaOH solution (10%) to remove the polymerization inhibitor and then distilled under reduced pressure before use. Copper(I) bromide was purified by stirring in glacial acetic acid, washing with methanol, and then drying under vacuum at 80 °C. All other solvents were used as-received without further purification.

### 2.2. ATRP of St and AN

Linear ATRP: St (5.21 g, 50 mmol), AN (2.65 g, 50 mmol), *t*-BBiB (0.28 g, 1.25 mmol), Bpy (0.59 g, 3.75 mmol) and Cu<sup>I</sup>Br (0.18 g, 1.25 mmol) were placed in a 100 mL round-bottomed flask equipped with a stir bar. The toluene was added only as an internal standard for GC measurements. The flask was sealed with a rubber

septum, and the contents in the flask were placed under vacuum and then back-filled with argon more than five times to remove the oxygen. The reaction mixture was then stirred at 70 °C. Samples (~0.5 mL) of the reaction mixture were taken at regular intervals and diluted into 1 mL of THF, and the polymerization was stopped by exposing the reaction to air. The mixture rapidly changed from brown to green, indicating termination of the polymerization due to the aerial oxidation of Cu(I) to Cu(II). The conversion of the reactants was determined by GC. Molecular weights and polydispersities were obtained from GPC measurements. The different copolymer composition was adjusted by choosing the appropriate [St]/[AN] ratio, with molar ratio of [Monomers]/[*t*-BBiB]/[Cu<sup>I</sup>Br]/[Bpy] kept as 80:1:1:3 in all syntheses.

Typical branching ATRP: the mixture of DVB (0.81 g, 5 mmol), AN (4.42 g, 83.33 mmol), St (8.68 g, 83.33 mmol), *t*-BBiB (1.24 g, 5.56 mmol), Bpy (1.17 g, 7.5 mmol) and Cu<sup>I</sup>Br (0.36 g, 2.5 mmol) were stirred in a 100 mL round-bottomed flask and trace of toluene was also added for GC measurements. The following treatments, polymerization procedures and analysis methods were similar to those carried out in the linear copolymerization. Molecular weight of the branched copolymer was measured by GPC analysis coupled with MALLS. The molar ratio of [DVB]/[*t*-BBiB]/[St]/[AN]/[Bpy]/[Cu<sup>I</sup>Br] was 0.9:1:15:15:1.35:0.45, except stated elsewhere.

### 2.3. Analysis and characterization

<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> using a 300MHz Bruker ARX 300 spectrometer with TecMAG processing software. The branched copolymer compositions,  $F_{St}$ , were calculated based on <sup>1</sup>H NMR spectra. Molecular weight and molecular weight distribution were obtained by GPC using Waters 1515 isocratic HPLC pump, a Waters 717PLUS autosampler, and a Waters 2414 differential refractometer with 5μ Waters Styrogel columns (guard, 0.5HR, 4EHR, 1HR). The data were processed using Polymer Standards Service software against linear polystyrene standards. MALLS was conducted on Wyatt min DAWN TRISTRA light scattering photometer. The  $dn/dc$  values of the branched copolymers were determined using an Optilab REX ( $\lambda = 640$  nm) interferometric refractometer (Wyatt) in batch mode at 35 °C. A series of six copolymer solutions with different concentration (the highest being  $1 \text{ g L}^{-1}$ ) in HPLC grade THF eluent were successively injected using a syringe injection, and the resulting signals were analyzed using the Wyatt software. The  $dn/dc$  values were calculated to be  $0.151 \pm 0.0022 \text{ mL g}^{-1}$ . The number average molecular weight,  $M_{n,b}$ , of the branched copolymer was calculated using the weight average molecular weight,  $M_{w,MALLS}$ , according to the literatures [28,29]. Conversion of reactants was measured by GC analysis, using an HP6890 with DB-5 column (length 30 m). The carrier gas was argon at 1 mL/min, and the temperature was increased from a starting value of 100 °C at sample injection to a maximum of 230 °C at 10 °C/min. The linear copolymer composition,  $F_{St}$ , was calculated from monomer conversion by GC analysis. Intrinsic viscosity was measured by Ubbelohde viscometer in THF at 25 °C.

## 3. Results and discussion

### 3.1. Linear ATRP of St and AN

In order to select a suitable feed composition to study the development of branching, the linear ATRP of styrene and acrylonitrile in different feed compositions was firstly performed.

Figs. 1 and 2 show the kinetic analysis results. The semi-logarithmic plots of monomer conversion vs. time were linear with  $f_{St} = 0.25$  and 0.50, indicating their conversion by first-order kinetics. For  $f_{St} = 0.75$ , besides relatively lower slope compared with that of  $f_{St} = 0.25$  and 0.5, the slope against time appeared to

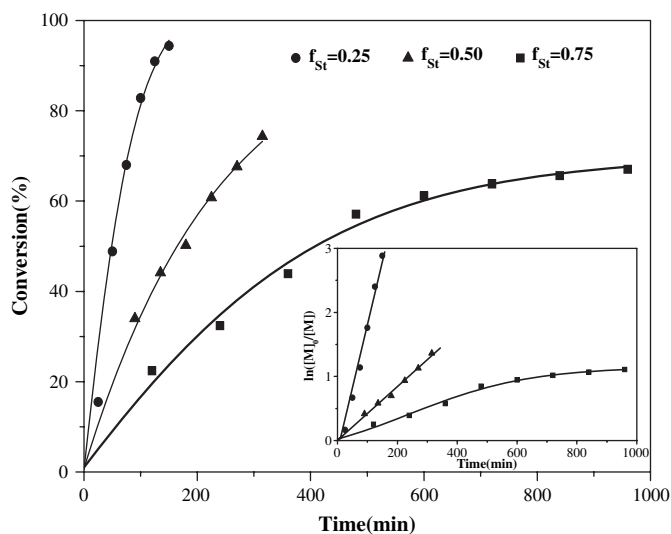


Fig. 1. Kinetics for the linear ATRP of St and AN.

decrease and the monomer conversion increased very slowly after about 720 min of polymerization. As a summary, the feed compositions had vital effects on the polymerization rate and monomer conversion. Particularly, the polymerization exhibited some fast polymerization rate at relatively lower  $f_{St}$  and marked polymerization retardation was observed in the late stage at feed composition  $f_{St} = 0.75$ . Although the mechanism of the retardation is beyond the scope of this study, it must be taken into consideration the following branching copolymerization.

Fig. 3 illustrates the dependence of molecular weight and molecular weight distribution on monomer conversion. The linear increase of molecular weight against monomer conversion and the relatively narrow molecular weight distribution indicated a negligible contribution from chain transfer or other side reaction under the polymerization conditions.

The composition of copolymer from living polymerization is not the same as that from conventional radical polymerization. In conventional radical copolymerization, the reactivity ratios of St and AN are different, and therefore the composition of the copolymer will deviate from the feed composition except at the azeotropic feed composition of 63% styrene and 37% AN in mol. At

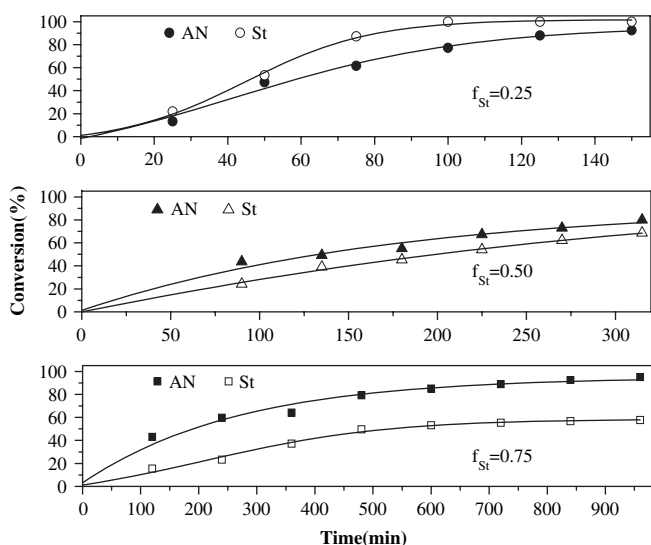


Fig. 2. Monomer conversion against polymerization time for the linear ATRP of St and AN.

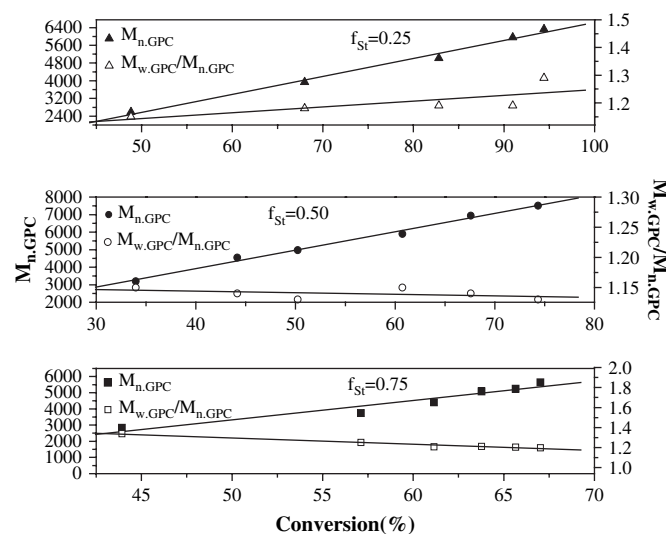


Fig. 3. The molecular weight analysis results for the linear ATRP of St and AN.

azeotropic feed composition, no compositional drift was observed throughout the copolymerization [16]. Fig. 4A–C shows the copolymer compositions ( $F_{St}$ ) as a function of monomer conversion. As the polymerization proceeded,  $F_{St}$  approached the values of  $f_{St}$ . The tendency of  $F_{St}$  with monomer conversion implied the presence of gradients in the copolymer chains due to the large difference in the monomer reactivity ratios as reported by Matyjaszewski [30,31]. Because of the polymerization retardation at the feed composition  $f_{St} = 0.75$ ,  $F_{St}$  remained almost constant around 0.64 when monomer conversion reached 40%.

### 3.2. Branching ATRP of St and AN

Branching copolymerization of St and AN was performed at the feed composition  $f_{St} = 0.5$ , since the polymerization could be well controlled and gave high monomer conversion in moderate

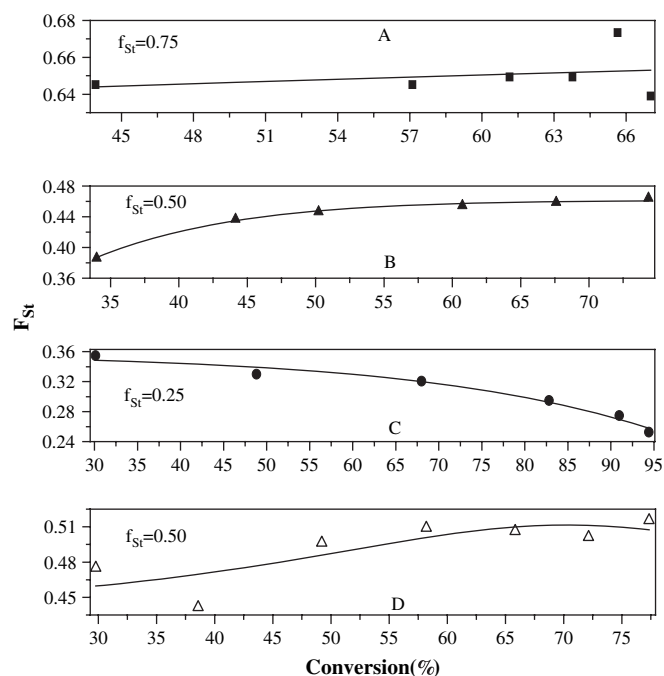


Fig. 4. The variation of polymer composition with monomer conversion for the ATRP of St and AN.

polymerization rate as observed in linear copolymerization. Our choice of DVB as the branching agent was based on Sherrington's report that the most regular branched material with lowest molecular weight distribution could be prepared [32].

The conversion of the double bonds was calculated based on the conversion of monomers (St, AN and DVB), assuming that the polymerization of the pendent vinyl group had negligible contribution to the conversion of the double bonds. Fig. 5 shows the results of the kinetic analysis. The slope of the semilogarithmic plot of the double bond conversion vs. time appeared to increase with time, and the polymerization deviated from the ideal case. Zhu et al. suggested that this phenomena was caused by an increase in radical concentration based on their electron spin resonance (ESR) analysis [20,26,33].

Fig. 6 shows the conversion of reactants vs. polymerization time. The conversion of initiator was much faster than that of DVB, St and AN, and no free *t*-BBiB could be detected after only 30 min polymerization. It could conclude that the rate of initiation was much faster than propagation, resulting in efficient initiation and avoiding the formation of polydispersity primary chains with some chains significantly longer than the average which cross-linked even more easily at relatively low conversion. Also, the relatively slow conversion of DVB compared with *t*-BBiB suggested that quite a few saturated primary chains without pendent vinyl groups formed at the early stage of polymerization. The conversion of DVB was slightly faster than that of St and AN, which derived from the fact that reaction of only one of its double bonds was sufficient to remove the free DVB from the reaction mixture, leaving a pendent vinyl group.

### 3.3. Development of branching

In order to probe the development of branching with conversion, i.e. to answer the question that at what monomer conversion does the branching take place and become significant? the polymerization process was monitored and analyzed by using GPC coupled with MALLS in detail.

One of the citations of living polymerization is that the molecular weight increases proportionally to monomer conversion. This linear relation between molecular weight and monomer conversion was observed in the preceding linear copolymerization. Assuming no pendent vinyl groups participate in the polymerization, the theoretical molecular weight of the primary chain,  $M_{n,l}$ ,

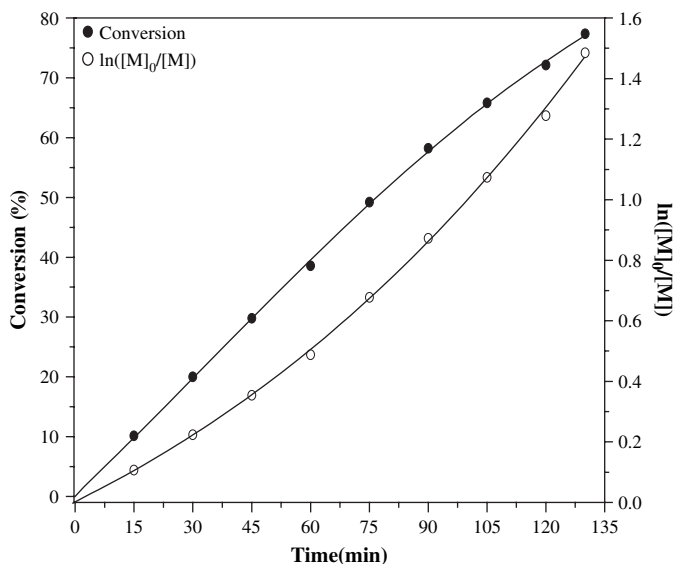


Fig. 5. Kinetics for the branching ATRP of St and AN.

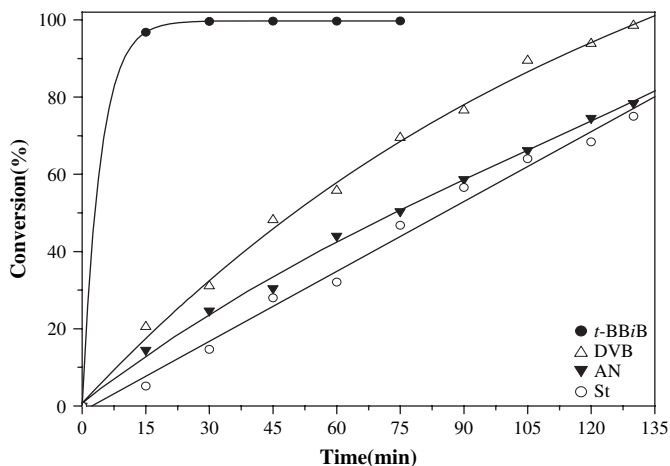


Fig. 6. Conversion of the reactants at various polymerization times for the branching ATRP of St and AN.

formed at the same conversion can be calculated according to Eq. (1).

$$M_{n,l} = 224 + ([St]_0 \times Conv_{St} \times 104 + [AN]_0 \times Conv_{AN} \times 53 + [DVB]_0 \times Conv_{DVB} \times 130) / [t-BBiB]_0 \times Conv_{t-BBiB} \\ = 224 + (1560 \times Conv_{St} + 795 \times Conv_{AN} + 117 \times Conv_{DVB}) / Conv_{t-BBiB} \quad (1)$$

Here 224, 104, 53 and 130 are the molecular weights of *t*-BBiB, St, AN and DVB, respectively.

Fig. 7 illustrates the comparison of the measured molecular weight with  $M_{n,l}$  at the same monomer conversion. At monomer conversion lower than 40%, the molecular weight increased more or less linearly with conversion, closely resembling the linear regression for their linear copolymerization. The polydispersity also remained relatively narrow values at around 1.2–1.3. After that, a sharp increase in molecular weight appeared and molecular weight distribution became much wider. Acceptable and reasonable explanation to this sudden change and deviation can only be attributed to the occurrence of the linking of primary chains through the polymerization of pendent vinyl groups. Actually, the linking reaction doubled the molecular weight of the resulting macromolecules and made the polydispersity wide. More seriously, the formed macromolecules by linking the primary chains contained much more initiate groups and pendent vinyl groups compared with the primary chains bearing only one initiate site. So

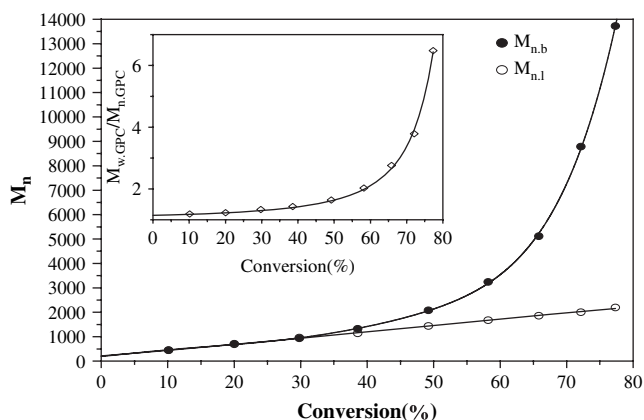


Fig. 7. Variation of molecular weight and its distribution with monomer conversion.

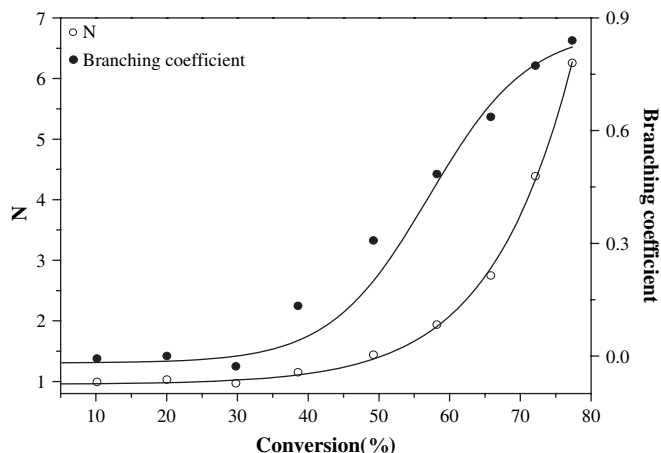


Fig. 8. Change of the average number of primary chain in one macromolecule and branching coefficient with conversion.

they took advantages over the primary chain in participating in the following polymerization, including initiating and being initiated by another macromolecule. Based on the molecular weight analysis, it could be concluded that branching occurred at about 40% monomer conversion.

The average number of primary chain per macromolecule can be simply identified as  $N = M_{n,b}/M_{n,l}$ , which will give a much more direct picture to the onset and development of branching. According to the theory of gelation pointed out by Flory, the branching coefficient can be expressed as  $[1 - (M_{n,l}/M_{n,b})]$  [27].  $M_{n,b}$  should approach infinity and the branching coefficient equals to one unit at the gel point,  $M_{n,b}$  should be equal to  $M_{n,l}$  and the branching coefficient is zero before branching. Fig. 8 shows the results. As expected, at monomer conversion less than 40%, the average number of primary chain in one macromolecule remained almost one and the branching coefficient was zero, proving again that no linking reaction through the polymerization of pendent vinyl groups. The average number of the primary chain per macromolecule rose rapidly after monomer conversion reached 50%, implying that the

most significant branching took place in this stage, while the branching coefficient also rose rapidly. These results coincided well with the inference from the growth of molecular weight. Finally, branched macromolecules bearing about six primary chains were prepared.

Further evidence that the most significant branching occurs mainly at the middle stage of the reaction, relating to monomer conversion up to 50%, is shown in Fig. 9. The figure shows the evolution of the molecular weight and its distribution with monomer conversion. At monomer conversion lower than 50%, the GPC traces were almost monomodal, closely resembling the linear polymerization. However, the GPC traces converted into multimodal as monomer conversion increased, which corresponded to the formation of macromolecules bearing more than one primary chain. A remarkable shift of the trace to much higher molecular weights appeared near 80% monomer conversion.

Fig. 10 illustrates the  $^1\text{H}$  NMR spectra of the resulting polymers at monomer conversion 38.6% and 49.2%. Signals at around 7.0 ppm, excepting signal at 7.26 ppm relating 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 5.25 ppm and 5.75 ppm come from the pendent vinyl groups; the area of this peak is expressed as  $S_2$ . Signals at chemical shift 4.4 ppm are attributed to the halogen end groups. Signals from 0.9–3.0 ppm are relating to the main chain, the total area of these peaks is expressed as  $S_3$ .

The copolymer composition,  $F_{\text{St}}$ , and the number ratio of the pendent vinyl group to monomer unit,  $N_{\text{Pendent vinyl group}}/N_{\text{Monomer unit}}$ , can be calculated according to Eqs. (2) and (3).

$$F_{\text{St}} = [N_{\text{St}}/(N_{\text{St}} + N_{\text{AN}})] = (S_1/5)/(S_3/3) \quad (2)$$

$$N_{\text{Pendent vinyl group}}/N_{\text{Monomer unit}} = [S_2/(S_3/3)] \times 100\% \quad (3)$$

Here, 5 and 3 mean that one benzene ring has five protons and one monomer unit contributes three protons to the main chain.  $N_{\text{St}}$  and  $N_{\text{AN}}$  are the number of the monomer unit of styrene and AN in the copolymer, respectively.

The copolymer composition is shown in Fig. 4D.  $F_{\text{St}}$  approached the feed composition as the monomer conversion increased,

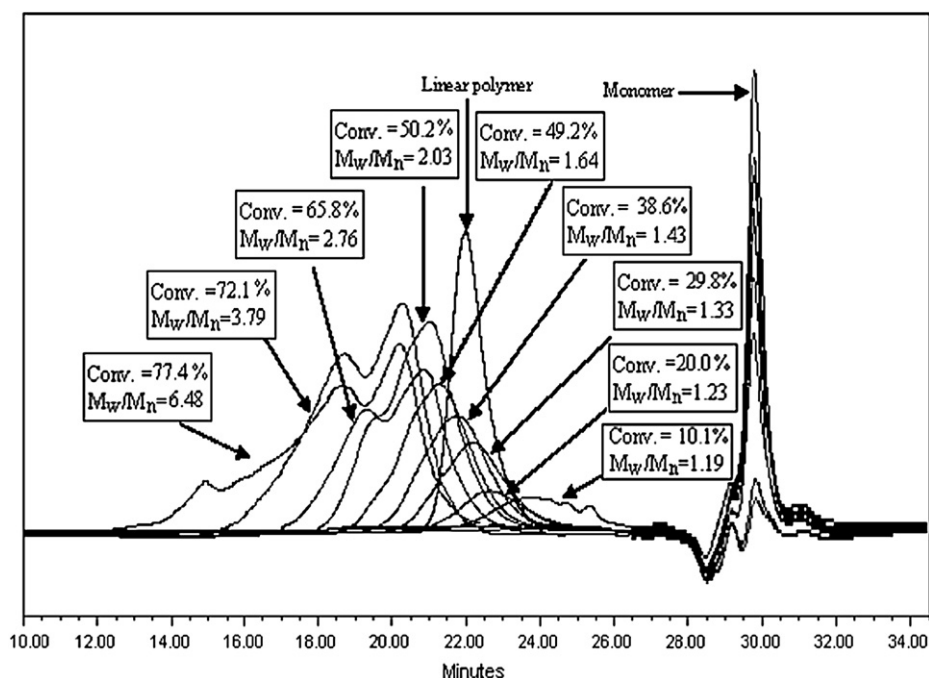


Fig. 9. Overlay of GPC chromatograms of the samples at various polymerization time.

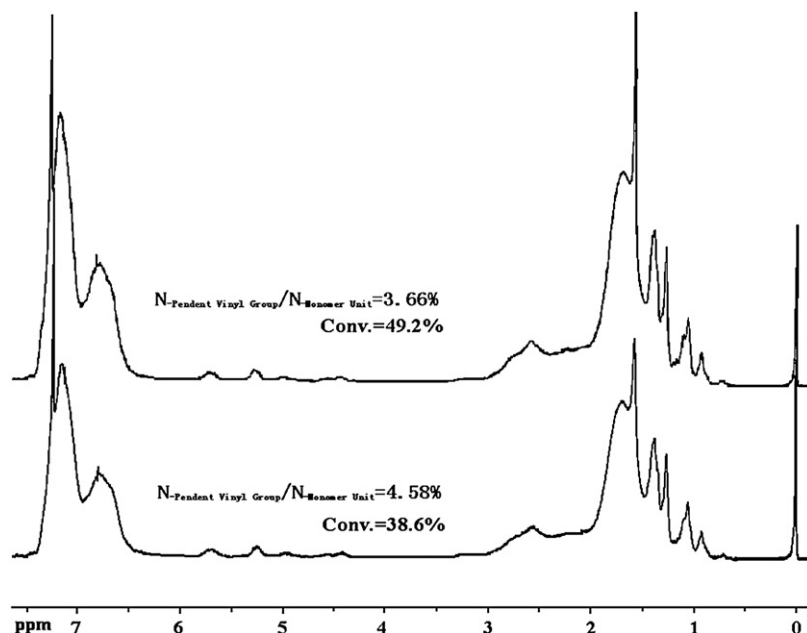


Fig. 10.  $^1\text{H}$  NMR spectra of the resulting copolymers.

proving the existence of gradients in the primary chain. The calculated values of  $N_{\text{Pendent vinyl group}}/N_{\text{Monomer unit}}$  were 4.58% and 3.66% at monomer conversion 38.6% and 49.2%, respectively.

Based on the hypothesis of no polymerization of the pendent vinyl groups, the theoretical ratios can be calculated based on GC analysis according to Eq. (4).

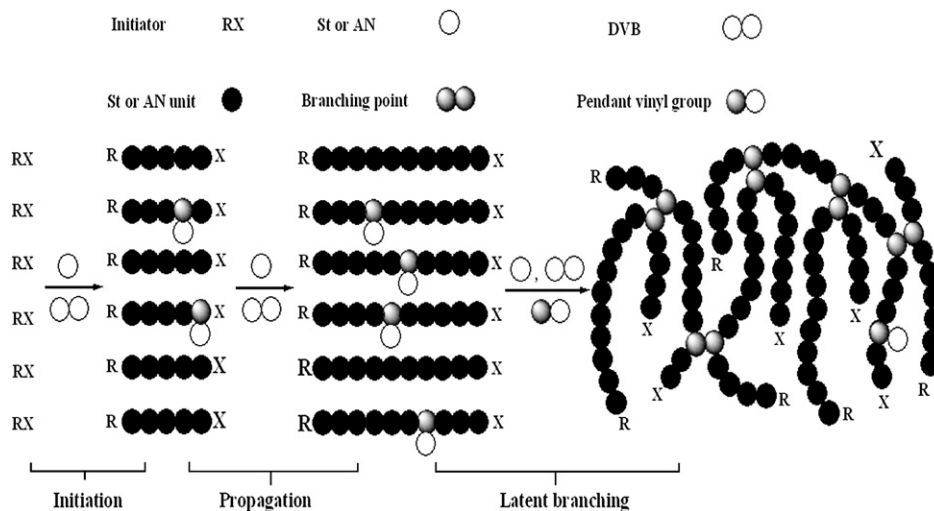
$$\begin{aligned}
 N_{\text{Pendent vinyl group}}/N_{\text{Monomer unit}} &= \left\{ \frac{[\text{DVB}]_0 \times \text{Conv}_{\text{DVB}}}{([\text{AN}]_0 \times \text{Conv}_{\text{AN}} + [\text{St}]_0 \times \text{Conv}_{\text{St}})} \right\} \times 100\% \\
 &= \left[ \frac{0.9 \times \text{Conv}_{\text{DVB}}}{15(\text{Conv}_{\text{AN}} + \text{Conv}_{\text{St}})} \right] \times 100\% \quad (4)
 \end{aligned}$$

The values from Eq. (4) were 4.40% and 4.29%, respectively. Comparing the ratios calculated from NMR and GC analyses can also give us some clues to the onset of branching; 4.58% was slightly bigger than 4.4%, this unordinary deviation should attribute to imprecise integration, which proved again no branching at this

stage. Consequently, marked decreased value from NMR analysis at monomer conversion 49.2% identified the occurrence of branching.

Unfortunately, the content of the pendent vinyl group will become too low to be detected precisely as the polymerization proceeds. So the integration in NMR analysis will become inaccurate and quantitative determination to study the kinetics of branching will be unreliable.

The scenario of the polymerization process, especially the development of branching can be outlined in Scheme 1. At the early stage relating to monomer conversion less than 40%, primary chains with low polydispersity formed from the polymerization of St, AN and DVB, and only a part of the primary chains contained pendent vinyl group. When monomer conversion was up to 40%, the pendent vinyl groups participated in polymerization, which resulted in the linking of the primary chains statistically to start the branching. The branching became significant at monomer conversion up to 50%, giving rise to a steep increase in molecular weight and width in molecular weight distribution.



Scheme 1. Illustration of the development of branching by ATRP.

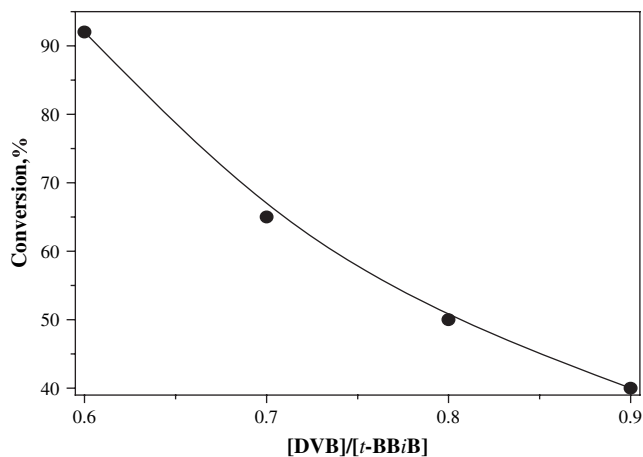


Fig. 11. Dependence of branching on the ratio of [DVB]/[t-BBiB].

### 3.4. Effects of DVB concentration on branching and preparation of branched copolymer

Fig. 11 illustrates the dependence of branching on DVB concentration. For a selected ratio of [St]/[AN]/[t-BBiB] = 15:15:1, the concentration of DVB had vital effects on branching, relatively high dosage of DVB gave rise to an early onset of branching.

The molecular weight data of the resulting polymer are summarized in Table 1. For a given reaction time, both molecular weight and molecular weight distribution increased steadily with increasing DVB content. Finally, the molecular weight and molecular weight distribution fell at a ratio of [DVB]/[t-BBiB] = 1, reflecting the formation of a small amount of very high molecular weight material (possibly microgel), which was not detected in the GPC analysis. Indeed, excess of DVB gave rise to gelation. In all cases, the branching coefficient also rose with increasing DVB content, as expected. It should be emphasized here that the  $M_{n,i}$  used to calculate the branching coefficient was the apparent molecular weight ( $M_{n,GPC}$ ) of the linear copolymer with the same polymerization time at the same feed composition, therefore the branching coefficient here was just an approximate and reference value.

At a selected ratio of [DVB]/[t-BBiB], the feed ratio of St to AN affected not only the rate of polymerization but also the level of branching. The fastest polymerization was also observed at St/AN feed ratio of 10/40. Polymers with high molecular weight

Table 1

Summary of the branched copolymers prepared with varying concentration of the branching agent<sup>a</sup>

[t-BBiB]/[DVB]/ [St]/[AN]	T (h)	$M_{n,GPC}/$ $10^3$	$M_{w,GPC}/$ $10^4$	$M_w/$ $M_n$	$M_{w,MALLS}/$ $10^4$	$M_{w,MALLS}/$ $M_{w,GPC}$	$(M_{n,b} - M_{n,i})/M_{n,b}$
1/0.6/15/15	2	5.9	1.1	2.2	1.4	1.3	0.48
1/0.75/15/15	2	7.7	2.3	3.0	4.2	1.8	0.76
1/0.8/15/15	2	7.7	2.4	3.2	4.5	1.9	0.76
1/0.9/15/15	2	7.8	3.0	3.8	10.1	3.4	0.88
1/0.95/15/15	2	9.0	5.8	6.5	19.9	3.4	0.89
1/1.0/15/15	2	9.5	4.6	4.9	14.4	3.1	0.89
1/1.1/15/15	2	Gelation					
1/0.9/40/10	6.3	6.7	1.3	1.9	2.7	2.1	
1/0.9/30/20	3.0	8.9	2.3	2.5	5.0	2.2	
1/0.9/25/25	2.5	9.5	3.0	3.2	7.7	2.6	
1/0.9/20/30	1.5	11.2	7.2	6.4	22.6	3.1	
1/0.9/10/40	0.9	9.7	14.8	15.2	77.7	5.3	
1/0.9/40/10	6.5	Gelation					
1/0.9/30/20	3.2	Gelation					
1/0.9/20/30	1.8	Gelation					
1/0.9/10/40	0.95	Gelation instantly					

<sup>a</sup> Polymerization was performed without toluene used as the internal standard in kinetic studies.

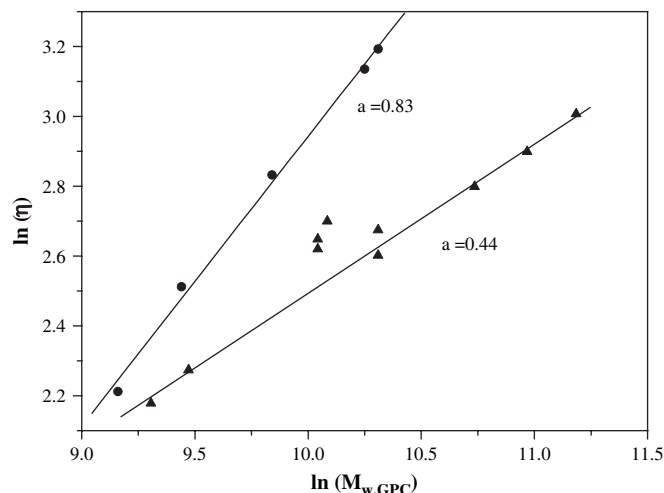


Fig. 12. Mark-Houwink plot of the branched copolymer (▲) and linear copolymer (●) in THF at 25 °C.

( $M_{w,MALLS} = 77.7 \times 10^4$ ) and high branched architecture ( $M_{w,MALLS}/M_{w,GPC} = 5.3$ ) were attained only after 0.9 h. However, the slowest polymerization rate, 6.3 h, was observed when the St/AN feed ratio was 40/10. The resulting polymer had also relatively lower molecular weight ( $M_{w,MALLS} = 2.7 \times 10^4$ ) and lower level of branching ( $M_{w,MALLS}/M_{w,GPC} = 2.1$ ).

Usually, the branching characteristics can be obtained using Mark-Houwink equation,  $\eta = KM^a$ , which has been developed from basic geometry and fundamental polymer solution theory. Fig. 12 shows the results. The intrinsic viscosity of the branched copolymer was lower than that of linear copolymer of similar apparent  $M_{w,GPC}$ . In addition, the slope of the branched copolymer was also smaller than that of the linear copolymer (exponent  $\alpha_B = 0.44$  and  $\alpha_L = 0.83$ , respectively), indicating a decreased level of interaction between polymer and solvent and proving their compact and branched structure.

## 4. Conclusion

The copolymerization of St and AN using ATRP was studied in detail. The linear copolymerization experiment proved that the feed composition had vital effects on the polymerization process, polymerization at  $f_{St} = 0.5$  was well controlled and gave high monomer conversion in moderate polymerization rate. When divinylbenzene was introduced as the branching agent, the development of branching strongly depended upon the feed composition, particularly the ratio of the initiator to the branching agent. Primary chains bearing pendent vinyl groups with low polydispersity formed mainly at the early stage then were statistically linked through the polymerization of the pendent vinyl groups to start the branching at the middle or late stage. Relatively high concentration of the branching agent gave rise to some early occurrence of branching. Too much high level of the branching agent resulted in gelation. At the selected ratio of [DVB]/[t-BBiB]/[St]/[AN]/[Bpy]/[Cu<sup>I</sup>Br] = 0.9:1:15:15:1.35:0.45, the branching started at about 40% monomer conversion and became significant at about 50% monomer conversion. Branched copolymer with gradient structure in their primary chains was prepared by statistically linking about six primary chains near 80% monomer conversion.

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