

# Studies on the Preparation of Branched Polymers from Styrene and Divinylbenzene

Honglan Tang, Fanghong Gong, Chunlin Liu, Qiang Ren, Yang Yang, Bibiao Jiang, Chao Liu, Jianhai Chen

Department of Materials Science and Engineering, Jiangsu Polytechnic University, Changzhou 213016, China

Received 11 February 2006; accepted 6 June 2006

DOI 10.1002/app.25837

Published online 28 May 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The self-condensing vinyl polymerization of styrene and an inimer formed *in situ* by atom transfer radical addition from divinylbenzene and 2-bromoisobutyl-*tert*-butyrate using atom transfer radical polymerization technique was studied. To study the polymerization mechanism and achieve high molecular weight polymer in a high polymer yield, the polymerization was carried out in bulk at 80°C. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy and gel permeation chromatography (GPC) coupled with multiangle laser light scattering (MALLS) were used to monitor the polymerization process and characterize the solid polymers. It is proved that the

polymerization shows a “living” polymerization behavior and the crosslinking reaction has been restrained effectively due to the introduction of styrene. Polymers with high molecular weight ( $M_{w, \text{MALLS}} > 10^5$ ) can be prepared in high yield (near 80%). Comparison of the apparent molecular weights measured by GPC with the absolute values measured by MALLS indicates the existence of branched structures in the prepared polymers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3323–3327, 2007

**Key words:** branched polymer; ATRP; divinylbenzene; inimer; self-condensing vinyl polymerization

## INTRODUCTION

Hyperbranched polymers have received great attention in recent years,<sup>1</sup> because they have a special structure, large number of terminal groups, and physical properties different from their linear analogues, such as small hydrodynamic volume and low melt viscosity. They can be used as processing additives to decrease the melt viscosity of certain plastics<sup>2–4</sup> and macroinitiators.<sup>5</sup>

The synthesis of hyperbranched vinyl polymers can be achieved by self-condensing vinyl polymerization (SCVP), first reported by Fréchet et al. in 1995.<sup>6</sup> Then, Hawker et al. and Matyjaszewski and coworkers extended this method to the living radical polymerization field.<sup>7–9</sup> But the synthesis of hyperbranched polymers by SCVP needs to prepare inimers in advance. The preparation process is tedious and the polymer yield is much low. To simplify the process, Baskaran<sup>10</sup> has attempted to synthesize hyperbranched polymers by *in situ* formation of

inimer from anionic initiators with divinylbenzene through anionic SCVP. It is well known that the polymerization condition of anionic is very rigorous and costly, and also the monomers suitable for anionic polymerization are limited. Consequently, our group has studied the preparation of hyperbranched polymers through atom transfer radical polymerization of an *in situ* formed inimer from ATRP initiator and divinylbenzene (DVB). Unfortunately, the polymerization is much sensitive to crosslinking and the double bond conversion is less than 60%.<sup>11</sup> Sherrington and coworkers reported the synthesis of branched poly(methyl methacrylate) via controlled/living polymerization exploiting ethylene glycol dimethacrylate as branching agent.<sup>12</sup> In this article, styrene was introduced as comonomer, and DVB was used as branch monomer. The atom transfer radical polymerization for branched polymers from inimer formed *in situ* was investigated. As expected, the crosslinking reaction has been restrained effectively due to the introduction of styrene and branched polymer of high molecular weights in a polymer yield near 80% has been prepared.

## EXPERIMENTAL

### Material

DVB (mixture of 1,3- and 1,4-isomer and 20% ethylstyrene) (Fluka, Switzerland), 2-bromoisobutyl-*tert*-butyrate (BIBTB) (Shanghai Chemical Corporation,

Correspondence to: B. Jiang (jiangbibiao@jpu.edu.cn).

Contract grant sponsors: Natural Science Foundation of China; CNPC; contract grant number: 20574032.

Contract grant sponsor: CNPC; contract grant number: CInnovation Fund (05E7009).

Contract grant sponsor: The Key Laboratory of Changzhou Polymer Material.

*Journal of Applied Polymer Science*, Vol. 105, 3323–3327 (2007)  
© 2007 Wiley Periodicals, Inc.

Shanghai, China), and 2,2'-bipyridine (BPY, an analytical reagent) (Shanghai Chemical Corporation, Shanghai, China) were used without further purification. Copper(I) bromide (CuBr, an analytical reagent) (Shanghai Chemical) was purified by stirring in acetic acid, and then washed with methanol and dried under vacuum. Styrene was distilled at reduced pressure before use. All the solvents were analytical reagents and used as received.

### Typical polymerization procedure

DVB (0.3506 g, 2.125 mmol, 0.85 equiv), BIBTB (0.5689 g, 2.5 mmol, 1 equiv), styrene (5.2083 g, 50 mmol, 20 equiv), CuBr (0.1613 g, 1.125 mmol, 0.45 equiv), and BPY (0.3435 g, 2.25 mmol, 0.9 equiv) were added to a dry 100-mL round bottom flask with a magnetic stir bar. The flask was cycled between vacuum and argon (6 times) to remove oxygen. Then the flask was sealed and placed in a preheated, thermally regulated oil bath at  $(80 \pm 1)^\circ\text{C}$ . Polymerization aliquots were analyzed by using  $^1\text{H-NMR}$  and gel permeation chromatography (GPC) coupled with multiangle laser light scattering (MALLS) measurement to monitor the double bond conversion and molecular weight growth. Finally, the flask was removed from the oil bath and allowed to cool for a few minutes. Petroleum ether was added to extract the unreacted monomers for the determination of polymer yield. Then tetrahydrofuran was added to dissolve the polymer under stirring. After filtration of the solution to remove the catalyst, alcohol was added to the filtrate to precipitate the resulting polymer. The polymer was dried under vacuum at  $40^\circ\text{C}$  for 24 h.

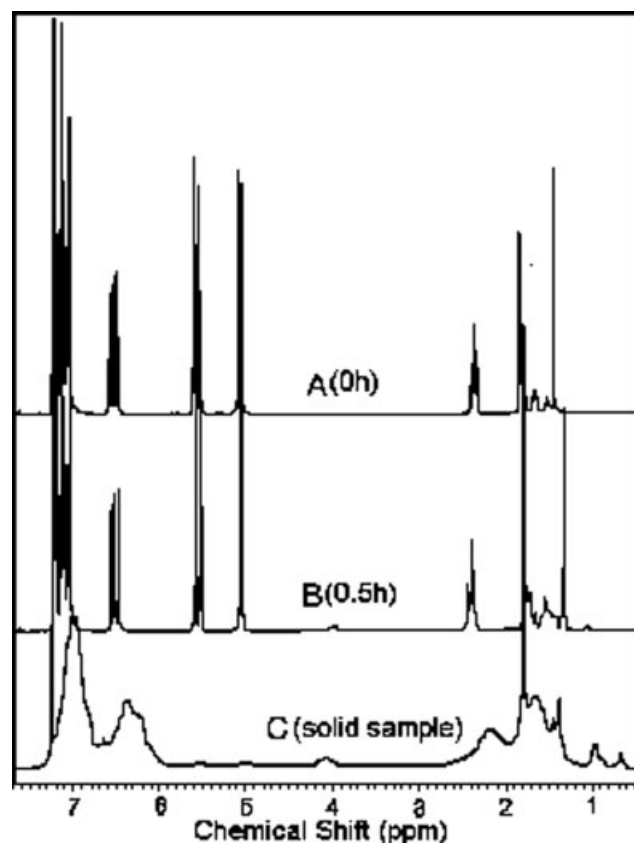
### Characterization methods

The  $^1\text{H-NMR}$  spectra were taken on a Bruker ARX-300 type NMR spectrometer at room temperature in  $\text{CDCl}_3$ . GPC was performed on a Waters GPC line coupled with MALLS at room temperature in tetrahydrofuran. Conversion of double bond was monitored by  $^1\text{H-NMR}$  using cyclohexanone as an internal standard. Gas chromatography (GC) was conducted on HP6890 with DB-5 column.

## RESULTS AND DISCUSSION

### Polymerization behavior of the system of styrene and DVB

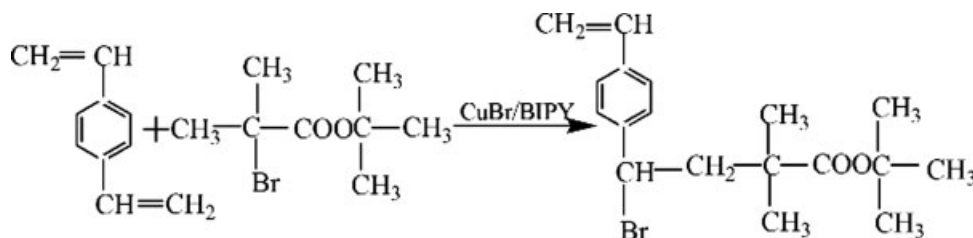
Figure 1(A,B) shows the respective  $^1\text{H-NMR}$  spectra of the polymerization samples at 0 and 0.5 h. The signals at chemical shifts of 6.9–7.3 ppm correspond to the protons of the benzene ring, and the signals at chemical shifts of 6.75, 5.75, and 5.25 ppm are attributed to the protons of the double bonds. The signals



**Figure 1**  $^1\text{H-NMR}$  spectra of the polymerization aliquots and obtained solid polymer sample.  $[\text{DVB}]/[\text{BIBTB}]/[\text{styrene}]/[\text{CuBr}]/[\text{BPY}] = 0.85/1/20/0.45/0.90$ ;  $[\text{styrene}]/[\text{cyclohexanone}] = 11.5/1.0$  in volume; polymerization at  $80^\circ\text{C}$ .

at chemical shift of 2.5 ppm are assigned to the protons of  $-\text{CH}_2\text{COCH}_2-$  of cyclohexanone. The signals between chemical shifts of 1.3 and 1.75 ppm are assigned to the protons of  $-\text{CH}_2-$  and  $-\text{CH}_3$  in the initiator and cyclohexanone. The methyl protons geminal to bromine in the initiator, at chemical shift of 1.9 ppm, are shifted upfield, at chemical shift of 1.3 ppm, as the bromine is removed and monomer added. In Figure 1(B), the new peak at chemical shift of 4.0 ppm is associated with the halogen end groups after the initiator initiating DVB and styrene to start the polymerization (Scheme 1).

Although introducing cyclohexanone as the internal standard will decrease polymerization rate, it does not influence to study the polymerization behavior. The conversion of the double bonds is plotted in Figure 2, where  $[A]$  represents the total concentration of the double bonds. The linear relationship between  $\ln([A]_0/[A])$  and polymerization time indicates that the concentration of active species remains constant and the polymerization exhibits a "living" polymerization behavior. It is also observed that the polymerization system is still soluble and no gel material is present after 10-h polymerization,



**Scheme 1** The procedure of initiator BIBTB initiating DVB.

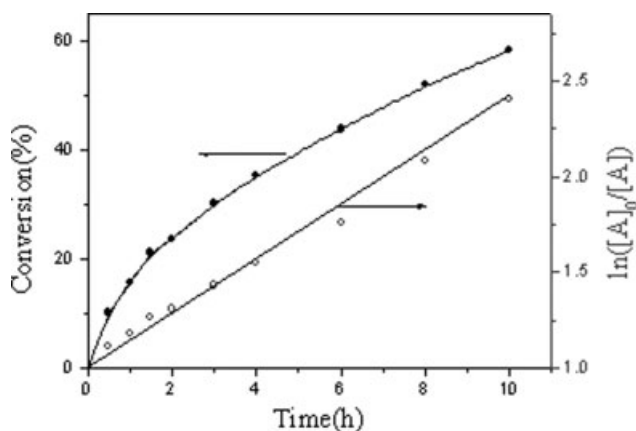
which is contrast to our previous studies that the system became a gel after only 3-h reaction.<sup>11</sup> The primary reason may be that the number of pendant vinyl groups in oligomers decreases when styrene has been introduced as comonomer. The pendant vinyl groups participate in polymerization giving rise to the coupling of oligomers, which results in the formation of branched structures and high molecular-weight polymers rapidly and crosslinking material finally.

For more information to probe the polymerization behavior, the polymerization aliquots were also analyzed by GPC. Figure 3(A,B) illustrates the results. The signals in region 1 correspond to the mixture of monomers (styrene and DVB), initiator, and the inimer formed *in situ*. The signals from regions 2 to 6 are assigned to oligomers of different molecular weight. The peaks in regions 7 and 8 are from macromolecules. It must be emphasized that while the conversion is low, high molecular-weight polymers, regions 7 and 8, have been observed. Because GC analysis has proved that the conversion of BIBTB reaches 100% after about 2-h polymerization, the signal in region 1 is still present throughout the polymerization, which indicates the existence of styrene and DVB in the whole polymerization processes. All

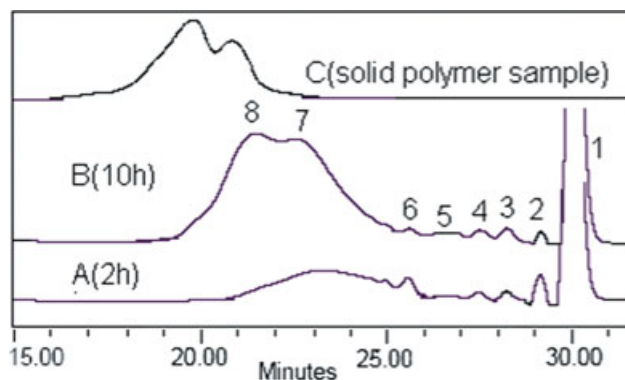
these experimental results are similar to those of ordinary SCVP of inimer preprepared.<sup>6,9,13</sup> Surprisingly, the amount of components 2–6 are much lower compared with their higher or lower analogues, suggesting that the coupling of growing oligomers is the major reaction pathway and the coupling of oligomers will proceed rapidly regardless the limited reactivity of pendant vinyl groups.

For a selected radical derived from halogen end group, it can initiate not only the double bond of DVB or styrene, but also the pendant vinyl group undergoing polymerization. Apparently, radicals formed will tend to initiate double bonds of monomers rather than the pendant vinyl groups due to their relatively lower reactivity. However, the fact is not the case; as stated in our previous paper,<sup>11</sup> the actual case should counter the number of the vinyl groups in the selected molecules when which type double bond will take advantage to participate in polymerization is considered.

Although the polymerization rate is finally affected by the total concentration of monomers and pendant vinyl groups, it is undoubted that oligomers bearing several double bonds and halogen end groups have advantage to take part in polymerization. The relatively high amount of component 1



**Figure 2** Conversion of double bond on the polymerization time by ATRP. [DVB]/[BIBTB]/[styrene]/[CuBr]/[BPY] = 0.85/1/20/0.45/0.90; [styrene]/[cyclohexanone] = 11.5/1.0 in volume; polymerization at 80°C.



**Figure 3** Overlay of GPC chromatograms of the system at various conversions. [DVB]/[BIBTB]/[styrene]/[CuBr]/[BPY] = 0.85/1/20/0.45/0.90; [styrene]/[cyclohexanone] = 11.5/1.0 in volume; polymerization at 80°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
**Results of the Polymerization of Styrene and Divinylbenzene (at 80°C in Bulk)**

Feed ratio <sup>a</sup>	Time (h)	Yield (%)	$M_n$ GPC	$M_w$ GPC	$M_w$ MALLS	$M_w$ GPC/ $M_n$ GPC	$M_w$ MALLS/ $M_w$ GPC
0.75 : 1 : 20 : 0.45 : 0.90	6.5	71.6	7640	26,460	115,900	3.46	4.38
0.85 : 1 : 20 : 0.45 : 0.90	6.5	79.1	8670	37,103	128,900	3.46	3.47
0.95 : 1 : 20 : 0.45 : 0.90	6.5	70.0	10,784	129,107	907,800	11.97	7.03
0.85 : 1 : 15 : 0.45 : 0.90	8.5	20.6	4966	7231	9973	1.46	1.35
0.85 : 1 : 30 : 0.45 : 0.90	8.5	75.5	7155	28,810	38,920	4.05	1.35

<sup>a</sup> Feed ratio: DVB : BIBTB : styrene : CuBr : BPY.

throughout the whole polymerization supports these statement and explanation strongly, since these fractions correspond to initiator, DVB, styrene, inimer bearing only one double bond and halogen end group. Based on the aforementioned statement and explanation, it should be easy to understand and accept the presence of high molecular-weight polymers after only 2-h polymerization and the very low amount of components 2–6 derived from the rapid coupling reaction of oligomers bearing several pendant vinyl groups and halogen end groups.

#### Characterization of the polymers from styrene and DVB

It has been found that the mole ratio of DVB to initiator has a vital effect on the atom transfer radical polymerization preparing hyperbranched polymers in our previous work.<sup>11</sup> Furthermore, the polymerization system would suffer crosslinking much more when relatively high ratios were adopted. Consequently, the mole ratio of DVB to BIBTB from 0.75 to 0.95 was adopted to prepare branched polymers of high molecular weight in high polymer yield.

Figure 1(C) presents a typical <sup>1</sup>H-NMR spectrum of the solid polymer. The signals at chemical shifts of 6.75, 5.75, and 5.25 ppm corresponding to the double bond were still present, which proves the presence of the pendant vinyl groups although the mole ratio of DVB to BTBTB is less than 1.0. These results are similar to hyperbranched polymers from inimer preprepared.<sup>6–9,13</sup> It has been concluded in our previous work that one macromolecule of the solid polymers from DVB bears several pendant vinyl groups, and the presence of excessive pendant vinyl groups gives rise to the rapid gelation, and only relatively low-molecular weight hyperbranched polymers can be obtained at low monomer conversion.<sup>11</sup> However, the intensity of these peaks related to the pendant vinyl groups is very weak as illustrated in Figure 1(C), which confirms that the introduction of styrene as a comonomer can really decrease the concentration of the pendant vinyl groups and restrain the crosslinking reaction. As a

result, it should be reasonable to expect that branched polymers with high molecular weight can be prepared at relatively high monomer conversion. The signals at chemical shift 4.0 ppm ascribe the halogen end groups.

Figure 3(C) illustrates the representative GPC trace of the solid polymer samples. Two peaks corresponding to the components 7 and 8 (high-molecular weight polymers) are shown in Figure 3(B). This is similar to branched vinyl polymers achieved by SCVP, first reported by Fréchet et al.<sup>6</sup> The apparent molecular weights obtained by GPC are determined against linear polystyrene standards, and the absolute real values for a branched polymer are most likely higher than the apparent values, as branched polymers have a smaller hydrodynamic volume. It is generally accepted that light scattering measurements are highly effective in the characterization of polymers containing branched structures.<sup>11,13</sup> The  $M_w$  values determined by MALLS will differ from those obtained by standard GPC analysis. Table I shows a comparison of the apparent molecular weights obtained by GPC with conventional polystyrene calibration and the absolute molecular weights obtained by MALLS for different solid polymer samples. The results do confirm the existence of branched structures. As expected, while [DVB]/[BIBTB]/[Styrene]/[CuBr]/[BPY] = 0.85 : 1 : 20 : 0.45 : 0.9, polymer with high molecular weight ( $M_w$  MALLS = 128,900, much higher than our previous work<sup>11</sup>) is obtained in high yield (79.1%) after 6.5-h polymerization.

#### CONCLUSIONS

The preparation of branched polymers from commercially available DVB and styrene by atom transfer radical polymerization has been studied. The polymerization proceeds by a SCVP mechanism evidenced by <sup>1</sup>H-NMR and the presence of branched structures is confirmed by comparison of the apparent molecular weights from GPC with the absolute values from MALLS. Most importantly, in a sharp contrast to previous studies of hyperbranched poly-

mers from inimer formed *in situ*, crosslinking reaction is restrained effectively in this polymerization. As expected, branched polymer of high molecular weight in a polymer yield near 80% is prepared at last.

## References

1. Gao, C.; Yan, D. *Prog Polym Sci* 2004, 29, 183.
2. Kim, Y. H.; Webster, O. W. *Macromolecules* 1992, 25, 5561.
3. Schmaljohann, D.; Pötschke, P.; Hässler, R.; Voit, B. I.; Froehling, P. E.; Mostert, B.; Loontjens, J. A. *Macromolecules* 1999, 32, 6333.
4. Ren, Q.; Li, A. Y.; Jiang, B. B.; Zhang, D. L.; Chen, J. H. *J Appl Polym Sci* 2004, 94, 2425.
5. Brenner, A. R.; Voit, B. I. *Macromol Chem Phys* 1996, 197, 2673.
6. Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* 1995, 269, 1080.
7. Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. L. *J Am Chem Soc* 1995, 117, 10763.
8. Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* 1996, 29, 1079.
9. Matyjaszewski, K.; Gaynor, S. G. *Macromolecules* 1997, 30, 7034.
10. Baskaran, D. *Polymer* 2003, 44, 2213.
11. Gong, F. H.; Tang, H. L.; Liu, C. L.; Jiang, B. B.; Ren, Q.; Yang, Y.; Chen, J. H. *J Appl Polym Sci* 2006, 101, 850.
12. Isawre, F.; Cormack, P. A. G.; Sherrington, D. C.; Armes, S. P.; Butun, V. *Chem Commun* 2004, 1138.
13. Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J Polym Sci Part A: Polym Chem* 1998, 36, 955.