

Preparation of Heat-Resistant Branched Poly(styrene-*alt*-NPMI) by ATRP with Divinylbenzene as the Branching Agent

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ABSTRACT: Heat-resistant branched poly(styrene-*alt*-NPMI) has been prepared via atom transfer radical polymerization (ATRP) of styrene (St) and *N*-phenyl maleimide (NPMI) with divinylbenzene (DVB) as the branching agent in anisole at 80°C. Gas chromatography (GC) was used to determine the conversion of the reactants. Triple detection gel permeation chromatography (TD-GPC) was used to analyze the copolymers. The results show that the polymerization yields primary chains predominately in the early stages and the formation of branched molecules occurs mainly when conversion is higher than 50%. As

expected, higher dosage of DVB in our investigation range favors the formation of polymers with higher degree of branching. All the resulting branched poly(styrene-*alt*-NPMI)s have glass transition temperature (T_g) above 175°C, extrapolated initial weight loss temperature (T_i) above 410°C and statistic heat-resistant index above 200°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 977–982, 2011

Key words: branched polymer; ATRP; NPMI; heat-resistance

INTRODUCTION

Branched polymers are intrinsically globular (at sufficient molecular weight) and do not have entangled chains, which gives rise to their low intrinsic viscosity.^{1–6} Due to their low intrinsic viscosity, branched polymers are suggested as novel melt modifier and used in the preparation of polymer blends with reduced blend viscosity. The reduction in polymer melt viscosity can enhance output rate and/or decrease power consumption for polymer processing. The reduced viscosity of the blend of linear polymers with branched polymers are attributed mainly the interference of physical entanglements between linear polymers by the globular-shaped branched polymers. The original synthesis of branched polymer involves the polycondensation of AB_x ($x \geq 2$) type monomers, each resulting molecule possesses one group A and

$(x-1)n+1$ group B; where n is the degree of the polymerization.^{7–9} In 1995, Frechet et al. reported the self-condensing vinyl polymerization (SCVP) of the AB^* monomer to branched polymer, where **A** is a vinyl group and B^* is a functional group that can be transformed into an active center, such as cationic,¹⁰ radical,^{11–13} or anionic,^{14,15} to initiate the polymerization of **A**. In addition to the aforementioned two main routes, there are also some notable methods have been reported,^{16,17} such as multibranching ring-opening polymerization of latent AB_x monomers and A_2+B_3 methodology. The synthesis of branched polymer by atom transfer radical polymerization (ATRP) of AB^* monomers has received much attention in the past decade because of the variability of vinyl monomers and mild polymerization conditions.^{18–21}

In 2000, Sherrington and coworkers²² prepared branched poly(methyl methacrylate) via conventional radical polymerization using a multifunctional vinyl comonomer as the branching agent in the presence of a thiol chain transfer agent to inhibit gelation. In 2004, they²³ synthesized branched poly(methyl methacrylate)s via controlled/living polymerization with ethylene glycol dimethacrylate as the branching agent. Our group²⁴ prepared branched polystyrene from the copolymerization of styrene with divinylbenzene (DVB) via ATRP. Zhu,²⁵ Armes²⁶ and our group²⁷ elucidated the development of branching in the ATRP of vinyl and divinyl monomers.

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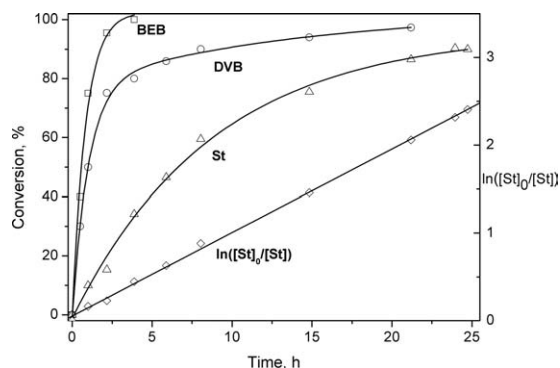


Figure 1 The kinetic data of the branching copolymerization BEB1-St24-NPMI25-DVB1, in anisole at 80°C.

N-phenyl maleimide (NPMI) can copolymerize with acrylonitrile and styrene to produce heat-resistant ABS.²⁸ However; maleimide-based copolymers are poor in molding processability due to their poor fluidity. Branched maleimide-based copolymers are expected to act as the melt modifier. Jiang et al.²⁹ synthesized branched copolymers of 4-(chloromethyl) styrene and *N*-cyclohexyl maleimide via ATRP. But their work still based on the SCVP of expensive 4-(chloromethyl) styrene.

The research interest of our group is the synthesis of cost-effective branched polymer that can be used as melt modifier to linear polymers.^{5,30} In this work, we focused on the one pot synthesis via ATRP of heat-resistant branched poly(styrene-*alt*-NPMI) with DVB as the branching agent. Blending using branched maleimide-based copolymers will be reported in subsequent article.

EXPERIMENTAL

Materials

Copper (I) bromide (CuBr, AR grade, from Shanghai Chemical Reagent Corporation) was purified by stirring in acetic acid, washing with methanol, and then drying under vacuum. Styrene was distilled under reduced pressure before use. DVB (mixture of 1, 3- and 1, 4-isomers and 20% ethyl styrene, DVB) and (1-bromoethyl) benzene (97%, BEB) were purchased from Aldrich and used as received. NPMI, a commercial product (Wuxi Xinghong Chemicals, Jiangsu province, China), was recrystallized twice from dry ethanol and dried under vacuum. Other materials are analytical reagents and used as received.

Branching atom transfer radical copolymerization of styrene and NPMI

NPMI (10.39 g; 60 mmol), styrene (6.0 g, 57.6 mmol), DVB (0.3906 g; 2.4 mmol), BEB (0.4579 g; 2.4 mmol), Bpy (1.1246 g; 7.2 mmol), copper (I) bromide (0.3443 g;

2.4 mmol), and anisole (11.18 g) were added into a 100 mL dry round bottom flask with a magnetic stir bar. The flask was cycled with argon five times to eliminate the moisture and oxygen, then sealed with a rubber septum and placed into an oil bath at 80°C \pm 1°C. Samples (\sim 0.2 mL) of the reaction mixture were taken at regular intervals, diluted into 2 mL of THF and exposed to the air to terminate the reaction. The conversion of the reactants, and molecular weight and viscosity were determined using gas chromatography, ¹H-NMR and TD-GPC respectively. The final samples were dissolved with acetone, filtered and precipitated in ethanol to yield solid polymers. The products were dried under vacuum at 50°C. In all synthesis, [BEB] : [CuBr] : [Bpy] is 1 : 1 : 3.

Linear atom transfer radical copolymerization of styrene and NPMI

Linear copolymerization was conducted without DVB at the same condition as that in the branching copolymerization.

Characterization methods

GC was conducted on HP-6890 with DB-5 column. TD-GPC was performed on a GPC line consisting of a Waters 1515 isocratic HPLC pump and Waters Styragel HR 4e, HR 1 and HR 0.5 column, a 703-T mini DAWN tristar light scattering detector operating at 690 nm (Wyatt), a on-line ViscoStar viscometer (Wyatt) and a Waters 2414 refractive index detector at 25°C. The eluent was tetrahydrofuran with a flow rate of 1 mL/min. The dn/dc values of the resulting copolymers were determined using an Optilab rEX ($\lambda = 690$ nm) interferometric refractometer (Wyatt) in off-line mode at room temperature. The dn/dc values of BEB₁-St₂₄-NPMI₂₅-DVB₁, BEB₁-St₄-NPMI₅-DVB₁ branched polymer and BEB₁-St₂₅-NPMI₂₅ linear copolymer were calculated to be

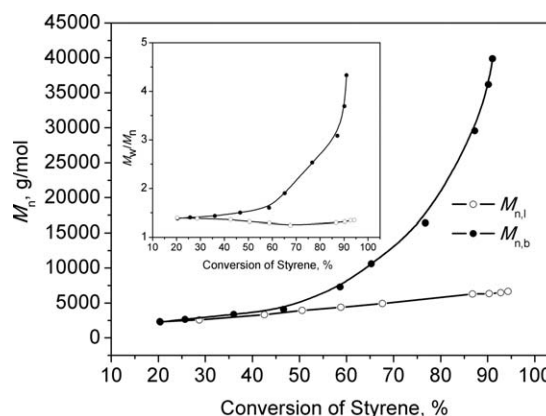
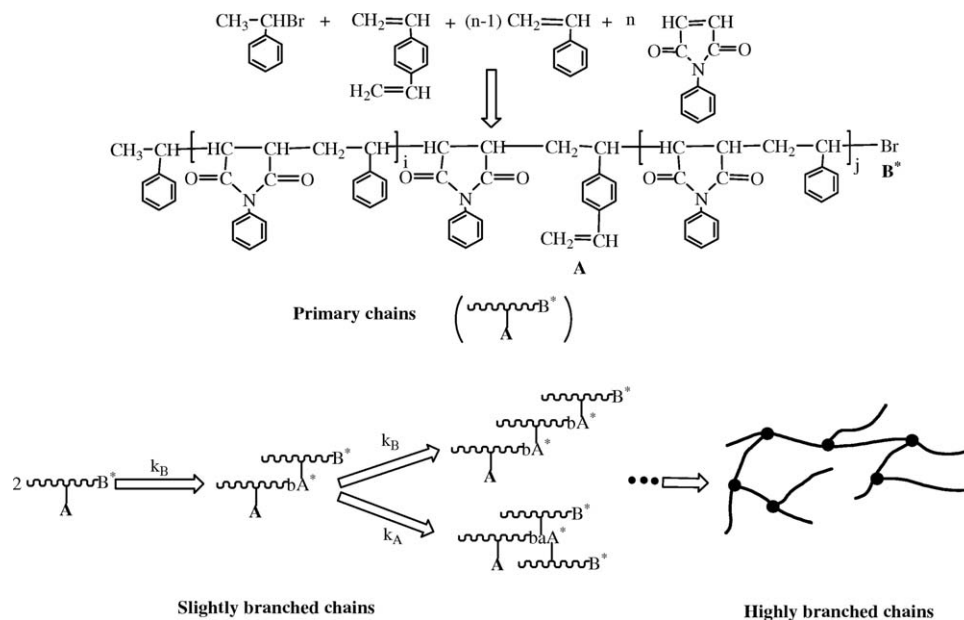


Figure 2 Variation of the molecular weight and polydispersity with styrene conversion. BEB1-St25-NPMI25 (○), and BEB1-St24-NPMI25-DVB1 (●).



Scheme 1 Schematic formation of the branched copolymer via ATRP of styrene and NPMI.

0.1575 ± 0.0009 , 0.1545 ± 0.0012 and 0.1594 ± 0.0036 mL g^{-1} , respectively. The number average molecular weight, $M_{n,b}$, of the copolymer was calculated using the weight average molecular weight, $M_{w,\text{MALLS}}$, according to the literatures,³¹ $M_n = M_{w,\text{MALLS}} / (M_{w,\text{GPC}} / M_{n,\text{GPC}})$. Thermal gravimetry (TG) and derivative thermal gravimetry (DTG) analysis were carried out on SDTQ-600 thermogravimetric analyzer under N_2 atmosphere in the temperature range of 50–600°C, at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was performed on a PE-7 thermal analysis system under N_2 atmosphere with a temperature range of 50–250°C, at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Kinetics of atom transfer radical copolymerization and development of branching

Alternating copolymers can be prepared by radical copolymerization of an electron-rich monomer and an electron-poor monomer through the formation of charge transfer complex (CTC). Chen et al.³² and Jiang et al.³³ prepared alternating copolymers of N-substituted maleimide and styrene via ATRP.

Solvent is necessary to decrease the vitrification effect in the final stage of the polymerization due to the high rigidity of maleimide based copolymers. Anisole was chosen as the solvent since it has good solubility to maleimide based copolymers and its polarity is also appropriate to maintain the CTC in our reaction system.

It is reasonable to consider that the conversion of NBMI is the same as that of styrene due to their alternating reaction. Figure 1 shows the kinetic data

of the polymerization. The linear semilogarithmic plot of monomer conversion versus time proves their consumption by first-order kinetics and implies a constant radical concentration during the reaction. This result indicates that the introduction of anisole in the reaction is enough to maintain control even at high monomer conversion. However, we found that it took longer time for the branching polymerization to reach the same conversion as compared with the linear one. For example, 90% conversion was attained within 24 h and 18 h for the branching and the linear polymerization respectively, which should be due to the fast increase in the viscosity of the branching reaction system.²⁶

Figure 2 illustrates the variation of the molecular weight and polydispersity with conversion. The molecular weight of the linear copolymer increased

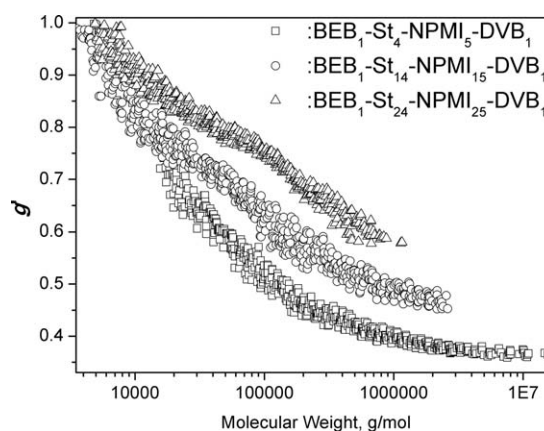


Figure 3 Variation of the Zimm branching factor with molecular weight across the full molecular weight range of the final products. BEB1-St_x-NPMI_y-DVB₁ copolymers.

TABLE I
Molecular Weights and Branching Characteristics of the Branched Copolymers

Sample	Feed ratio ^a	Conv.St (%)	$M_{n,b} \times 10^{-4}$ (g/mol)	M_w/M_n	N_b	ρ_b (%)	$[\eta]$ (mL/g)	g'
A	25 : 24.7 : 1 : 0.3	94.2	0.94	1.46	1.44	0.6	5.89	0.96
B	25 : 24.4 : 1 : 0.6	92.1	1.72	3.25	2.7	1.4	12.95	0.89
C	25 : 24 : 1 : 1	91.6	3.99	4.33	6.3	2.5	20.32	0.70
D	15 : 14 : 1 : 1	92.5	3.43	4.62	8.9	3.2	17.14	0.62
E	5 : 4 : 1 : 1	95.6	2.35	5.13	17.7	9.8	11.66	0.50

^a The feed ratio is expressed as [NPMI] : [St] : [BEB] : [DVB].

linearly with monomer conversion, and the polydispersity decreased gradually from 1.39 to 1.24. As regarding to the branching copolymerization, the molecular weights are only some bigger than those of the linear reference, the polydispersity also increased slowly (<1.5), indicating some branching but not significant. The molecular weights deviated markedly from those of the linear reference and the polydispersity became broad when conversion was 50–60%, but no steep increase in the molecular weight occurred, implying the coupling mainly come from the primary chains, giving rise to the formation of small and slightly branched molecules. A steep increase in molecular weight and rapid broadening in polydispersity occurred above 60% conversion, suggesting the coupling between branched molecules became significant.

Based on the above results, we can give a scheme to outline the formation of the branched copolymer (Scheme 1). Of course, the product must be mixture with different molecular weights and degree of branching because of the statistical nature of the process.

Influence of DVB dosage on the degree of branching

Following Zhu,²⁵ Billingham and Arms,²⁶ also Flory,⁷ the average number of the primary chain per molecule, N_b , and the branching density, ρ , can be calculated using eqs. (1) and (2).

$$N_b = \frac{M_{n,b}}{M_{n,l}} \quad (1)$$

$$\rho = \frac{138.5}{M_{n,b}} (N_b - 1) \quad (2)$$

where $M_{n,b}$ and $M_{n,l}$ are the molecular weight of the branched copolymer and the linear reference at the same conversion. 138.5 is the average molecular weight of NPMI and styrene. The $M_{n,l}$ for a particular monomer conversion was interpolated from the linear regression in Figure 2.

As regarding to the degree of branching, the Zimm branching factor, g' where for polymers of the

same molecular weight, is used as the qualitative indicator.^{34,35}

$$g' = IV_{\text{Branched}}/IV_{\text{Linear}} \quad (3)$$

where IV is the intrinsic viscosity of the polymer.

For linear styrene/NPMI alternating copolymers, the following equation was derived from several samples prepared in this work.

$$[\eta] = 1.77 \times 10^{-2} M_w^{0.614} \quad (4)$$

A plot of g' as a function of each molecular weight slice of the final branched polymers is shown in Figure 3. These data show that the sample is branched across the whole of its molecular weight distribution and that branching increases as the molecular weight increases. It suggests that the higher molecular weight species have much developed branching structure than that of lower molecular weight. Also, polymer prepared at higher dosage of DVB has higher degree of branching.

Table I summarizes the results. It is clear that N_b and ρ rise rapidly with increased DVB feed ratio at similar conversion. The polydispersity is also broader at high DVB concentration. Polymer prepared at higher dosage of DVB provided higher degree of

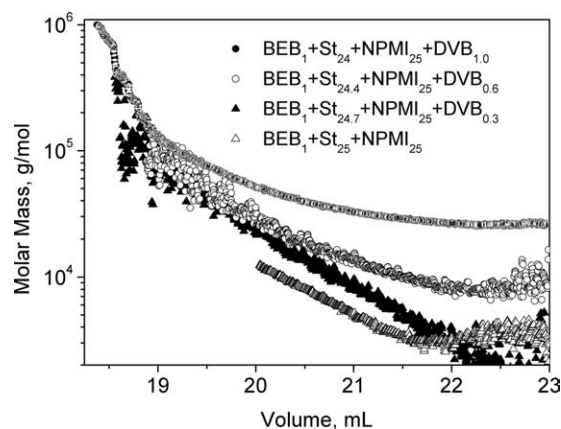


Figure 4 Relationship between molar mass and GPC elution volume for the copolymers. BEB1-Stx-NPMI25-DVB copolymers.

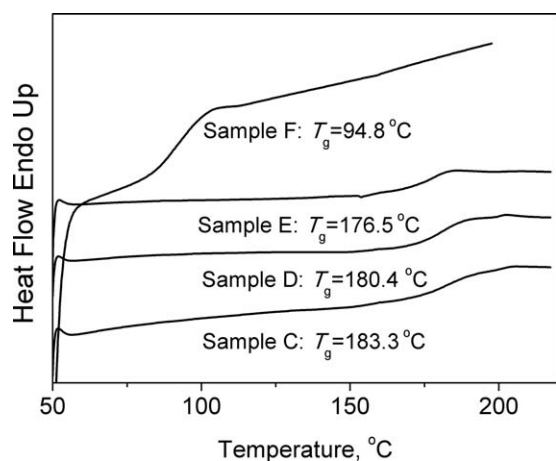


Figure 5 DSC curves of the branched copolymers. Sample C, D, E, and F correspond to the samples in Table II.

branching and smaller value of g' as we expected. Of course, the degree of branching expressed as g' is just a value in average similar to molecular weight of polymer. The relatively lower molecular weight of polymer D and E may be explained mainly by the steric effect at high conversion.

Figure 4 illustrates the relation between GPC elution volume and molecular weight data for the linear copolymer and polymer A, B, and C in Table I. It is clear that for a given elution volume, the molecular weights of the branched copolymers are higher than those of the linear copolymer because the branched copolymer has more compact structure than the linear one. At the same elution volume in Figure 4, polymer A and C have the lowest and highest molecular weight respectively in the three branched copolymers, due to their different degree of branching.

Thermal properties of the resulting branched poly(styrene-*alt*-NPMI)s

The thermal properties of the resulting copolymers are our big concern in this study. Branched copolymers with different degree of branching were investigated. For comparison, branched polystyrene pre-

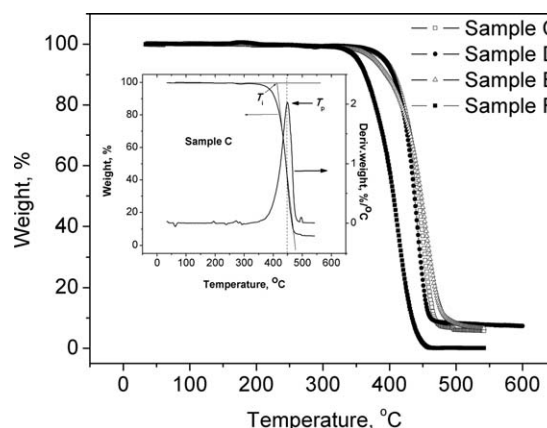


Figure 6 TG curves of the branched copolymers. Sample C, D, E, and F correspond to the samples in Table II. Initial weight loss temperature T_i is the temperature corresponding to the point of intersection of the baseline and the tangent line at T_p . T_p is the temperature with the fastest weight-losing rate determined by DTG.

pared at styrene₅₀-BEB₁-DVB₁ was also investigated. The DSC, TG curves and corresponding results of all the samples are shown in Figures 5 and 6 and Table II, respectively.

The branched polystyrene has glass transition temperature (T_g) of 94.8°C. The three branched poly(styrene-*alt*-NPMI) samples have glass transition temperature (T_g) higher than 175°C though the T_g decreases slightly with the increase of degree of branching. Higher degree of branching of a polymer means the presence of more terminal groups, free volume and so results in the lower T_g . The three branched poly(styrene-*alt*-NPMI) samples have extrapolated initial weight loss temperature (T_i) above 400°C and statistic heat-resistant index (T_s) above 200°C, which are much higher than those of branched polystyrene. The 5% weight loss temperature of the sample E is much lower than those of the samples C and D, indicating the weight-losing rate of the sample E is the faster in the early stages. The labile carbon-halide moieties in polymers prepared by ATRP usually undergo degradation first.³⁵ The more carbon-halide moieties present in the polymer, the more weight-losing percentages may be detected

TABLE II
TG and DSC Results of the Branched Copolymers

Sample	[NPMI] : [St] : [BEB] : [DVB]	$M_n \times 10^{-4}$ (g/mol)	T_g (°C)	T_i^a (°C)	T_5^a (°C)	T_{30}^a (°C)	T_s^b (°C)
C	25 : 24 : 1 : 1	3.99	183.3	417.0	392.0	431.1	203.6
D	15 : 14 : 1 : 1	3.43	180.4	415.8	392.4	427.0	202.4
E	5 : 4 : 1 : 1	2.35	176.5	414.8	377.0	431.4	200.7
F	0 : 50 : 1 : 1 ^c	3.76	94.8	366.0	353.6	390.8	184.2

^a T_i : initial weight loss temperature; T_5 : 5% weight loss temperature; T_{30} : 30% weight loss temperature.

^b $T_s = 0.49[T_5 + 0.6(T_{30} - T_5)]$.

^c Polymerization to synthesize branched polystyrene.

in the lower temperature. The sample E has the most carbon-bromide moieties, so the weight losing rate is the fastest in the early stages.

CONCLUSIONS

Analysis of the changes in the molecular weight and polydispersity of the copolymer indicates that the ATRP of styrene and NPMI with DVB as the branching agent mainly yields primary chains in the early stages, and the formation of branched chains occurs mainly when conversion is higher than 50%. Higher dosage of DVB favors the formation of polymers with higher degree of branching in our investigation range. All the resulting copolymers show improved thermal stability as compared with polystyrene, their glass transition temperature (T_g) and statistic heat-resistant index are above 175°C and 200°C respectively.

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