

Synthesis of Branched Polystyrene and Poly(styrene-*b*-4-methoxystyrene) by Nitroxyl Stable Radical Controlled Polymerization

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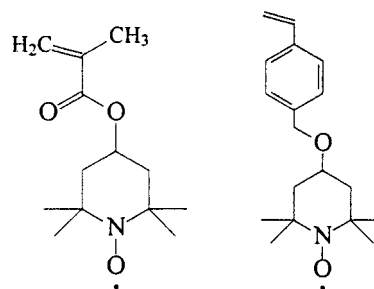
ABSTRACT: Branched polystyrene was synthesized through controlled radical polymerization of styrene in the presence of 4-(4'-vinylphenylmethoxy)-2,2,6,6-tetramethyl-1-piperidinyloxy (STEMPO) which possesses a nitroxyl stable radical and a polymerizable vinyl group. During the polymerization, STEMPO played the role of branching agent since it can polymerize as well as trap the propagating radical. The resulting polymer contained a labile covalent C–ON bond at each branch point and had broad molecular weight distribution. After being heated with phenylhydrazine, the GPC profile of the product became narrower due to cleavage of the branch points. The molecular weight of the cleaved product was proportional to monomer conversion, demonstrating a controlled growth of primary chains. ¹H NMR showed that, in the polymerization of deuterated styrene, the signal intensity of vinyl groups in STEMPO decreased at a constant rate with increasing monomer conversion. ESR measurement illustrated that the labile C–ON bonds at branch points were subject to thermal homolysis. The branched product was used as a macroinitiator for radical polymerization of 4-methoxystyrene. The resulting copolymer possessed a branched architecture of diblock primary chains with controlled length and narrow distribution.

Introduction

Branched polymers are generally formed through three mechanisms, i.e., step polymerizations of monomer in the presence of a small amount of multifunctional branching agent, chain transfer in radical polymerizations, and copolymerization of monomer and macromonomer. None of these approaches can control the branched structure, such as the length of the primary chain and the distribution of branched units along the polymer backbone.

Recently, there has been much effort to synthesize well-defined polymers through radical polymerizations mediated by nitroxyl stable free radicals such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy).^{1–3} This includes the syntheses of block⁴ and graft^{5,6} copolymers, star-shaped polymers,⁷ and hyperbranched polymers.⁸ A unimolecular initiator containing an alkoxyamine was introduced by Hawker.³ During the polymerization, the functional group and the precursor architecture of the alkoxyamine and resulting stable radical are retained at the end of primary chain. A number of TEMPO and alkoxyamine derivatives such as hydroxy,⁹ epoxy,¹⁰ and vinylic hydrocarbon^{8,11} functionalized as well as polymeric¹² and dendritic¹³ TEMPOs and alkoxyamines were synthesized and were used to prepare end-functional polymers,⁹ block^{10,14} copolymers, branched polymers and polymer brushes,¹¹ dendritic-linear,¹³ and hyperbranched⁸ polymers.

In studying the kinetics of stable free radical controlled polymerization (SFRP),¹⁵ we developed a rate enhancement technique in which a polymerizable nitroxide, 4-methacryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxy (MTEMPO), was used as the counter radical.¹⁶



MTEMPO

STEMPO

During the polymerization, MTEMPOs polymerize onto the chain and thus have lower diffusibility to trap propagating radicals. While the resulting polymerization rate was accelerated, the molecular weight distribution (MWD) was quite broad,¹⁶ in contrast to the usual narrow MWD observed in SFRP. Preliminary analytical results show that a branched polystyrene was formed.^{16,17}

In the present work, we synthesized a branched polystyrene with well-defined architecture. Here “well-defined” is referred to controlled length and narrow length distribution of primary chains, as well as controlled number of branches, and more homogeneous distribution of branch points than that achieved by conventional radical polymerization. We polymerized styrene in the presence of 4-(4'-vinylphenylmethoxy)-2,2,6,6-tetramethyl-1-piperidinyloxy (STEMPO) instead of MTEMPO because the propagating radical formed by MTEMPO has a higher tendency to disproportionate with another nitroxyl stable radical via “hydrogen transfer”, as in TEMPO-mediated radical polymeriza-

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Table 1. Polymerizations of Styrene and Styrene-*d*₈ in the Presence of a Stable Radical

entry	recipe			polymerization results				
	styrene/g, mol	radical/g, mmol	AIBN/g, mmol	conversion	$M_n/10^4$ g/mol	d	$[\eta]_n^{dL}/g$	α^e
1 ^a	27.10, 0.26	0.15, 0.87	0.12, 0.73	81% (21.5 h)	1.8	1.2	0.11	0.74
2 ^b	27.10, 0.26	0.37, 1.30	0.18, 1.09	85% (22 h)	1.3	1.8	0.10	0.60
3 ^b	27.10, 0.26	0.25, 0.87	0.12, 0.73	87% (21.5 h)	3.3	2.6	0.18	0.59
4 ^{b,c}	4.75, 0.04	0.04, 0.14	0.02, 0.12	75% (11.5 h)	3.5	2.3		

^a System using 4-hydroxy-TEMPO. ^b Systems using STEMPO. ^c System using styrene-*d*₈ as monomer. ^d Number-average intrinsic viscosity. ^e Mark-Houwink value.

tion of methacrylates.¹⁸ The branched structure synthesized in this work is distinct from that by Hawker^{6,8} in that the former is thermally reversible (see Discussion).

Experimental Section

Materials. Styrene (Yonghua Special Chemicals Co. Ltd., 99%), styrene-*d*₈ (ACROS, 98+ atom % D), and 4-methoxystyrene (TCI, 96%) were distilled under reduced pressure. AIBN (Shanghai 4th Factory of Chemicals, 99%) was recrystallized from methanol. 4-Hydroxy-TEMPO (BASF, 99%) was recrystallized from cyclohexane. 4-Chloromethylstyrene (ACROS, 90%) and phenylhydrazine (Shanghai Main Factory of Chemicals, 98%) were used as received.

Instrumentation. The molecular weight, M_n , and polydispersity index, $d = M_w/M_n$, of the final products were determined by gel permeation chromatography (GPC) on a Waters 590 GPC system equipped with two AM GEL columns (5 μ m, linear) and a detector Viscotek model T60 which gives viscosity data and the light scattering (LS) results, using THF as eluent at a flow rate 1 mL/min at 30 °C. The concentration was detected by an external RI detector. LS angle: 90°. Laser wavelength: 670 nm. M_n and d of other samples were measured on three Waters Styragel columns (pore size: 10², 10³, and 10⁴ Å in series) in a Water 2010 system. THF was used as eluent at a flow rate of 1 mL/min at 40 °C. The elution time was detected by a Waters 410 RI detector. The columns were calibrated by narrow polystyrene standards.

¹H NMR measurements were carried out on a Bruker (400 MHz) NMR instrument using CDCl₃ as the solvent and tetramethylsilane (TMS) as the reference.

ESR measurements were carried out on a Bruker ER 200D-SRC spectrometer, operating with an X-band standard cavity (~9.67GHz), at temperatures of ambient, 80, 90, 95, and 100 °C. The concentration of nitroxyl radical was obtained by calibration with standard solution of 4-hydroxy-TEMPO. Instrument parameters: modulation frequency = 100 kHz; modulation amplitude = 1.25 G; microwave power = 20 mW. The receiver gain was set depending on the concentration of nitroxyl radical in different samples.

Monomer conversions were determined by thermogravimetric analysis (TGA) following Veregin's method¹⁹ on a NETZSCH TG209 instrument. The temperature was elevated from 25 to 510 °C at a rate of 20 K min⁻¹. The weight loss above 275 °C gave the polymer content.

Synthesis of STEMPO. 4-Chloromethylstyrene (5.50 g, 0.036 mol) was added dropwise under vigorous stirring to an aqueous NaOH solution (50%, 8 mL) of *N*-tetrabutylammonium bisulfate (1.02 g, 0.003 mol). Then 4-hydroxy-TEMPO (5.17 g, 0.03 mol) was added in several batches over 15 min. The mixture was stirred for 24 h at room temperature before diluting with 20 mL of water and extracting with chloroform. The organic layer was separated and washed with water, dried over MgSO₄, and evaporated. The crude product was purified by column chromatography (Al₂O₃, ethyl acetate/*n*-hexane = 3/17). Red crystals; yield: 85%; mp: 47–48 °C. UV max (ethyl ether): 260 and 460 nm. IR: ν [cm⁻¹] = 1630 (C=C), 1360 (N–O). ESR: $g = 2.0063$, $a = 16.0$ G (toluene). MS (EI): 288. Calcd for C₁₈H₂₆NO₂: C, 75.24; H, 9.09; N, 4.86. Found: C, 75.02; H, 8.92; N, 4.74.

Polymerization. Homopolymerization of Styrene (Take STEMPO-Mediated Styrene Polymerization (Styrene/STEMPO

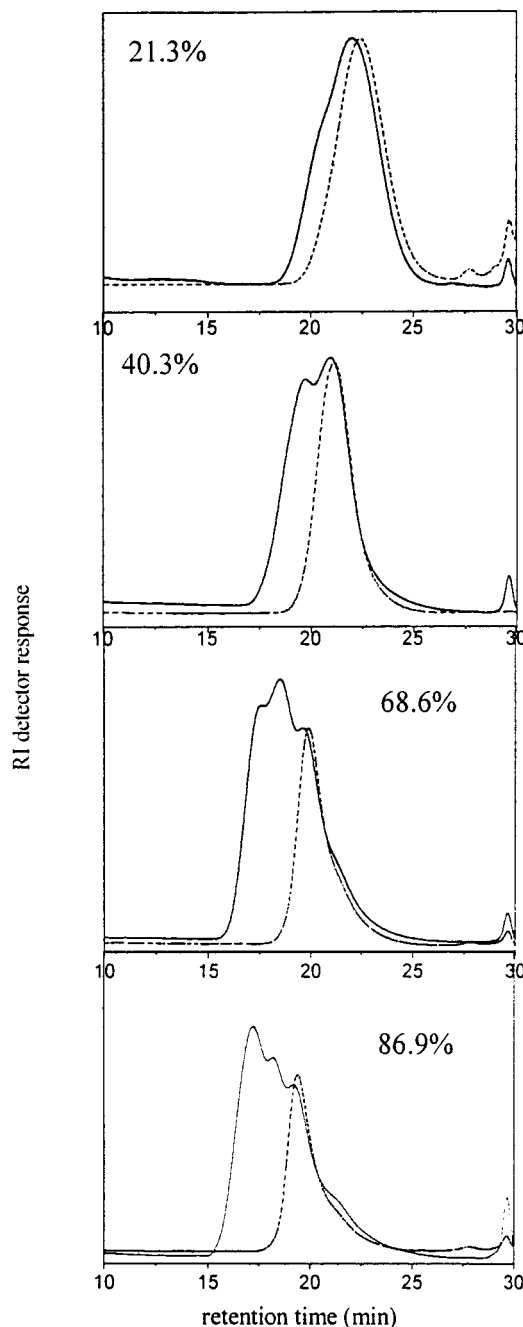
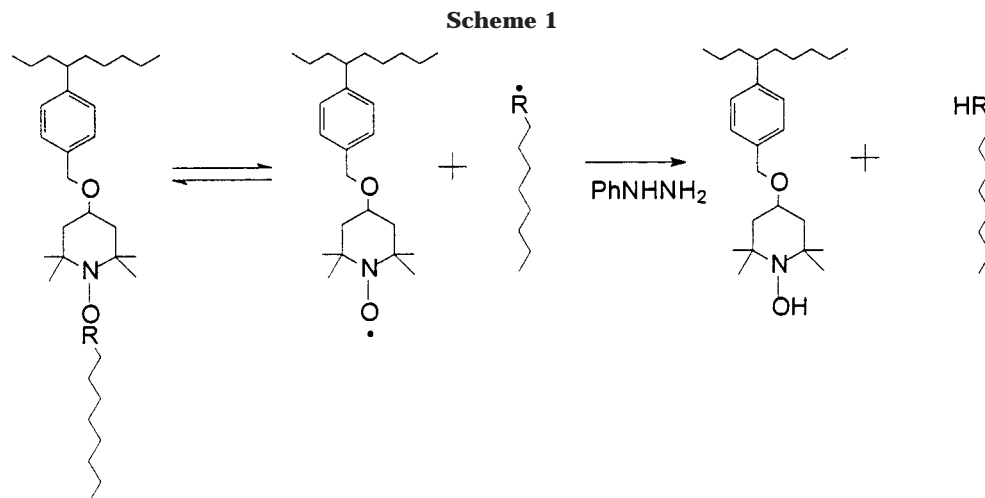


Figure 1. GPC profiles of the products of STEMPO-mediated styrene radical polymerization at various conversions before (solid) and after (dashed) treatment with phenylhydrazine. Polymerization conditions: styrene (27.10 g, 0.26 mol), AIBN (0.12 g, 0.73 mmol), STEMPO (0.25 g, 0.87 mmol). Temperature: 120 °C.

= 300/1, Entry 3 in Table 1) as an Example). A solution of styrene (27.10 g, 0.26 mol), AIBN (0.12 g, 0.73 mmol), and STEMPO (0.25 g, 0.87 mmol) was degassed through three freeze–thaw cycles. Then the mixture was thermostated at



120 °C under a nitrogen atmosphere. The samples were taken from the system at 2, 4, 11.4, and 21.5 h and then quenched into liquid nitrogen to stop the polymerization. The final product was dissolved in THF and precipitated into methanol three times. Final conversion 87% (21.5 h, by TGA), $M_n = 3.3 \times 10^4$ g/mol, and $d = 2.6$ (by LS).

The other polymerizations were carried out under similar conditions, and the results are summarized in Table 1.

Block Copolymerization of Styrene and 4-Methoxystyrene. The precipitated product (4 g, $M_n = 1.97 \times 10^4$ g/mol by GPC after cleavage) of entry 3 in Table 1 and 4-methoxystyrene (4 g, 0.03 mol) were dissolved in toluene (11.5 mL). After degassing by three freeze-thaw cycles, the solution was thermostated at 120 °C. The samples were taken from the system at 12, 16, 20, 26, and 32 h and then quenched into liquid nitrogen to stop the polymerization. The final product was dissolved in THF and precipitated into methanol three times. Final conversion 88% (32 h, by TGA), $M_n = 2.8 \times 10^4$ g/mol, $d = 1.4$ (by GPC on cleaved product).

Posttreatment with Phenylhydrazine (Take the Cleavage of the Product of Entry 3 in Table 1 as an Example). The product (1 g, $M_n = 3.3 \times 10^4$ g/mol, $d = 2.6$ by LS) of entry 3 was dissolved in 1 mL of chlorobenzene before the addition of phenylhydrazine (1 g, 9.2 mmol). The mixture was thermostated at 120 °C for 1 h and then precipitated into methanol. A white powder was obtained, $M_n = 1.6 \times 10^4$ g/mol, $d = 1.3$ (by GPC).

Results and Discussion

Synthesis of Branched Polystyrene. Styrene radical polymerizations were carried out in bulk at 120 °C, using AIBN as initiator, in the presence of a stable free radical. Figure 1 shows the GPC profiles of the resulting polymers (solid line) at different monomer conversions in a STEMPO-mediated system (entry 3 in Table 1). The peaks shift to higher molecular weights with increasing monomer conversion. However, the molecular weight distributions are quite broad, exhibiting multimodal GPC profiles even at 21.3% conversion. This is quite different from the narrow GPC peak commonly observed in SFRP. We believe that this is due to the formation of a branched product through two elementary reactions, i.e., by trapping of growing chain radicals by a polymerized STEMPO (pendent) and by polymerization of dormant chains possessing vinyl end groups as macromonomers. Both of these reactions lead to branches linked by weak C-ON bonds.

The formation of a branched structure was proved by viscosity data in Table 1 obtained by GPC measurement equipped with a viscosity detector. The calculated Mark-Houwink values for entries 2 and 3 are 0.60 and

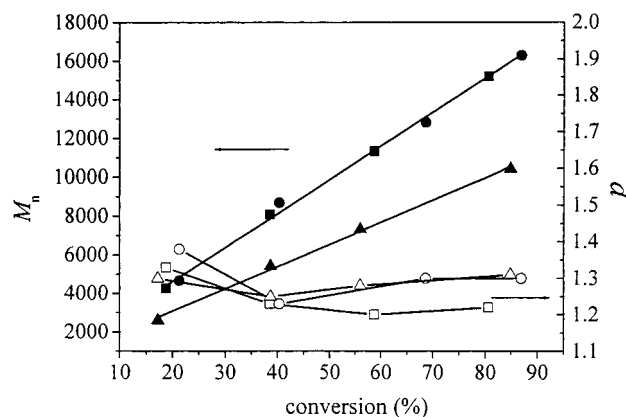


Figure 2. Dependence of molecular weight, M_n (filled scatterers), and polydispersity index, d (open scatterers), on monomer conversion in styrene radical polymerizations in the presence of 4-hydroxy-TEMPO (■ and □, monomer/nitroxide = 300/1) or STEMPO (samples after cleavage) with the feeds of monomer/STEMPO = 300/1 (● and ○) and 200/1 (▲ and △). The reaction conditions are the same as in Figure 1.

0.59, well below 0.74 for the reference system (entry 1), a typical value for linear polymer in good solvent. The second method to demonstrate the branched structure is the cleavage of the product into linear chains by reducing agents such as phenylhydrazine as shown in Scheme 1 in which the thermally produced nitroxyl and a carbon-centered radicals are permanently terminated.^{20,21}

In all cases, the cleavage was completed within 1 h in chlorobenzene, as indicated by narrow GPC traces (dashed lines in Figure 1) and the fall of M_n to steady values. The peaks of the cleaved products correspond to the component with the longest retention time of the sample before cleavage (Figure 1). In addition, the branched fraction increases steadily with monomer conversion (solid lines in Figure 1) and is dominant in the final product.

Figure 2 shows that the M_n of the primary chains increases linearly with monomer conversion. The results of STEMPO- and 4-hydroxy-TEMPO-mediated systems agree well for systems with constant feed ratio, i.e., monomer/nitroxide = 300/1. The polydispersity index, d , is well below 1.5, the lowest value of conventional radical polymerizations. Furthermore, the molecular weight of the cleaved product depends on the feed concentration of nitroxyl radicals. A feed ratio of monomer to STEMPO of 300/1 produces a higher M_n of

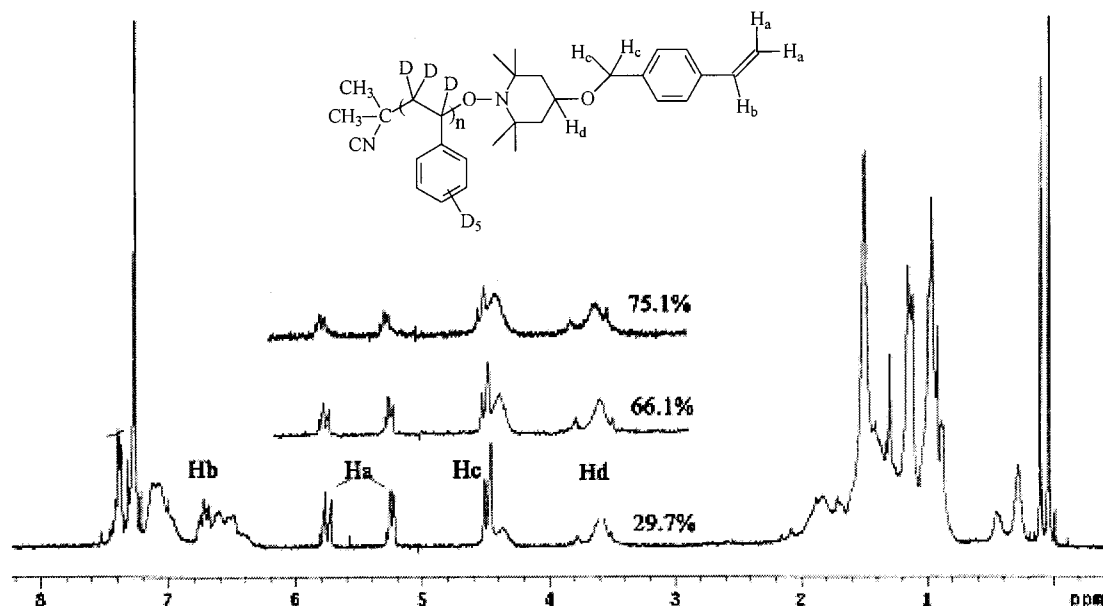


Figure 3. ^1H NMR spectra of the products of styrene- d_8 polymerization in the presence of STEMPO at different monomer conversions as indicated in the figure. The ratio of monomer to STEMPO = 300/1.

primary chains than a ratio of 200/1. This is because the number of nitroxyl radicals determines the number of living chains.²²

Copolymerization of the vinyl groups in STEMPO and in styrene was investigated by ^1H NMR. Deuterated styrene (styrene- d_8) was polymerized in the presence of STEMPO under the same condition of undeuterated monomer. The conversion was determined by monitoring the intensity of vinyl protons of STEMPO. However, residual hydrogen in the deuterated monomer would interfere with integration of the NMR spectra if the samples were taken directly from the reaction mixture. Therefore, the samples were purified by three cycles of dissolving in THF and precipitating in methanol to remove unreacted monomer. The loss of STEMPO was negligible since the concentration of uncoupled STEMPO molecules was very low. In Figure 3, the signals at $\delta = 5.2$ and 5.7 ppm are assigned to the two vinyl hydrogens (H_a). That around 4.4 ppm is assigned to the methylene hydrogens (H_c) between phenyl ring and oxygen in STEMPO. The conversion of the double bond in STEMPO is given by

$$C_{\text{STEMPO}} = (A_{\text{Hc}} - 2A_{\text{Ha}})/A_{\text{Hc}}$$

in which A is the area under the denoted signal.

There are some uncertainties about the signals at 5.0 – 6.0 ppm. The methine proton(s) adjacent to $-\text{ON}$ at the end of the dormant chains are also located at around 5.1 ppm. Furthermore, the dormant chains can decompose to "dead" polymers with ω -vinyl groups whose chemical environment is quite similar to that of the vinyl group of STEMPO. However, the possibility that the atom(s) on these groups are hydrogen is very low. Therefore, we ruled out interference by these hydrogens.

Figure 3 shows that the relative intensity of H_a with respect to H_c decreases as the polymerization proceeds. The plot of C_{STEMPO} against monomer conversion in Figure 4 is approximately linear, indicating that the vinyl group in STEMPO polymerizes at a constant rate with monomer conversion. Since almost all living chains have been formed at the beginning of the polymeriza-

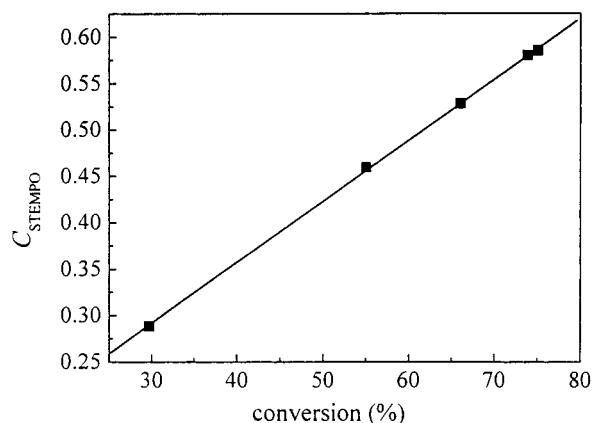
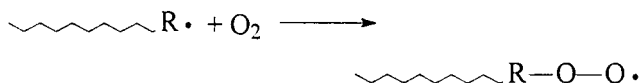


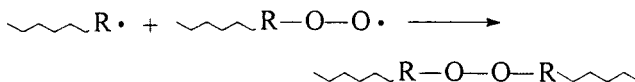
Figure 4. Plot of conversion of vinyl group in STEMPO, C_{STEMPO} , against monomer conversion in STEMPO-mediated styrene- d_8 polymerization.

tion, and these living chains grow simultaneously with monomer conversion, we deduce that the branch points are randomly distributed along the primary chain.

ESR Measurement. The branched polystyrene containing C–ON bonds at its branch points can undergo thermally reversible homolysis/recombination. Under atmospheric conditions, the initially released carbon-centered radical by homolysis of alkoxyamine can be readily trapped by molecular oxygen solvated in toluene,²³



The resulting oxygen-centered radical will not combine with the nitroxyl stable radical, but with another carbon-centered radical,²³



Therefore, according to Bon et al.,²³ the concentration

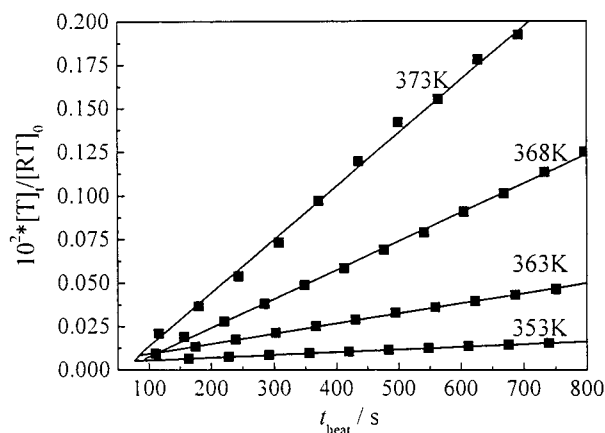


Figure 5. Dependence of dissociated fraction of polymeric alkoxyamine on heating time, t_{heat} , at different temperatures as measured by ESR. The sample is the linear product of entry 1 in Table 1 at 81% conversion.

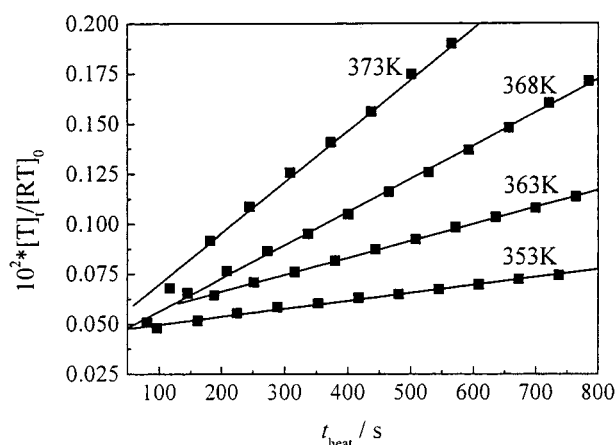


Figure 6. Dependence of dissociated fraction of alkoxyamine in branched polystyrene on heating time, t_{heat} , at different temperatures in ESR measurement. The sample is the product of entry 3 in Table 1 at 87% conversion.

of nitroxyl stable radical ($[T]$) measured by ESR is a pseudo-first-order function of heating time (t_{heat}) within the initial period of heating,

$$[T]/[RT]_0 = k_a t_{\text{heat}} + C$$

where $[RT]_0$ is the initial concentration of alkoxyamine. k_a is the rate constant of alkoxyamine homolysis, and C is an integration constant. In the case of branched polystyrene, $[T]$ and $[RT]$ do not stand for free molecules but for nitroxyl and alkoxyamine moieties, respectively, in macromolecules.

The cleavage of a linear polystyrene and its branched analogue at various temperatures in toluene was monitored by ESR. The results are plotted in Figures 5 and 6, respectively. The first-order kinetics within the initial 800 s is inconsistent with Bon's results²³ on small molecule and linear polymeric alkoxyamines. Figure 7 shows the Arrhenius plots determined by ESR, which have activation energies of 166 and 102 kJ/mol for the linear and branched products, respectively. The activation energy for the linear polystyrene is somewhat larger than that previously reported,^{23,24} possibly due to the larger M_n of the sample in this work. The E_a of the branched polystyrene is, however, quite low. This may be because the energy state of alkoxyamine in branched sample is higher due to conformational en-

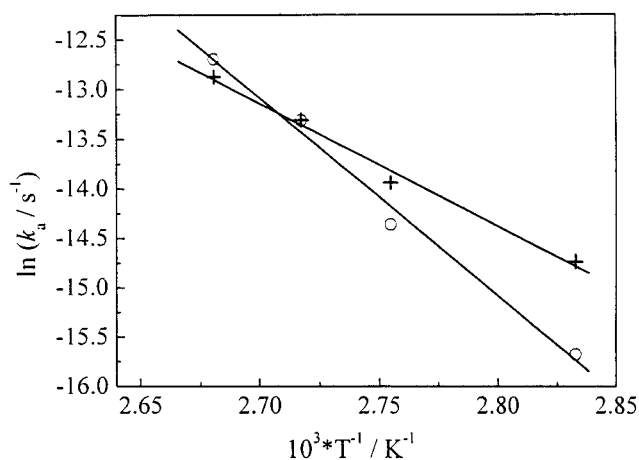


Figure 7. Arrhenius plots of the dissociation of alkoxyamine in linear (○) and branched (+) polystyrene.

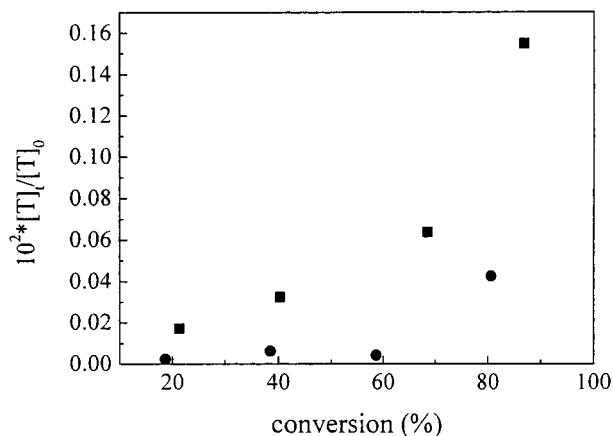


Figure 8. Dependence of uncoupled fraction of nitroxyl stable radical during styrene radical polymerization in the presence of STEMPO (■, entry 3 in Table 1) and 4-hydroxy-TEMPO (●, entry 1 in Table 1). ESR measurement was performed at room temperature.

tropic constraints. A supporting result by ESR is drawn in Figure 8. The concentration of the uncoupled species during the polymerization in the branched polystyrene is larger than that in the linear product of the reference system. Nevertheless, the percentage of uncoupled nitroxide is as low as 0.16% and therefore does not make remarkable change on the branched structure of the product.

Radical Polymerization Using Branched Polystyrene as a Macroinitiator. As demonstrated by ESR measurement, the branched polystyrene thermally cleaved into stable and carbon-centered radicals, with the latter capable of initiating further polymerization. Therefore, we used the branched polystyrene as a macroinitiator for the polymerization of 4-methoxystyrene in toluene without any classical radical initiator. When the mixture was heated at 120 °C, its viscosity increased with reaction time. The product was purified by three cycles of dissolving in THF and precipitating from methanol. Figure 9 shows the ¹H NMR spectrum of the product. The methoxy hydrogen is clearly shown at $\delta = 3.8$ ppm. The molecular weight of the branched polystyrene increased with conversion. These products were posttreated with phenylhydrazine at 120 °C, resulting in a lower molecular weight and narrower GPC peaks. Figure 10 plots the dependence of M_n and d of the cleaved product on monomer conversion. M_n

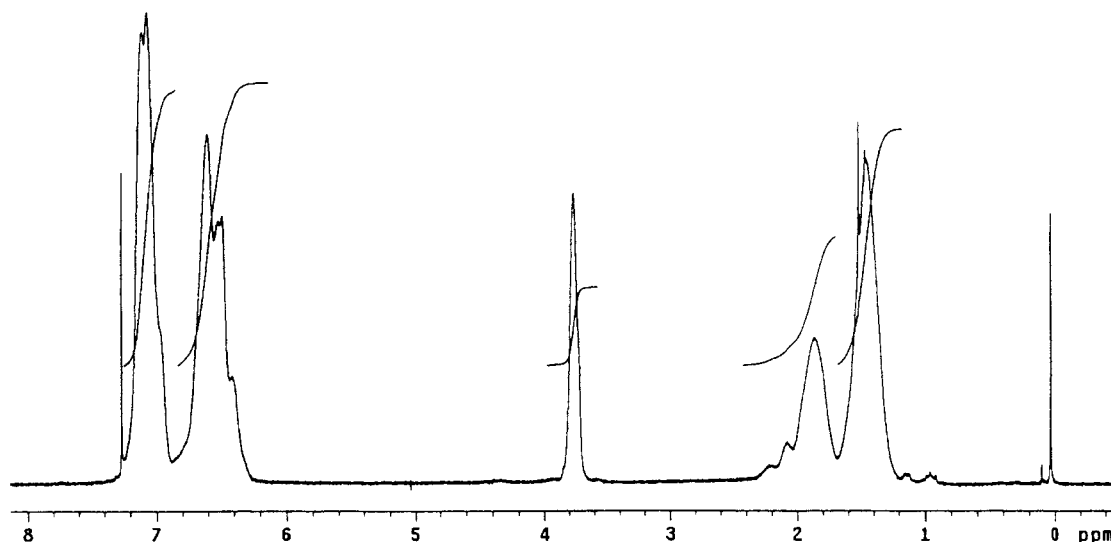


Figure 9. ^1H NMR spectrum of the product of 4-methoxystyrene polymerization initiated by the branched polystyrene macroinitiator.

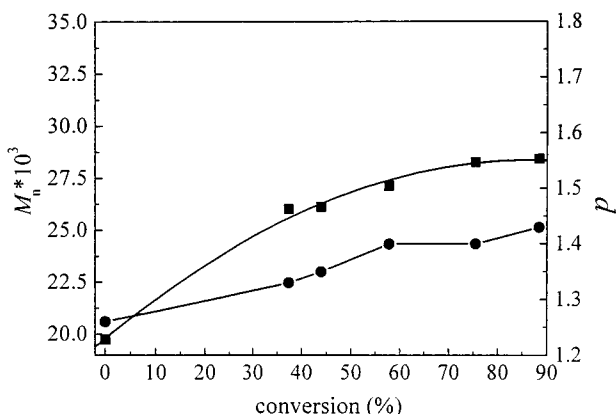


Figure 10. Dependence of the molecular weight of the block copolymers after cleavage, M_n (■), and the polydispersity index, d (●), with the conversion of 4-methoxystyrene.

seems to increase with monomer conversion in a decaying instead of a linear fashion. The reason for this is unclear at present. This and the increasing polydispersity (up to 1.4) indicate that control of the block copolymerization is less effective than the polymerization of the first block.

Concluding Remarks

The nitroxyl stable radical bearing a vinyl group acts as both a counter radical and a branching agent. Radical polymerization of styrene in the presence of STEMPO yields a "living" branched polystyrene in which the length of primary chains increases with monomer conversion and display narrow distribution. The branch points are randomly distributed along the primary chain.

The branch points of the branched polymers can undergo thermally reversible homolysis/recombination reactions. It can therefore be used as a branched macroinitiator to prepare copolymers with diblock branches. Further propagation takes place near the branching point. Therefore, the resulting block copolymer has the second block close to the branching point, the inner part of the whole structure. The poly(styrene-*b*-methoxystyrene) synthesized in this work is a precursor of branched poly(styrene-*b*-hydroxystyrene), an am-

phiphilic block copolymer with promising special properties which will be reported in a subsequent paper.

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