

Free-Radical Bulk Polymerization of Styrene with a New Trifunctional Cyclic Peroxide Initiator

Wei-Chen Sheng,¹ Jian-Yi Wu,² Guo-Rong Shan,¹ Zhi-Ming Huang,¹ Zhi-Xue Weng¹

¹Polymer Reaction Engineering Division, State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China

²Department of Chemical Engineering, College of Jiaxing, Jiaxing 314000, Zhejiang, China

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ABSTRACT: The bulk free-radical polymerization of styrene in the presence of a new cyclic trifunctional initiator, 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane, was studied. Full-conversion-range experiments were carried out to assess the effects of the temperature and initiator concentration on the polymerization kinetics, molecular weight, and polydispersity. Gel permeation chromatography was used to measure the molecular weight and the molecular weight distribution of polystyrene. When this multifunctional initiator was used for styrene polymerization at higher temperatures, it was possible to produce polymers with higher

molecular weights and narrower molecular weight polydispersity at a higher rate. This showed that the molecular weight and polydispersity were influenced by the initiator concentration and the polymerization temperature in an unusual manner. Moreover, polystyrene, obtained with trifunctional peroxide, had O—O bonds in the molecular chains and was investigated with differential scanning calorimetry and gel permeation chromatography. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1035–1042, 2004

Key words: initiators; radical polymerization; polystyrene

INTRODUCTION

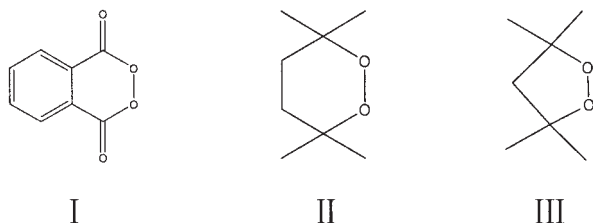
Styrene (STY) is a monomer that can be thermally polymerized. The thermal polymerization of STY leads to a certain rate/molecular weight relationship at a given temperature. Usually, the rate of polymerization can be increased by an increase in the temperature at the expense of the molecular weight of the polymer.¹ Over the years, improvements in reactor technology and heat removal have resulted in better rate performance for polymer production. Monofunctional initiators (azo compounds or peroxides) are widely used for polymerizations of different monomers as described, for instance, in Gao and Penlidis,^{2,3} Sanchez and Myers,^{4,5} or any industrial initiator catalogue.⁶ The bulk or less solvent free-radical polymerization of STY at higher temperatures with the aid of appropriate initiators is of significant industrial importance because they bring about increased polymerization rates and narrower polydispersity. Monofunctional organic peroxides offer limited improvement because the molecular weight is inversely proportional to the polymerization rate in ordinary free-radical polymerization with common initiators. Extensive research has been carried out^{7,8} for improving the

rate/molecular weight balance. Difunctional initiators and their advantages over monofunctional ones are also well documented in the literature, especially for polystyrene (PS) production, as discussed in Sanchez and Myers,^{4,5} Kamath,⁷ Kamath and Harpell,⁹ Kim and Choi,¹⁰ Choi et al.,¹¹ Villalobos et al.,^{12,13} Dhib et al.¹⁴ and Cavin et al.^{15,16} Studies involving difunctional perketals in ethylene polymerization¹⁷ have shown increased levels of high-molecular-weight components in the products. In rubber-modified PS, difunctional peroxides not only increase the weight-average molecular weight (M_w) but also broaden the molecular weight distribution.^{18,19} Mixtures of symmetrical difunctional initiators²⁰ and mixtures of difunctional and monofunctional initiators²¹ have been studied in the free-radical polymerization of STY. However, the addition of diperoxides as initiators is a new alternative for the production of high polymerization rates without the lowering of the molecular weight of the final products. The potential advantage of using these difunctional initiators is that high polymer molecular weights and high polymerization rates can be obtained simultaneously through the control of the radical concentrations through the sequential decomposition of the two labile groups of the initiator molecule through optimal reactor temperature programming.^{12,21–23}

The rate and molecular weight balance can be extended by the use of sequentially decomposing initiators. A peroxide unit is incorporated into the PS

Correspondence to: Z.-X. Weng (wengzx@cmsce.zju.edu.cn).

chain during the initial stage of polymerization, and this peroxide unit may reinitiate in the other direction to enhance the molecular weight at a later stage. However, very few multifunctional initiators are commercially available, and they are seldom found in the literature.^{24,25} The feature of multifunctional peroxides is perhaps related to productivity improvements and the ability to increase molecular weights at the same time in comparison with a lower functional initiator under similar conditions.



Cyclic peroxides are a class of peroxides producing diradicals theoretically. However, anomalous results have been reported for peroxides with formulas I–III, which cannot initiate the polymerization of STY after decomposition.²⁶ This article describes the kinetic behavior of the free-radical polymerization of STY with a novel type of trifunctional peroxide initiator under conditions similar to those of industrial processes. The effects of the reaction temperature and the concentration of different initiator mixtures on the polymerization rate and molecular weight were investigated to increase the monomer conversion and optimize new routes of polymer synthesis with a new class of cyclic peroxide initiators.

EXPERIMENTAL

Materials

Bulk polymerization experiments were carried out in Pyrex ampules with an inner diameter of 3 mm.²⁷ STY was purified by the standard method.²⁸ 3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TETMTPA) and di-*tert*-butyl peroxide (DTBP) were supplied by Akzo Nobel.

Thermal decomposition of TETMTPA

The kinetic data for the thermal decomposition reaction of the peroxide and its polymeric peroxide were measured in solvents by differential scanning calorimetry (DSC) with a peroxide concentration below 0.02 mol/L.²⁹ The data were analyzed with methods reported by Sheng.³⁰

Polymerization

An appropriate amount of the initiator was dissolved in STY with a cyclic initiator concentration of 0.0050–

0.0150 mol/L, and equal amounts of the resulting solution were placed in glass ampules. The cooled ampules were purged with nitrogen to remove oxygen and were sealed *in vacuo*. All the ampules were immersed in a temperature-regulated oil bath at the predetermined temperature to start the reaction. The conversion of the pure thermal polymerization of STY was measured under the same conditions for comparison. PS obtained with TETMTPA was dissolved in methyl methacrylate (MMA) to synthesize PS-*b*-poly(methyl methacrylate) (PMMA) with the aforementioned methods. Homopolymers of STY and MMA, produced as byproducts of the preparation of PS-*b*-PMMA, were purified by extraction with cyclohexane and acetonitrile.

After predetermined intervals, the samples were taken out and treated as follows.

Characterization

After the polymerization, the polymer samples were dissolved in tetrahydrofuran (THF) and precipitated by the addition of excess ethanol. This procedure was repeated several times to ensure the complete elimination of the unreacted monomer. The samples were dried *in vacuo*, and the monomer conversion was measured gravimetrically. The molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC, Waters Co., USA) with three Ultrastaygel columns from Waters (10^3 , 10^4 , and 10^5) with THF as a solvent at 25°C. These columns were calibrated with six narrow-polydispersity PS samples of known molecular weight. THF was pumped at a flow rate of 1.0 mL/min at 25°C. A PerkinElmer DSC-7 (Perkin Elmer Co., USA) differential scanning calorimeter was used to study the thermal decomposition of O—O bonds. The NMR spectra were recorded with an Advance DMX 500-MHz (Bruker Co., Germany) spectrometer with CDCl_3 as a solvent at 20°C.

Thermal decomposition of the polymers with O—O bonds

To verify the existence of the O—O bonds in the polymers initiated by TETMTPA, we thermally decomposed the polymers at a scanning rate of 10°C/min by DSC.

To determine the location of the O—O bonds in the polymers polymerized with TETMTPA, we thermally decomposed the polymers at 180°C for 0.5 h, which is much higher than the 0.1-h half-life temperature of the initiator and lower than the decomposition temperature of PS; the molecular weights of the decomposed polymer segments were determined with GPC.

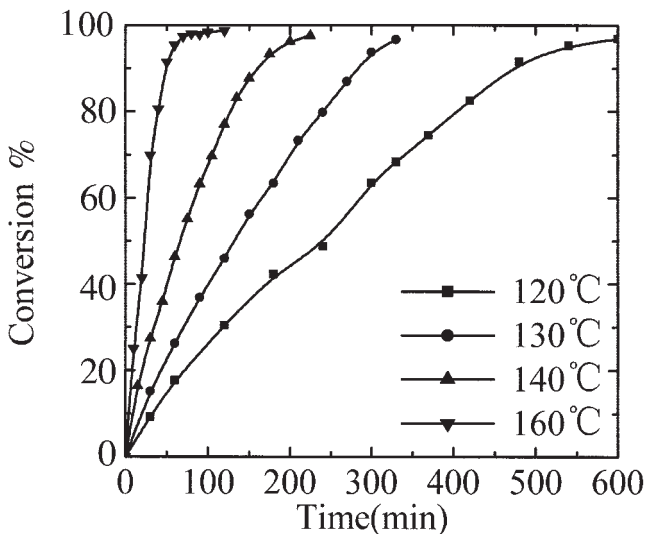


Figure 1 Effect of the temperature on conversion–time plots of STY polymerization at an initial initiator concentration of 0.0050 mol/L.

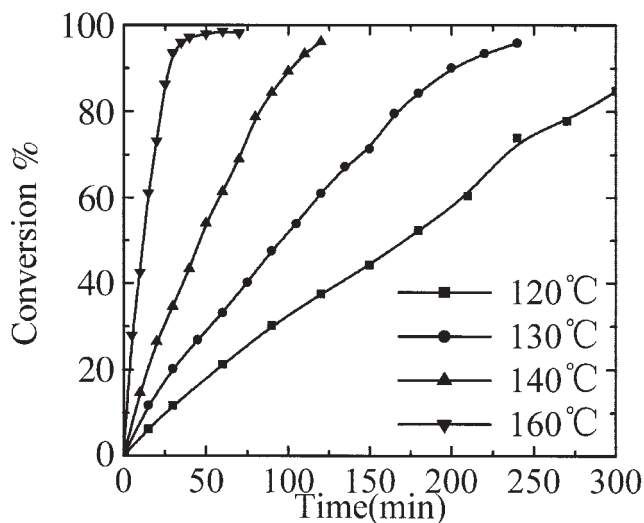


Figure 2 Effect of the temperature on conversion–time plots of STY polymerization at an initial initiator concentration of 0.0150 mol/L.

RESULTS AND DISCUSSION

Thermal decomposition of cyclic peroxide

The kinetics of the thermal decomposition reaction were measured in monochlorobenzene at different heating rates. The behavior obeyed first-order kinetic law in all cases. The effect of the scanning rate on the rate constant was also studied, and the linearity of each equation showed that the activation parameters and frequency index were not affected by the scanning rate over a wide range. The decomposition rate constant (k_d) and half-lifetime in monochlorobenzene for peroxide were calculated with an Arrhenius equation: $k_d = 1.02 \times 10^{15} \exp(-150230/RT)$, where R is the universal constant, J/mol · K; and T is the temperature, K.

Effect of the temperature on the polymerization of STY in the presence of cyclic peroxide

Figures 1 and 2 present the effect of the temperature on the monomer conversion for TETMTPA concentrations of 0.0050 and 0.0150 mol/L, respectively. The slopes of the conversion–time plots at low conversions can be used to compare their relative rates. The polymerization rate increased more quickly for every 10°C increase in temperature because of the Arrhenius dependence of the rate on the temperature. Interestingly, the final conversions of these curves all approached 100%, but the higher the polymerization temperature was, the closer the final conversion was to 100%.

Figures 3 and 4 show the trends of M_w of PS prepared at different temperatures with initiator concentrations of 0.0050 and 0.0150 mol/L, respectively. For both initiator concentrations, the observed M_w values were lower for

reactions at higher reaction temperatures, as expected. The molecular weight increased slightly with the conversion increasing at higher temperatures. In the entire conversion range, the molecular weight gradually increased because the active species decreased, the system viscosity increased, termination reactions involving polymeric radicals became diffusion-controlled, and the termination rate constant decreased considerably with an increase in the monomer conversion.^{23,31,32} However, there was a small decrease in the molecular weight as the reaction reached its limiting conversion level at higher

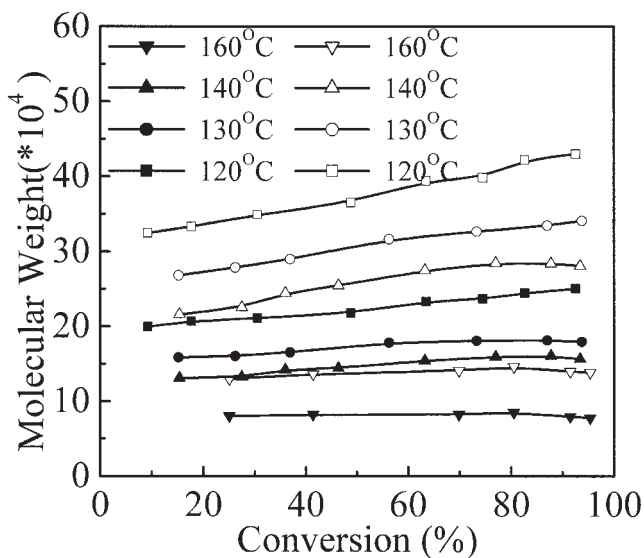


Figure 3 Effect of the temperature on the molecular weight/conversion plots of PS at an initial initiator concentration of 0.0050 mol/L. The solid symbols represent M_n , and the open symbols represent M_w .

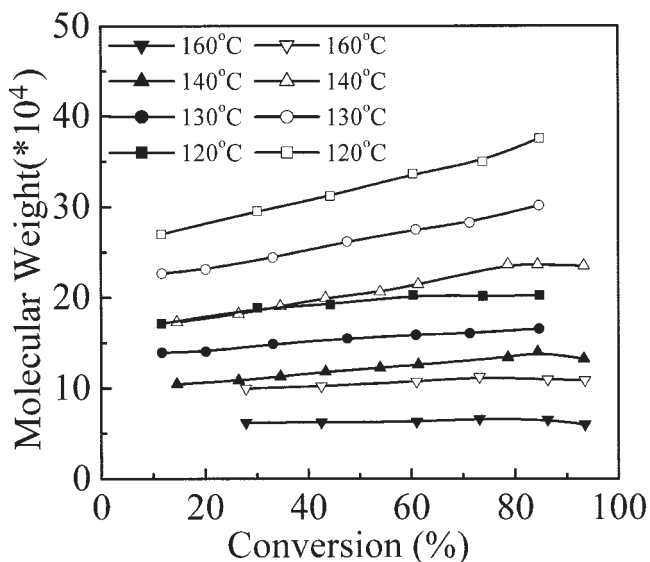


Figure 4 Effect of the temperature on the molecular weight/conversion plots of PS at an initial initiator concentration of 0.0150 mol/L. The solid symbols represent M_n , and the open symbols represent M_w .

reaction temperatures. These results are not clearly understood yet. The polydispersity appeared to be affected by the temperature too. With the temperature increasing, the polydispersity index at the same conversion increased first and then decreased. Figures 5 and 6 present this effect for polymerization at 0.0050 and 0.0150 mol/L, respectively. This observation was different from that of Villalobos et al.¹² and Choi et al.¹¹ They found that polydispersity decreased monotonously with the temperature increasing for difunctional initiators and that an

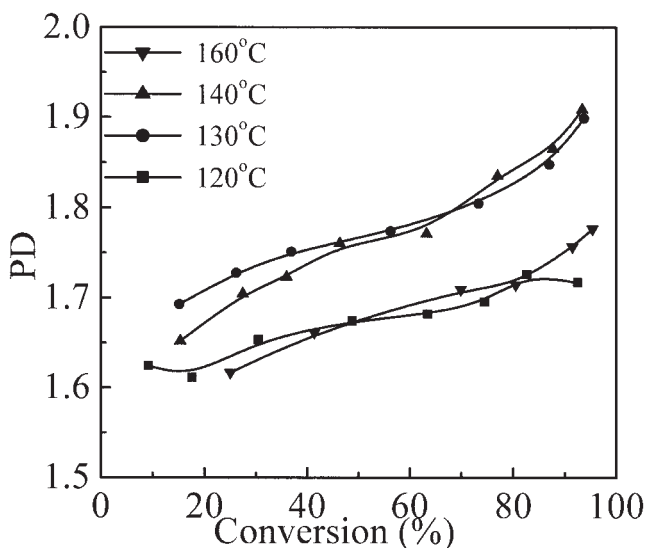


Figure 5 Effect of the temperature on the polydispersity-conversion plots of PS at an initial initiator concentration of 0.0050 mol/L.

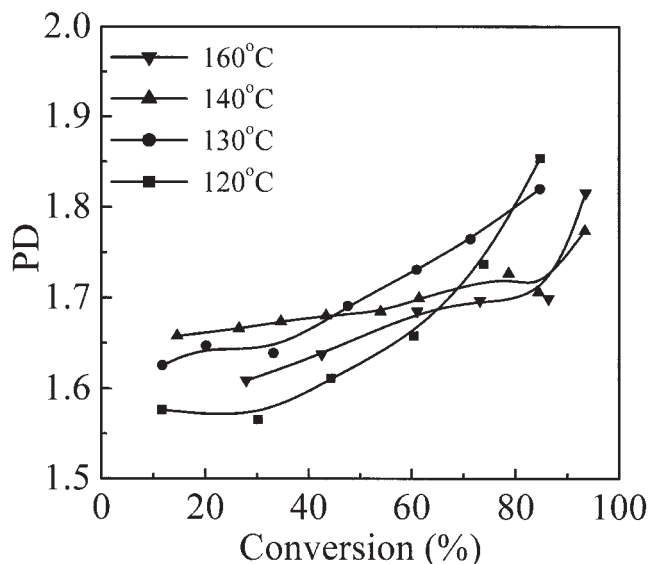


Figure 6 Effect of the temperature on the polydispersity-conversion plots of PS at an initial initiator concentration of 0.0150 mol/L.

increase in the polymerization rate caused by an increase in the temperature or an increase in the initiator concentration caused a decrease in the polydispersity. The reason is that the difunctional initiators produced two monoradicals, causing lower molecular weights, whereas the diradical led to higher molecular weights. In this study, TETMTPA decomposed to generate diradicals, whereas thermal initiation produced monoradicals. The phenomenon of the polydispersity index first increasing and then decreasing with the temperature increasing was rooted in the increase in the proportion of thermal initiation. When thermal initiation was dominant, the polydispersity index decreased.

Effect of the TETMTPA concentration on the polymerization of STY

Figure 7 shows monomer conversion/time plots at different TETMTPA concentrations at 140°C. The polymerization rate increased with the initiator concentration. However, the exponential of the initiator concentration affecting its rate was slightly less than 0.5 because of accompanying thermal initiation. The molecular weight decreased and polydispersity also decreased a little at higher initiator concentrations. Also, the molecular weight decreased somewhat at the end of polymerization. The effects of the initiator concentration on the molecular weight and polydispersity index are shown in Figures 8 and 9, respectively. The effects of thermal initiation are also shown in Figures 7–9. Figure 9 shows that the polydispersity rarely changed with the conversion for thermal initiation; this was similar to the findings of Arai et al.³³ Interestingly, the higher the TETMTPA concentration was, the narrower the molecular

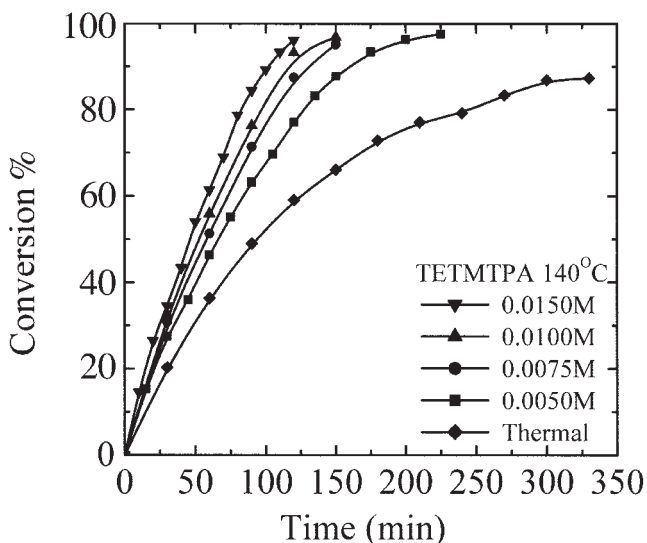


Figure 7 Effect of the initiator concentration on the conversion-time plots of STY polymerization at 140°C.

weight polydispersity was. This is unique for the cyclic trifunctional peroxide TETMTPA because more diradicals generate in higher concentrations to cause propagation from two directions, which leads to higher molecular weights and narrower polydispersities for the same effect of thermal initiation.

Comparison of STY polymerizations initiated with TETMTPA and thermally

Figures 10 and 11 show M_w -conversion (or rate) plots for comparisons of thermal and TETMTPA initiations.

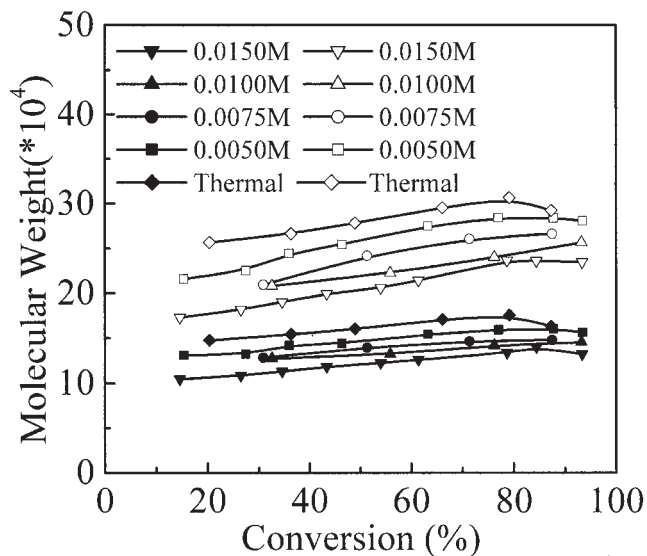


Figure 8 Effect of the initiator concentration on the molecular weight/conversion plots of PS at 140°C. The solid symbols represent M_n and the open symbols represent M_w .

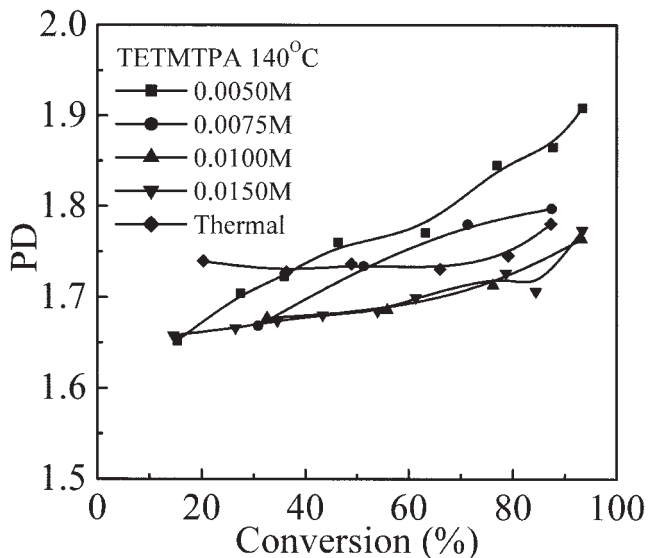


Figure 9 Effect of the initiator concentration on the polydispersity-conversion plots of PS at 140°C.

There were obvious M_w -rate advantages for polymerizations initiated with TETMTPA in comparison with those initiated thermally.

Synthesis of polymers with TETMTPA

The decomposition of TETMTPA and the synthesis of PS are shown in Scheme 1. There are two possible routes for the polymerization initiated with TETMTPA: the sequential decomposition of three peroxide groups step by step (A, B, and C) and the simultaneous decomposition of three peroxide groups at the

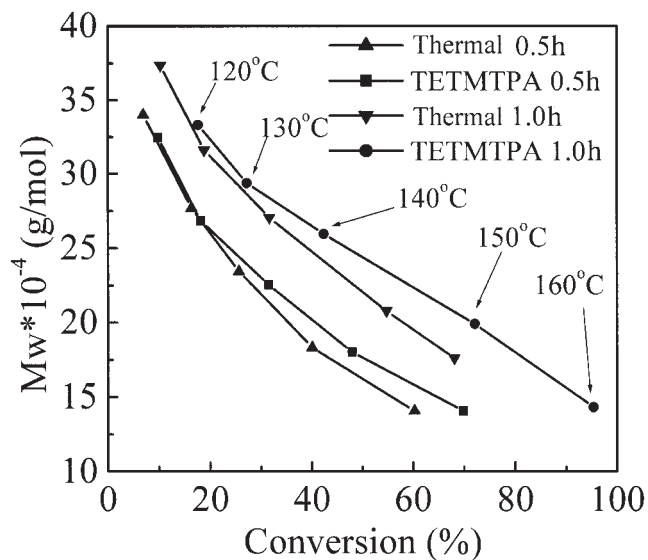


Figure 10 Comparison of M_w -conversion plots for PS initiated thermally and by TETMTPA at different temperatures and at an initial initiator concentration of 0.0050 mol/L.

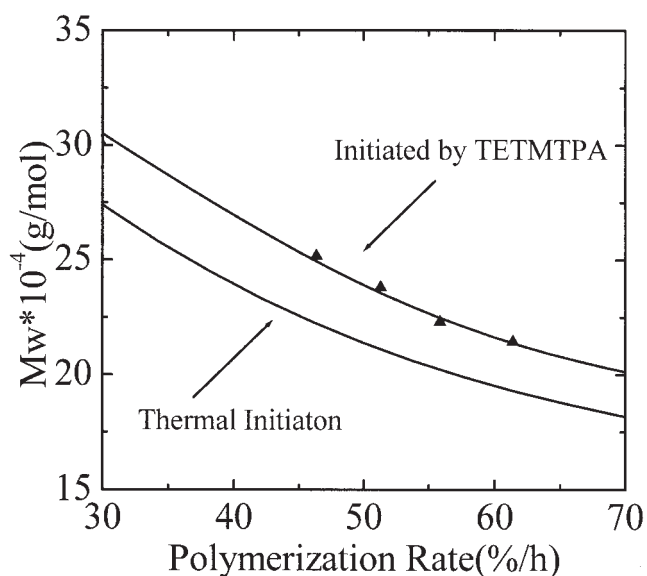


Figure 11 Comparison of M_w -rate plots for PS initiated thermally and by TETMTPA at 140°C at initiator concentrations of 0.0050, 0.0075, 0.0010, and 0.0150 mol/L.

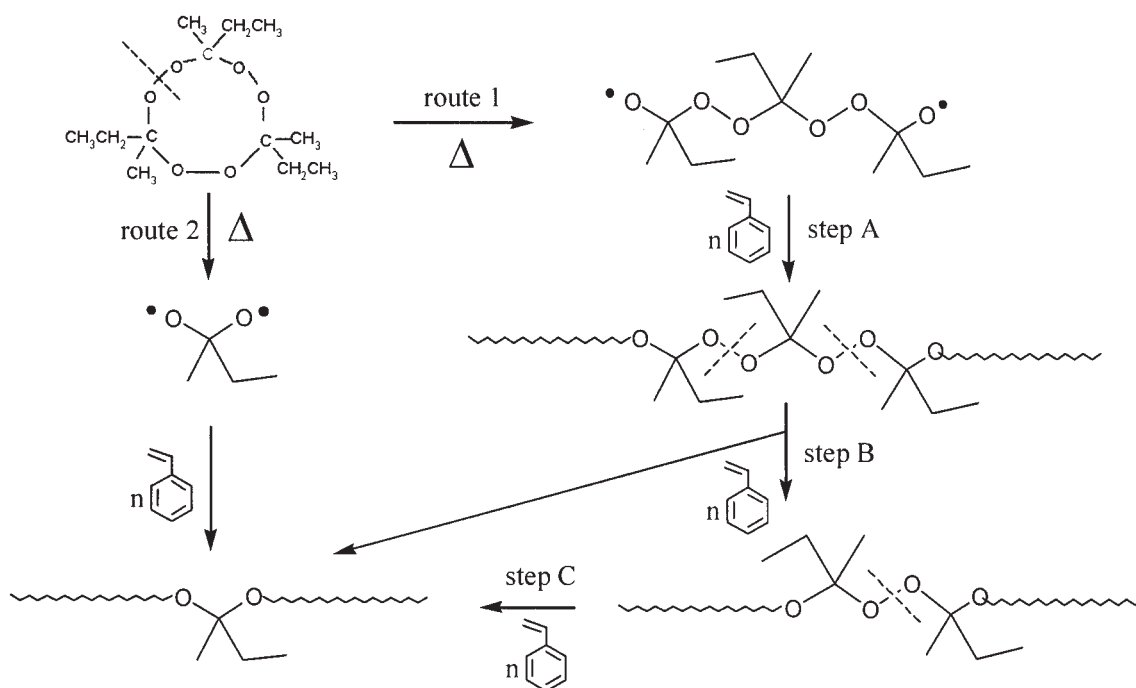
same time. On the basis of the k_d value for the TETMTPA employed in this study and the propagation rate constant, the decomposition of O—O bonds in the radical chain can be negligible during the propagation of radical chains. This means that only when the radical chains with uncomposed O—O bonds are terminated do the O—O bonds in the chains decompose. Therefore, route 2 seldom arises. First, the O—O

bonds in TETMTPA decompose and initiate the polymerization as shown in step A. After termination, the second O—O bond in the polymer chains decomposes again and reinitiates the polymerization of STY as step B and then as step C. Therefore, polymers with O—O bonds can be formed during the polymerization process.

Thermal decomposition of polymers with O—O bonds

Several studies were carried out to demonstrate that the gradual decomposition of TETMTPA and increase in M_w arose from undecomposed peroxides in the polymer chain. The formation of polymers with O—O bonds in steps A and B was verified by differential thermal analysis. The DSC traces are shown in Figure 12. PS initiated by TETMTPA produced an exothermic peak around 210°C, the same as that of pure peroxide, and no such peak was found for PS polymerized by thermal initiation and by a conventional organic peroxide. This meant that some O—O bonds remained in PS chains polymerized with TETMTPA and decomposed again to give the DSC exotherm. This firmly validated the sequential decomposition route of TETMTPA.

In the polymerization with unsymmetrical difunctional initiators, two different slopes were observed at low and intermediate conversions, which were due to the different thermal stabilities of the two peroxide groups.^{12,34–36} However, this behavior was not ob-



Scheme 1 Polymerization of STY with TETMTPA.

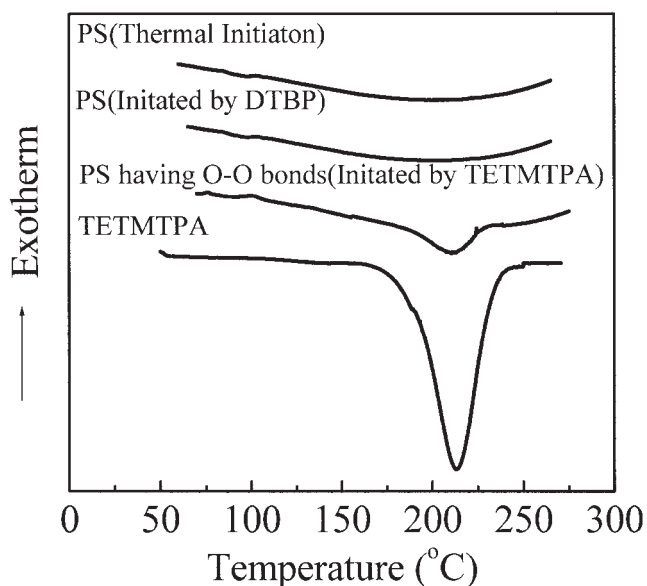


Figure 12 DSC curves of TETMTPA and PS initiated in different ways.

served for the trifunctional cyclic initiators used in this study, and this indicated that there was no substantial difference in the reactivity of the two or three peroxide groups contained by initiator molecules under isothermal conditions. The second feature was that there was only one exothermic peak when peroxide was heated from 40 to 280°C with DSC. This showed that the three O—O bonds in TETMTPA and the O—O bonds in the polymers had the same activity.

All these results corroborated the fact that TETMTPA decomposed and initiated polymerization via route 1 presented in Scheme 1.

On the other hand, for better insight into the position of the peroxy segments in the backbone of polymers polymerized with TETMTPA, the polystyrene peroxide (PSP) active polymers obtained at 100°C and at the TETMTPA concentration of 0.3M were decomposed at 130°C for 20 h in chlorobenzene to thermally destroy the O—O bonds in the polymer chains, and the molecular weights of the polymers, before and after thermal destruction, are listed in Table I. It was postulated that all the O—O bonds ruptured, and so on average the percentage of polymer chains with

O—O bonds in all the polymer chains could be expressed as follows: $R = [(m/M) - (m/M_0)] / (m/M_0) = M_0/M - 1$, where m is the mass of the polymers, M_0 is the molecular weight of the polymers before heating, and M is the molecular weight after heating.

The tabulated data show that the molecular weight of the polymers after thermal destruction was some lower than before. This can be explained as follows: some O—O bonds in the former polymer chains decomposed and led to the formation of two or three chains from an original chain. This also means that O—O bonds in the polymers initiated with TETMTPA were located in the middle of the polymer chains. Otherwise, a significant reduction in the molecular weight would not have been observed. Because the O—O bonds in PSP had the same decomposition activity as those in TETMTPA, they also decomposed during the polymerization, and so there were fewer than two O—O bonds in each polymer chain. This can be explained by the decrease in R during the polymerization process. Therefore, the molecular weight after thermal destruction was larger than a third of that before thermal destruction. From the low-conversion data, we find that the molecular weight was halved if R was 100%; this means that every polymer chain had one O—O bond on the average.

Moreover, when the same PS was heated in the presence of another monomer, it acted as a macroinitiator, conducting the formation of a block copolymer.

Characterization of PS-*b*-PMMA

The $^1\text{H-NMR}$ spectrum of the resulting system showed the characteristics signals of PS [1.43 (—CH₂—), 1.84 (>CH—), 6.4–6.8 (o-protons), and 6.9–7.2 ppm (p- and m-protons)] and PMMA [0.8–1.1 (—CH₃), 1.89 (—CH₂—), and 3.65 ppm (—OCH₃)], thereby confirming the formation of PS-*b*-PMMA.

CONCLUSIONS

This is the first detailed report of STY bulk polymerization by a new cyclic trifunctional peroxide initiator (TETMTPA). Full-conversion polymerizations were carried out over a range of temperatures and initiator concentrations. The performance of TETMTPA was

TABLE I
Molecular Weight and its Distribution Before and After the Thermal Treatment of PS Initiated by TETMTPA

No.	Conversion (%)	Before			After			R (%)
		M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	
1	8.76	54,878	98,094	1.79	27,692	53,381	1.93	98.17
2	19.8	57,629	104,105	1.81	29,898	58,534	1.96	92.75
3	29.3	59,892	108,919	1.82	36,067	71,611	1.99	69.21
4	48.8	63,431	113,409	1.79	45,915	91,325	1.99	29.51

also evaluated with respect to the conversion, molecular weight, dispersion, and polymer structural characteristics. The polymerization of STY with TETMTPA obeyed expected polymerization trends with respect to the effects of the temperature and initiator concentration. The experimental data revealed that TETMTPA presented typical multifunctional initiator behavior and could be used to produce PS with higher molecular weights and narrower molecular weight polydispersity at a higher reaction rate.

Finally, polymer samples produced with TETMTPA had an exothermic peak with DSC, whereas polymers with a monofunctional initiator and thermal initiation had no such peak. The molecular weight of the polymers before heating was somewhat higher than that after heating. This provided evidence of the existence of a few O—O bonds in the polymer chains. The content of O—O in the polymer chains decreased with conversion.

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