Controlled Radical Polymerization of Styrene in the Presence of a Polymerizable Nitroxide Compound

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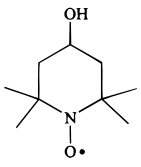
ABSTRACT: Styrene is polymerized in the presence of 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxy. The polymerization rate is higher than that using 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy as counterradical. However, the molecular weight does not increase linearly with monomer conversion and the ultimate polydispersity is rather high. After posttreating with ascorbic acid, the molecular weight decreases and a narrow polydispersity is obtained. A branched or hyperbranched structure was thus suggested.

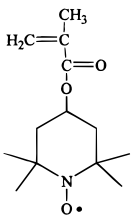
Introduction

In recent years, living free radical polymerizations mediated by a stable free radical such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) have attracted much attention[1−5] because they produce polymers with narrow molecular weight distributions[2,6−8] and well-defined structures[9−15] using mild reaction conditions. Several groups[6,7,16−22] accounted for controlled molecular weight and architecture by an equilibrium between propagating and dormant chains. The low concentration of propagating radicals suppresses the probability of irreversible biradical termination. However, a very low concentration of propagating radicals also decreases the polymerization rate, especially when stable radicals accumulate after part of the propagating radicals irreversibly terminate.[22,23]

Generally, two methods have been used to enhance the rate of living free radical polymerization. First, camphorsulfonic acid,[24,25] 2-fluoro-1-methylpyridinium *p*-toluenesulfonate,[23,26] dicumyl peroxide,[27] and *tert*-butyl hydroperoxide[28] can be added to consume excess TEMPO. Alternatively, a more sterically hindered stable radical, such as di-*tert*-butyl nitroxide,[29−32] attains a higher polymerization rate because it reversibly couples at a slower rate with propagating radicals. This paper investigates the radical polymerization of styrene mediated by 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxy (MTEMPO), which may act as both a stable



HTEMPO



MTEMPO

radical and monomer. Thus, the concentration of low molecular weight MTEMPO should be decreased as the reaction proceeds. The polymeric nitroxyl radical should be more sterically hindered and should have a low diffusibility and therefore be less efficient at trapping propagating chain radicals.

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Experimental Section

Materials and Instrumentation. Styrene was freshly distilled before use. Benzoyl peroxide (BPO) was recrystallized from chloroform/methanol. MTEMPO was prepared using a method described previously.[33] HTEMPO was received from BASF and recrystallized from cyclohexane before use.

Gel permeation chromatography (GPC) was performed on a Waters instrument equipped with three Waters Styragel columns (pore size: 10^2, 10^3, and 10^4 Å) in series, using THF as eluent at 1 mL/min at 35 °C and polystyrene as the standard.

Polymerizations. A solution of styrene (41.6 g, 0.4 mol), benzyol peroxide (0.290 g, 1.2 mmol), and MTEMPO (0.288 g, 1.2 mmol) was heated at 120 °C under nitrogen atmosphere. An aliquot of about 0.5 mL of the mixture was extracted at a predetermined time and dried in a vacuum at 50 °C. The weight loss gave the monomer content at the time when the sample was taken.

For comparison, parallel polymerizations were also carried out using double the amount of MTEMPO (0.576 g, 2.4 mmol) and using HTEMPO (0.206 g, 1.2 mmol).

Results and Discussion

Kinetics. To determine the utility of MTEMPO, styrene was also polymerized in the presence of HTEMPO for comparison (curve 2 in Figure 1). The polymerization rate of the system using MTEMPO (curve 1) is faster than that using an equimolar amount of HTEMPO, which demonstrates that MTEMPO is less efficient at trapping propagating radicals. For a system using double the amount of MTEMPO (curve 3), although the polymerization rate is lower at the early stage, the monomer conversion catches up to that of curve 2 at 22 h or so. This again supports the point that some of the MTEMPO has polymerized and that the polymeric nitroxide is less efficient at trapping propagating radicals.

Molecular Weight and Distribution. The molecular weight increases linearly with monomer conversion in a living polymerization, since the concentration of propagating chains is constant. Curves 2 and 3 in Figure 2 are linear. For 0.0261 M MTEMPO mediated polymerization, however, the molecular weight growth "accelerates" at high conversion (Figure 2, curve 1). The molecular weight using 0.0261 M MTEMPO is thus much higher, about 3-fold of that using equimolar HTEMPO, at the end of the polymerization. As shown by the GPC traces in Figure 3, the product has a multimodal distribution and the polydispersity index is high. The abnormally high molecular weight and polydispersity can be explained by a branching reaction

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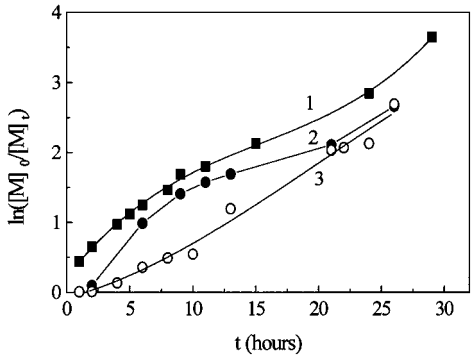


Figure 1. Kinetics of controlled radical bulk polymerization of styrene in the presence of (■) 0.0261 M and (○) 0.0522 M MTEMPO and (●) 0.0261 M HTEMPO. The amount of BPO is 0.0261 M.

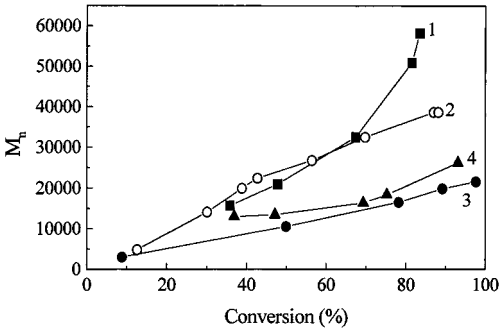


Figure 2. Growth of molecular weights with monomer conversion in controlled radical bulk polymerization of styrene in the presence of (■) 0.0261 M and (○) 0.0522 M MTEMPO and (●) 0.0261 M HTEMPO. After posttreatment with ascorbic acid, the points on curve 4 (▲) resulted from corresponding points on curve 1.

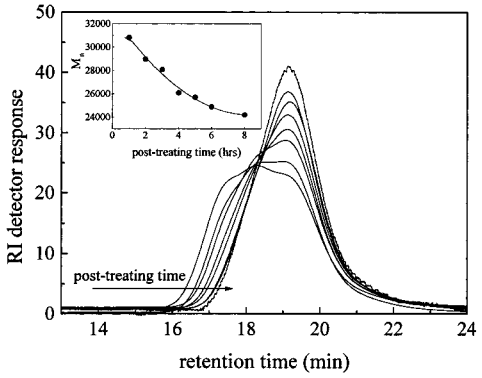
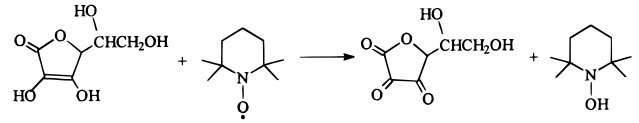


Figure 3. GPC traces of the final product of curve 1 in Figure 1 at different posttreating time with ascorbic acid. The inset shows the change in calculated molecular weight.

between a propagating chain radical and a chain-bonded nitroxide (Scheme 1, reaction 6). Branching can also occur by unsaturated ends of dormant chains to propagating radicals as in polymerization of a macromonomer (Scheme 1, reaction 4).

The hypothesis of branching reactions is correlated by a decrease in molecular weight and polydispersity after the product was heated with ascorbic acid at 120 °C in chlorobenzene. Ascorbic acid reacts readily with nitroxyl radicals:[34]



Scheme 1

initiator homolysis:

(1) $I \rightarrow 2R_0^{\bullet}$

chain propagation:

(2) $\sim R_j^{\bullet} + M \longrightarrow \sim R_{j+1}^{\bullet}$

(3) $\sim R_j^{\bullet} + M\text{-}T \longrightarrow \sim R_j M^{\bullet} \xrightarrow{+nM} \sim R_{j+n+1}^{\bullet}$

(4) $\sim R_i^{\bullet} + \sim R_j\,T\text{-}M \longrightarrow \sim R_i M^{\bullet} \xrightarrow{+nM} \sim R_{i+n+1}^{\bullet}$

reversible trapping of chain radical by stable radical:

(5) $\sim R_j^{\bullet} + M\text{-}T \rightleftharpoons \sim R_j T\text{-}M$

(6) $\sim + \sim R_i^{\bullet} \rightleftharpoons$

irreversible termination to form dead chains:

(7) $\sim R_i^{\bullet} + \sim R_j^{\bullet} \longrightarrow \sim P_{i+j}$ or $\sim P_i + \sim P_j$

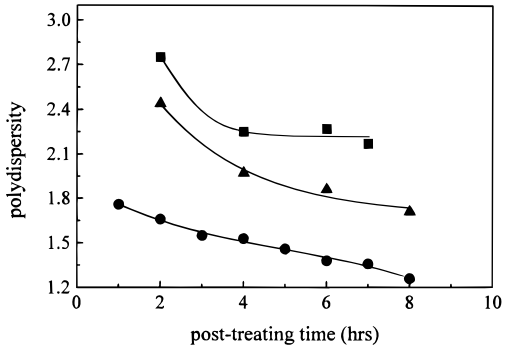


Figure 4. Decrease in polydispersity with posttreating time for three samples taken from the polymerization of curve 1 in Figure 1, at the conversions of 36.9% (■), 75.2% (▲), and 93.1%-(●).

Whenever a labile NO−C linkage in the product undergoes homolytical fission, the released stable radicals are most likely reduced by ascorbic acid present in the reaction medium. The branched structure should eventually be degraded to linear chains. In Figure 3, as the posttreating time increased, the high molecular weight component of the multiheaded curve before treatment was reduced and finally disappeared to give a unimodal curve. Correspondingly, the molecular weight decreased monotonically with posttreating time (Figure 3, inset). The peak position of the final unimodal is identical to the lower molecular weight component of the initial product. This indicates that the polymerization product is a mixture of branched and linear polymers.

After treatment with ascorbic acid, the molecular weight of the product increases almost linearly with monomer conversion (curve 4 in Figure 2). The polydispersity index decreases with conversion (Figure 5), similar to HTEMPO-mediated living free radical polymerization of styrene. The final polydispersity of 1.2 demonstrates that the polymerization of styrene is controlled in the presence of MTEMPO.

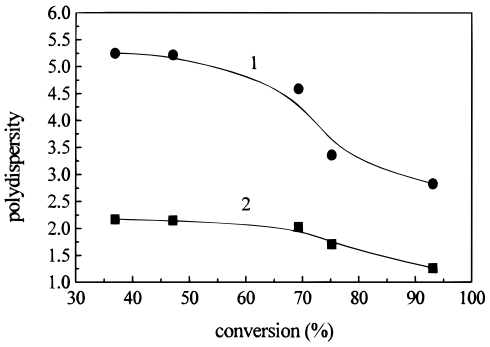
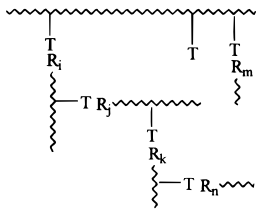


Figure 5. Plot of the polydispersity vs monomer conversion for system of curve 1 in Figure 1 before(●) and after (■) posttreatment with ascorbic acid for 8 h.

Brief Discussion of the Reaction Mechanism and the Product Structure. The GPC results indicate that MTEMPO acts as both monomer and stable radical. The polymeric nitroxyl radical can still trap the propagating radical, although it may be less efficient than free MTEMPO. Scheme 1 outlines our mechanism for the MTEMPO-mediated styrene polymerization:

In Scheme 1, I is the radical initiator, R_j represents chain radical with length *j*, M is the monomer, M−T is MTEMPO with M being the methacrylate moiety, and T is the nitroxide moiety. Reactions 4 and 6 result in branched molecules. Additional side chains may be attached to these side chains. Hence, the product may have a branched or hyperbranched structure as follows:



This structure is similar to the hyperbranched structures reported previously by living free radical polymerization.[35−37] However, in our product a labile NO−C bond links every graft point. This linkage may also undergo reversible association/dissociation at higher temperature as a dormant chain does in the polymerization.

Conclusion

The rate of nitroxide-mediated radical polymerization of styrene was enhanced by using a polymerizable counterradical, MTEMPO. After the product was posttreated with ascorbic acid, the molecular weight increased linearly and the polydispersity decreased with monomer conversion, indicating that the polymerization was controlled. We accounted for the results of molecular weight and distribution by a reversibly branched or hyperbranched structure.

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