

NITROXIDE MEDIATED FREE RADICAL POLYMERIZATION PROCESS – AUTOPOLYMERIZATION

MICHAEL K. GEORGES,* R. ANDREW KEE, RICHARD P. N. VEREGIN, GORDON K. HAMER AND PETER
M. KAZMAIER

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, Canada

The autopolymerization of styrene in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical), with and without organic acids, such as benzoic acid and camphorsulfonic acid, was studied. Broad polydispersities are obtained in the absence of acid, whereas narrower polydispersities are obtained in their presence. The significance of these results for the synthesis of narrow polydispersity polystyrene by the TEMPO-mediated living polymerization process is discussed.

INTRODUCTION

It has been demonstrated that a living nitroxide stable free radical mediated polymerization process can be used to synthesize resins with narrow polydispersities.^{1–3} This result has very important consequences because it provides the opportunity to make resins of controlled and predictable molecular weights, previously inaccessible by a free radical polymerization process. In addition, it permits the synthesis of resins of complex architecture with controlled chain length for each component. Since the reaction is conducted above 100 °C, the contribution of thermal or autopolymerization to the outcome of the polymerization process is of considerable interest. In this paper, we present results for the autopolymerization of styrene under the reaction conditions required for the nitroxide-mediated free radical polymerization process. The effects of camphorsulfonic acid (CSA) and benzoic acid (BA) on the autopolymerization reaction are highlighted because of their importance to the process. BA is inherently present in the reaction mixture as a by-product of benzoyl peroxide (BPO) dissociation and CSA is added to the reaction mixture to increase the rate of polymerization.

The autopolymerization of styrene has been studied extensively and is generally accepted to occur according to the Mayo mechanism⁴ outlined in Scheme 1. The reaction begins with a Diels–Alder cycloaddition between two styrene molecules to produce product **1**, which then undergoes a one electron transfer reaction with another styrene monomer to form the two benzylic

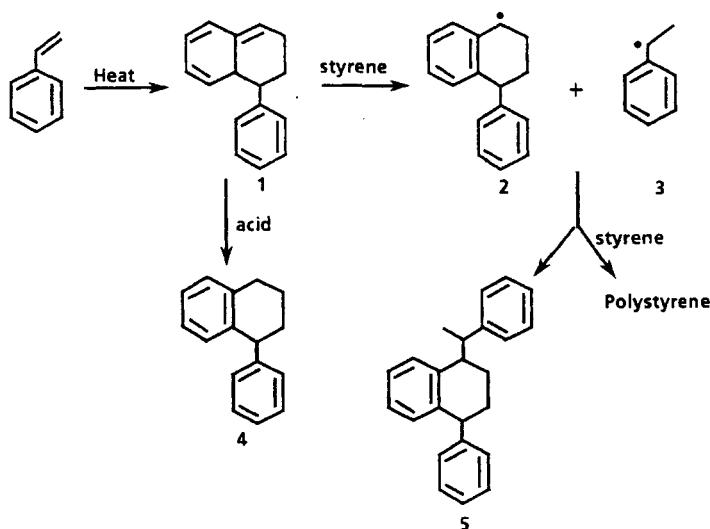
radical products **2** and **3**. Products **2** and **3** can combine to form **5** or add monomer to initiate polymerization.

We studied the autopolymerization of styrene in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) with and without added CSA and BA. It has been reported that strong organic acids, such as CSA, can reduce autopolymerization by converting the Diels–Alder product **1** into the innocuous product **4** (Scheme 1).⁵ Whereas it was reported⁵ that CSA had no effect on the rate of polymerization of styrene, we have found that CSA significantly increases the rate of the TEMPO-mediated free radical polymerization.⁶ We were also interested in the influence that benzoic acid might have on autopolymerization because it is present in the TEMPO-moderated free radical polymerization as a by-product of the reaction between TEMPO and the BPO initiator.⁷

EXPERIMENTAL

Materials and Equipment. All reactions were performed under argon with stirring in three-necked reaction flasks equipped with an argon inlet and outlet and a condenser. The reaction flasks were heated in an oil bath maintained at 125 or 130 °C for up to 39 h. Analytical samples were obtained by briefly removing the condenser and withdrawing the sample with a disposable pipette. Reagents and monomers were used as received. Benzoyl peroxide, TEMPO, camphorsulfonic acid and benzoic acid were purchased from Aldrich. Molecular weights and polydispersities were estimated by gel permeation chromatography (GPC) using a Waters/Millipore liquid chromatograph equipped with a Waters Model 510 pump, Ultrastaygel

* Author for correspondence.



Scheme 1. Mayo mechanism for the autopolymerization of styrene

columns of pore size 10^4 , 2×500 and 100 \AA , and a Waters Model 410 differential refractometer. A flow-rate of 0.8 ml min^{-1} was used and samples were prepared in tetrahydrofuran. Polystyrene standards were used for calibration. Molecular weights were determined for samples before they were purified by precipitation into methanol. Percentage conversion was determined by gas chromatographic analysis using a Perkin-Elmer SIGMA 2000 gas chromatograph with a Perkin-Elmer LCI-100 laboratory computing integrator. The columns used were Carbowax 20M supplied by Supelco.

Polymerizations. One set of autopolymerization reactions were performed by heating solutions of styrene (15 ml) and TEMPO (0.10 g) at 130°C for 39 h without acid, with BA (0.08 g, 0.66 mmol) or with CSA (0.076 g, 0.32 mmol). A second set of experiments were conducted in an oil-bath maintained at 125°C with solutions of styrene (15 ml) and TEMPO (0.10 g) with either BA (0.08 g, 0.66 mmol) or CSA (0.056 g, 0.24 mmol).

3. RESULTS AND DISCUSSION

The molecular weights, polydispersities (PD) and monomer conversions for the products of the first set of autopolymerization experiments performed at 130°C for 39 h without acid, with BA and with CSA are summarized in Tables 1, 2 and 3, respectively. It is evident that in all cases extensive autopolymerization occurs after 39 h, even in the presence of TEMPO. The polydispersity of the product is influenced by whether acid is present and by the identity of the acid. Thus, the products from the reaction with no added acid show the

broadest polydispersities and while those from the reaction with added BA have the narrowest polydispersities. These results are further emphasized by comparing the GPC plots of the final sample of the autopolymerization performed in the presence of BA

Table 1. Autopolymerization of styrene at 130°C in the presence of TEMPO

Sample	Time (h)	M_n	M_w	PD	Conversion (%)
I	15	1326	2750	2.07	10
II	23	2086	3887	1.86	22
III	39	1658	4289	2.58	32

Table 2. Autopolymerization of styrene at 130°C in the presence of TEMPO and benzoic acid (0.66 mmol)

Sample	Time (h)	M_n	M_w	PD	Conversion (%)
I	15	2419	3398	1.40	3
II	23	4535	6556	1.46	30
III	39	7304	10326	1.41	58

Table 3. Autopolymerization of styrene at 130°C in the presence of TEMPO and camphorsulfonic acid (0.32 mmol)

Sample	Time (h)	M_n	M_w	PD	Conversion (%)
I	15	4897	8923	1.82	10
II	23	6731	11672	1.73	28
III	39	9596	15509	1.61	48

with the final products of the reaction without acid and with CSA (Figures 1 and 2, respectively). What is noteworthy is the distinct tailing of the distribution at low molecular weight for all products, with the product formed in the absence of acid showing the most significant tailing. The least amount of tailing is observed for the sample formed in the presence of BA. This would suggest that BA has some effect on minimizing the amount of autopolymerization, even though it increases the rate of polymerization of a TEMPO-terminated polystyrene. This can be seen in a plot of the negative natural logarithm of conversion versus time (Figure 3), which shows an increase in the rate of polymerization for the reaction with BA relative to the polymerization without acid. Interestingly, for the first 15 h there appears to be very little or no autopolymerization for the BA-catalyzed reaction. It is possible that early in the autopolymerization reaction, BA is very efficient at converting all of product 1 into product 4 (Scheme 1). Later in the reaction, possibly owing to the decrease in the concentration of BA, some of 1 is converted into 2 and 3, which initiate chains that are then catalyzed by BA to add monomer at an accelerated

rate. If this is the case, it would suggest that the amount of BA required to increase the rate of reaction is less than that which is required to prevent autopolymerization. Further experiments are in progress to study this possibility. However, for the question at hand, it would appear that in the presence of BA, autopolymerization should not be a concern for the nitroxide-mediated free radical polymerization of styrene if the reaction is completed in less than about 15 h.

The reaction with CSA gives the product with the highest molecular weight because of its ability to increase the rate of polymerization of TEMPO-terminated polystyrene.⁶ The polydispersities are slightly broader than those obtained with BA. A comparison plot of the GPC distributions of the reaction with BA and CSA (Figure 2) shows a distinct broadening in the distribution for the CSA polymerization reaction, which is not evident in the BA distribution. This would suggest that more autopolymerization occurs in the presence of CSA than BA. Buzanowski *et al.*⁵ reported that although CSA promotes the aromatization of 2 to 4, it also promotes the Diels-Alder reaction increasing the probability of forming products 2 and 3 (Scheme 1).

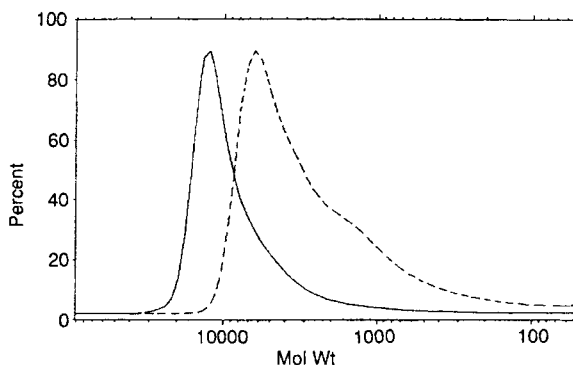


Figure 1. GPC Comparison plot of the products from the autopolymerization of styrene without acid (---) and with BA (—) at 130 °C

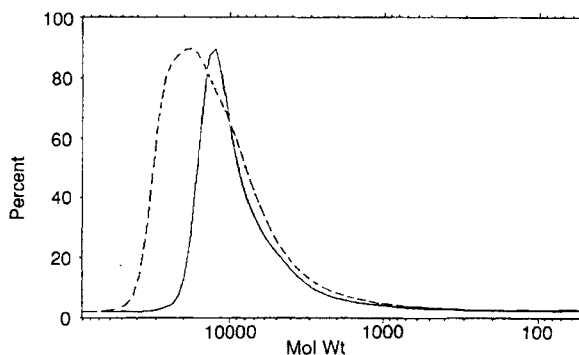


Figure 2. GPC comparison plot of the products from the autopolymerization of styrene with CSA (---) and with BA (—) at 130 °C

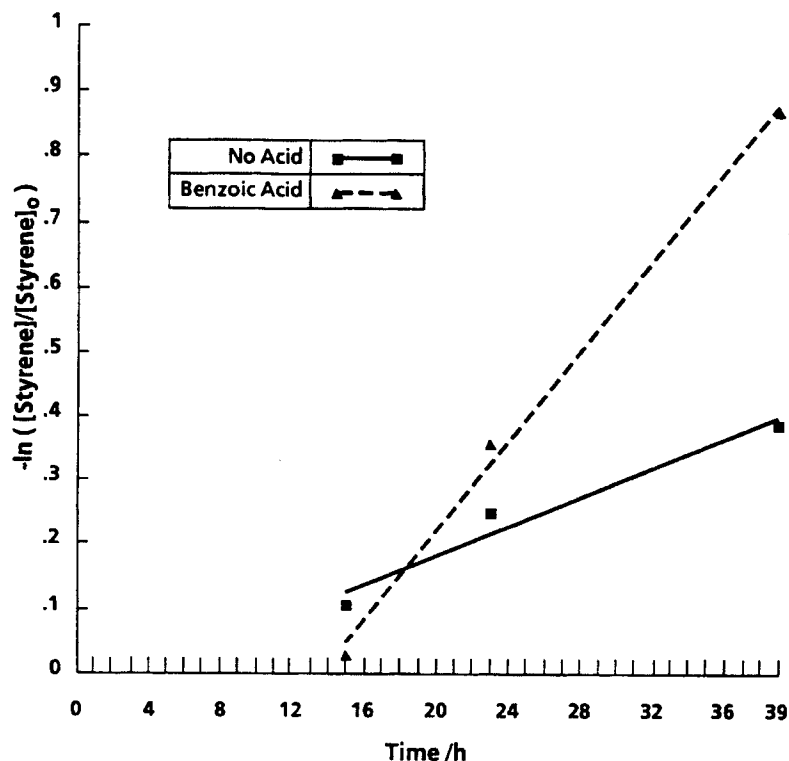


Figure 3. $-\ln(\text{conversion})$ vs time for the autopolymerization of styrene (■) in the absence of acid and (▲) in the presence of BA

Note that at 30% conversion (Tables 1–3), the molecular weights increase going from the reaction with no acid to BA and to CSA. The number of chains initiated in each reaction must, therefore, decrease in the same order. The broader polydispersity of the CSA reaction relative to the BA reaction would seem to suggest that even though the CSA reaction results in the initiation of fewer chains, they are initiated over a longer time period. Alternatively, CSA is destroying some of the nitroxide, reducing its effectiveness at controlling the polymerization.

The autopolymerization reactions with BA and CSA were repeated, at a slightly lower temperature (125 °C rather than 130 °C), where the amount of CSA was reduced so that the rates of the two reactions would be approximately the same. The physical properties of the resulting resins are listed in Table 4 and a GPC comparison plot of the molecular weight distributions is presented in Figure 4. The molecular weights of the two samples are approximately the same, allowing a direct comparison of the shapes of the molecular weight distributions for the two products. Again, it is evident that the reaction with the BA provides resin with narrower polydispersity

than the reaction with CSA, even when the rate of reaction and the molecular weights are about the same.

Finally, it should be pointed out that although the autopolymerization reaction in the presence of TEMPO can be controlled by BA to provide narrow polydispersity resins, the polydispersities are never as narrow as those that are obtained by a BPO initiated, TEMPO-mediated polymerization. This can be seen in the GPC comparison plot (Figure 5), which shows a TEMPO-terminated polystyrene prepared at 125 °C over 45 h,¹ and the product obtained from the autopolymerization of styrene in the presence of BA (Table 2, sample III).

Table 4. Autopolymerization of styrene at 125 °C in the presence of TEMPO with added benzoic acid (0.66 mmol) and camphorsulfonic acid (0.24 mmol)

Sample	Time (h)	M_n	M_w	PD	Conversion (%)
BA	29	6504	9578	1.47	42
CSA	29	5303	8596	1.62	40

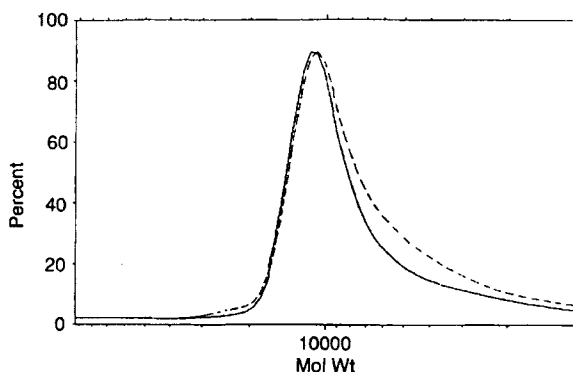


Figure 4. GPC comparison plot of the products from the autopolymerization of styrene with CSA (---) and with BA (—) at 125 °C

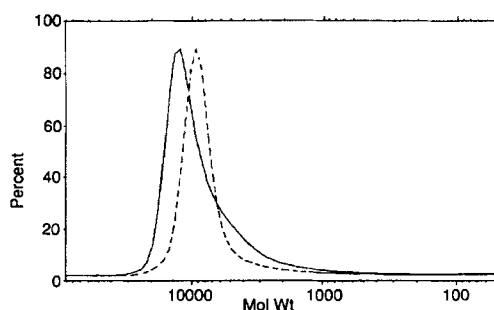


Figure 5. GPC comparison plot of the product from the autopolymerization of styrene with benzoic acid (—) with the product of BPO-initiated, TEMPO-mediated polystyrene polymerization (---)

CONCLUSIONS

It has been demonstrated that autopolymerization of styrene occurs at temperatures above 100 °C even in the presence of TEMPO, although the amount is dependent on both the reaction time and the absence or presence of an organic acid. However, in contrast to results reported earlier by other workers,⁸ broad polydispersity polystyrenes are always obtained when styrene is heated above 100 °C in the presence of TEMPO with no added acid. In the presence of either CSA or BA, narrower polydispersity resins are obtained although BA is more effective than CSA at

controlling the polydispersity. This result is significant for the BPO initiated, TEMPO-mediated living polymerization of polystyrene to produce narrow polydispersity resins. It would suggest that one of the keys to the success of this reaction is the presence of benzoic acid, produced as a by-product of benzoyl peroxide dissociation. However, this may not be the end of the story, since BPO initiated, TEMPO-mediated polymerizations of styrene provide resins with much narrower polydispersities than can be achieved by the autopolymerization of styrene in the presence of BA, even when the former reaction is allowed to continue for up to 69 h.¹

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