

# Radical Styrene Polymerization in the Presence of Trace Levels of Sulfonic Acids

Bryan R. Matthews, William Pike, Jose M. Rego, P. D. Kuch, D. B. Priddy

Dow Polystyrene R&D, 438 Building, Dow Chemical Company, Midland, Michigan 48667

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**ABSTRACT:** The bulk polymerization of styrene in the presence of the vinyl functional sulfonic acid 2-sulfoethylmethacrylate (SEM) was found to have utility for making polystyrenes with narrow polydispersity, bimodal polydispersity, and ultrahigh molecular weight at fast polymerization rates. Narrow polydispersity polymers were made by the addition of SEM to nitroxide-mediated polymerizations. Bimodal polydispersity polymers were made by the ultrahigh molecular weight component being made in the presence of SEM in the absence of an initiator and the low molecular weight component being made in the presence of an initiator and/or chain-transfer agent.

Ultrahigh molecular weight monomodal polystyrenes were prepared at much faster polymerization rates than possible via spontaneous polymerization in the absence of SEM. SEM was found to be more effective, by an order of magnitude, than camphor sulfonic acid on a weight basis and, because it is copolymerized into the polymer chain, should not lead to corrosion problems during fabrication of the polymer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 869–875, 2003

**Key words:** polystyrene; oligomers; radical polymerization

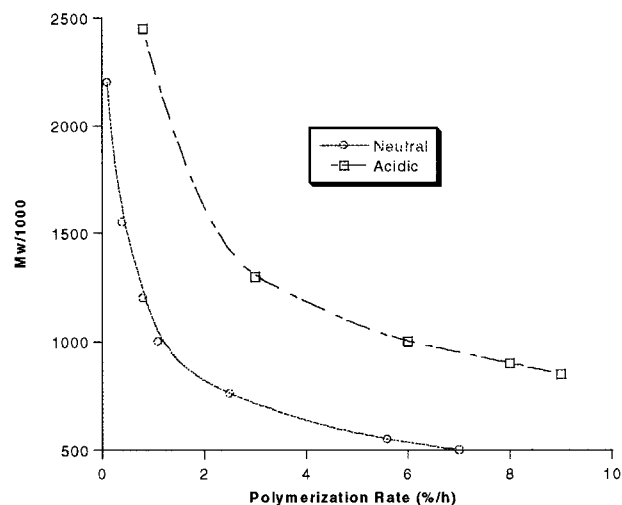
## INTRODUCTION

Previously, we reported that spontaneous bulk styrene polymerization in an acidic environment results in a significant shift of the normal spontaneous polymerization rate versus the molecular weight (Fig. 1).<sup>1</sup> This effect results from acid-catalyzed isomerization of the highly reactive free-radical precursor (Mayo intermediate) to phenyltetralin (Scheme 1). Thus, certain acids act as polymerization inhibitors. However, the isomerization is not quantitative, allowing some initiating radicals to form. If the temperature is increased, the rate of polymerization increases. At a higher temperature, the rate of propagation increases, whereas the rate of termination (by radical coupling) is lower than normal because of the lower concentration of polystyryl radicals. Moreover, Pryor and Coco<sup>2</sup> estimated the chain-transfer constant of the Mayo dimer to be about 10. Thus, lowering its concentration during styrene polymerization increases the polymer

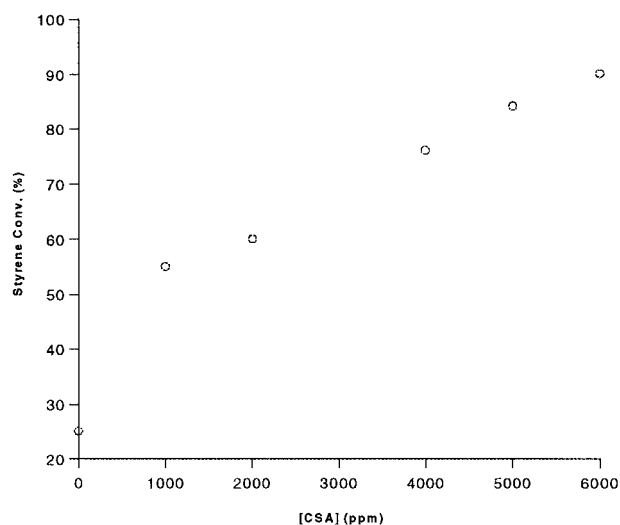
chain length. These effects are cumulative, yielding the net result that ultrahigh molecular weight polystyrene (PS) can be produced at polymerization rates about 5 times faster than spontaneous styrene polymerization carried out in a neutral environment.

After screening a variety of acids, we learned that there is an optimum acid strength to achieve the maximum effect on polymerization. If the acid is too strong (e.g., methane sulfonic acid), cationic polymerization takes place. If the acid is too weak (e.g., acetic acid), no effect is observed. We were also faced with solubility issues; that is, many sulfonic acids were found to be insoluble in styrene. During our initial screening study, the acid selected for further study was camphor sulfonic acid (CSA) because it is quite soluble in styrene, does not cause cationic polymerization, and is very effective at relatively low concentrations (i.e., 0.01–0.05% w/w). However, the effect of CSA is catalytic, so PS produced in its presence is contaminated by fugitive residual CSA. We were concerned about potential problems of residual acid (e.g., mold corrosion) in the polymer and began looking for a way to solve this problem. We decided to evaluate copolymerizable sulfonic acids so that the acid residues would be immobilized in the polymer.<sup>3</sup>

Correspondence to: D. B. Priddy.



**Figure 1** Polymerization rate versus the molecular weight for spontaneous bulk styrene polymerization under neutral and acidic conditions.



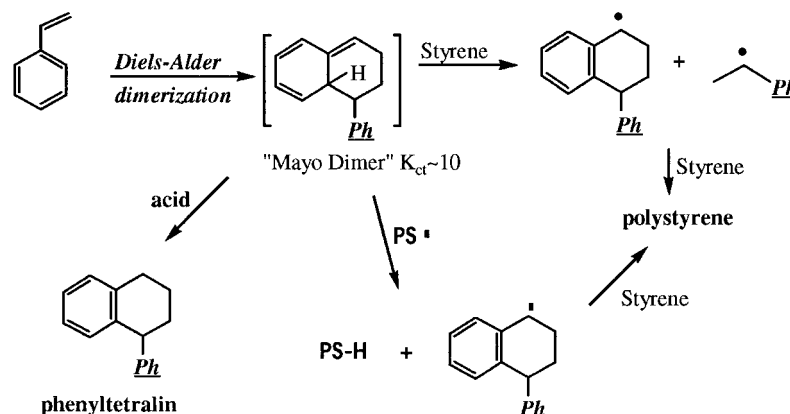
**Figure 2** Effect of the CSA concentration on nitroxide-mediated styrene polymerization (130°C, 5.5 h).

A further objective of this study was to investigate the utility of acid-catalyzed styrene polymerization for making PS of controlled polydispersity, such as narrow and bimodal polydispersity.

Narrow polydispersity polystyrenes [NPDPS; weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ ) < 1.5] are typically prepared by the addition of stable free radicals to the polymerization. However, this generally greatly retards the polymerization rate. Thinking that the polydispersity could be narrowed, Georges et al.<sup>4</sup> found that the addition of stable nitroxyl radicals to the polymerization greatly reduces the polydispersity (<1.5) and that the addition of CSA along with the nitroxyl radical dramatically increases the rate of polymerization (Fig. 2). However, CSA concentrations of 0.1–0.6% w/w were used. This concentration range is

about an order of magnitude higher than that used in our work<sup>1</sup> and would likely cause problems (e.g., mold corrosion) if left in the polymer. A copolymerizable acid should help to eliminate potential problems caused by high levels of fugitive sulfonic acid residues in NPDPS produced with the nitroxide/acid-mediated polymerization process.

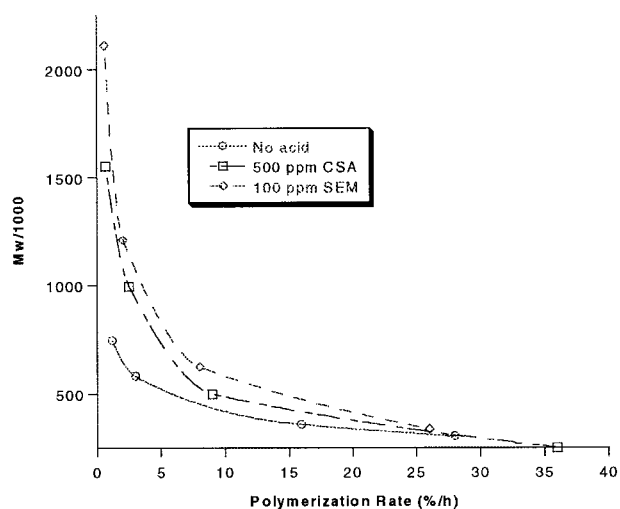
The improved strength and rheological properties of bimodal polydispersity polystyrene (BPDPS) was demonstrated by Wesselmann.<sup>5</sup> BPDPS was prepared by unstabilized styrene being warmed at 60°C for 5 days to form a syrup containing 10% PS ( $M_w = 1,400,000$ ). This syrup was then fed into a continuous bulk polymerization reactor along with a peroxide initiator to produce BPDPS. However, BPDPS has not yet been commercialized because of a lack of a com-



**Scheme 1** Acid-catalyzed isomerization of the Mayo dimer to phenyltetralin.

**TABLE I**  
Data Obtained from Ampule Polymerizations with Various Levels of SEM at Several Temperatures Compared with 500 ppm CSA

| CSA (ppm) | SEM (ppm) | Temperature (°C) | Time (h) | Solids (%) | Rate (%/h) | $M_w/1000$ | $M_n/1000$ |
|-----------|-----------|------------------|----------|------------|------------|------------|------------|
| 0         | 0         | 90               | 17       | 20         | 1.2        | 743        | 388        |
| 0         | 10        | 90               | 17       | 16         | 0.9        | 885        | 433        |
| 0         | 25        | 90               | 17       | 14         | 0.8        | 1146       | 475        |
| 0         | 50        | 90               | 17       | 13         | 0.8        | 1608       | 739        |
| 0         | 75        | 90               | 17       | 11         | 0.7        | 1909       | 807        |
| 0         | 100       | 90               | 17       | 10         | 0.6        | 2109       | 797        |
| 0         | 0         | 110              | 2        | 6          | 3          | 579        | 289        |
| 0         | 10        | 110              | 2        | 7          | 3.5        | 656        | 344        |
| 0         | 25        | 110              | 2        | 5          | 2.5        | 871        | 441        |
| 0         | 50        | 110              | 2        | 5          | 2.5        | 1107       | 544        |
| 0         | 75        | 110              | 2        | 4          | 2          | 1248       | 618        |
| 0         | 100       | 110              | 2        | 4          | 2          | 1210       | 579        |
| 0         | 0         | 130              | 1        | 16         | 16         | 357        | 181        |
| 0         | 10        | 130              | 1        | 14         | 14         | 370        | 191        |
| 0         | 25        | 130              | 1        | 13         | 13         | 394        | 196        |
| 0         | 50        | 130              | 1        | 11         | 11         | 551        | 287        |
| 0         | 75        | 130              | 1        | 10         | 10         | 494        | 252        |
| 0         | 100       | 130              | 1        | 8          | 8          | 623        | 313        |
| 0         | 0         | 150              | 0.5      | 14         | 28         | 303        | 153        |
| 0         | 10        | 150              | 0.5      | 25         | 50         | 254        | 130        |
| 0         | 25        | 150              | 0.5      | 22         | 44         | 260        | 132        |
| 0         | 50        | 150              | 0.5      | 21         | 42         | 280        | 140        |
| 0         | 75        | 150              | 0.5      | 12         | 24         | 308        | 152        |
| 0         | 100       | 150              | 0.5      | 13         | 26         | 336        | 171        |
| 500       | 0         | 90               | 17       | 12         | 0.7        | 1550       | 710        |
| 500       | 0         | 110              | 2        | 5          | 2.5        | 995        | 455        |
| 500       | 0         | 130              | 1        | 9          | 9          | 498        | 238        |
| 500       | 0         | 150              | 0.5      | 18         | 36         | 251        | 118        |



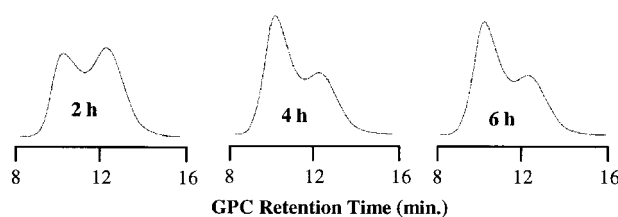
**Figure 3**  $M_w$  versus the polymerization rate (from data in Table I) for spontaneous styrene polymerization catalyzed by 500 ppm CSA versus 100 ppm SEM.

mercially viable process. One of our objectives was to see if the addition of acid to radical styrene polymerization might improve the feasibility of preparing BPDPS.

**EXPERIMENTAL**

**Materials**

2-Sulfoethylmethacrylate (SEM) was purchased from Hampshire Chemical Corp. (Lexington, MA) and was



**Figure 4** GPC curves of BPDPS produced by styrene polymerization at 140°C in the presence of 100 ppm SEM and 1000 ppm BPO.

**TABLE II**  
**Results of Styrene Polymerization**  
**at 140°C in the Presence of 100 ppm SEM**  
**and 1000 ppm BPO**

| Polymerization Time (h) | Conversion (%) | $M_w/1000$ | $M_w/M_n$ |
|-------------------------|----------------|------------|-----------|
| 2                       | 38             | 350        | 4.0       |
| 4                       | 55             | 540        | 4.2       |
| 6                       | 62             | 525        | 3.9       |

used as received. Styrene (Dow Chemical Co., Midland, MI) contained 3 ppm *t*-butylcatechol. All other materials were obtained from Aldrich Chemical Co. (Milwaukee, WI) and were used as received.

### Polymerizations

#### Ampoules

The styrene solutions were placed in a glass ampoules (5-mm inner diameter  $\times$  9-mm outer diameter  $\times$  30 cm). The ampoules were sealed *in vacuo* with a freeze-thaw technique and were then inserted into 1-cm holes in an electrically heated aluminum block. After the desired thermal exposure, the ampoules were removed from the heating block, cooled, and opened. A portion of the polymer syrup was analyzed with gel permeation chromatography (GPC), as previously described. The rest of the syrup was used to gravimetrically determine the percentage (w/w) of PS contained in the syrup with vacuum-oven (<4 mmHg) devolatilization at 215°C.

#### Lab Pot

Polymerizations were carried out with an electrically heated kettle with a volume of 2 L. The agitator was a hollow auger, as previously described.<sup>6</sup> The reactor was charged with 1200 g of styrene and SEM, and the

reactor was pressurized to 20 psi with nitrogen. After isothermal heating at the desired temperature and time, initiator dissolved in ethylbenzene (EB) was added, and heating continued, following a temperature ramp. Samples of the reactor contents were collected periodically, and the monomer conversion percentage and molecular weight of PS in the polymerization mixture were determined.

## RESULTS AND DISCUSSION

The copolymerizable acid selected for evaluation was SEM. This acid was chosen because of its commercial availability and good styrene solubility. The performance of SEM was compared with CSA by polymerization in glass ampoules (Table I). The data show that 100 ppm of SEM allows the preparation of high molecular weight PS at faster rates than 500 ppm of CSA (Fig. 3).

### Preparation of BPDPS

We were able to use acid-catalyzed styrene polymerization to make BPDPS in two ways: (1) polymerizing styrene in the presence of both an initiator and SEM at a temperature significantly above the 1-h half-life temperature of the initiator and (2) polymerizing styrene in the presence of SEM without an initiator to make ultrahigh molecular weight PS and then adding an initiator and/or chain-transfer agent to form low molecular weight PS. With the first option, 1000 ppm benzoyl peroxide (BPO) was added along with 100 ppm SEM to styrene. The ampoules were heated at 140°C, and an ampoule removed after 2, 4, and 6 h. The GPC curves of the three PS samples and analytical results are shown in Figure 4 and Table II, respectively.

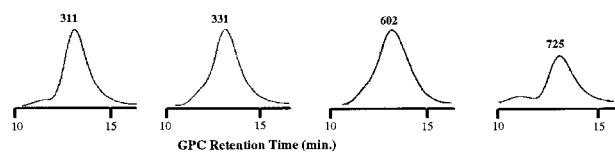
Heating the mixture of styrene, BPO, and SEM at 140°C quickly decomposed the BPO and formed

**TABLE III**  
**Results of the Preparation of BPDPS in the Lab Reactor**

| Run number | Conversion/time (%/h) | High fraction $M_w/1000$ | Polymerization temperature (°C) | SEM (ppm) | Final % PS | Final $M_w/1000$ | Final $M_w/M_n$ |
|------------|-----------------------|--------------------------|---------------------------------|-----------|------------|------------------|-----------------|
| 311        | 6/2                   | 1200                     | 120                             | 100       | 76         | 210              | 3.4             |
| 331        | 14/2                  | 800                      | 125                             | 25        | 77         | 249              | 3.8             |
| 602        | 16/2                  | 725                      | 130                             | 50        | 70         | 284              | 4.0             |
| 725        | 8/16                  | 2400                     | 90                              | 100       | 59         | 500              | 6.0             |

TABLE IV  
 Lab Reactor Runs with Isothermal First Stage to Make High-Molecular-Weight PS Followed by Second-Stage Addition of Initiator and Chain-Transfer Agent with a Temperature Ramp to Make Low-Molecular-Weight PS

| Run number | SEM (ppm) | Temperature/time before second addition (°C/h) | EB after second addition (%) | Temperature profile after second addition (°C/min)   | tBPB in second addition (% w/w) | DtBPB in second addition (% w/w) | nDM in second addition (% w/w) |
|------------|-----------|--|------------------------------|--|---------------------------------|----------------------------------|--------------------------------|
| 311        | 100       | 120/2  | 20                           | Hold 120 for 40<br>Ramp to 130 over 120  | 0.5                             | 0.5                              | 0                              |
| 331        | 25        | 125/2  | 20                           | Ramp to 135 over 40<br>Ramp to 145 over 40<br>Ramp to 155 over 40<br>Hold 120 for 40<br>Ramp to 130 over 120                           | 0.4                             | 0.4                              | 0                              |
| 602        | 50        | 130/2  | 15                           | Ramp to 135 over 40<br>Ramp to 145 over 40<br>Ramp to 155 over 40<br>Ramp to 135 over 42<br>Ramp to 140 over 42<br>Hold at 140 for 122 | 0                               | 0.3                              | 0.8                            |
| 725        | 100       | 90/16  | 20                           | Ramp to 150 over 42<br>Ramp to 118 over 48<br>Ramp to 122 over 96<br>Ramp to 124 over 48<br>Ramp to 130 over 48<br>Ramp to 138 over 48 | 0.5                             | 0                                | 0.5                            |



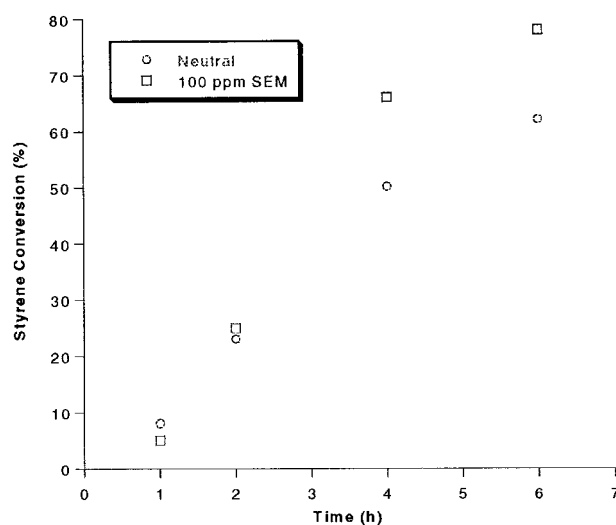
**Figure 5** GPC curves showing BPDPS made in lab reactor experiments.

low molecular weight PS. Once the BPO was consumed, only spontaneous polymerization took place that, in the presence of SEM, led to the formation of ultrahigh molecular weight PS. As the polymerization progressed, the ratio of the high molecular weight component in the bimodal blend increased relative to the low molecular weight component.

The other option was to conduct the acid-catalyzed spontaneous polymerization to make the ultrahigh molecular weight PS first and then make the low molecular weight component. This was demonstrated with a lab reactor, as described in the Experimental section. The  $M_w$  value of the high molecular weight component was controlled by temperature and SEM concentration. The  $M_w$  value of the low molecular weight component was controlled by the amount of the initiator, *t*-butylperbenzoate (*t*BPB) or di-*t*-butylperoxide (*Dt*BP), and the chain-transfer agent, *n*-dodecylmercaptan (*n*DM), added to the reactor after the high  $M_w$  component had been produced. The run conditions and molecular weight data are summarized in Tables III and IV. The GPC curves of BPDPS produced from four lab-pot runs are shown in Figure 5.

#### Effect of SEM on Nitroxide-Mediated Radical Polymerization

Experiments to determine the effect of SEM on nitroxide-mediated styrene polymerization were carried out at 140°C with and without SEM (100 ppm). 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO; 1500 ppm)



**Figure 6** Effect of SEM on the styrene conversion during nitroxide-mediated (1500 ppm TEMPO) styrene polymerization at 140°C.

was used as the nitroxyl radical. The results of the experiment are summarized in Table V. The presence of SEM clearly accelerated the polymerization rate and resulted in the formation of higher molecular weights (Figs. 6 and 7).

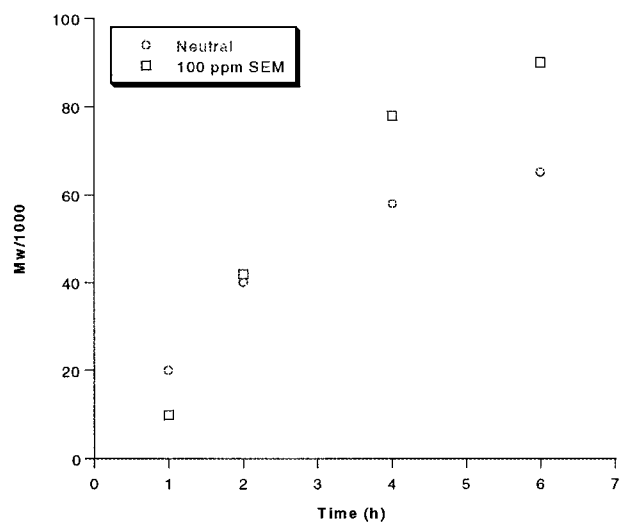
## CONCLUSIONS

SEM is an excellent alternative to CSA for providing an acidic environment during bulk styrene polymerization. SEM is more effective, by about an order of magnitude, than CSA on a weight basis and offers the added advantage of copolymerizing into the polymer, which should minimize the potential for corrosion problems during fabrication of the final polymer.

Acid-catalyzed polymerization technology offers the ability to make BPDPS via bulk radical polymerization in one reactor, a feat previously difficult to

**TABLE V**  
Results of Ampule Experiments to Determine the Effect of SEM on Nitroxide-Mediated Spontaneous Styrene Polymerization

| SEM (ppm) | TEMPO (ppm) | 1-h Conversion | 1-h $M_w$ | 2-h Conversion | 2-h $M_w$ | 4-h Conversion | 4-h $M_w$ | 6-h Conversion | 6-h $M_w$ |
|-----------|-------------|----------------|-----------|----------------|-----------|----------------|-----------|----------------|-----------|
| 0         | 1500        | 8.5            | 19        | 24             | 39        | 49             | 57        | 62             | 64        |
| 100       | 1500        | 5              | 10        | 26.4           | 41        | 65             | 75        | 79             | 89        |



**Figure 7** Effect of SEM on the PS  $M_w$  during nitroxide-mediated (1500 ppm TEMPO) styrene polymerization at 140°C.

accomplish. BPDPS is known to have an improved toughness/melt-processing balance over monomodal PS. Also, the addition of SEM to nitroxide-mediated styrene polymerization increases both the polymerization rate and final molecular weight of the resulting PS.

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