

# Nitroxide-Mediated Free Radical Polymerization of Styrene. Absence of the Gel Effect<sup>†</sup>

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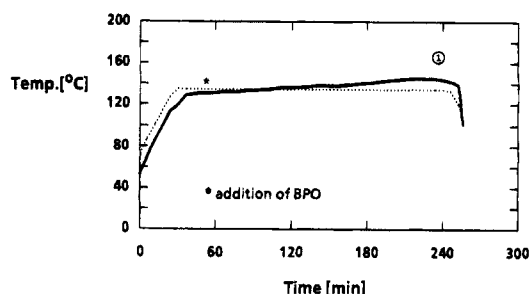
**Introduction.** In conventional bulk free radical styrene polymerization the rate of polymerization is governed by the equation

$$R_p = k_p(fk_d[I]/k_t)^{1/2}[M] \quad (1)$$

up to about 30% monomer conversion which can be considered as the onset of the gel (or Trommsdorff) effect.<sup>1</sup> The main feature of the gel effect is that  $R_p$  increases with conversion instead of decreasing as monomer is consumed. Under isothermal polymerization conditions this rate increase is attributed to a decrease in the termination rate constant ( $k_t$ ) which results in an increase in radical concentration. The rate increase for styrene homopolymerization, as measured by O'Driscoll and Huang,<sup>1</sup> under isothermal conditions, could be as high as 15 times over the rate expressed by eq 1. Due to the exothermic nature of styrene polymerization ( $-\Delta H = 17.0$  kcal/mol), it is a challenge to assure isothermal polymerization conditions at high monomer conversion even at the smallest laboratory scale (1–10 g of monomer).<sup>1,2</sup> In the case of a nonisothermal styrene polymerization, the onset of the gel effect is moved to a lower degree of conversion and the relative rate increase is higher than in the isothermal case, making the system more prone to thermal runaway.<sup>1</sup> For nonisothermal styrene polymerization, the reaction temperature ( $T_r$ ) is directly proportional to  $R_p$  and, therefore, provides a good measure of the extent of polymerization.

We have recently introduced the use of nitroxide-stable free radicals to mediate free radical polymerizations (SFRP) to produce narrow polydispersity resins.<sup>3–5</sup> Polymerizations are initiated at temperatures such that the initiator half-life is a few minutes or less,<sup>6</sup> allowing almost simultaneous chain initiation. Narrow-polydispersity resins result, in part, because irreversible termination by coupling, although probably not completely eliminated, is reduced. This work suggested that since initiation and termination are controlled, stable free radical-mediated polymerizations should not exhibit a gel effect, rendering it safer to perform than a conventional free radical polymerization process.<sup>7</sup> To test this hypothesis, bulk polymerizations of styrene were performed in a 1-L bench-scale reactor (440 g of styrene) under nonisothermal reaction conditions.

**Experimental Section.** Bulk polymerization of styrene was carried out in a 1-L jacketed reactor (Büchi autoclave BEP 280) equipped with a reflux condenser. The reactor was charged with monomer and heated to reaction temperature under a gentle nitrogen purge with stirring. When the initial reaction temperature in Table 1 was reached, the initiator was added, which



**Figure 1.** SFRP reaction exotherm (solid line) and reactor jacket temperature (dotted line) for reaction 1. Start of the reaction is the addition of BPO to the reactor as denoted with the asterisk. Note that the reaction exotherm reached a maximum at about 200 min and started to decrease due to the monomer consumption. The final monomer conversion was 84.6% by GC analysis. The final polymer had  $M_w = 33\,000$  and  $PD = 1.40$ . Other conditions are described in Table 1.

denoted the start of the reaction. Time zero conversion was zero in all reactions, as determined by gravimetry. An anchor agitator (75 mm diameter) was used at 200 rpm for all reactions except for experiment 6 where a turbine agitator (46 mm diameter) was used. Heat transfer characteristics of the reactor system were determined from control experiments. It was found that the stainless steel (SS) reactor (84 mm diameter) had about 5 times more efficient heat transfer than the 1-L glass reactor (82 mm diameter, with 9 mm wall thickness). The reactor jacket temperature was held constant throughout the course of the polymerization reaction. The reaction temperature was monitored using a resistance temperature detector (RTD) connected to the distributed control system (DCI-4000). Samples were periodically removed from the reactor for analytical purposes. Molecular weights were determined in tetrahydrofuran by gel permeation chromatography using Ultrastaygel columns calibrated with polystyrene standards. All chemicals were used as received. Camphorsulfonic acid was used in SFRP to enhance the polymerization rates and make them comparable to the conventional free radical rates.<sup>8</sup>

**Results and Discussion.** We have found that under conditions described in Table 1 the gel effect is strongly suppressed in the SFRP system to the extent that it could not be distinguished from the reaction exotherm. The increase in reaction temperature in reactions 1 and 2 (Figures 1 and 3) was probably due to the poor heat transfer at high monomer conversion rather than to the gel effect. It is well-known that heat transfer constants decrease due to increases in reaction mixture viscosity.<sup>9</sup> Therefore, when conventional styrene polymerization was carried out under similar process conditions, reactions 3–6, the uncontrollable reaction exotherm seems to be unavoidable (Figures 2 and 3). Reactions 3 and 4 (Figure 2) illustrate the effect of jacket temperature on the reaction exotherm in a glass reactor. Although the BPO half-life at 91 °C is 1 h (Table 1), it did not take more than about 15 min for the runaway exotherm to occur in reaction 3. This could be due to the relatively poor heat transfer in a heavy-walled glass autoclave.

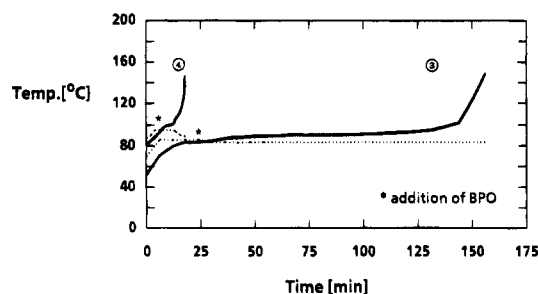
Using the conversion–time data from Figure 3, the polymerization rates were calculated for reactions 2 and 5 using a method described by O'Driscoll and Huang.<sup>1</sup> The initial polymerization rates ( $R_{p,0}$ ) were found to be comparable:  $R_{p,0} = 7.8 \times 10^{-4}$  mol L<sup>-1</sup> s<sup>-1</sup> for reaction 2;  $R_{p,0} = 5.6 \times 10^{-4}$  mol L<sup>-1</sup> s<sup>-1</sup> for reaction 5. As the reaction progressed in conventional polymerization

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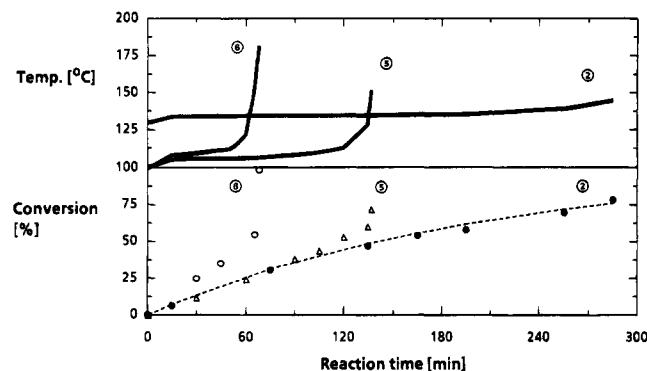
Table 1. Experimental Conditions for Styrene Polymerization in Bulk<sup>a</sup>

reaction	initiator ( $T_{1/2}$ , 1 h)	concn (M)	$T_{r,0}$ (°C)	$T_j$ (°C)	remark
1	BPO/TEMPO/CSA	(3.30/4.30/2.40) $10^{-2}$	130	135	glass reactor
2	BPO/TEMPO/CSA	(3.30/4.94/1.72) $10^{-3}$	130	135	SS reactor
3	BPO (91 °C)	0.033	80	83	glass reactor
4	BPO (91 °C)	0.033	83	95	glass reactor
5	TAEC (117 °C)	0.015	104	105	SS reactor
6	TAEC (117 °C)	0.030	103	105	SS reactor

<sup>a</sup> BPO = benzoyl peroxide (LUCIDOL 98, Elf Atochem); TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical (Aldrich); CSA = camphorsulfonic acid (Aldrich); TAEC = *O*-*t*-amyl-*O*-(2-ethylhexyl) monoperoxycarbonate (LUPERSOL TAEC, Elf Atochem);  $T_{r,0}$  = initial reaction temperature;  $T_j$  = reactor jacket temperature;  $T_{1/2}$ , 1 h = 1 h half-life temperature (Elf Atochem data).



**Figure 2.** Conventional free radical polymerization exotherm (solid line) for reactions 3 and 4. Jacket temperature is shown with a dotted line. Reactions were quenched with toluene after reaching the maximum. The final monomer conversion in 3 was 89.1% (by GC analysis), and the final polymer had  $M_w = 70\,500$  and  $PD = 1.92$ . The product of reaction 4 was not analyzed. Other conditions are described in Table 1.

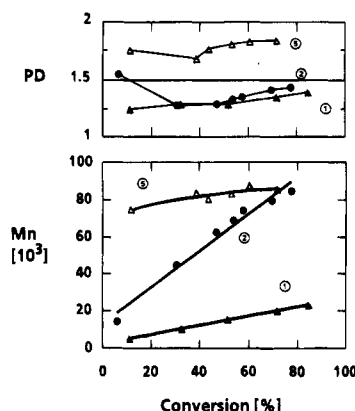


**Figure 3.** SFRP reaction 2 (●) compared to conventional free-radical polymerization reactions 5 (Δ) and 6 (○): comparison of conversion and reaction exotherm. The jacket temperature was held constant as shown in Table 1. Reactions 5 and 6 were quenched with toluene after reaching the maximum temperature. The broken line represents the calculated monomer conversion for SFRP reaction 2 using  $k_{obs} = 0.00492 \text{ min}^{-1}$ .

(reaction 5), the rate started to slowly increase after about 40% monomer conversion, reaching  $R_p = 8.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  at 60% conversion. At 72% monomer conversion, the gel effect resulted in about a 10-fold increase in the rate of reaction 5 ( $R_p = 83.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ ). For comparison, the rate of SFRP reaction 2 was  $R_p = 2.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  at 60% conversion and  $R_p = 3.8 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  at 77.5% conversion. Thus, the SFRP rate was virtually unchanged during the course of styrene polymerization, which confirms a living polymerization mechanism. The monomer consumption in SFRP can be represented by eq 2 as shown by Veregin et al.<sup>10</sup>

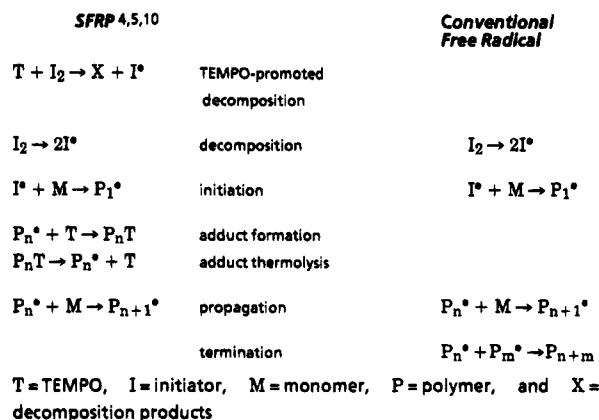
$$-d[M]/dt = k_p[P^*][M] = k_{obs}[M] \quad (2)$$

where  $k_{obs} = k_p[P^*]$  is the observed pseudo-first-order rate constant for styrene polymerization by the SFRP



**Figure 4.**  $M_n$  and polydispersity (PD) versus monomer conversion for SFRP reactions 1 (Δ) and 2 (●) and conventional free radical polymerization reaction 5 (Δ). This plot illustrates the “living” nature of SFRP compared to the conventional free radical polymerization.

## Scheme 1



mechanism, and  $[P^*]$  is the polymer radical concentration. As shown in Figure 3, calculated monomer conversion agrees well with the experimental conversion for  $k_{obs} = 0.00492 \text{ min}^{-1}$ .

Increase in polymer  $M_n$  in SFRP is linear with monomer conversion, as shown for reactions 1 and 2 in Figure 4, in contrast to the conventional free radical polymerization reaction 5. This fact along with the relatively narrow polydispersities in reactions 1 and 2 compared to that of reaction 5 supports a living polymerization mechanism of SFRP.

Reasons for the absence of the gel effect in SFRP styrene polymerization become apparent if one compares the SFRP mechanism to the conventional free radical mechanism as shown in Scheme 1.

Since the irreversible termination by dead polymer, which is common in the conventional styrene polymerization, is strongly suppressed in the SFRP,<sup>10</sup> no gel effect could be detected in the SFRP. Even when the polymerization is performed at relatively high reaction

rates, by adding CSA, no gel effect is evident. This result may have significant benefits for industrial scale bulk styrene polymerizations where not only the concern of runaway reactions would be minimized but also less expensive reactors of simpler design could be used.

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### References and Notes

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