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Characteristics of the Stable Free Radical Polymerization of Styrene in the Presence of 2-Fluoro-1-methylpyridinium *p*-Toluenesulfonate

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ABSTRACT: The behavior of the stable free radical moderated polymerization of styrene in the presence of 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (FMPTS) has been examined. The rate enhancement has been found to be the result of the decrease of free nitroxide (TEMPO) concentration that shifts the equilibrium between capped and growing chains toward the growing free radical form. The decrease in TEMPO concentration was shown to be coupled to the presence of FMPTS. The system is sensitive to the initiator employed and the timing of the addition of FMPTS. If the polymerization rate change due to the change in TEMPO concentration is accounted for, a secondary polymerization retarding influence of FMPTS was observed.

Introduction

In a previous communication[1] we reported that the addition of 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (FMPTS) significantly enhanced the observed rate of polymerization during a stable free radical polymerization (SFRP). Subsequently, the importance of the post-initiation stable free radical concentration on the observed rate and the methodology for in-situ monitoring of this concentration was described.[2] The latter work derived a mathematical relationship between the observed rate of polymerization and the residual stable free radical concentration. This understanding has been applied to the rate enhancement observed in the SFRP system upon addition of camphorsulfonic acid (CSA).[3] The current submission seeks to extend that understanding to the styrene polymerization employing FMPTS. The observed rate of polymerization was found to be inversely proportional to the free TEMPO concentration, and this concentration was lowered by the addition of FMPTS. The ability of FMPTS to influence the equilibrium between growing and dormant chains is significant. This equilibrium is the basis of controlled or “living” free radical polymerization and provides control over the molecular weight distribution.[4,5] FMPTS also reduces the rate of thermal initiation of styrene during the course of the stable free radical polymerization.[6] By accounting for the change in free TEMPO concentration due to the presence of FMPTS, we have been able to observe a secondary effect, a minor reduction in rate with increasing levels of the salt. Thus, there is an optimal FMPTS concentration, since in addition to its rate enhancement via TEMPO removal, it also slows the polymerization when considered independently of the TEMPO concentration.

Experimental Section

The details of the polymerization, molecular weight determination, conversion analysis, and ESR spectroscopy have been previously published.[1,2] The accurately weighed amount of FMPTS was added as dry crystals 5 min after the addition of the initiator, and 10−15% of the monomer was reserved to wash the FMPTS into the reaction flask. Five minutes after the addition of the salt to the reaction flask, an aliquot was taken and placed into an ESR tube and transferred to the spectrometer.

Results and Discussion

[TEMPO] Control of Polymerization Rate. Figure 1 examines two reaction variables as they affect the apparent rate of polymerization. The rate can clearly be affected by the initial TEMPO concentration and by the presence of FMPTS. Not surprisingly, there is a synergistic effect of using less TEMPO, coupled with the presence of FMPTS, to provide the fastest rate. Figure 2 examines the same four polymerizations as Figure 1; here rather than conversion, the concentration of TEMPO is recorded against time during the course of the polymerization. This is the ESR signal appropriately integrated and calibrated to measure the TEMPO free radical not bound to the polymer chain end. The data is shown by the points; a curve of the form $[T] = [T]_0 bt^s$ has been fitted to the data. The first signal is obtained about 15 min into the polymerization, after initiation has occurred and most of the TEMPO introduced into the polymerization has reacted with the styryl radical. The fraction of TEMPO remaining has a profound effect on the rate as can be seen by comparing the corresponding polymerizations between Figures 1 and 2. Clearly, the lower the TEMPO concentration the faster the rate of polymerization. There is, of course, a practical limit, as too little TEMPO would allow the polymerization to go out of control and proceed, at least in part, conventionally. Recent work[7] has explored very low levels of TEMPO relative to the initiator. There is a small increase in polydispersity as the initial level of TEMPO is reduced; this is likely due to the lower efficiency of capture of the free radicals produced during initiation. We have coined the term, germination efficiency, for the yield of this step. The overall number of living free radical chains is the product of the initiator efficiency and the germination efficiency. The FMPTS also contributes to the disappearance of TEMPO. This offers the advantage of allowing higher TEMPO levels to be used with initiation. Then the TEMPO level can be lowered with the delayed addition of FMPTS to increase the rate.

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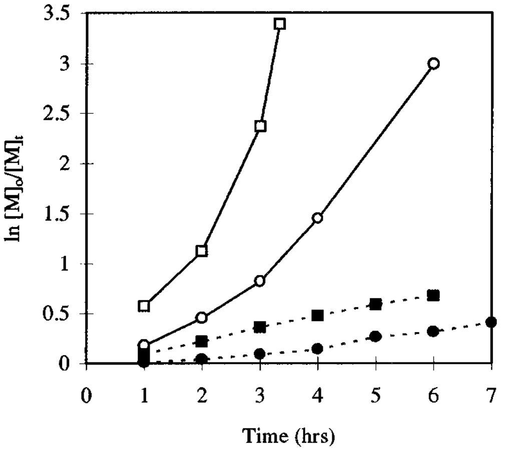

Figure 1. Observed rate of polymerization with FMPTS (solid lines) and without (dashed lines) at 125 °C and molar ratio of TEMPO:BPO of 1.3:1 (○,●) and 1.1:1 (□,■). The lines shown are a guide to the eye only.

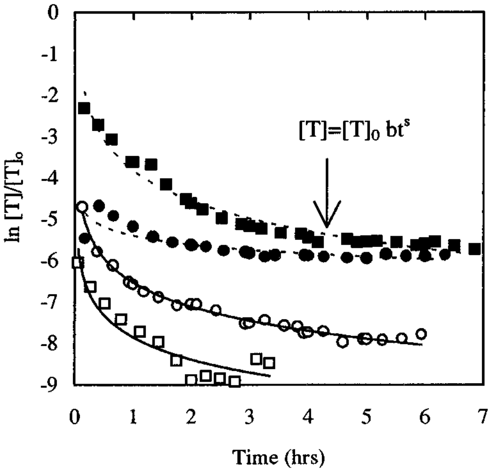

Figure 2. [TEMPO] Decay with FMPTS and molar ratio of TEMPO:BPO of 1.3:1 (○) and 1.1:1 (□); without FMPTS and ratios 1.1:1 (●) and 1.3:1 (■) corresponding to data of Figure 1.

Longer TEMPO lifetimes were observed in the presence of FMPTS when compared with CSA. To take advantage of this, polymerizations were conducted with a lower TEMPO to BPO ratio. The molar ratio in the first set of experiments, illustrated in Figure 1, was 1.3: 1.0. Subsequent polymerizations used 1.25 mmoles of TEMPO for a molar ratio to BPO of 1.1:1.0. The transition and gain in rates are shown by Figures 1 and 2.

Temperature Effects. Figure 3 is, once again, ESR data showing the change in TEMPO concentration over the course of six polymerizations. The impact of the FMPTS addition is illustrated in the ESR data; the free TEMPO concentration at 1−2 h is 10−20 times lower with the addition of FMPTS. The data for both of the polymerizations, with and without FMPTS, at 135 °C, is particularly interesting as it shows a gradual increase in the amount of TEMPO. This may be reflected in the FMPTS rate data at 135 °C in Figure 4, where the increase in rate from 125 °C to 135 °C is not nearly as great as it is from 115 °C to 125 °C. Nor does the 135 °C data display the same curvature as does the other data, reflecting the fact that the TEMPO level is not continuing to decrease. While the rate and [TEMPO] data can be reconciled, it is more difficult to define what is occurring at a molecular level. For the TEMPO concentration to rise it must have a source, and the largest possible one is from the capped chains. If at 135 °C there is a chain termination event that is more prevalent than at lower temperatures, then an increase in TEMPO concentration would occur as dead chains release TEMPO molecules. However, at these low TEMPO levels, if the difference in concentration between 125 and 135 °C is entirely due to dead chains, this would account for less than 1% of the total polymer chains in the system. Autopolymerization is another possible influence on the TEMPO level and polymer molecular weight distribution. As a source of free radicals, autopolymerization is expected to consume TEMPO;[8] however at 135 °C the nitroxide concentration rises over time, suggesting a free radical termination, or extinction that releases TEMPO is more prevalent at the higher temperature. This occurs despite an increase in the rate of autopolymerization with temperature.[9] Examination of the data in Table 1 shows that little discernible difference exists between the molecular weights of the polymerizations at 125 and 135 °C; the polydispersities (PD) are virtually identical, and at equivalent conversions the molecular weights are within 5% of each other. Thus, routine GPC analysis may detect, but not quantify, subtle differences in chain

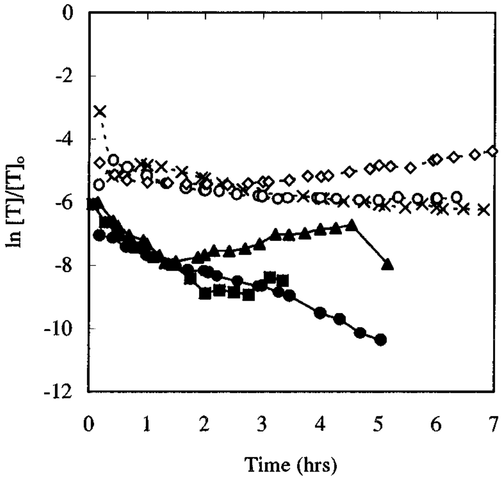

Figure 3. Temperature influence on [TEMPO] decay with FMPTS (solid points: (●) 115 °C; (■) 125 °C; (▲) 135 °C) and without FMPTS (open points: (×) 115 °C; (○) 125 °C; (◇) 135 °C). All experiments were conducted with a 1.1:1 molar ratio of TEMPO to BPO. The lines shown are a guide to the eye only.

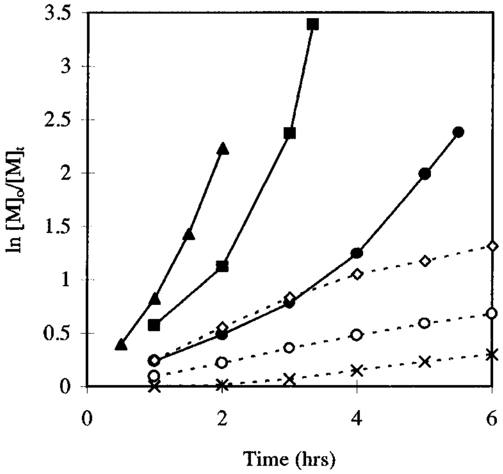

Figure 4. Temperature influence on the observed rate corresponding to polymerizations shown in Figure 3. FMPTS (solid points: (●) 115 °C; (■) 125 °C; (▲) 135 °C) and without FMPTS (open points: (×) 115 °C; (○) 125 °C; (◇) 135 °C). The lines shown are a guide to the eye only.

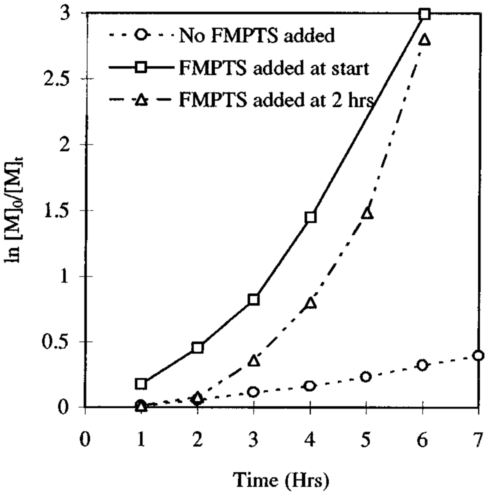

Figure 5. Conversion vs time with late addition of FMPTS compared to early FMPTS addition and no FMPTS. Polymerization at 125 °C and 1.3:1 molar ratio of TEMPO to BPO. The lines shown are a guide to the eye only.

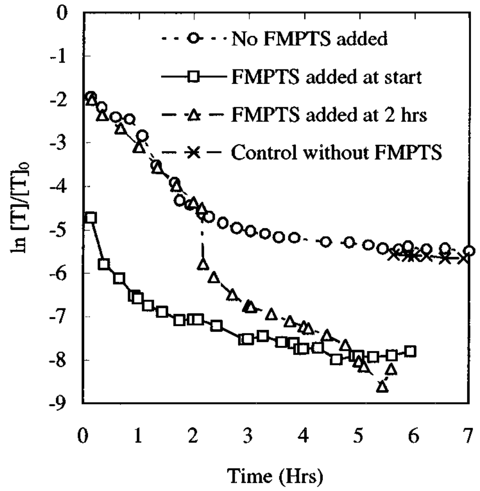

Figure 6. [TEMPO] decay with FMPTS observed with late addition of FMPTS corresponding to the polymerizations in Figure 5. The lines shown are a guide to the eye only.

Table 1. Temperature Effects on Molecular Weight in the Presence of FMPTS

	135 °C		125 °C		115 °C	
time (min)	Mn	PD	Mn	PD	Mn	PD
30	7705	1.53				
60	13651	1.39	10023	1.59	4299	3.31
90	20068	1.36				
120	23334	1.35	18196	1.39	10559	1.87
180			24773	1.32	15387	1.64
210			26642	1.33		
240					19357	1.58
300					22674	1.57
330						

distributions. The poorer PDs are obtained at the lower temperature, 115 °C, leading to speculation that a slower exchange rate and propagation rate may allow competing processes to exert more influence on the molecular weight distribution.

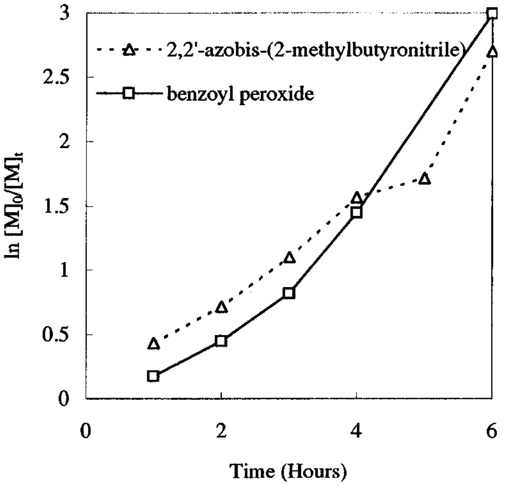

Figure 7. Observed rate with azo and peroxide initiators in the presence of FMPTS polymerization at 125 °C and 1.3:1 molar ratio of TEMPO to initiator. The lines shown are a guide to the eye only.

Table 2. Initiator Influence on Molecular Weight

	2,2′-azobis-(2-methylbutyronitrile)			benzoyl peroxide		
time (min)	Mn	PD	conv %	Mn	PD	conv %
60	5623	1.48	35	3481	1.77	16
120	9809	1.29	51	10037	1.36	36
180	12438	1.32	67	16397	1.28	56
240	15656	1.26	79	21855	1.28	76
300	17770	1.24	82			
360	18369	1.26	93	27884	1.28	95

Timing of FMPTS Addition. In Figures 5 and 6, the effect of a much later addition of FMPTS, 2 h after the polymerization start, is described in terms of the rate of polymerization and the TEMPO concentration. The picture is quite clear, showing a rapid drop in TEMPO concentration and the attendant increase in polymerization rate upon the FMPTS addition. Figure 6 requires some explanation. The polymerization was sampled and monitored in the usual manner. After the addition of FMPTS, it was resampled and this later sample, the lower line (open triangles), was recorded in the ESR. As a check, the original sample was held at temperature during this period, and returned to the ESR cavity for the last hour. This sample is indicated in the "Control without FMPTS" in the figure (×'s). The other samples are a FMPTS free control (open circles), and a polymerization with the typical addition period for FMPTS, 5 min after the initiator (open squares). The rapid effect of the FMPTS addition is particularly striking; within minutes of the late addition, it has reduced the difference in [TEMPO] between the FMPTS free polymerization and the early FMPTS addition by half. A total of 2−3 h more are required to match the nitroxide level and rate of the early addition polymerization, but it is achieved.

Influence of the Initiator. The influence of initiator in a FMPTS accelerated, TEMPO-mediated, styrene polymerization was briefly examined. As a comparison to benzoyl peroxide, 2,2′-azobis-(2-methylbutyronitrile) was used at the same 1.11 mmol level at 125 °C. As can be seen in Table 2, the choice of initiator does not make a large difference in the polymerization rate although early in the polymerization the azo initiator provides both higher conversion and higher molecular weight: an observation that is difficult to simultaneously rationalize on the basis of either a change in initiator efficiency or the more rapid decomposition of azo initiator. The peroxide generates a broader initial molecular weight distribution, but this is not unusual at these low conversions and molecular weights. The conversion data are also plotted in Figure 7, which is not altogether remarkable until one considers the TEMPO concentration data of Figure 8.

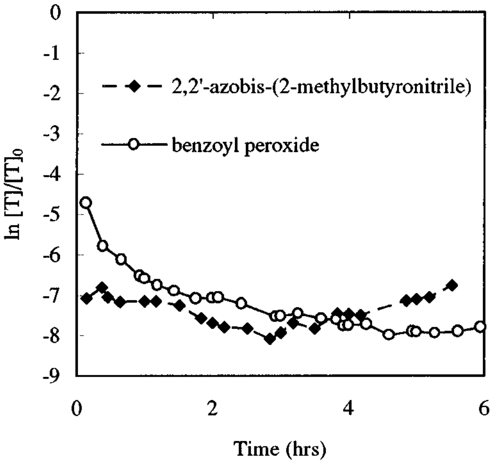

Figure 8. [TEMPO] decay with different initiators corresponding to the polymerizations in Figure 7. The lines shown are a guide to the eye only.

The TEMPO concentration in Figure 8 accounts for the attributes of both polymerizations. In the presence of an azo initiator the TEMPO concentration drops much more rapidly. The more rapid thermolysis of the azo initiator relative to the peroxide can account for some of the TEMPO consumption. As well, the lower M_n of the azo polymerization, 18K vs 28K for the BPO polymerization, at equivalent conversions (93% and 95% respectively) indicates that the azo initiator is more efficient. So the high efficiency and rapid decomposition of the azo initiator consume sufficiently more of the TEMPO to accelerate the rate. However, the gradual decay of TEMPO concentration does not appear to occur in the azo-initiated polymerization, the TEMPO concentration remains constant, perhaps even rising in the later stages of the polymerization.[10] In the BPO-initiated polymerization, the TEMPO concentration decays to a level below that of the azo polymerization. This accounts for how the BPO polymerization makes up lost ground and reaches an equivalent degree of conversion. FMPTS removal of TEMPO still appears to be the significant factor in determining the rate of polymerization, but the factors provided by the different initiators in determining how FMPTS affects the TEMPO consumption are not understood. The use of classical polymerization initiators, such as peroxy or azo compounds, can be avoided through the use of nontraditional initiating systems, such as benzylic nitroxides.[11] As Scaiano[12] and co-workers have pointed out, this approach still results in a population, or pool, of free nitroxide that controls the polymerization, even though these latter unimolecular systems have an initial 1:1 ratio of nitroxide to polymerizable radical and avoid the consideration of initiation and germination efficiencies. We have previously,[2] as does Scaiano,[12] remarked on the importance of considering the work of Beckwith, Bowry, and Ingold,[13] who investigated the influence of polar species on the reaction between nitroxides and other free radicals. These workers illustrated that the reaction is not simply diffusion controlled.

Quantitating the [TEMPO] Influence. The polymerization rate is accelerated by the disappearance of TEMPO and this can be included in the rate expression:

$$\frac{d[M]}{dt} = -k\frac{[M]}{[TEMPO]} \tag{1}$$

In Figure 2 the TEMPO decay was fitted to a curve,

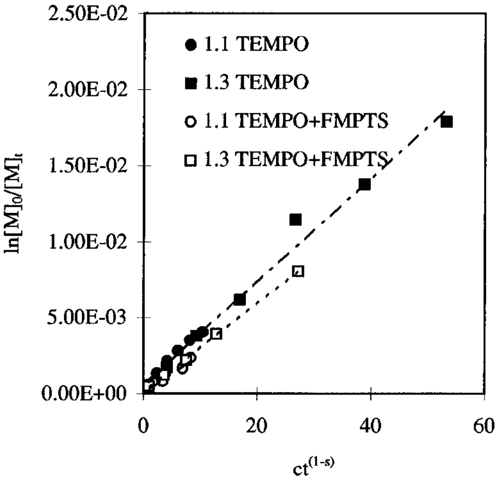

Figure 9. [TEMPO]-corrected polymerization rates with and without FMPTS at two ratios of TEMPO to BPO. The lines shown are best linear least-squares fits.

where b and s are constants, and s determined empirically to be about −1:

$$[TEMPO] = [TEMPO]_0\, bt^S \tag{2}$$

The TEMPO decay expression can be combined with the rate expression and rearranged:

$$\int\frac{d[M]}{[M]} = -k\int\frac{dt}{[TEMPO]_0\, bt^S} \tag{3}$$

Integration provides the expression

$$\ln\left\{\frac{[M]_0}{[M]_t}\right\} = kct^{(1-S)} \tag{4}$$

where

$$c = \left\{\frac{1}{b(1-S)[TEMPO]_0}\right\} \tag{5}$$

On the basis of this analysis, Figure 9 is a plot of

$$\ln\left\{\frac{[M]_0}{[M]_t}\right\} \text{ vs } ct^{(1-S)} \tag{6}$$

The x-axis in Figure 9 is a corrected time that accounts for variations in TEMPO concentration among the four polymerizations. Comparing this plot with the same data plotted without correcting for the variation in TEMPO level as shown by Figure 1, one easily sees how the free TEMPO accounts for the major differences in polymerization rates. Careful examination of the plot in Figure 9 will reveal that the FMPTS-containing polymerizations (open symbols), when considered independently of the FMPTS influence on TEMPO levels, appear to be slightly slower than the polymerizations without FMPTS (closed symbols). This apparently insignificant difference takes on more importance after one considers the following.

FMPTS Concentration. The influence of the FMPTS concentration on the rate of polymerization is a revealing feature of its mechanism. In Figure 10 the change of TEMPO concentration with polymerization time is once again plotted: the typical level of FMPTS along with twice and half that amount, respectively. These data appear to be reasonable since, as more FMPTS is

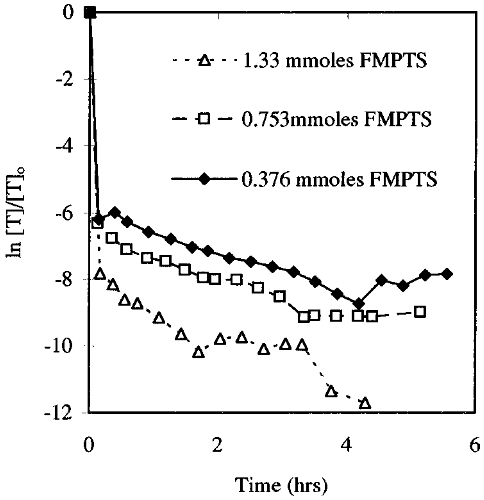

Figure 10. [TEMPO] decay at different FMPTS concentrations. Polymerizations were conducted at 120 °C and a molar ratio of TEMPO to BPO of 1.1:1. The lines shown are a guide to the eye only.

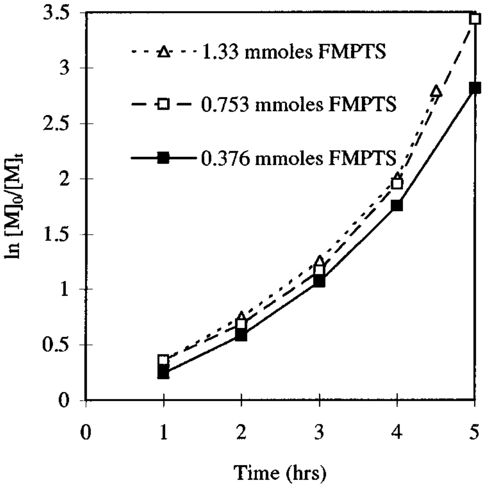

Figure 11. Change in polymerization rates with FMPTS concentration corresponding to the polymerizations of Figure 10. The lines shown are a guide to the eye only.

Table 3. Influence of FMPTS Level on Molecular Weight

	Half FMPTS		Normal FMPTS		Twice FMPTS	
time (h)	Mn	PD	Mn	PD	Mn	Pd
1	5472	1.85	8858	1.70	14229	2.91
2	11549	1.50	15995	1.40	17680	2.33
3	17022	1.42	20514	1.39	17686	2.06
4	22731	1.37	24621	1.39	26013	1.55
4.5					26533	1.62
5	25943	1.35	30213	1.31		

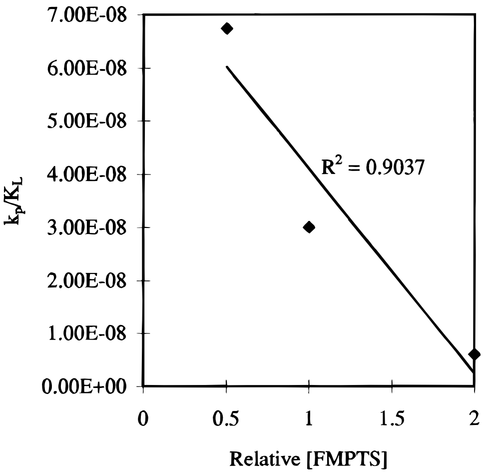

Figure 12. FMPTS concentration influence on the [TEMPO] corrected rate. The line shown is a best linear least-squares fit. The [TEMPO] corrected observed rate k_p/K_L represents the ratio of the exchange rate between capped and living chains (K_L) with the propagation rate k_p. More details of this derivation are provided in ref 2.

added, more TEMPO is removed from the polymerization medium. However, Figure 11 tells a different story in that there is very little difference in the observed polymerization rates at the three FMPTS levels. The rates of the 1 and 2× FMPTS polymerizations are virtually identical, while the half-normal FMPTS level is only slightly slower and within experimental error equivalent to the other two polymerizations. Consideration of the data in Table 3 is also important, for it points out the risk of having too little TEMPO in the polymerization. At first glance one might expect that if free TEMPO slows the polymerization, then once the newly initiated chains are captured, total elimination of the remaining TEMPO might be advantageous. The double FMPTS experiment in Figure 11 shows that very low levels of TEMPO are reached, yet the polydispersity data for this polymerization within Table 3 indicates that the impact of too little TEMPO is a broadening of the molecular weight distribution. Thus it would appear that a minimum level of TEMPO is required to maintain control over the polymerization.

Secondary Effect of FMPTS. Could FMPTS also have a negative impact on the polymerization rate? The double FMPTS experiment indicates that despite the low TEMPO level something keeps the rate of polymerization in check. Similarly, with half FMPTS levels and higher TEMPO concentration the polymerization rate is not as slow as one might expect. The same application of eq 6 to the polymerization data that led to Figure 9 can be made with these three polymerizations. This obtains the observed polymerization rates corrected for TEMPO concentration (the slope of the plot of $\ln([M]_0/[M]_t)$ vs $ct^{(1-S)}$) which in turn have been plotted against the relative FMPTS level as shown by Figure 12. This plot suggests that increasing FMPTS levels slows the polymerization. One mode of action could be the suppression of an autopolymerization component of the overall rate of conversion, as suppression of autopolymerization has been observed with FMPTS.[6] However camphorsulfonic acid (CSA) also reduces styrene autopolymerization,[14] yet it appears to enhance the polymerization rate after accounting for the change in nitroxide concentration.[3]

If we return to the data first presented in Figures 4 and 5, again correcting the rates for TEMPO concentration, and plotting against inverse temperature, there is a suggestion that FMPTS raises the activation energy of the polymerization. This analysis indicates a significant difference in activation energies: 154 kJ/mol with FMPTS vs 115 kJ/mol without FMPTS. These values suggest that the minor differences observed in the rates with and without FMPTS in Figure 9 could have an origin other than statistical variance. The mechanism, or even the mode of action, of what is termed the second effect of FMPTS is not known.

Conclusion

We have shown that the primary determinate of polymerization rate in the SFR polymerization of styrene is the post-initiation TEMPO level. A salt, 2-fluoromethylpyridinium toluenesulfonate, increases the polymerization rate by gradually consuming the free TEMPO after initiation. The polymerization attributes may also be affected by the initiator type, peroxide or azo compounds, long after they themselves have been consumed. Monitoring the polymerization by ESR, in addition to determining the molecular weights and conversions throughout the polymerization, is an important tool in elucidating mechanistic features. FMPTS also has a retarding secondary effect on the rate that is masked by its pronounced rate enhancement through TEMPO consumption. A minimum TEMPO level helps to preserve control over the polydispersity during the polymerization.

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