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Rate Enhancement of Living Free-Radical Polymerizations by an Organic Acid Salt

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The first publication[1] from this laboratory describing the polymerization of styrene in the presence of a nitroxide stable free radical (SFR) to provide polymers with narrow molecular weight distributions (MWD) required 69 h to achieve 90% conversion at 125 °C. Subsequently, the polymerization rate was improved by performing the reaction in the presence of a strong organic acid, camphorsulfonic acid (CSA).[2] CSA was initially employed as a means to reduce the autopolymerization of styrene,[3] which, as a competing reaction with the stable free-radical-mediated propagation, can lead to a broadening of the MWD. The role of benzoic acid, a byproduct in the promoted and thermal dissociation of benzoyl peroxide (BPO), in the SFR polymerization is described later[4] as an inhibitor of the styrene autopolymerization, but it does not dramatically enhance the rate of the SFR-mediated polymerization.

While we have made good progress in increasing the rate of the nitroxide-mediated living free-radical polymerization and in extending the scope of the polymerization to include copolymers,[5,6] we remained interested in exploring the scope of polymerization rate enhancement due to polar additives. In the course of this exploration, it was found that 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (FMPTS) provides faster rates of 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy, free radical (TEMPO) moderated polymerization than does CSA.

The polymerizations were conducted in mechanically stirred Morton flasks in a Neslab constant-temperature bath held at the set point to within ±0.1 °C. All the polymerizations employed 0.288 mol of styrene (Fluka) and 1.11 mmol of benzoyl peroxide (Aldrich), except where noted, and were conducted under argon. The rate-enhancing additive (CSA or FMPTS) was added after initiation is believed to be largely complete. With the exception of TEMPO, which was sublimed, all reagents were used as received. The conversion data were determined on a TA Instruments 2950 thermogravimetric analyzer by comparing the weight loss due to monomer vaporization below 260 °C to the decomposition of polymer above that temperature. The molecular weight data were determined by gel permeation chromatography (GPC) employing tetrahydrofuran as eluent at 0.8 mL min^{-1} through four Waters Ultrastryagel columns (100, 2 × 500, 400 Å) and a Waters 410 RI detector. Polydispersities (PDs) were taken as the ratio of M_w to M_n. The data analysis was accomplished on a Waters 860 system. Electron spin resonance (ESR) spectra were obtained using a Bruker ESP300 spectrometer and ER4111 variable-temperature accessory. Details of the ESR method were published previously.[7]

Figure 1 shows the relative rates of polymerization of styrene at 125 °C initiated by BPO in the presence of 1.47 mmol of TEMPO, with either (A) FMPTS (0.54 mmol), (B) CSA (0.54 mmol), or (C) in the absence of either acid or salt. The data demonstrate that the addition of a small amount of FMPTS to the polymerization provides substantially higher rates of conversion (particularly, at higher conversions) than CSA at the same concentration. Interestingly, the higher rate of conversion with FMPTS compared to CSA is achieved without significantly increasing the PD compared to the control without salt or acid or compared to CSA.

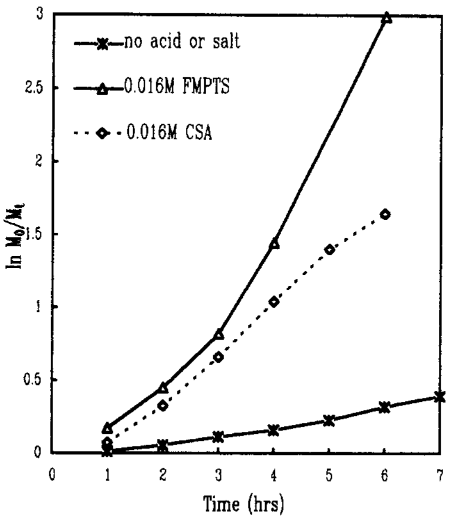

Figure 1. Semilogarithmic plot of M_0/M_t with polymerization time for bulk polymerization of styrene at 125 °C with a TEMPO/BPO ratio of 1.3 and FMPTS, CSA, or control without acid or salt.

While it is not within the scope of this communication to understand the mechanism by which FMPTS increases the rate of polymerization, a series of ESR experiments was performed to monitor whether the TEMPO is consumed by FMPTS and CSA.[6] Our current understanding[7] of the mechanism of the nitroxide-mediated polymerization suggests that the rate of polymerization will be inversely proportional to the TEMPO concentration. Samples of 0.020 M TEMPO in xylene with or without FMPTS (at the same 2.8:1 mole ratio of TEMPO:FMPTS used in the above polymerization) were shake in an ESR tube for about 5 min in the hot xylene to dissolve the FMPTS and then placed in the variable-temperature Dewar in the ESR cavity maintained at 135 °C. The concentration of TEMPO was determined from the ESR spectrum every 10 or 15 min measured over 2.5 h. TEMPO in xylene alone showed no decay within the limits of experimental error, while the TEMPO with FMPTS showed only a very slight decay in TEMPO concentration ([TEMPO]). The decay was first order in TEMPO, giving a linear semilogarithmic plot of ln([TEMPO]) with time (r^2 = 0.984 for 11 data points). The rate constant for the decay was (6.0 ± 0.6) × 10^{-6} s^{-1} (error is 95% confidence level). That is, at a concentration of 0.007 M FMPTS, only 3.2% of the total TEMPO is consumed in 1 h (the half-life is about 32 h). Addition of benzoic acid to the above reaction does not show any increase in rate of TEMPO consumption. The direct effect of FMPTS on TEMPO is not large enough to explain the dramatic effect of FMPTS on the rate of polymerization.

Previous ESR work[8] shows that TEMPO is consumed rapidly by CSA: even at 95 °C, the rate constant for TEMPO decay at 0.007 M CSA is about 2.4 × 10^{-3} s^{-1},

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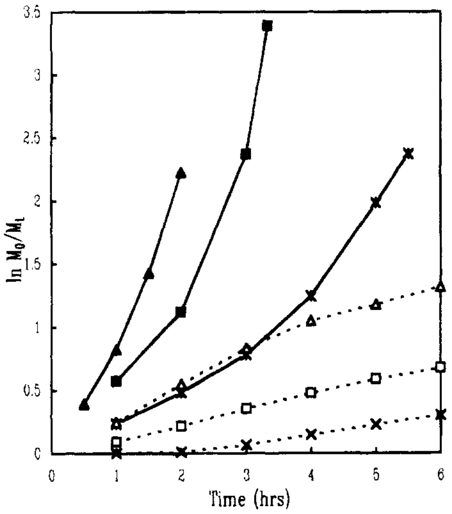

Figure 2. Semilogarithmic plot of M_0/M_t with polymerization time for bulk polymerization of styrene with a TEMPO/BPO ratio of 1.1 with 0.016 M FMPTS (solid lines) and without FMPTS (dotted lines) at 135 °C (triangles), 125 °C (squares), and 115 °C (×'s).

or a half-life of only 5 min, compared to 32 h for FMPTS. Unlike the consumption of TEMPO by FMPTS, it is clear that the consumption of TEMPO by CSA is fast enough to increase the rate of polymerization by this effect alone.

Subsequently, to take advantage of the longer lifetime of TEMPO in the presence of FMPTS, polymerizations were conducted with a lower TEMPO to BPO ratio; the molar ratio in the first set of experiments was 1.3:1.0, the following experiments used 1.25 mmol of TEMPO for a molar ratio to BPO of 1.1:1.0. The reduction of TEMPO in of itself should again lead to higher polymerization rates.[7] In Figure 2 the effect of temperature on the FMPTS polymerizations is explored in comparison to salt (and acid) free controls.

Lowering the TEMPO concentration and increasing the temperature do show the expected increase in rates. The higher PD with less TEMPO is expected, as more polymer chain coupling would be anticipated as the concentration of chain ends increases when the concentration of TEMPO decreases.[7] The influence of FMPTS concentration on the polymerization at 120 °C (Figure 3) is interesting in that on first glance the polymerization does not appear sensitive to FMPTS levels; however, there is a distinct broadening of the molecular weight distribution at the higher FMPTS level without an appreciable increase in polymerization rate. This higher PD is consistent with the observation made earlier with increasing levels of CSA.[2]

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 1, the choice of initiator does not make a large difference in the polymerization rate although initially 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 initially generates a broader initial molecular weight distribution, but we are not yet able to ascribe this to an initiator effect per se or the result of higher molecular weights and/or conversions coupled with a GPC artifact.

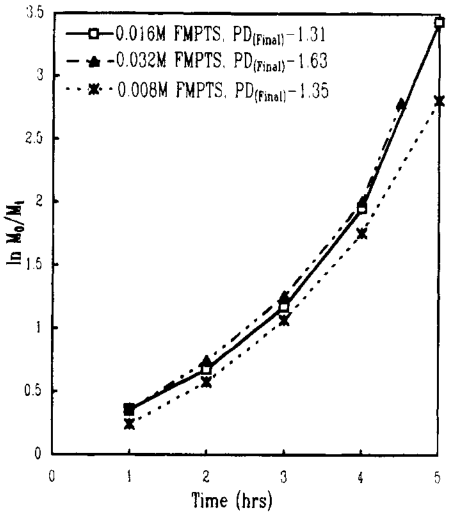

Figure 3. Semilogarithmic plot of M_0/M_t with polymerization time for bulk polymerization of styrene at 120 °C with a TEMPO/BPO ratio of 1.1 with varying FMPTS concentrations.

Table 1. Influence of Initiator Type on Molecular Weight Growth and Conversion during a SFR Polymerization of Styrene in the Presence of FMPTS

time (min)	2,2′-azobis(2-methylbutyronitrile)			benzoyl peroxide		
	M_n	PD	conv (%)	M_n	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

In summary, the addition of small amounts of FMPTS to a SFR-mediated polymerization provides an increase in polymerization rate over that of CSA. The apparent consumption of TEMPO by FMPTS is less than that of CSA. The mechanistic role of FMPTS in the polymerization is not understood and work is in progress to elucidate it.

Supporting Information Available: GPC molecular weight data with respect to time of the polymerizations in four tables (4 pages). Ordering information is given on any current masthead page.

References and Notes

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(6) The potential for the rate enhancement to be the result of an impurity in the FMPTS cannot be entirely discounted; however, we have measured the polymerization rate of the

likely acidic impurity, toluenesulfonic acid, under stable free-radical polymerization conditions at 125 °C and found its observed rate to be about 60% of that of CSA. Thus it is not likely that a small portion of TSA accounts for the rate enhancement. The Aldrich catalog states the impurity in FMPTS as up to 5% 2-hydroxy-1-methylpyridinium *p*-toluenesulfonate. The effect of this compound alone has not been investigated, but the very low effective concentration of any impurity should be noted.

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