# Polymerization Control Through the Free-Radical Retrograde-Precipitation Polymerization Process

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ABSTRACT: In this article, we present results of our work in a novel polymerization process [called the free-radical retrograde-precipitation polymerization (or FRRPP) process] that occurs at temperatures above the lower critical solution temperature. In this process, conversion-time plots for styrene polymerization in ether show autoacceleration at the beginning, followed by a relatively long period of reduced conversion rate starting at conversions as low as 30% and at operating temperatures way below the glass transition of the reacting system. Molecular weight and polydispersity index data also indicate early autoacceleration (in the form of overshoots in these values), whereas the latter period of slow conversion rate is accompanied by stable levels of molecular weight and polydispersity index. Polymer radical concentration measurements show an initial sharp rise, followed by an asymptotic value, even after almost all the initiator molecules have already decomposed into radicals. With end-group analyses of product polystyrene and polymer radical data, we calculate a proportion of live polymeric radicals to asymptote at levels of 80-84% of all polymeric species, even after almost all initiator molecules have already decomposed into radicals. All the data presented herein verify the postulate of a controlled polymerization mechanism for the FRRPP process. Our results have become the basis for an *anti-gel effect phenomenon* that is derived from prior theoretical and experimental observations, in which phenomenological diffusivities vanish at the spinodal curve of the phase envelope. The universality of this behavior in FRRPP systems is manifested from similar observations in styrene polymerization in acetone and methacrylic acid polymerization in water. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 761-774, 1999

# **INTRODUCTION**

Within the past several years, we have been studying the physicochemical and product material aspects of free-radical precipitation polymerization reaction systems, wherein phase separation occurs above the lower critical solution temperature (LCST).<sup>1</sup> In contrast with the conventional precipitation polymerization process<sup>2–4</sup> that involves phase separation below the upper critical solution temperature, we call this new process a free-radical retrograde-precipitation polymerization (FRRPP) process (Fig. 1). The added complication of retrograde precipitation could be offset by tighter control of reactor operating conditions and polymer molecular properties. Also, the relatively low operating pressures typically needed are not of great economic disadvantage, inasmuch as commercial implemen-

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Polymer concentration

**Figure 1** Binary phase diagram for a typical amorphous polymer-solvent system showing phase curves for conventional [temperature below the upper critical solution temperature (UCST)] and retrograde (temperature above the LCST) precipitation processes. Retrograde precipitation would involve going from point A to B.

tation can be affected using typical commercial autoclave polymerization reactors. In fact, this work includes a system that has been shown to undergo retrograde precipitation polymerization in an atmospheric reactor system.

From an earlier work,<sup>1</sup> we proposed the following features of the FRRPP process:

- 1. Gradual increase of conversion *vs.* time, even under gel effect conditions
- 2. Local heating around the radical site
- 3. Reduced rate of propagation, as well as the rate of radical-radical termination
- 4. Relatively narrow molecular weight distributions
- 5. The existence of live radicals that could be exploited for production of block copolymers.

In an experiment involving a polystyrene(PS)styrene-ether system, we were able to observe indirectly the possible occurrence of hot regions in the reactor fluid. Also, the product polymer had a narrow molecular weight distribution. A second experiment involving the PS-styrene-acetone system showed that, at the beginning of the polymerization process, there was an accumulation of polymer with almost the same molecular weight and the same polydispersity index of 1.4. In another experiment involving the same PS-styreneacetone system, an increase in average molecular weight was observed long after almost all the initiator molecules have decomposed. Also, the results suggested a gradual increase in conversion vs. time. Finally, an experiment was conducted to make a block copolymer (which was believed to contain methyl methacrylate-butyl acrylate-methyl methacrylate triblock copolymer due to existence of rubbery plateau in a dynamic mechanical analyzer) through the sequential addition of monomers.

In this article, we present results that indicate that the FRRPP process involves polymerization control based on vanishing component diffusivities and high concentrations of trapped live polymer radicals. Such control over the polymerization rate is oppposite to what has been normally observed under gel effect conditions<sup>5</sup>; thus, we call the unique physicochemical mechanism of the FRRPP process an *anti-gel effect phenomenon*.

### THEORY

#### **Free-Radical Chain Polymerization**

Conventional free-radical chain polymerization kinetics has been known to occur with the following mechanism<sup>6</sup>:

Initiation by thermolysis of species, I

$$I \xrightarrow{k_d} 2R^{\bullet} + G \uparrow$$
$$R^{\bullet} + M \to P_1^{\bullet}$$
$$2R^{\bullet} \to R - R$$

where either the desired primary radical  $P_1^{\bullet}$  or the undesired initiator fragment R - R are formed. The gaseous species, G, is either nitrogen (if I is an azo initiator) or carbon dioxide (if I is a peroxide).

Propagation

$$P_k^{\bullet} + M \xrightarrow{k_p} P_{k+1}^{\bullet}$$

Chain Transfer

$$P_j^{\bullet} + XA \rightarrow P_{j-} - X + A^{\bullet}$$

where *XA* is either a chain transfer agent, solvent, polymer, initiator, or monomer. Termination

$$P_{n}^{\bullet} + P_{m}^{\bullet} \xrightarrow{k_{lc}} P_{n+m}$$

$$P_{n}^{\bullet} + P_{m}^{\bullet} \xrightarrow{k_{ld}} p_{n}^{-} + P_{m}^{\bullet}$$

The rate of consumption of the monomer, M, is considered to be primarily due to the propagation reaction. Thus,

$$\frac{d[M]}{dt} = -k_p[P_k^{\bullet}][M] \tag{1}$$

From the quasi-steady-state approximation (QSSA), the rate of primary radical generation from the initiator equals the rate of radical termination. If we assume the absence of chain transfer reactions, quasi-stead-state approximation and eq. (1) result in

$$\frac{d[M]}{dt} = -K(t)[M] \tag{2}$$

where

$$K(t) = k_p \left(\frac{f}{k_t}\right)^{1/2} (k_d[l])^{1/2}$$
(3)

During the gel effect condition, a dramatic increase in K(t) is observed due to the drop in  $k_t$  by orders of magnitude, compared with the drop in  $k_p$  and [I]. Note that [I] can be obtained from the first-order decomposition of the initiator

$$[I] = [I]_o \exp(-k_d t) \tag{4}$$

#### **Phase Separation Thermodynamics and Kinetics**

For two liquid phases in equilibrium, concentrations of coexisting phases (superscripts "and") obey the following relationship<sup>7</sup>



**Figure 2** Ternary phase diagram for amorphous polymer-solvent-nonsolvent system at constant temperature showing the positions of both the binodal and spinodal curves. Both equilateral (a) and right triangular (b) diagrams are shown.

$$\mu_i' = \mu_i'' \tag{5}$$

where  $\mu_i$  is the chemical potential of component *i*. The loci of the phases in equilibrium (polymerrich and polymer-lean phases) at a particular temperature constitute the binodal curve. The spinodal curve can be obtained from

$$\det\left[\frac{\partial\mu_i}{\partial\phi_j}\right]_{n-1} = 0 \tag{6}$$

where  $\phi_j$  is the volume fraction of component *j*. The order of the determinant in eq. (6) is n - 1, where *n* is the total number of components. Figure 2 shows the relative position of the spinodal curve in the phase envelope for a ternary system that applies to an amorphous polymer-solventnonsolvent system.

When a homogeneous solution is brought to a concentration inside the spinodal curve, it will not be stable to any fluctuation however small in amplitude. The solution undergoes a spontaneous transformation called spinodal decomposition, where the new phases are formed by a continuous flux of like molecules or polymer segments against the direction of concentration gradient (uphill diffusion). This has been shown to imply a negative diffusivity for a binary system. Outside the spinodal curve, phenomenological diffusivities have been shown to be positive, in which material fluxes follow the direction of concentration gradient (downhill diffusion).<sup>8</sup> It is therefore not suprising that eq. (6) results in vanishing mutual diffusivity for a binary system. For a ternary system, it was also theoretically shown that phenomenological diffusivities vanish for all the components.<sup>9</sup> These results imply that a general multicomponent system will have all phenomenological diffusivities vanishing at the spinodal curve.

Vanishing diffusivities along the spinodal curve was invoked in explaining data on sorption of cyclohexanol in PS, wherein very little weight change was detected at increasing penetrant activity.<sup>10</sup> In this work, we will use the same concept as part of the explanation for the control of propagation rate in the FRRPP process.

# **EXPERIMENTAL**

### **Materials and Preparation Procedures**

Styrene and methacrylic acid (MAA) monomers were purchased from Aldrich Chemicals (Milwaukee, WI), and they contain the usual amounts of inhibitors. For phase equilibria studies, these inhibitor-laden monomers were used as is. However, for polymerization studies, they were purified with a double distillation technique under reduced pressure. Analytical grade-mixed xylenes was purchased from Aldrich Chemicals, and used as received. Water used in the experiments was double-distilled, whereas analytical grade ether, acetone, and isopropanol were purchased from Fisher Scientific (Pittsburgh, PA), and used as is. Sorbitan monolaurate (Span 20), used as surfactant, was obtained from Aldrich Chemicals without further purification. Initiators, 2,2'-azobis(2amidinopropane) dihydrochloride (V-50) and 4,4"-

azobis (4-cyanopentanoic acid) (V-501) were obtained from Wako Chemical Co. (Osaka, Japan). They were used without further purification. Primary standard PS used for phase equilibria studies was purchased from Pressure Chemical Co.

# Phase Equilibria of Polymer-Monomer-Solvent Systems above the LCST

In this section, the experimental procedure for the determination of the ternary phase envelope will be described for the styrene-PS-ether system. The same procedure and apparatus have been used in the MAA-poly(MAA)-water system.

Ternary phase envelopes were determined with specially designed apparatus. The mixture was contained in a heavy-walled tube with the outer diameter of 2.54 cm and an effective length of 20.32 cm. The tube had a tailored Teflon® stopper through which a channel with different diameters in different sections was cut to fit the requirement of a silicone rubber seal. A needle of precision syringe could penetrate the silicone rubber seal without breaking the sealing of the tube (Fig. 3). The air in the tube was taken out by vacuum before the experiment, and the tube was mounted in the water bath with different temperature to determine the volume needed for filling the vacuum tube with ether. Then, preweighed polymer was transferred into the tube. A small Teflon<sup>®</sup>-coated magnetic stirrer was put into the tube for stirring. The tube was capped with the specially designed Teflon® stopper and then subjected to vacuum. A clear water bath with magnetic stirrer was maintained within  $\pm 0.1$  °C of the required temperature. A syringe pump full of styrene or ether was used to meter fluids accurately that were introduced inside the tube. A He-Ne laser beside the bath was installed to facilitate the determination of the endpoint. The fluids (monomer or solvent) could be added from the precision air-tight syringe into the tube to change the compositions of the mixture. The cloudpoint curve (CPC) was determined by adding monomer to the point of clarity of the turbid solution. This is facilitated by visual comparison of the laser beam passing the working fluid, with the aid of a black screen behind the tube. In practice, a black ruler with fine scales behind the tube was preferred. For a high concentration of the polymer sample, CPC was determined by adding solvent to the blur point or adding monomer to the phaseseparated system to the point where the solution



**Figure 3** Set up of the high-pressure tube used for the determination of ternary binodal curves containing the working sample and showing the laser beam passing through the tube.

became clear again. After every addition of a small amount of fluid, enough time was allowed to reach equilibrium. The accuracy of the air-tight precision syringe was  $\pm 0.01$  mL with one drop of the liquid of  $\sim 0.002$  mL. This procedure of determining the CPC is depicted in the trajectories in a ternary phase diagram (Fig. 4).

After CPCs were obtained, tie lines were determined by sampling for polymer compositions of the polymer-rich and polymer-lean phases.

### **Polymerization Experiments**

### **Polymerization of Styrene**

Styrene polymerizations took place at temperatures above the boiling point of the solvents, and a high-pressure reactor is used. The set up is a 300-mL mantle-heated high pressure reactor vessel [purchased from Parr Instruments, Inc. (Moline, IL)], and two high-pressure metering pumps [purchased from Fluid Metering, Inc. (Oyster Bay, NY)].<sup>1</sup> The range of recipes for polymerization of styrene in ether and acetone is given in Table I. Half of nitrogen-bubbled solvent was charged into the reactor first, and the temperature was ramped to 80°C in 30 min. The reactor was then pressurized to 70 psig with the nitrogen



**Figure 4** Types of trajectories followed by the composition scan system for determination of binodal curves. A-B-C-D-E-F-G-..., is the possible routine to generate the phase envelope. The curve that connects the points (such as C1, C2, ...), where the system becomes clear from turbid, or the curve that connects the points (P1, P2, ...), where the system becomes turbid from homogeneous solution is the CPC. The former is used for all of the systems.

gas before the rest of the nitrogen-bubbled reactant mixture was pumped into the reactor in  $\sim 2$ min. Samples were withdrawn at known times, cooled with dry ice, and purged with air to stop further polymerization reaction. Samples were then dried to constant weight for computation of conversion. Dried samples used for further analysis were purified by dissolving in toluene and washing with water to get rid of residual initiator fragments.

### Polymerization of MAA

The reactor used for the polymerization is a 2-L steam-jacketed glass reactor (purchased from ACE Glass Inc.) equipped with temperature con-

Table I	Range	of Starting	Compositions
for Styre	ene Poly	ymerization	

Chemicals	Amount	
Styrene	15–40 mL	
Ethyl ether (or acetone)	65–120 mL	
V-501	0.1–0.684 g	

Chemical	Amount	
MAA	12 mL	
Distilled water	120  mL	
V-50 initiator	0.06 g	
Mixed xylenes	225  mL	
Sorbitan monolaurate		
surfactant (Span 20)	17.25 g	

Table IITypical Recipe for Polymerizationof MAA through the FRRPP Process

troller, sampling system, and stirring motor as described elsewhere.<sup>11</sup>

Because poly(MAA) is an intractable gel when it phase separates, polymerization was accomplished by suspending MAA-water-initiator in mixed xylenes. Table II gives a typical recipe used. Liquid reactant components were bubbled with nitrogen gas for  $\sim 15$  min before they were used in the experiment. Mixed xylenes was first loaded into the reactor with surfactant and raised to the reaction temperature. Then, monomer and initiator were loaded in. Polymerization took place at 90°C under a nitrogen gas blanket. Samples were taken at different times, placed into an ice bath to quench the reaction, and exposed to air to stabilize the free radicals.

The liquid samples taken from the reactor were dried to constant weight. The dried material was ground in a mortar and pestle and washed with analytical grade isopropyl alcohol five to six times to extract the surfactant and unreacted monomer. The insolubility of poly(MAA) in isopropyl alcohol was reported,<sup>12</sup> and the solubility of the surfactant and monomer was verified experimentally. Washed samples were dried and used in subsequent molecular weight analysis.

#### Size Exclusion Chromatography

The molecular weights of the dried polymer samples from the reactor fluid were measured using a size exclusion chromatograph. The chromatography system has refractive index and multiangle light scattering detectors (Wyatt Technologies, Inc., Santa Barbara, CA). Thus, measured molecular weights were absolute, and there was no need to calibrate molecular weights after injecting a few samples. For the analysis of poly(MAA) samples, we used a glucose BR<sup>TM</sup> mixed bed column (Jordi Associates) with a molecular weight range of 10 g mol<sup>-1</sup> to 10 million g mol<sup>-1</sup>, and our carrier fluid was 80/20 v/v 0.1 NaOH solution/

dimethylsulfoxide mixture from high-pressure liquid chromatography grade materials. For the analysis of PS samples, we used a silica column (Supelco, Inc., Bellefonte, PA; LC-1 Supelcosil column) with high-pressure liquid chromatography grade toluene as carrier fluid.

# Polymer Radical Measurements and End-Group Analysis

### Spectrophotometric Analysis of PS Radicals

A spectrophotometer, Spec 20D (from Milton Roy, Inc.), was used for the determination of radical concentrations of PS samples produced through the FRRPP process in both ether and acetone. A 1-mL DPPH/toluene solution of concentration  $5.16 \times 10^{-6}$  mol mL<sup>-1</sup> was used to react with 1-mL PS samples in ether and acetone. Changes in transmitted light intensities (at 412 nm) were recorded as a function of time. Two regimes were observed: fast reaction regime and slow reaction regime (as illustrated in Fig. 5). Only the slow reaction regime was considered, inasmuch as the fast reaction regime is believed to be due to the reaction of DPPH with distinct low molecular weight polystyrene ( $\sim 1,000 \text{ g mol}^{-1}$  and < 5 wt %in the final solid product). Such low molecular weight species is pressumed to be due to thermal polymerization of styrene. Radical concentrations were then calculated from the light intensity differences using a calibration curve.

### End-Group Analysis of PS in Reactor

The purified PS samples were dissolved in chloroform. Then, the carboxylic end-groups of the PS



**Figure 5** Spectrophotometer intensity *vs.* time for the determination of concentration of PS radicals from the FRRPP system.

sample were titrated with 0.02N NaOH/ethanol solution using 0.5% phenolphthalein-ethanol solution (color changes from colorless to pink at pH > 8) at room temperature. The NaOH/ethanol solution was standardized with predried potassium acid phthalate. The carboxylic group concentrations were calculated from the amount of NaOH/ethanol solutions used.

A Mattson FT-IR (Galaxy-3000) was used to measure the amount of C=O and C-O groups in PS samples prepared from acetone and ether, and their characteristic peaks of 1711 cm<sup>-1</sup> and 1120 cm<sup>-1</sup> were chosen, respectively. The purified PS powder samples were mixed with KBr crystal powder, pressed into transparent thin films, and placed into the FT-IR machine for spectrum scan. Calibration lines were constructed by measuring spectra of standard PS/adipic acid and standard PS/n-butyl ether mixtures at different levels.

### *Electron Spin Resonance (ESR) for MAA Polymerization*

A Varian ESR spectrometer (model E-104B) was used to follow the free radical production/retention of polymerization processes. The spectrometer was coupled with a variable temperature Dewar flask to control the reaction temperature. The ESR signal was recorded and stored in a microcomputer. The resonant peaks were then doubledintegrated using Excel software and computed for the radical concentrations. Because water has a very high dielectric constant, it interferes with the ESR signal. So, to measure the polymer radical concentration of the MAA-water polymerization system, two approaches were taken: use of dry samples and low measuring temperatures. Dried samples were prepared in such a way that samples were taken out from the reactor at designed times, quenched into dry ice, then freezedried under vacuum. The powder polymer samples were then transferred into an ESR tube under a nitrogen blanket and flame-sealed. Samples for low temperature measurements were prepared in the same way as in situ polymerization samples, but the sample tubes were polymerized in a water bath and taken out at different reaction times. Then, they were quenched in liquid nitrogen before the spectrum scans were taken at −120°C.

Double-integrated ESR signals were calibrated using stable radical DPPH/toluene solutions of different concentrations. ESR signals for calibration were taken at room temperature.



**Figure 6** Ternary phase diagram for PS-styreneether system at 50° and 80°C, showing binodal curves and tie lines at 80°C and number average molecular weight of 400,000 g mol<sup>-1</sup>. All polymer samples used have polydispersity indices of 1.06 or less.

### RESULTS

# Phase Equilibria of Polymer-Monomer-Solvent Systems above the LCST

Figure 6 shows the ternary phase diagram for PS-styrene-ether system. The plot shows that the PS-styrene binary pair is homogeneous at all compositions. Also, PS phase separates in pure ether. As expected, the phase envelope is larger at 80°C, compared with that at 50°C. The shape of the phase envelope is a type 1 for ternary polymer systems, wherein the polymer dissolves in the monomer, and ether can only partially dissolve the polymer.<sup>13</sup>

Figure 7 shows the ternary phase diagram for poly(MAA)-MAA-water system. The behavior for this system is similar to that of the PS-styreneether system (Fig. 6), except for distortions in the shape of the phase curves. One of these deviations involves the formation of a polymer-rich phase as MAA is added to a dilute solution of poly(MAA) in water. The other is the formation of a LCST for the water-MAA binary pair between 80° and 90°C.

## **Polymerization of Styrene**

Figure 8 shows the conversion-time data for the batch reactor polymerization of styrene in ether



**Figure 7** Ternary phase diagram of the poly-(MAA)[PMAA]-MAA-water system showing binodal curves at 80° and 90°C and tie lines at 90°C.

and acetone both at 80°C. At this temperature, phase equilibria measurement (Fig. 6) suggests that the ether system is going to show phase separation at low conversions. On the other hand, we know that the LCST of PS in acetone is at  $67^{\circ}$ C.<sup>14</sup> We note that the half-life of the V-501 initiator used in the ether system is ~ 130 min.<sup>15</sup> Herein, we observe a sharp rise in conversion at the beginning, followed by a period of reduced



**Figure 8** Conversion-time plot for polymerization of styrene (st) in ether and acetone at 80°C. Starting reactor compositions are: 14 g/81 g/0.222 g for styrene/ ether/V-501 and 36 g/71 g/0.684 g for styrene/acetone/ AIBN.



**Figure 9** Number-average molecular weight (mw) for the ether-based FRRPP system at 80°C. Starting reactor composition is the same as in Figure 8.

conversion rate. The onset of reduced conversion rate for ether- and acetone-based systems occur at  $\sim 30\%$  and 65%, respectively. Corresponding values of the number-average molecular weight (Fig. 9), as well as polydispersity index (Fig. 10) for the ether system, show sharp rises at the initial autoacceleration period. When conversion-time data showed reduced conversion rate, molecular weight and polydispersity data showed stable values. What is remarkable is the overshoot between the initial autoacceleration period and reduced conversion rate period, particularly that the polydispersity index stabilized at 1.7–1.8 levels.

### **Polymerization of MAA**

Figure 11 shows the conversion-time data for batch reactor polymerization of MAA at 90°C. It is



**Figure 10** Polydispersity index (PDI) for the etherbased FRRPP system at 80°C. Starting reactor composition is the same as in Figure 8.



**Figure 11** Conversion-time plot for polymerization of MAA at 90°C. Starting reactor compositions are given in Table II.

worth noting herein that the half-life of the V-50 initiator used is 9 min.<sup>15</sup> Again, there is an initial autoacceleration period, followed by a reduced conversion rate at 70% conversion. In terms of molecular weights (Fig. 12), the system first goes into a maximum at  $\sim 140,000$  g mol<sup>-1</sup>, before it goes into an asymptote at  $\sim 120,000$  g mol<sup>-1</sup>. In Figure 13, the polydispersity index goes into a maximum at a value of 2.0 before it drops to an asymptotic value of  $\sim 1.3$ . It is worth noting that the maximum in polydispersity index is coincident with the rise of the molecular weight toward its maximum value (Fig. 12), and right between the initial autoacceleration period and reduced conversion rate period. In a previous work,<sup>11</sup> the maximum in polydispersity with conversion did not show a maximum, probably because the ini-



**Figure 12** Number average molecular weight *vs.* time for batch polymerization of MAA at 90°C. Starting reactor compositions are given in Table II.



**Figure 13** Polydispersity index *vs.* time for the batch polymerization of MAA at 90°C. Starting reactor compositions are given in Table II.

tiator was added into the reactor containing monomer already. In this work, monomer that is added with initiator would polymerize at a relatively high monomer concentration at the start. This results in broadening of the molecular weight distribution. When the components are uniformly mixed in the system, better control over the molecular weight distribution is obtained, as seen from the leveling off of the polydispersity index at 1.3. The leveling off of the polydispersity index at 1.3 (Fig. 13) is also coincident with the asymptote of the molecular weight at 120,000 g mol<sup>-1</sup>.

### **PS Radical and End-Group Measurements**

Figure 14 shows the evolution of radical concentration for the polymerization of styrene in ether



**Figure 14** Evolution of radical concentration for polymerization of styrene (st) in ether and acetone at 80°C. Starting reaction compositions are the same as in Figure 8.



**Figure 15** Radical evolution data (xylene-free basis) for polymerization of MAA in water at 90°C. Starting reaction composition for both systems is given in Table II.

and acetone under FRRPP conditions. Again, radical concentrations go into a sharp rise and end with stable values. Also, there are overshoots in radical concentrations between these two time regimes. For the MAA system (Fig. 15), a similar behavior was observed with a less pronounced overshoot.

Figure 16 shows evolution of [COOH], [C=O], and [C-O] species in PS samples that were polymerized using carboxy-functional V-501 initiator, and acetone and ether as solvents. Note that, for the PS samples made with ether [Fig. 16(a)], the near coincidence of the [COOH] and [C=O] readings indicates that indeed C=O is in the COOH group. For the acetone system [Fig. 16(b)], the C=O group detected indicates substantial chain transfer to acetone. For the PS samples made with ether, very low [C-O] readings imply that there is practically no chain transfer to ether.

### DISCUSSION

As seen from our phase equilibria and polymerization results, the entry of the FRRPP system into the phase envelope can be linked with the reduction in conversion rate. From conversiontime data alone, it is evident that the FRRPP system has very good reaction control after the onset of phase separation, even though it goes into autoacceleration at the beginning of the reaction.

The overshoot in number-average molecular weight (Figs. 9 and 12) and polydispersity index

(Figs. 10 and 13) at low conversions seems to be unique for the FRRPP system, so are their subsequent drop to almost constant values. In bulk and solution polymerization systems, sharp rises in number-average molecular weight and polydispersity index occur as a consequence of the gel effect.<sup>5</sup> Before the gel effect, bulk and solution systems closely follow the quasi-steady-state approximation,<sup>6</sup> whereby the rate of formation of radicals from decomposition of initiator molecules is almost balanced by the rate of termination. In the FRRPP system, deviations from this approximation are already observed, even at low conversions. Because phase separation might have already been occurring, then the propagating radicals could actually be within high polymer concentration domains. This means that these



**Figure 16** Evolution of [COOH], [C=O], and [C-O] for the polymerization of styrene in (a) ether and (b) acetone at 80°C. Starting reaction composition is the same as in Figure 8.



**Figure 17** Temperature-ternary composition diagram showing the proposed reaction pathway OABC, in which the BC segment occurs due to local heating. The solid curve is the binodal or CPC, whereas the dashed curve is the spinodal curve. Segment AB is the tie line. Segment OA occurs because it normally takes the system to reach the spinodal curve before phase separation takes place spontaneously. The segment OAB is in the SMP plane, whereas the segment O'A'B'C' is in the base plane. Segment BC is vertical.

domains could be at their gel effect condition. However, in the FRRPP systems, the end of the sharp rise in conversion-time data does not coincide with the glass effect. In the PS-styrene-ether system, the polymer-rich phase can be conservatively taken to contain  $\sim$  47 wt % PS, 5 wt % styrene with the rest as ether (Fig. 6). This corresponds to a glass transition temperature of  $-52^{\circ}$ C, which is well below that of the operating temperature of 80°C. In the poly(MAA)-MAA-water system, this occurs at 60-70% conversion (Fig. 11). Taking 16 wt % polymer and 5 wt % monomer for the polymer-rich phase at the operating temperature of 90°C (from Fig. 7), the Fox Equation<sup>16</sup> results in an overall  $T_g$  of 18°C. In the calculations,  $T_g$  or  $T_m$  values are 160°C for poly-(MAA),<sup>17</sup> 100°C for PS,<sup>16</sup> 16°C for MAA,<sup>18</sup> –31°C for styrene,  $^{18}$  –116°C for ether,  $^{18}$  –95°C for acetone,<sup>18</sup> and 0°C for water.<sup>18</sup>

If we allow for the possibility that the polymerrich domains are at a higher temperature (because direct measurements of higher temperatures and vapor pressures from the reactor have been reported in the past<sup>1</sup>), then phase behavior could force it into a high polymer concentration. This can explain the reduction of the termination rate coefficient, but not the propagation rate coefficient. However, it is well-known that adjacent to the boundary of the phase envelope for liquidliquid phase separation in amorphous systems is the spinodal curve.<sup>7</sup> In this case, polymer-rich domains that are originally in the phase boundary will be driven toward the spinodal curve by local heating (Fig. 17). This is in agreement with the fact that a very small phase envelope (Fig. 6) would have been seen at the operating temperature of 80°C for the PS-styrene-ether system with a PS molecular weight of  $5.000-11,000 \text{ g mol}^{-1}$ (Fig. 9); with higher temperatures than the operating bulk fluid temperature, a bigger phase envelope would in fact be in existence in the vicinity of the polymer radical sites. The seemingly smaller phase envelope for the reactive system was also observed in the poly(MAA)-MAA-water system,<sup>19</sup> which is again consistent with local heating from polymer radical sites. From past modeling<sup>8</sup> and experimental<sup>10</sup> work in binary polymer systems, we found that a system in the spinodal curve has a vanishing mutual diffusivity. In a ternary system (such as what we have in our polymerization systems), Cahn and Murrell<sup>9</sup> showed that phenomenological diffusivities of all the components vanish at the spinodal curve. Thus, whereas there is ample Brownian motion of the various small molecules and polymer seg-



**Figure 18** Plot of  $k_p (f/k_t)^{1/2}$  vs. conversion for the styrene-PS-ether FRRPP system at 80°C showing the drop in ordinate values during the period when the system exhibited a decrease in conversion rate starting at 25% conversion.



**Figure 19** Plot of  $k_p (f/k_t)^{1/2}$  vs. conversion for the MAA-poly(MAA)-water FRRPP system at 90°C showing the drop in ordinate values during the period when the system exhibited a decrease in conversion rate starting. The condition involving use of one-half the surfactant is based on the proportion of Span 20 shown in Table II.

ments, radical sites that are starved of the monomer cannot propagate much further because monomer molecules do not move away from their high concentration regions. The result is a reduction of the propagation rate coefficient. In Figure 18, the plot of  $k_p (f/k_t)^{1/2}$  vs. conversion shows the extent of the reduction of the propagation rate coefficient, compared with the termination rate coefficient for the ether-based system. This is made even more convincing by the fact that, when we obtained the initiator efficiency, f, from molecular weight data, we found that the trend in Figure 18 remains unchanged (with values of f between 0.9 and 0.5 up to 35% conversion). Figure 18 can be compared with the result of an ordinate value of 0.025 for the AIBN-initiated polymerization of styrene, based on the classical theory of chain polymerization kinetics.<sup>20</sup> The calculation procedure for ordinate values is based on the use of eqs. (3) and (4) to our conversion data. In the slowdown period starting at 25% conversion, the drop in ordinate values is another way of looking into the effect of vanishing mass fluxes in the system. Because it happens to be the opposite of the rise in ordinate values for a gel effect situation, we call the physicochemical mechanism of our work an anti-gel effect phenomenon. Similar calculations for acetone-based styrene and the water-based MAA reaction systems all result in a similar drop of ordinate values as in Figure 18 (Figs. 19 and 20).

Another important consequence of the previously described anti-gel effect mechanism is the effectiveness at which it can trap live polymer radicals. This is seen as a stable value of the radical concentration after the onset of phase separation (Figs. 14 and 15). To determine the amount of polymer radicals compared with dead polymer species, we used the results of end-group analyses of carboxylic acid from the initiator, carbonyl group from the carboxylic end group of the initiator and from acetone by chain transfer, and the C—O bond from the ether group by chain transfer. Essentially, we have the following possible product polymer species after all initiator fragments have already been removed:

[A]:	HOOC	$\mathbf{PS}$	COOH
[ <i>B</i> •]:	HOOC	$\mathbf{PS}$	Radical
[C]:	HOOC	$\mathbf{PS}$	Solvent
$[D^{\bullet}]$ :	Solvent	$\mathbf{PS}$	Radical
[E]:	Solvent	$\mathbf{PS}$	Solvent

If there is no chain transfer, then a unique functional group in the solvent will not be detected by subsequent infrared spectroscopy of the polymer materials. In general, the total polymer radical concentration,  $[P^{\bullet}]$ , would be

$$[P^{\bullet}] = [B^{\bullet}] + [D^{\bullet}] \tag{7}$$

To determine the fraction of live polymer radical relative to all polymer species, X, we could look into the following two cases. Case I. No Chain Transfer (i.e.,  $[C] = [D^{\bullet}] = [E] = 0$ )

$$X = \frac{[P^{\bullet}]}{[A] + [B^{\bullet}]} \tag{8}$$



**Figure 20** Plot of  $k_p (f/k_t)^{1/2} vs.$  conversion for the styrene-polystyrene-acetone FRRPP system at 80°C showing the drop in ordinate values during the period when the system exhibited a decrease in conversion rate.



**Figure 21** Time evolution of *X*, the fraction polymer radical compared with all polymeric species, for case I situation for acetone- and ether-based FRRPP systems. st = styrene.

$$[B^{\bullet}] = [P^{\bullet} \tag{9}$$

and from the [COOH] balance,

$$[COOH] = 2[A] + [B^{\bullet}]$$
 (10)

Thus,

$$X = \frac{2[P^{\bullet}]}{[\text{COOH}] + [P^{\bullet}]} \tag{11}$$

Case II. Extreme Chain Transfer to Acetone (i.e.,  $[A] = [B^{\bullet}] = 0$ )

$$[D^{\bullet}] = [P^{\bullet}] \tag{12}$$

and the following balances for [COOH] and [C=0]

$$[\text{COOH}] = [C] \tag{13}$$

$$[C = O] = 2[C] + [D^{\bullet}] + 2[E]$$
(14)

results in

$$X = \frac{2[P^{\bullet}]}{3[P^{\bullet}] + 4[\text{COOH}] + [C=0]}$$
(15)

With the plots of  $[P^{\bullet}]$  (Fig. 14), [COOH], [C=O], and [C-O] vs. time (Fig. 16), values of X vs. time for case I were obtained and shown in Figure 21 for the polymerization of styrene in acetone and ether. Because [C-O] is almost 0 [Fig. 16(a)], case I data is closely followed by the ether system. It is therefore worth noting that, for this system, the proportion of polymer radical, compared with all polymeric species, can be as high as 84%. Also, the value of X seems to have reached an asymptote at 80-84% levels, when almost all initiator molecules have already decomposed into radicals. Asymptotic behavior with time for X (Fig. 21) and for  $[P^{\bullet}]$  (Fig. 14) in the ether system indicates a living radical aspect of the FRRPP process. Also, the fact that this occurs at values of X closer to 100% than 50% indicates the potential of the FRRPP process in the generation of high yields of block copolymers from freeradical chemistry. For acetone, the significant amount of [C==0] in the product means that chain transfer is quite substantial. A look at both case I and case II situations for the acetone system indicates that the proportion of polymer radicals relative to all polymeric species can be as low as 18% (Fig. 22).

# **CONCLUSIONS**

We have therefore shown in this work that the FRRPP process involves a unique polymerization control mechanism. We have also shown that this mechanism involves the formation of high polymer concentrations in the polymer-rich domains of the phase-separated system. Strong arguments were introduced to link the formation of high polymer concentrations to the postulate that the polymer-



**Figure 22** Time evolution of *X*, the fraction polymer radicals compared with all polymeric species, for case I (no chain transfer) and case II (extreme chain transfer) situations for the acetone-based FRRPP system.

rich domains are at a higher temperature than the overall fluid. This drives the polymer-rich domains (where most of the polymer is present) into the spinodal curve, where phenomenological diffusivities of all the components have been known to vanish. Thus, both rates of termination and propagation decrease to the extent that  $k_p(f/k_t)^{1/2}$  drops drastically to levels that can be below that of ideal conventional free-radical chain polymerization process. This is the reason why we call this an *anti-gel effect phenomenon*. It is also evident from this work that the FRRPP system can result in live polymer radicals that are in the order of 80–84% of all polymeric species.

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