

# Free-Radical Retrograde-Precipitation Copolymerization of Vinyl Acetate and Acrylic Acid

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**ABSTRACT:** Free-radical chain polymerization kinetics of vinyl acetate (VA) and acrylic acid (AA) exhibit some unusual control features. The VA radicals have a high rate of chain transfer leading to relatively sluggish propagation rates. Polymerization of AA, however, is prone to autoacceleration behavior in bulk, solution, and precipitating media. Thus, conventional statistical copolymerization of VA and AA would result in the preferential formation of high AA content copolymer. However, when the reaction medium is chosen in such a way that the copolymer precipitates above the lower critical solution temperature (LCST), propagation control and even monomer sequence control are obtained. Under these conditions, when the VA charge is much greater than

AA, a tapered block copolymer (VA-t-AA) is obtained. We report a single stage polymerization process for the synthesis of such materials. The presence of VA-t-AA products is verified by emulsification, solubility, fractionation, size exclusion chromatography, NMR, and thermal analyses. In addition, propagation control can virtually eliminate formation of bimodal MWD and random/homopolymer materials that are associated with various chain transfer mechanisms in conventional polymerization routes. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3872–3882, 2009

**Key words:** addition polymerization; block copolymers; copolymerization; fractionation of polymers; surfactants

## INTRODUCTION

Free-radical polymerization of vinyl acetate (VA) and acrylic acid (AA) comprise some of the more difficult systems from a segmental control standpoint. Poly(vinyl acetate) radical ends are highly reactive and can react readily with VA monomer, VA segments in a polymer, initiators, and a variety of solvents.<sup>1</sup> AA, however, has been known to readily exhibit autoacceleration behavior when polymerized in solution.<sup>2</sup> As an academic exercise, it is desirable to be able to control the monomer distribution during the copolymerization of VA and AA. From an economic standpoint, it is worth noting that AA is one of the least expensive synthetic free-radical monomer that can be used to produce hydrophilic polymers. Also, VA is one of the least expensive room-temperature-liquid synthetic free-radical monomers that can be used to produce a relatively polar hydrophobic polymer.

In this article, we present a single-stage procedure that is used to produce a tapered block copolymer material based on VA and AA monomers. The method that is used to generate this novel material is the so-called free-radical retrograde-precipitation polymerization (FRRPP) process,<sup>3</sup> wherein the reaction fluid undergoes phase separation above the lower critical solution temperature (LCST). From our early work, we proposed the following mechanism 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.

Recently, we have been able to elucidate some of the underlying concepts behind this mechanism.<sup>4</sup> We found that the exotherm of the polymerization reaction may be strong enough to raise the local temperature of the reaction zone to the spinodal curve of the phase diagram, whereby mutual diffusivities have been found to vanish. This would result in the slowdown of the propagation reaction, until

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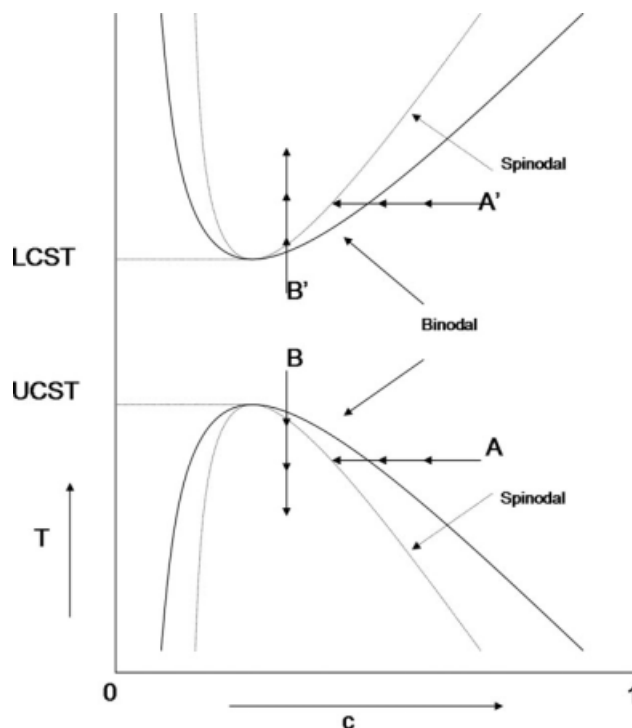
the reaction zone temperature drops to a condition a little below the spinodal curve. Further propagation would raise the reaction zone temperature toward the spinodal curve again. We propose that such cyclic incremental heating and cooling in the vicinity of the spinodal curve leads to the control of the propagation of chains. The precipitated condition also results in the slowdown of polymer radical termination, if conditions are such that chain transfer is minimized. In more recent work,<sup>5</sup> we showed that the approach of the reaction zone to the spinodal curve may not be the only factor contributing of reaction control.

Because the reaction rate is controlled, the polymer-rich domain growth has also been found to be under good control if domain interaction is minimized.<sup>6</sup> In a well-mixed vessel, some nanometer-sized polymer particles have been obtained when a crosslinker was included with the reaction recipe. When the reaction was carried out in a quiescent fluid, a large number of nano-sized particles were obtained even without the use of a crosslinker.

### Theoretical considerations

#### Single-stage copolymer formation

According to the literature,<sup>7</sup> reactivity ratios for AA (1)/VA (2) copolymerization are:  $r_1 = 2.0$  and  $r_2 = 0.1$ . This means that from a reactivity standpoint, AA-radical ends will want to react with AA monomer while VA-radical ends will also want to react with AA monomer. Thus, if there exists a 50/50 mole ratio of AA-to-VA in the reactor fluid, AA will tend to add into a growing copolymer chain at 20 times faster than VA. This implies a very active AA monomer, which is the reason why it was well-known that VA/AA copolymers with AA contents greater than 10 wt % cannot be produced efficiently. The reactivity of AA monomer would normally result in AA-rich and AA-poor chains, due to chain termination. If the introduction of AA in the reactor is controlled, then the reaction of VA will allow the overall control of the propagation rate while keeping polymer radicals live. This will result in the possibility of producing relatively high AA-content copolymers, as opposed to mixtures of AA and VA rich polymers with relatively low incorporation of comonomers into each set. Further, if a significant proportion of AA is added to the reactor while initiation is taking place so it can be incorporated into most initiated chains until all initiator molecules are exhausted, the longevity of the polymer radicals makes it possible to continue propagation with VA monomer to produce tapered block copolymers. This is possible due to the novel features shown by the FRRPP process as described in previous work<sup>4,6</sup>



**Figure 1** Typical phase diagram of amorphous polymer-small molecule systems, showing phase separation below the upper critical solution temperature (UCST) and above the lower critical solution temperature (LCST). Points outside the phase envelopes (such as A, A', B, and B') correspond to single-phase behavior, wherein the fluid appears to be transparent. Phase separation (or precipitation) can be induced by entering the phase envelope through composition (A or A' trajectories) or temperature (trajectories B or B') changes. Entering the lower phase envelope through A and B trajectories will induce conventional precipitation (CP), while entering the upper phase envelope through trajectories A' and B' will induce retrograde precipitation (RP).

including long lived free radicals and evidence of polymerization control.

#### Polymerization experiments

The concept behind the above-mentioned procedure can be explained through a typical binary amorphous polymer-solvent phase diagram shown in Figure 1.<sup>8-10</sup> Upper and a lower phase envelopes are shown at constant polymer molecular weight and pressure. At zero pressure and infinite polymer molecular weight, the highest point in the lower phase envelope is the upper critical solution temperature (UCST); the lowest point in the upper phase envelope is the LCST.

Within a phase envelope are the solid binodal curve and the dashed spinodal curve. The spinodal curve is always inside the phase envelope compared to the binodal curve. The binodal curve indicates the compositions of the phases in equilibrium; these

TABLE I  
Chain Transfer Constants From VA and AA Radical Ends at Various Temperatures

Polymer radical ends	Chain transfer constants ( $\times 10^4$ )	Temperature, °C				
		60	70	80	100	130
VA	$C_M$	2.1, 2.4, 2.5, 2.6, 2.8	2.4, 2.9			
	$C_I$ to AIBN	550				
	$C_P$				6.6	9.2
	$C_S$ to EtOH	25	26.3			
	$C_S$ to <i>n</i> -buOH	20				
AA	$C_S$ to <i>t</i> -buOH		0.46, 0.5, 1.3			
	$C_S$ to EtOH		4.38			
	$C_S$ to <i>n</i> -buOH	2.91	5.85			
	$C_S$ to <i>t</i> -buOH	0.17	0.712			

compositions are obtained from the intersection of a horizontal line with two points in the curve. A horizontal line is drawn because at equilibrium, the temperature, pressure, and chemical potential are the same for both phases.<sup>11</sup> Within the spinodal curve is the so-called spinodal region, wherein phase separation will occur spontaneously.<sup>12</sup> The region between the binodal and spinodal curve is the metastable region (or supersaturation region), wherein phase separation will occur only if the system is activated by finite temperature or composition perturbations.<sup>13</sup>

When a system within the single-phase region outside the envelopes such as A, A', B, or B' (which will appear transparent) is slowly brought inside the envelope by composition (A or A' trajectories) or temperature (B or B' trajectories) changes, phase separation (appearance of a turbid fluid) will not occur until the condition is closer to the spinodal curve than the binodal curve. However, if the system starts within the spinodal curve and is slowly brought outside the envelope, turbidity will disappear when the system is at the binodal curve. Thus, the disappearance of turbidity on dropping of the temperature is the basis of our determination of the binodal point in the upper phase envelope.

The choice of solvents for PVA-based FRRPP synthesis has been narrowed by looking into the various chain transfer constants.<sup>7,14</sup> Table I shows values of these constants. High rates of chain transfer are detrimental to polymerization control as they can lead to radical delocalization and relatively quick termination.

The transfer constants are based on the following equation for the overall chain transfer constant,  $C_X$

$$C_X = C_M + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} + C_P \frac{[P]}{[M]} \quad (1)$$

Here,  $C_M$ ,  $C_I$ ,  $C_S$ , and  $C_P$  are chain transfer constants to monomer, initiator, solvent, and polymer, respectively. The effect of  $C_X$  is seen from the following equation

$$\frac{1}{P_n} = \frac{1}{P_{n0}} + \sum C_X \frac{[X]}{[M]} \quad (2)$$

We can see that normally the object is to minimize  $C_X$ , maintain the radical ends of the polymer. At about 10–20 wt % monomer charge, it can be seen that  $C_S$  can dominate the equation for both EtOH and *n*-buOH. We chose to use azeotropic *t*-buOH/water as the solvent at an operating temperature of 65°C.

#### Emulsification, dissolution, and fractionation studies

Since the VA-*t*-AA polymers produced by this process are amphiphilic, their ability and efficiency to form emulsions can serve as an effective measure of their presence relative to homopolymer and random contaminants. Block copolymers, even if tapered, have much higher interfacial activity than their random analogs. Differences in the ability to form emulsions can serve as effective measures of the relative amounts of block copolymers.

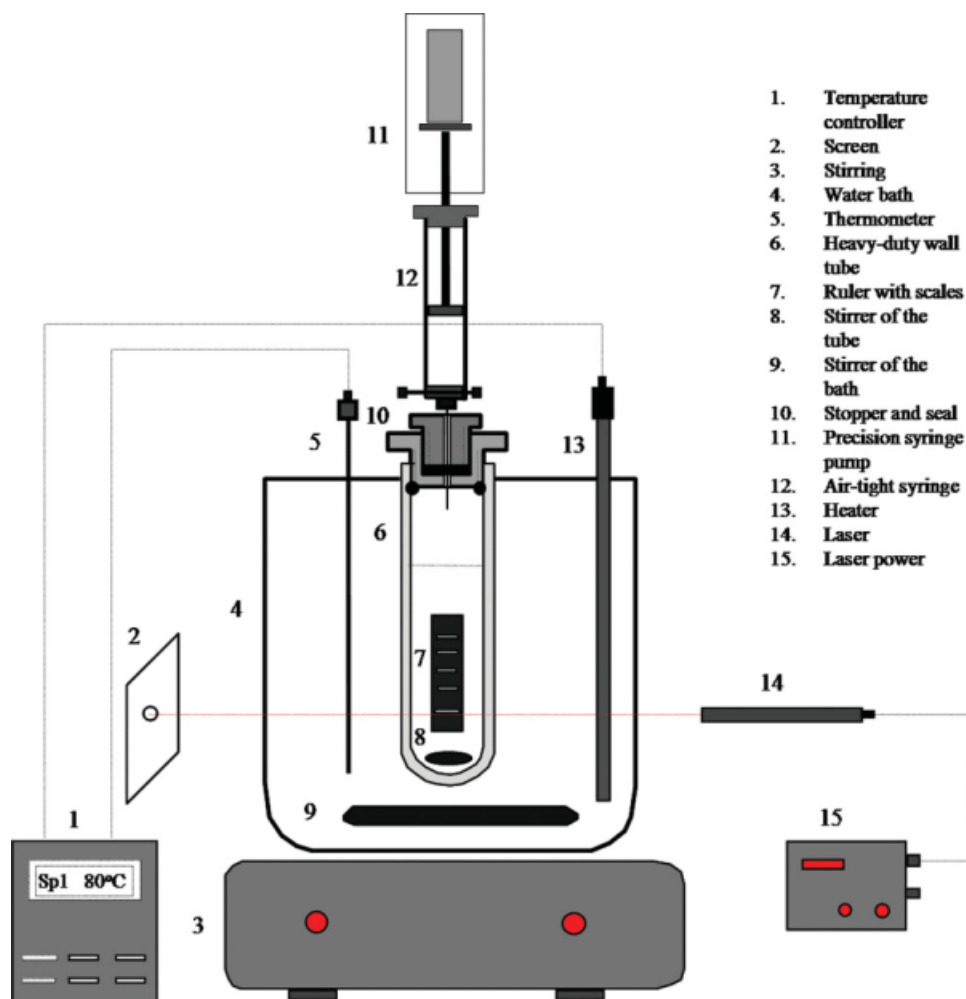
Further, the solubilities of copolymers in mutual as well as selective solvents for the different components can also serve as effective measures of composition as well as architecture. Block and random copolymers show differences in solubility in mutual and selective solvents as do the respective homopolymers.

Fractional precipitation, or fractionation, of the various polymer products as well different phases of an emulsion followed by subsequent compositional analysis can also provide information about the composition and architecture of the polymers. Such studies were conducted on selected products to further evaluate their structure and composition. Random and block copolymer products were compared.

## EXPERIMENTAL

### Phase equilibria work

The apparatus (Fig. 2) and procedure for doing phase equilibria work were described in our prior work.<sup>4,15</sup> Ternary phase envelopes were determined with a specially designed apparatus that consisted of



1. Temperature controller
2. Screen
3. Stirring
4. Water bath
5. Thermometer
6. Heavy-duty wall tube
7. Ruler with scales
8. Stirrer of the tube
9. Stirrer of the bath
10. Stopper and seal
11. Precision syringe pump
12. Air-tight syringe
13. Heater
14. Laser
15. Laser power

**Figure 2** Schematic experimental setup for phase diagram generation. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

a heavy-duty-wall tube with the outer diameter of 2.54 cm and effective length of 20.32 cm. Sometimes, a reference tube containing the solution with about the same polymer concentration of the sample, but with a composition in the homogeneous solution region, would also be used to the presence and extent of cloudiness. The sample tube had a tailored Teflon<sup>®</sup> stopper through which a channel with different diameters in different sections was cut to accommodate a silicone rubber seal. The needle of a precision syringe could penetrate the silicone rubber without breaking the sealing of the tube.

For each cloud point determination, a specific amount of 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<sup>®</sup> stopper and then subjected to vacuum. A clear water (or glycol) bath with magnetic stirrer was maintained within  $\pm 0.1^\circ\text{C}$  of the required temperature. A syringe pump was used to accurately meter the solvents in the syringe into the tube. A He-Ne laser beside the bath was in-

stalled to facilitate the determination of the end point. If the reference tube was used, the laser was adjusted so that the laser beam passed reference and sample tubes simultaneously. The solvents could be added from the precision air-tight syringes into the tube to change the compositions of the mixture in the sample tube.

The cloud point curve (CPC) was determined by either adding a component fluid or changing the bath temperature to the point of clarity of the turbid solution. The end point was determined by comparing the laser beam passing the solution in the sample tube and the reference tube or by the visual observation of cloudiness with the help of a black ruler with a fine scale behind the tube.

### Polymerization experiments

Polymerization experiments were conducted using a 1-L glass reactor that was operated at a slightly positive pressure with a nitrogen gas blanket. Such a device is similar to one described in an earlier



publication,<sup>4</sup> with the additional feature that the glass reactor used can be pressurized to about 40 psig (as specified by the manufacturer, Ace Glass Ltd.).

Formation of VA/AA copolymer is accomplished with the reactor containing all the monomers and then starting the reaction by adding the initiator solution. The idea is that most of the AA will react at the early stage and subsequent chain extension will occur with VA addition. The solvent is azeotropic *t*-butanol/water and initiator is VA-044. These experiments were conducted using reduced amounts of initiator to minimize premature polymer-polymer termination of AA-containing chains; thus, minimizing the formation of random copolymer.

Two separate polymerizations were performed to produce a tapered block copolymer with 6 wt % AA (B6-1 and B6-2) in a 1-L glass reactor system. The reactor was initially charged with the following reagents: 310.7 g azeotropic *t*-butanol/water, 2 g AA, and 72.4 g VA. Then, the temperature was raised to 65°C in 30 min while slowly purging the reactor with nitrogen gas. After the operating temperature was reached, the reactor was sealed and the following was added into the reactor fluid for a period of 20 minutes: 0.129 g VA-044 dissolved in 10 g distilled water, 43.3 g azeotropic *t*-butanol/water. If higher proportions of AA was needed in the product, more AA were initially charged in the reactor and/or some AA were included with the initiator charge. Normally, this produces a significant amount of random copolymers as well. When AA was added into the reactor after chain extension (when almost all initiator molecules have been exhausted), tapered triblocks were obtained. Random copolymers were produced when AA was almost continuously added into the reactor during the period when initiator molecules are being decomposed into radicals. A summary of reactant sequence addition and the corresponding products are shown in Table II.

The naming convention used for the polymer samples is based on their proposed architecture of the polymers. Solid products that are believed to contain block as well as random chains have been named with the "BR" designation, such as a BR11-1 which is the first product that contains 11 wt % AA. Tapered triblock copolymers were assigned designations such as B9B-1 or BR17B-1. If the product is believed to be mostly random copolymer material, then an "R" designation is used, such as the R20-1 product which contained 20 wt % AA.

Samples were taken at various stages of the experiments. Conversion was obtained by gravimetric means, i.e., by obtaining the weight % polymer from weights of reactor fluid samples and dry solid weights. Polymer compositions obtained from NMR studies (Varian 400 MHz spectrometer) were com-

pared with the % monomer charge, to calculate monomer conversion to polymer. To determine molecular weight distribution of polymer samples, a size exclusion chromatograph was used (Waters 150 CV.) with mixed bed columns (styragel, Waters Associates). The mobile phase used was THF, and molecular weights were obtained based on narrow molecular weight distribution polystyrene standards. Data were analyzed using Waters Millennium software. Thermal properties were evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed on air-dried sample using TA Instruments DSC 2920. TGA was performed using TA instruments TGA 2950. Data were analyzed using TA Universal Analysis software.

### Emulsification, dissolution, and fractionation studies

Emulsification was done by heating the reactor fluid and replacing vaporized volatile organics with ammonia-water up to pH = 7. Usually, sludge is formed on the walls of the evaporating vessel. It was found that all the samples formed an emulsion while hot but separated into supernatant and precipitate layers on cooling to room temperature. On an overall basis, mixtures have 5–10 wt % solids.

To determine AA compositions of polymer samples and products, a 400-MHz Varian NMR spectrometer was used. Particle size distributions of the ammonia-neutralized VA/AA self-emulsions were measured using a Leed & Northrop Microtrac Particle Size Analyzer.

Solubilities of products were also investigated using various solvents. Solids from supernatant and residues were collected and dried on aluminum weighing pans.

Fractionation was done by preparing 1 wt % dried solid samples in 100 g THF. The precipitant, cyclohexane, was then added into the solutions at the rate of 1 drop/sec while continuously being mixed with a magnetic stirrer bar. After a specific amount of precipitant was admixed into the solution, the precipitate was separated out using a centrifuge (<1000 RPM). Precipitant residues at the bottom of centrifuge tubes were dissolved on THF, dried and weighed, to obtain fractionation curves, such as the one shown in Figure 6.

## RESULTS

### Cloudpoint measurements

In the reporting of our experimental data, phase separation below the upper critical solution temperature (UCST) will be referred to as conventional

**TABLE II**  
**Recipe and Properties Correspondence with VA-AA Product Codes**

Product code	Wt % AA	Copolymer mixture	Initial reactor charge	Initiator solution	Monomer mixture after chain extension
B6-1	6	Tapered diblock	310.7 g azeotropic <i>t</i> -butanol/water, 2 g AA, 72.4 g VA	0.129 g VA-044, 10 g distilled water, 43.3 g azeotropic <i>t</i> -butanol/water	None
B6-2	6	Tapered diblock	349.7 g azeotropic <i>t</i> -butanol/water, 2 g AA, 71.6 g VA	0.129 g VA-044, 10 g distilled water, 43.3 g azeotropic <i>t</i> -butanol/water	None
B6-3	6	Tapered diblock	328.3 g azeotropic <i>t</i> -butanol/water, 2 g AA, 71.9 g VA	0.3325 g VA-044, 1.65 g AA, 20.7 g VA, 10 g distilled water, 94.6 g azeotropic <i>t</i> -butanol/water	None
BR11-1	11	Tapered diblock + random	310.2 g azeotropic <i>t</i> -butanol/water, 4 g AA, 71.6 g VA	0.133 g VA-044, 10.4 g distilled water, 42.4 g azeotropic <i>t</i> -butanol/water	None
B4-1	4	Tapered diblock	302.2 g azeotropic <i>t</i> -butanol/water, 2 g AA, 72.1 g VA	0.126 g VA-044, 10 g distilled water, 43.9 g azeotropic <i>t</i> -butanol/water	None
B9B-1	9	Tapered diblock + tapered triblock	346.2 g azeotropic <i>t</i> -butanol/water, 2 g AA, 72.3 g VA	0.3037 g VA-044, 10 g distilled water, 12.9 g VA, 1.4 g AA, 79.5 g azeotropic <i>t</i> -butanol/water	0.3 g AA, 2.77 g VA, 7.23 g azeotropic <i>t</i> -butanol/water
BR17B-1	17	Tapered diblock + tapered triblock + random	389.0 g azeotropic <i>t</i> -butanol/water, 4.5 g AA, 95.3 g VA	0.5557 g VA-044, 15 g distilled water, 250.5 g azeotropic <i>t</i> -butanol/water, 38.4 g VA	2 g AA, 20.8 g azeotropic <i>t</i> -butanol/water, after removal of 448.9 g reactor samples
BR11-1	11	Tapered diblock + random	310.2 g azeotropic <i>t</i> -butanol/water, 4 g AA, 71.6 g VA	0.133 g VA-044, 10.4 g distilled water, 42.4 g azeotropic <i>t</i> -butanol/water	None, but longer chain extension time than BR36-1
BR20-1	20	Tapered diblock + random	376.4 g azeotropic <i>t</i> -butanol/water, 3 g AA, 70.2 g VA	0.3 g VA-044, 70.1 g methanol	None, but shorter chain extension time than BR20-1
BR36-1	36	Tapered diblock + random	376.4 g azeotropic <i>t</i> -butanol/water, 3 g AA, 70.2 g VA	0.3 g VA-044, 70.1 g methanol	None, but shorter chain extension time than BR20-1
R20-1	20	Random	327.7 g azeotropic <i>t</i> -butanol/water, 3 g AA, 70.2 g VA	0.5957 g VA-044, 15.4 g distilled water, 116.8 g azeotropic <i>t</i> -butanol/water	10.2 g AA, 59.4 g VA, 290.8 g azeotropic <i>t</i> -butanol/water added gradually after a relatively short chain extension time (2 hrs and 27 min)

TABLE III  
Retrograde Precipitation (RP) and Conventional Precipitation (CP) for PVA and PMMA in Alcohol/Water Mixtures

Polymer/solvent system	Results	Normal boiling temperature, °C
9.1 wt % PVA (medium MW) in azeotropic ethanol/water (95.5 wt % ethanol)	CP at 45°C, and RP at 64°C	78.1
6.8 wt % PVA (medium MW), and azeotropic <i>n</i> -butanol/water (62 wt % <i>n</i> -butanol)	RP at 71°C	92.4
6.4 wt % PMMA (inherent viscosity of 0.45) in 3 g <i>t</i> -butanol, 1.4 g water	CP at 46°C, RP at 68°C, and LCST at around 57°C	
6.3 wt % PVA (medium MW) in azeotropic <i>t</i> -butanol/water (88.3 wt % <i>t</i> -butanol)		79.9
7.7 wt % PVA (medium MW) in 1.8 g <i>t</i> -butanol, 0.8 g water	RP at 97°C	

precipitation (or CP), whereas inverse-temperature phase separation above the LCST will be referred to as retrograde precipitation (RP). CP and RP are composition dependent and practically pressure-independent in our systems. The lowest RP temperature at the composition range and zero pressure is the formal designation for the LCST.

Results of the cloud point measurements using alcohol-based solvents that were suitable for this work are shown in Table III below. Other alcohol/water solvent systems were also examined but have not shown the RP behavior below about 100°C. The PVA solution in azeotropic ethanol/water phase separated above the LCST of at 71°C, whereas the PVA solution with azeotropic *t*-butanol/water had an LCST at 97°C. These results suggest that polymerization of VA and VA/AA monomer mixtures can be investigated using both azeotropic ethanol/water and *t*-butanol/water, bearing in mind that the addition of a small amount of AA in the mixture and the formation of VA-AA copolymer would shift the RP values in the reaction vessel. Also, much lower values of the chain transfer constants to *t*-butanol (Table I) could be an overriding factor to favor the use of azeotropic *t*-butanol/water over azeotropic ethanol/water as reactor solvent.

During the polymerization of VA (86.8 g) in azeotropic *t*-butanol/water (370–375 g) at 65°C that was initiated by VA-044 (0.4884 g VA-044 in 43 g distilled water), the reaction fluid started to turn turbid 3 min after all reactants were introduced (for 35 minutes). The turbidity level increased for 3 h. The level of turbidity decreased after 6 hrs, which corresponds to 18 times the initiator half-life. A similar observation of the turbidity was obtained during the polymerization of VA/AA in *t*-butanol/water at 65°C. The difference is that in the polymerization of VA/AA, the reactor fluid was generally more turbid than that in VA homopolymerization. For the homopolymerization of VA in azeotropic ethanol/water at 75°C, the reactor fluid remained relatively clear. However, during copolymerization of VA and AA at

the same temperature, the reactor fluid became turbid.

#### Kinetics of PVA homopolymer and copolymer formation

Polymerization of VA in azeotropic EtOH and *t*-BuOH seemed to show the effects of chain transfer in these systems. For the EtOH-based system that was polymerized at 75°C with about 10 wt % actives, a bimodal MWD was obtained with a low MW peak at 2–3 kDaltons. This is consistent with the numbers obtained from eqs. (1) and (2), based on the chain transfer constant values obtained in the literature (Table I). For the *t*-buOH-based systems, the following product molecular weight characteristics were obtained: (a) for an operating temperature of 70°C, a bimodal MWD was obtained at peak MWs of 109 kDaltons (49% area) and 56 kDaltons (49% area); and, (b) for an operating temperature of 65°C, a unimodal peak was obtained with a number-average and peak molecular weight of 127 kDaltons, with a slight lower MW shoulder at about 60–70

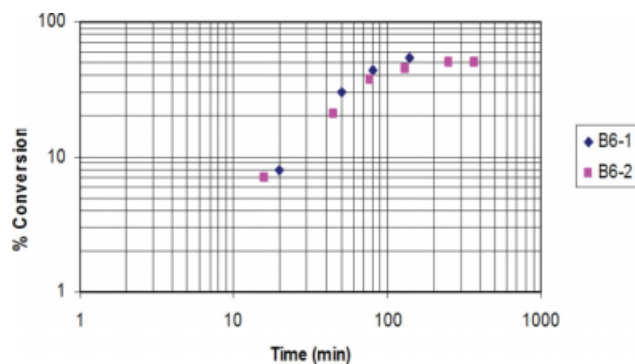


Figure 3 Conversion-time plots for VA-*t*-AA copolymer products with 6 wt % AA content. Note that the initiator (VA-044) has a half-life of 30 min at the operating temperature of 65°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

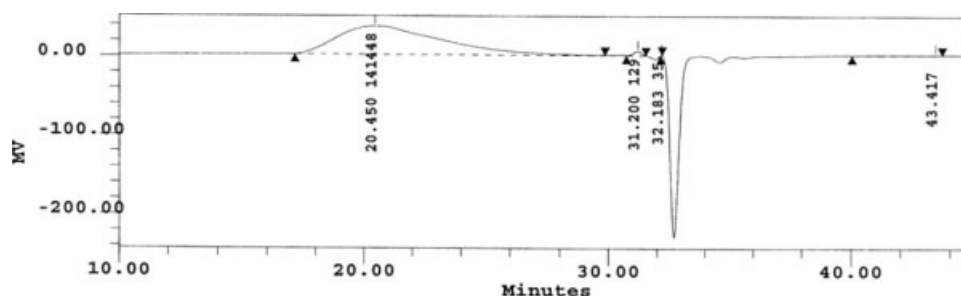


Figure 4 GPC plot of the B6-1 tapered VA-AA product, which contains 6 wt % AA.

kDaltons. Again, the lower MW peak and MW shoulder can be attributed to chain transfer effects.

Kinetic data for one of the experiments used for the formation of tapered VA/AA copolymer is shown in Figure 3. Time zero corresponds to the time when all initiator was added in. It is worth noting that the data indicates adherence to a sequence of two line segments in a log-log plot. The higher conversion rate segment corresponds to an autoacceleration index (slope) of 0.5–0.7, which indicates a retardation-type of behavior with slope less than 1.0. Note that an acceleration index of 0.5 was obtained for styrene-based FRRPP systems.<sup>16</sup> The higher conversion line segment is almost horizontal, which indicates the relative absence of chain extension. GPC analysis of the B6-1 product indicates a unimodal peak with number average MW of 42 kDaltons and PDI of 2.76 (Fig. 4).

#### Emulsification work

Table IV shows the result of the emulsification work. AA contents were obtained from <sup>13</sup>C NMR spectra, such as the one shown in Figure 5, wherein peaks at 178 and 171 ppm correspond to those of carbonyl carbons from AA and VA, respectively. It is evident that all materials that settled or coagulated had lower AA compositions than the supernatants. A

higher AA content in the emulsion (as in BR17B-1) did not guarantee a lower proportion of residue or sludge, although the B6-1 Product was made recently using a batch reactor method that has been shown (see also fractionation results) to result in relatively small random copolymer contamination. Moreover, the B6-1 Product had very little proportion of sludge and residue from the cold emulsion. This again points to a very small amount of random copolymer contamination. Finally, the GPC trace of the B6-1 emulsion is almost identical with that of the unemulsified B6-1 product (Fig. 4).

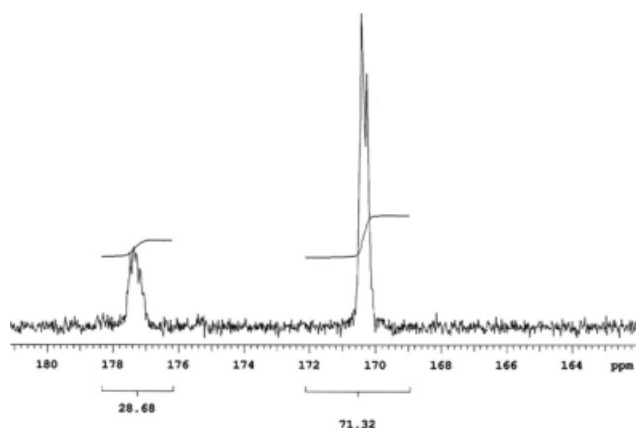
The emulsions were found to have relatively large average particle sizes. Most of them look white, except for the R20-1 product, which was translucent. These white relatively large emulsion particles indicate the possibility of liquid crystalline macromolecular assemblies, as it was found to occur in high molecular weight ethylene oxide-propylene oxide segmented block copolymer nonionic surfactants.<sup>17</sup> In an earlier publication, we reported that at 6.6 wt % in water, the B6-1 emulsion showed a bicontinuous structure with 5–10 μm repeat unit using an optical microscope. On dilution to about 20 times, 10–60 μm spherical domains were obtained.<sup>18</sup>

Another focus of the study of VA/AA copolymerization is the formation of emulsion products from materials with higher AA contents. The BR8B-1 run

TABLE IV  
Properties of Emulsified VA/AA Products

Product	Hot emulsions						
	Sludge		Supernatant emulsion at R.T.			Residue at R.T.	
	% AA	Wt % sludge relative to total solids	Mean particle diam., μm	Wt % relative to solids in hot emulsion	% AA	Wt % relative to solids in hot emulsion	% AA
B4-1	2.7	4	20	94	3.4	6	3.2
B9B-1	3.9	5	98	97	6.1	3	4.6
B6-1	1.3	1.5	97	~ 100	6.3	~ 0	
BR17B-1		3	40	77	14.1	23	10.4
BR11-1	7.8	11	196	~ 100		~ 0	
R20-1			91	90–95		5–10	





**Figure 5**  $^{13}\text{C}$  NMR spectrum of the B6-3 VA-t-AA product, wherein peaks at 178 and 171 ppm correspond to those of carbonyl carbons from AA and VA, respectively.

started in the same way as the B6-1 run, except that a little more AA was charged in the reactor. Then the fluid was cooled to room temperature. Then, some AA was added in, and the reactor fluid was heated back to 65°C in 1 hr. About 30 min after the reactor reached the operating temperature, the product was withdrawn. The BR11-1 follows the same procedure as the B6-1 product, except that a much greater amount of AA charge was used.

### Solubility tests and fractionation

VA/AA copolymer products were tested for their solubilities in a number of solvents, such as acetone, methanol, ethyl acetate, cyclohexane, THF, Toluene, water, pyridine, etc. Also, mixed solvents were used for solubility testing. THF and pyridine were found to dissolve all the products. Others are part of solvent/nonsolvent pairs for either PVA or PAA. Solvent/nonsolvent pairs are indicated in the literature,<sup>14</sup> and are shown in Table V. Given the variety of VA/AA copolymer composition and architecture and as a result of our solubility tests, we decided to

**TABLE V**  
Solvent/ Nonsolvent Pairs for PAA and PVA

Polymer	Solvent	Nonsolvent
PAA	MeOH	Ether
	MeOH	Ethyl acetate
	MeOH	Water
PVA	Acetone	<i>n</i> -Hexane
	Acetone	<i>n</i> -Heptane
	Acetone	<i>n</i> -Pentane
	Acetone	Water
	Acetone	Petroleum ether
	Ethyl acetate	Cyclohexane
	Methyl acetate	Petroleum ether
	MeOH	Water (for branched PVA at 35°C)

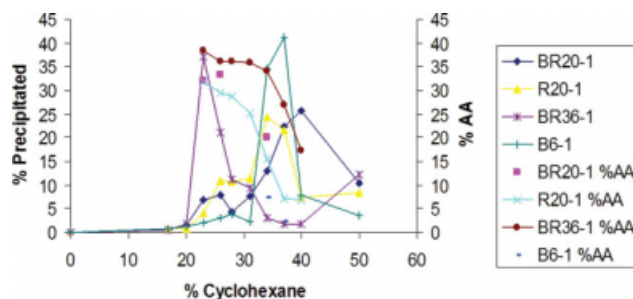
**TABLE VI**  
Results of Extraction of VA/AA Polymer Products Using Ethyl Acetate

VA/AA product	% Supernatant from ethyl acetate
B6-1	~ 100
BR11-1	69.8
B6-3	98.2
B6-2	~ 100
B9B-1	~ 100

use THF as solvent and cyclohexane as nonsolvent for fractionation work. Table VI is an outline of the results. The key to sample code names is shown in Table II, and is included as footnote A to Table IV.

As it can be seen in Table VI, there is a good correlation in the solubility behavior of B6-1, B6-2, B6-3, and B9B-1. If we compare the results of Tables IV and VI, it is evident that these three materials have relatively low amounts of VA/AA random copolymer; thus they have higher amphiphilic character. By comparison, materials with relatively high amounts of VA/AA random copolymer (such as BR11-1) resulted in incomplete solubility in ethyl acetate.

Results of fractionation work (Fig. 6) indicate broadening of fractograms for random copolymer materials. For other materials, no clear separations were obtained, probably due to the presence of significant amounts of tapered block copolymers. A random copolymer (R20-1 Product) and a block copolymer (B6-1 Product) have been fractionated for comparison. The results are also shown in Figure 6. It is evident that fractionally precipitated material from the random copolymer is much more distributed than that from the block copolymer. Curves for two samples (BR36-1 and BR20-1) are also shown to get an idea of random copolymer formation at a higher AA content. The two samples were taken at different times in the same reaction with BR36-1 coming first just after the addition of the initiator in



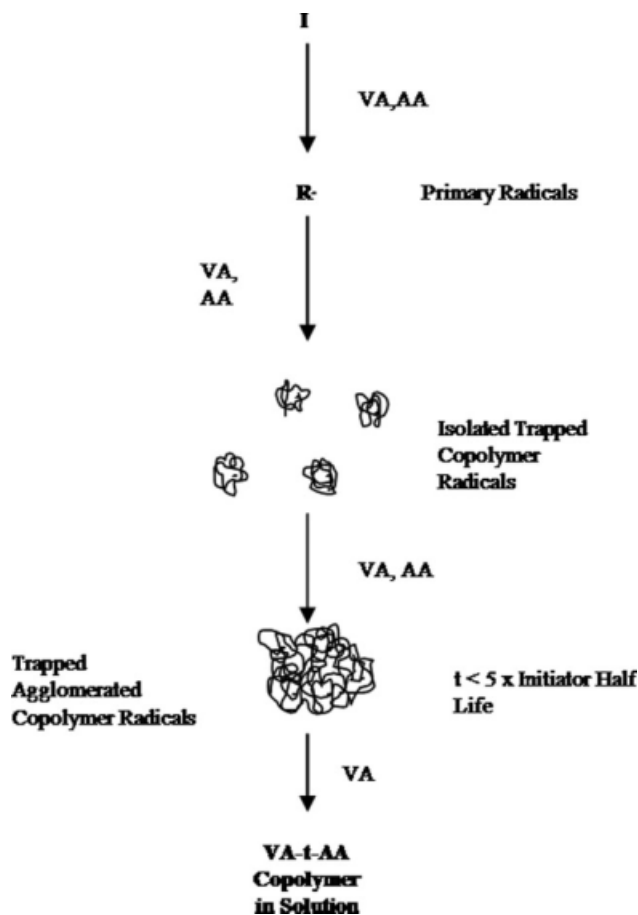
**Figure 6** Fractionation results for the VA-AA copolymers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the reactor (Table II). As shown in Figure 6, the random copolymer part of BR36-1 was reduced in BR20-1, based on the reduction of the peak at lower % cyclohexane precipitant. This indicates that the pre-made polymer in BR36-1 has helped in the formation of blockier BR20-1.

### Thermal analysis

DSC results on the B6-1 material indicated glass transition temperatures of 39.5–44.5 and 80.7–90.1°C. If, we neglect the formation of vinyl alcohol segments, this indicates about 56–66 wt % AA in the AA-rich block and 5–12 wt % AA in the VA-rich block, using the inverse-rule-of-mixtures or the Fox Equation.<sup>19</sup> TGA analysis indicated that this material retained 96% of its weight up to 218.75°C. A higher percentage VA blocky material, BR11-1, was found to have glass transition temperatures of 42 and 94°C. This translated to about 70 wt % AA in the AA-rich phase and 8 wt % AA in the VA-rich phase. For products that were understood to be almost truly random copolymers, a single glass transition between those of PVA (at 36°C) and (PAA at 106°C) was obtained. Thus, thermal analysis supports the result of the formation of either blocky materials or random copolymers in different experiments.

The assumption of insignificant formation of vinyl alcohol segments from the B6-1 product was investigated by tracking the pH of the reactor fluid. Since it is a valid to assume that all AA monomer has reacted and vinyl alcohol formation is accompanied by formation of acetic acid in the reactor fluid, then any free acid is going to be based on acetic acid. This is determined conveniently from a reactor fluid whereby the copolymer was allowed to settle to the bottom of the container, and the top layer would then be devoid of AA segments of the copolymer. In this case, we obtained a pH for the top layer of 5, which corresponds to a vinyl alcohol content of less than 0.001 wt %. To minimize formation of more vinyl alcohol segments during thermal analysis, the above-mentioned reported glass transition data were obtained during the first heating stage only. In fact, when a second heating stage was carried out, we observed an upward drift in all the transition temperatures, which indicates vinyl alcohol segment formation. Sometimes, a distinct glass transition temperature at 65°C for poly(vinyl alcohol) shows up during these subsequent heating cycles, and some of the high AA-content polymer samples turned into a pinkish watery gel after about 2 weeks in humid atmosphere. Thus, while it was possible to convert the VA segments into vinyl alcohol, it can be minimized for relatively low AA content (below 10 wt %) copolymer products.



**Figure 7** Mechanism of the formation of VA-t-AA copolymer.

## DISCUSSION OF RESULTS

The characterization data presented herein supports the formation of a tapered VA/AA block copolymer. The polymerization kinetics, interfacial properties, dissolution/fractionation profiles, and thermal characterization results provide a means to differentiate between random and block architectures. The characterization of this material was nontrivial as the product is not a “pure” block copolymer but was a tapered copolymer where the blocks were not synthesized in well defined stages as in other block copolymer synthesis procedures. This was a consequence of the approach and process used for its synthesis. This limited the ability for the utilization of more standard tools for block copolymer characterization, with the exception of thermal analysis.

It is well known that free-radical polymerization of AA tends to exhibit autoacceleration behavior,<sup>2</sup> especially under precipitating conditions. The presence of overwhelming amounts of VA compared to AA moderates this behavior and results in an autoacceleration index below 1 (Fig. 3). Also, the presence of AA in the reaction fluid resulted in increased turbidity. It could be proposed that PAA

could phase separate in the reaction fluid. However, this may not be plausible, since the reactor fluid became less turbid with time. Another possible explanation is localized temperature rise within the reactor due to the exotherm of the chain polymerization from the reactive acrylic acid radical ends, which could result in hot spots around these sites. The occurrence of hot spots has been cited in early studies of the FRRPP process as a factor in its propagation control.<sup>3</sup>

We believe that the high reaction rate of AA enhanced the FRRPP mechanism even though phase equilibria studies indicate that reactor temperatures are a little below RP temperatures (Table III). The other result of the formation of hot spots is the "caging" of the reactive sites, which will make them inaccessible to free AA molecules. Only newly initiated radicals are accessible to AA molecules, which will soon propagate in a controlled manner through the overwhelming presence of VA compared with AA and formation of hot spots. If the depletion of initiator decomposition is timed with the total consumption of AA, then mostly VA molecules will be available for chain extension after the initiator has been exhausted. As reactive sites start to cool to the operating temperature, the cage around them opens up for VA propagation. The overall effect of the combination of these reaction and transport mechanisms (Fig. 7) is the self-assembly of the monomer sequence in the copolymer product, in which AA reacts first with VA, followed by almost pure VA propagation and termination. Finally, propagation control has been achieved to moderate the increase of the average molecular weight to minimize intermolecular chain transfer reactions during the chain extension of the VA block.

## CONCLUSIONS

In this article, we report the discovery of a single-stage FRRPP method using industrially practicable operating conditions for the formation of a novel VA-AA tapered block copolymers (VA-t-AA) that exhibit amphiphilic material properties. The presence of block copolymer is verified through its interfacial, solution, and thermal properties and a mechanism has been proposed for polymerization control. The polymerization mechanism is based on the moderation of AA propagation through the over-

whelming presence of VA compared with AA and the trapping of the hot radical sites by precipitated unreactive polymer chains. As reactive sites start to cool to the operating temperature, the cage around them opens up for VA propagation. The overall effect of the combination of these reaction and transport mechanisms is the self-assembly of the monomer sequence in the copolymer product, in which AA reacts first with VA, followed by almost pure VA propagation and termination. Another consequence of this mechanism and its demonstration in the formation of VA-t-AA is that the FRRPP process could provide a way of overcoming the limitations of reactivity ratios in statistical copolymerization processes. This could be achieved by a combination of extended radical lifetimes and careful control of monomer concentrations.

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