

# Phase Behavior and Self-Assembly of Poly [*N*-vinylformamide-*co*-(acrylic acid)] Copolymers Under Highly Acidic Conditions

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**ABSTRACT:** Copolymers of *N*-vinylformamide and acrylic acid were synthesized by conventional aqueous free-radical polymerization. The phase behavior of the copolymer solutions was investigated through the addition of hydrochloric acid and the variation of the temperature. With a moderate content of *N*-vinylformamide, the copolymers showed complex phase behaviors. Under low-acidity conditions, a suspending liquid was formed, whereas under high-acidity conditions, the random copolymers could assemble into round nanoparticles with a broad particle size distribution. When the temperature was reduced, a much less cloudy solution that contained nanoparticles

became a milk-like suspending liquid, and this temperature-responsive phenomenon was reversible. This indicated that the formamide group was protonated under highly acidic conditions; the repulsive electrostatic forces compelled the aggregates to disperse. The amount of salt and excess acid influenced the particle size as well as the temperature-responsive behavior of the copolymers under highly acidic conditions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2802–2807, 2008

**Key words:** particle size distribution; phase behavior; self-assembly; water-soluble polymers

## INTRODUCTION

Stimuli-responsive polymers have received much attention for their intelligent and reversible behavior in response to environmental stimuli, such as variations in the solution pH,<sup>1–4</sup> temperature,<sup>5,6</sup> and salt concentration.<sup>7–9</sup> Typical pH-responsive polymers often contain weakly acidic or alkaline groups, and the charge density can be easily controlled through changes in the pH of the polymer solution. Poly(acrylic acid) (PAA)<sup>10,11</sup> and polysulfobetaine<sup>12</sup> have been reported to exhibit a transition temperature. This phase transition is believed to result from the breaking of intrachain and interchain interactions such as hydrogen bonding and electrostatic attractions that form at lower temperatures.

PAA has pH-, salt-, and temperature-responsive properties; copolymers with acrylic acid (AA) units can also be responsive to environmental stimuli. Recently, Mori et al.<sup>13</sup> reported that aqueous poly

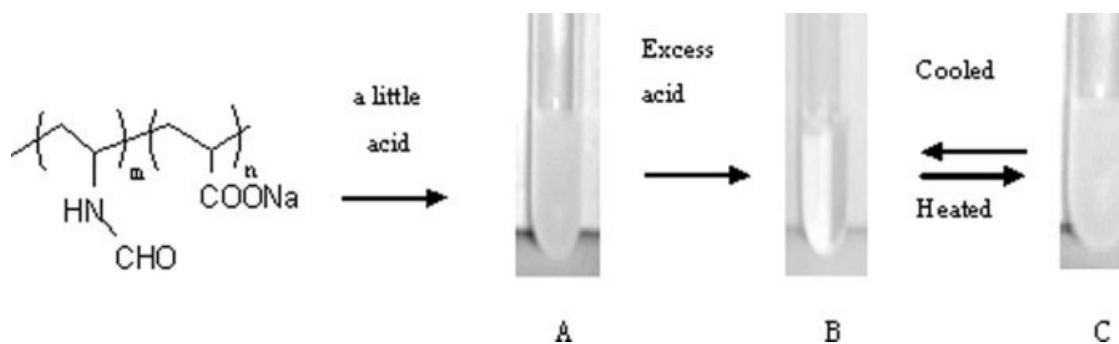
[*N*-vinylacetamide-*co*-(acrylic acid)] solutions have a unique phase-transition behavior in aqueous salt (Na<sub>2</sub>SO<sub>4</sub> or NaCl) solutions. In the presence of salt, copolymers containing more than 51 mol % *N*-vinylacetamide (NVA) showed a reentrant soluble–insoluble–soluble (S–I–S) transition with increasing temperature under acidic conditions (pH 2.2–3). Salts were indispensable for the unique phase behavior of the copolymers, but the explanation was not enough. In addition, the copolymerization of NVA and AA was essential for the unique phase-transition behavior because the S–I–S transition was not observed in the mixed homopolymer system [poly(*N*-vinylacetamide)/PAA]. It was concluded that introducing a hydrogen-bonding pair and a polymer with moderate hydrophobicity afforded a universal design for polymers with an S–I–S transition in aqueous solutions.<sup>13</sup>

*N*-Vinylformamide (NVF) is the lowest member of the *N*-vinylamide family and, as a precursor to amide- and amine-functional polymers, offers a unique mix of physical and chemical properties that make it highly attractive from both scientific and commercial perspectives. The structure of NVF is similar to that of NVA, but it is more hydrophilic because of the hydrogen-substituted methyl in NVA. In this study, the phase behavior and self-assembly of poly[*N*-vinylformamide-*co*-(acrylic acid)] (PNVFAA) copoly-

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**Scheme 1** Structure of PNVFAA and solution phenomena induced by acid and temperature. The concentration of the polymer solution was 10g/L.

mers were investigated by the addition of acid and the variation of the temperature. The influential factors were determined, and a mechanism of self-assembly and phase behavior was suggested.

## EXPERIMENTAL

### Materials

NVF (98%; Aldrich, Munich, Germany) and 2,2'-azobis(*N,N'*-dimethyleneisobutyramidine) dihydrochloride (VA-044, Wako Chemicals, Inc., Osaka, Japan) were used as received. AA was purified by distillation. All other reagents were analytical-grade and were used without further purification. Hydrochloric acid (6 mol/L) was used to adjust the acidity of the polymer solutions.

### Synthesis of the copolymers

The PNVFAA copolymers were prepared in an aqueous solution at 45°C with 0.1 mol % VA-044 as the initiator. The total monomer concentration of NVF and AA was held constant at 10 wt %. After a designated time, the polymerization was terminated, and the resulting polymer solution was precipitated into acetone. The polymers were further purified by reprecipitation into acetone followed by drying in an oven. The poly(*N*-vinylformamide) (PNVF) and PAA homopolymers were synthesized in the same way.

### NMR experiment

The <sup>1</sup>H-NMR spectra were taken on a Bruker (Fallanden, Switzerland) AV400 spectrometer operated at 400 MHz. All the samples were dissolved in D<sub>2</sub>O; for the PNVF homopolymer, 27, 50, and 70°C were chosen for the temperature-varying NMR experiments.

### Transmission electron microscopy (TEM)

TEM was performed on a JEOL (Tokyo, Japan) JEM-1011 transmission electron microscope operated at

an acceleration voltage of 100 kV. A drop of a very dilute solution (1 g/L) was placed on a TEM copper grid covered by a polymer support film precoated with a thin carbon film. Excess solution was blotted away with filter paper, and the samples were allowed to dry in an oven at about 100°C.

### Measurements of the dynamics

The dynamics were analyzed with a Lambda 900 ultraviolet-visible/near-infrared spectrometer (Perkin-Elmer Instruments, France). The samples (much less cloudy solutions) were frozen to form suspending liquids in a quartz container, with care taken to avoid overcooling, and set at the ambient temperature. Light transmittance was detected at 280 nm at intervals of 0.1 s.

### Particle diameter measurements

Particle diameter and distribution measurements were performed on a Brookhaven (Huntsville, AL) 90 Plus particle sizing instrument at 658.0 nm.

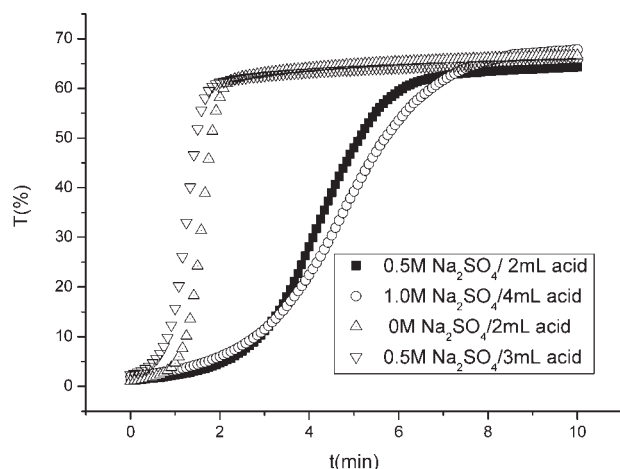
## RESULTS AND DISCUSSION

### NMR experimental analysis

The ratio of NVF to AA units in the copolymers was determined from the integral area of <sup>1</sup>H-NMR, and the results showed that the ratio was similar to that of the feed. The copolymer with a 60/40 molar ratio of NVF to AA was used for most of the experiments unless mentioned otherwise. The number-average molecular weight of PNVFAA(60/40) was 40,0000 g/mol (polydispersity index 1.52), and the other samples had the same magnitude of molecular weight.

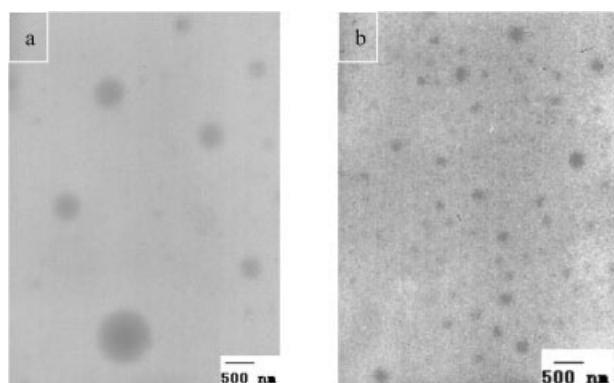
### Phase behavior of the solutions induced by acid and temperature

As shown in Scheme 1, the copolymer solution became a milk-like suspending liquid (state A) when

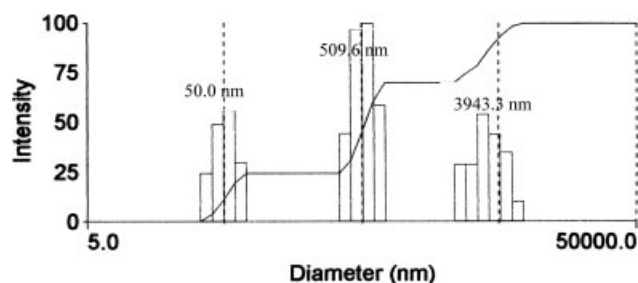


**Figure 1** Relationship between the light transmittance ( $T$ ) and time ( $t$ ) from state C formed at a low temperature to state B at the ambient temperature. The concentration of the polymer solution was 10 g/L.

the pH was adjusted to 2.5–3.0 by the addition of several drops of hydrochloric acid. However, with the addition of excess acid, the suspending liquid immediately became a much less cloudy solution (state B). With more acid, when dropping temperature, the solution became a suspending liquid as shown in Scheme 1 (state C). The temperature-sensitive behavior was reversible. The suspending liquid (state A) became a clear solution at a critical temperature (upper critical solution temperature)<sup>10</sup> upon heating, being similar to PAA,<sup>11</sup> and the solution was still clear when the temperature was up to 100°C (the phenomenon is not shown in Scheme 1); this meant that there was only one insoluble–soluble transition for PNVFAAs with heating. However, the poly[*N*-vinylacetamide-*co*-(acrylic acid)] copolymers showed one S–I–S transition with increasing temperature under acidic conditions.<sup>13</sup> One of the differences between the two systems was that PNVFAAs



**Figure 2** TEM images of the particles morphology in the much less cloudy solution (state B) at different sites on the same copper grid. The concentration of the polymer solution was 1 g/L.



**Figure 3** Multimodal size distribution in the much less cloudy solution (state B). The concentration of the polymer solution was 1 g/L, the concentration of  $\text{Na}_2\text{SO}_4$  was 0 mol/L, and the volume of acid was 2 mL.

just could flocculate (forming a milk-like suspending liquid) at pH 2.2–3.0, while the copolymers of NVA and AA were soluble. The results showed the phase behaviors were discriminated.

#### Self-assembly of the copolymers under highly acidic conditions

Figure 1 shows the relationship between the light transmittance and time from state C formed at a low temperature to state B at the ambient temperature. State B was not a completely transparent solution, the light transmittance was less than 100%, and TEM images showed that the copolymers formed round particles with a broad particle size distribution [Fig. 2(a,b)]. As shown in Figure 3, the particle diameter was distributed to three scales, and the mean diameters were 50.0, 509.3, and 3943.3 nm. Table I shows that the particle size and particle size distribution of PNVFAA were influenced by the amount of salt and excess acid. The particle size distribution was very broad, around 0.35–0.46, and the effective diameter fluctuated greatly. From Table I (entries 1 and 2 and entries 2 and 3), it could be concluded that more salt gave rise to bigger particles, whereas more acid gave rise to smaller particles. The particle size distribution was little influenced by the addition of salt and acid because the particle size was distributed to three

**TABLE I**  
Effects of the Salt Concentration and Amount of Excess Acid on the Effective Diameter and Particle Size Distribution

Number	Concentration of $\text{Na}_2\text{SO}_4$ (mol/L)	Volume of acid (mL)	Effective diameter (nm)	Particle size distribution
1	0	2	368.4	0.430
2	0.5	2	1206.7	0.456
3	0.5	3	472.0	0.343
4	1.0	4	7028.8	0.413

The concentration of the polymer solution was 10 g/L.

**TABLE II**  
Temperature Variation with Different Salt Concentrations and Excess Acid

Number	Concentration of Na <sub>2</sub> SO <sub>4</sub> (mol/L)	Volume of acid (mL)	T <sub>1</sub> (°C)	T <sub>2</sub> (°C)
1	0	2	11	7
2	0.5	2	16	8.5
3	0.5	3	5	-2
4	1.0	4	8	0

The concentration of the polymer solution was 10 g/L.

scales, as shown in Figure 3. When there was 1.0M Na<sub>2</sub>SO<sub>4</sub> in the solution, the effective diameter was up to 7000 nm; this indicated that the aggregation was severe with a high salt concentration.

#### Temperature-responsive behavior under highly acidic conditions

As shown in Scheme 1, under more highly acidic conditions, the much less cloudy solution (state B) could become a suspending liquid (state C) when it was cooled. For the transition from state B to state C, the transition temperatures depended on the Na<sub>2</sub>SO<sub>4</sub> concentration and the amount of excess acid (Table II). T<sub>1</sub> and T<sub>2</sub> were defined as the temperatures when states B and C were formed, respectively. With the same amount of excess acid, T<sub>1</sub> and T<sub>2</sub> with 0.5M Na<sub>2</sub>SO<sub>4</sub> were 16 and 8.5°C, that is, a little higher than the temperatures with no salt (entries 1 and 2). However, with the same concentration of salt, T<sub>1</sub> and T<sub>2</sub> with more acid were much lower (entries 2 and 3).

As shown in Figure 1, the time from state C to state B varied greatly under different conditions. From Figure 1, it was clear that the time was prolonged remarkably when salt was contained, and the time was much shorter when more acid was added. When there was 1.0M Na<sub>2</sub>SO<sub>4</sub> in the solution, although more excess acid (4 mL of excess acid) had been added, the time was still prolonged.

#### Mechanism of self-assembly and phase behavior

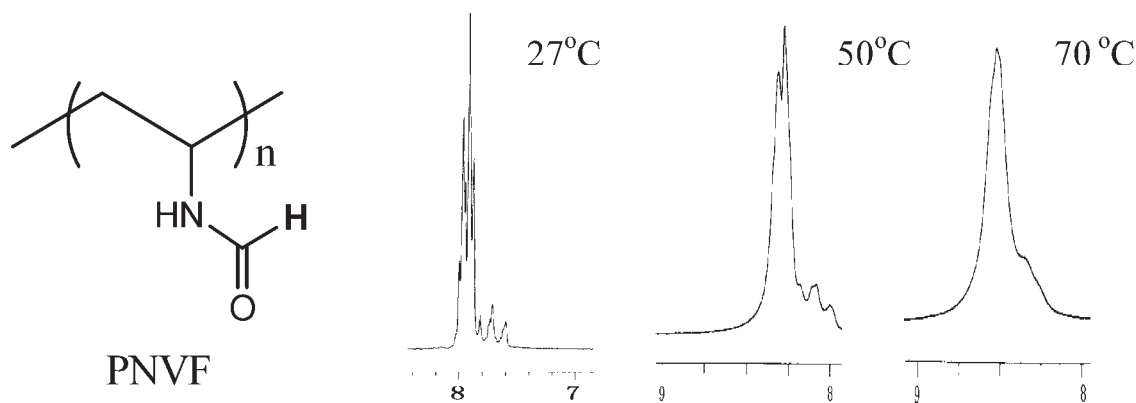
As mentioned by Mori et al.,<sup>13</sup> moderate hydrophobicity is one of the factors for an insoluble-soluble-insoluble phase transition; NVF being more hydrophilic than NVA might be one of the reasons for the different phase behaviors of PNVFAAs and poly[N-vinylacetamide-co-(acrylic acid)] copolymers when the temperature was varied. It could be concluded from Table III that NVF played an important role in the transition because PAA (entry 5) could form a suspending liquid with the addition of acid, but it could not become a much less cloudy solution with the addition of excess acid. The content of NVF in the copolymers had to be moderate because PNVF (entry 4) and the copolymers containing 80% NVF units (entry 2) also could not form a suspending liquid by the addition of acid, and the copolymer containing 20% NVF units (entry 3) experienced the same phenomenon as PAA when acid was added. The suspending liquid of the mixture of PNVF and PAA (entry 6) could not become a much less cloudy solution when excess acid was added, and this meant that the copolymerization of these two monomers was essential for the unique phase-transition behavior.

The temperature-varying NMR spectra for the proton of the aldehyde of PNVF are shown in Figure 4. As the temperature increased, the peak of the proton was broadened, implying that the interaction had been broken by heating. NMR experimentation identified the interaction as hydrogen bonding. The main peak shifted downfield with increasing temperature, as also found by Sato et al.<sup>14</sup> Figure 5 shows that the pH decreased with the concentration of PNVFAA increasing. As is well known, entanglements between chains of macromolecules are enhanced when the concentration of polymers is increased; therefore, we could believe that the formamide group hydrogen-bonded with carboxyl. The strong hydrogen bonding might be the reason for the PNVFAA copolymers flocculating at pH < 3.0.

**TABLE III**  
Phenomena Induced by the Addition of Acid and Variation of the Temperature with Different Polymer Constituents

Number	Polymer	Phenomena		
		From solution to state A	From state A to state B	From state B to state C
1	PNVFAA (60/40)	Detectable	Detectable	Detectable
2	PNVFAA (80/20)	Undetectable	—	—
3	PNVFAA (20/80)	Detectable	Undetectable	—
4	PNVF	Undetectable	—	—
5	PAA	Detectable	Undetectable	—
6	Mixture (PNVF/PAA)	Detectable	Undetectable	—

The concentration of the polymer solution was 10 g/L. *Detectable* means that the phenomenon could be detected as shown in Scheme 1. *Undetectable* means that the phenomenon could not be observed as shown in Scheme 1. A dash means that the experiment was not carried out anymore.



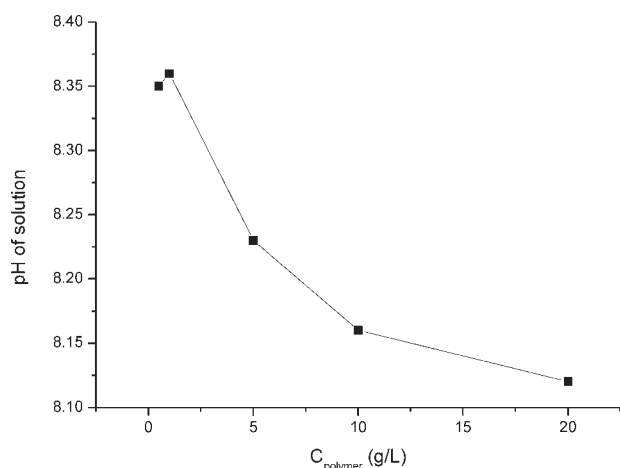
**Figure 4** Temperature-varying  $^1\text{H}$ -NMR spectra of the formamide group in PNVF.

Most of the carboxyls had to be protonated under highly acidic conditions because the degree of ionization of PAA was less than 1% at pH 2.5<sup>15</sup> and formed a hydrogen bond. Generally, the hydrogen bonding was still unbroken under this condition; that is, the unique phase behavior was not caused only by the units of AA in the copolymers. It is well known that PNVF can be hydrolyzed into poly(*N*-vinylamine);<sup>16</sup> however, the suspending liquid (state A) disappeared at once, and the hydrolysis could not be as rapid at the ambient temperature.<sup>17</sup> Under the highly acidic conditions, the formamide group might be protonated; consequently, the copolymers could behave as polyelectrolytes.<sup>18</sup>

The broad particle size distribution (see Table II) might be caused by two features: the polydispersity of the polymer molecular weight and the aggregation of particles. As shown in Table I, very big particles could be detected, so it was believed that aggregation was the main reason for the broad distribution. Some of the clusters might be impelled to

disperse nanosize round particles by increases in the hydrophilicity and repulsive electrostatic forces of the formamide groups after protonation. The addition of more salt screened the charge of PNVF<sub>AA</sub>, so more aggregation occurred. In contrast, adding more excess acid enhanced the repulsive electrostatic forces, and this let more clusters disperse to form nanoparticles, so the effective diameter was depressed.

The addition of salt screened the repulsive electrostatic forces, and the polymer chains were more flexible,<sup>17</sup> so the chains could find suitable sites to form stronger hydrogen bonds, and state C needed more time to change to state B when the temperature was elevated (see Fig. 1) to break the interaction. If there was no salt or more excess acid in the solution, the chains were more rigid because of the repulsive electrostatic forces, and it was difficult to form strong hydrogen bonds, so little time was needed. The reversible temperature-responsive behavior of states B and C might be aggregation and dispersion of the nanosize round particles.



**Figure 5** Effect of the polymer concentration ( $C_{\text{polymer}}$ ) on the pH of the polymer solution. The solution was aged overnight.

## CONCLUSIONS

Random copolymers of PNVF<sub>AA</sub> with a moderate number of NVF units showed complex phase behaviors under highly acidic conditions. The copolymers assembled to form round nanoparticles with a broad particle size distribution, and the particles contained a solution that became a suspending liquid when it was cooled. The effective diameter and temperature-responsive behavior depended on the amount of salt and excess acid. Acid could effectively depress aggregation, in contrast to the salt effect. Because the formamide groups might be protonated under highly acidic conditions, the copolymers behaved as polyelectrolytes. The repulsive electrostatic forces could compel the aggregates to disperse, whereas salt could screen the repulsive electrostatic forces and let particles aggregate.

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