Synthesis and Functionalities of Poly(*N*-vinylalkylamide). 13. Synthesis and Properties of Thermal and pH Stimuli-Responsive Poly(vinylamine) Copolymers

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ABSTRACT: The thermoresponsive and pH-responsive intelligent copolymers of *N*-vinylformamide (NVF) and *N*-vinylisobutyramide (NVIBA), and their derivatives with primary amino groups, were synthesized. Hydrolysis of poly(NVF), poly(NVIBA), and poly(NVF-*co*-NVIBA) to obtain poly(vinylamine) [poly(VAm)] was carried out under acidic conditions, at 30 °C in a transparent homogeneous solution system below the lower critical solution temperature (LCST) of poly(NVIBA). Poly(NVIBA)'s chemical structure was not affected at all by dissolution in 2 N HCl for 3 weeks, with complete retention of the side chains, whereas poly(NVF) was completely hydrolyzed after 2 weeks in 2 N HCl. The NVF unit of poly(NVF-*co*-NVIBA) was able to hydrolyze selectively, and it has become feasible to make poly(VAm-*co*-NVIBA). Aqueous hydrolyzed copolymer solutions (0.2 wt %) did not show LCSTs below $pK_a = 10.0$, although they became slightly turbid, whereas in the pH 12.0 (above pK_a), the copolymers clearly exhibited LCSTs. Above pK_a, the LCST increased successively depending on the poly(VAm) content of the copolymer. Hydrogels with stimuli-responsive property were prepared by hydrolysis of poly(NVF-*co*-NVIBA) hydrogel (NVF content; 30 mol %) in 2N HCl solution at 30 °C for 12 h. The hydrolyzed copolymers were found to exhibit thermal and/or pH responsiveness. The primary amine-containing polymers are intelligent polymers and can act as chemical modifiers.

Introduction

Water-soluble synthetic polymers have important roles as a variety of functional polymers, including biomaterials, stimulus-responsive materials, and chemical modifiers. Poly(vinylamine) (poly(VAm)) is one of the simplest and most important polymers due to significant modification possibilities. Poly(VAm), a linear polymer with all primary amine groups that are all bonded directly to the main chain, is of interest because of its pH-dependent polycationic nature. Poly(VAm) forms chelating complexes with various heavy metal ions,[1,2] serves as a support matrix to immobilize enzymes,[3] and acts as a flocculant.[4] Modified poly(VAm) is anticipated to be similarly useful in polymeric water-soluble dyes,[5] mimicking natural enzymes,[6] as a polymer surfactant,[7] etc. However, vinylamine monomer, as the simplest precursor to poly(VAm), is not available in the free state, because it tautomerizes so readily to acetaldehyde imine. Therefore, poly(VAm) has been synthesized only via indirect routes. It is most convenient to produce poly(VAm) from poly(*N*-vinylamide)s by hydrolysis.[5,8,9]

N-Vinylamides are fundamental derivatives of vinylamine that have amide bonds in their side chains in an inverted direction to the corresponding acrylamide derivatives. They are easily polymerized by radical polymerization, and the resulting polymers are regarded as simple protein models. This class of compounds includes many derivatives that are potential starting materials for water-soluble functional polymers.[10−15] Furthermore, it is possible to produce copolymers with a wide variety of functions. Some water-soluble polymers in the poly(*N*-vinylamide) class of compounds show a reversible phase-transition phenomenon.[12]

Poly(*N*-vinylisobutyramide) (poly(NVIBA)), a thermoresponsive water-soluble polymer, showed a lower critical solution temperature (LCST) at 39 °C.[12] Poly(NVIBA) has been considered to represent a simple but relevant protein model, similar to poly(*N*-isopropylacrylamide) (poly(NIPAAm))[16,17] with a LCST at 32 °C.[18−20] At these temperatures, poly(NIPAAm) makes coil-to-globule reversible transitions.[19] In addition, these transitions are induced by salt concentration,[22,23] surfactant addition,[24] saccharide addition,[25] solvent,[26] etc. A series of poly(acrylamide) derivatives having different alkyl groups in their side chains were synthesized, and their LCST behaviors were found to depend mainly on the polymer side chains.[27] The LCSTs of copolymers formed from NIPAAm with other *N*-alkylacrylamides have also been reported to be between 0 and 65 °C.[28,29] It is clear that the transition temperature of these polymers depends on the hydrophobic−hydrophilic balance.

A series of poly(*N*-vinylamide) derivatives having different alkyl groups on their side chains were polymerized and then copolymerized.[9,12,13] Their LCSTs were found to depend mainly on the polymer side chains. Poly(NVIBA) also exhibits protein-like behaviors. The addition of salt decreases the LCST of aqueous poly(NVIBA) solution almost linearly with the salt concentration and is dependent on the type of salt.[14] From changes observed in the light transmission data during temperature scanning and during pressure scanning of poly(NVIBA) and poly(NIPAAm) solutions, contour lines were made by connecting the midpoint of the light transmission change in the temperature−pressure dia-

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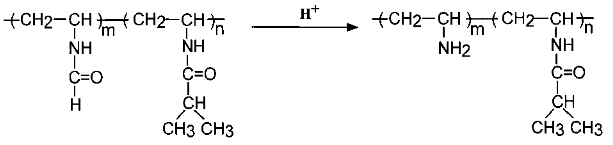
Scheme 1



poly(NVF-co-NVIBA) poly(VAm-co-NVIBA)

gram.[15] The result was almost identical to the ellipsoid diagrams obtained for the temperature–pressure dependence of protein denaturation.[30]

Hoffman defined intelligent polymers as those polymers that respond with large property changes to small physical or chemical stimuli.[31–33] He suggested temperature change, pH level, ions, electric fields, solvents, reactants, light or UV radiation, stress, recognition, and magnetic fields as examples of environmental stimuli. Moreover, Hoffman indicated that reversible and abrupt phase change in volume is a typical example of a sharp response to a stimulus for aqueous-based intelligent polymers in solution. However, he assumed that intelligent polymers should respond independently to several factors, such as temperature and pH.

Here we report on the results of the hydrolyses of poly(NVF), poly(NVIBA), the random copolymers of NVF and NVIBA [poly(NVF-*co*-NVIBA)], and copolymer gels, as summarized in Schemes 1 and 2. The expected hydrolysis product from both poly(NVF) and poly(NVIBA) is poly(VAm). Responsiveness to environmental stimuli, i.e., the thermal and pH responsiveness, of hydrolyzed copolymers and copolymer gels is discussed. Hydrolyzed copolymers and copolymer hydrogels undergo marked solubility changes in water in response to temperature and/or pH changes.

Experiment

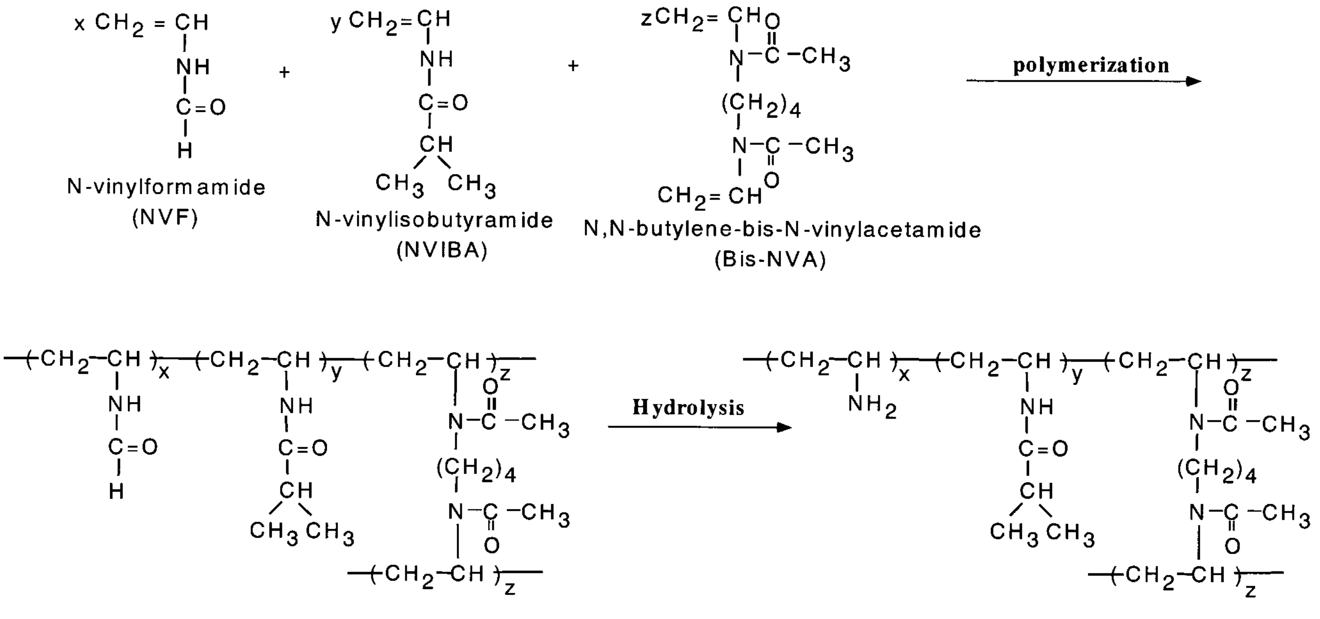
Materials. NVF (Mitsubishi Chemical, Co. Ltd.) was distilled under reduced pressure before use. NVIBA was synthesized according to a previously reported method.[12] The resulting monomer was purified by recrystallization from *n*-hexane and dried in vacuo at room temperature. *N*,*N*-butylenebis(*N*-vinylacetamide) (Bis-NVA) as a cross-linker was prepared according to the method reported previously.[14] 2,2′-Azobis(isobutyronitrile) (AIBN, Wako Pure Chemical Ind. Ltd.) was recrystallized from ethanol and dried in vacuo at room temperature. 2,2′-Azobis(*N*,*N*-dimethyleneisobutyramidine) dihydrochloride (VA-044, Wako Pure Chemical Ind. Ltd.) was used without further purification. Solvents were purified in the usual way prior to use. The wet cellulose dialysis tubing used was no. 1000 molecular weight cutoff from Spectrum Medical Industries, Inc.

Polymerization. The homopolymers and copolymers were prepared by free radical polymerization using azo initiators (1 mol % with respect to total monomer). The poly(NVF) and poly(NVIBA) were synthesized according to a previously reported method.[9] Copolymers with various compositions were also prepared from NVF and NVIBA in methanol at 60 °C for 24 h in sealed tube using AIBN as an initiator. The reaction mixture was then placed in cellulose dialysis tubing. Purification was achieved by continual dialysis at room temperature for several days against regularly replaced pure water. The polymers and copolymers were recovered by lyophilization.

Preparation of Hydrogel. Hydrogels were prepared by free radical polymerization with various mixtures of NVF with NVIBA and was carried out in methanol using Bis-NVA as the cross-linker, as is shown in Scheme 2. NVF and NVIBA (total monomer concentration; 3 mmol), Bis-NVA (1 mol % with respect to total monomer), and AIBN as a radical initiator were dissolved in 1.5 mL of methanol and bubbled with dry nitrogen gas for 10 min. The solutions were injected between double glass plates that were separated by a Teflon gasket (3 × 4 cm) (1.0 mm thickness). The solutions were polymerized at 60 °C for 24 h. After polymerization, the gel membranes were separated from the double glass plates and were cut into disks (10 mm diameter) using a cork borer. These gel membranes were then immersed in methanol to remove unreacted compounds at room temperature for several days against regularly replaced methanol. These gel membranes were then soaked in distilled water for 1 week at room temperature, with the water changed every day. Prior to measuring, the gel membranes were equilibrated in water and then recovered by lyophilization.

Hydrolysis. Hydrolysis of poly(NVF), poly(NVIBA), and poly(NVF-*co*-NVIBA) was carried out under acidic conditions as follows. The polymers (100 mg) were dissolved in 5 mL of

Scheme 2



poly(NVF-co-NVIBA) hydrogel poly(VAm-co-NVIBA) hydrogel

2 N HCl (2 wt % polymer concentration) and were kept at the given temperatures for the given time. After being neutralized, the polymer solutions were then placed in cellulose dialysis tubing. Purification was achieved by dialysis continued at room temperature for several days against regularly replaced pure water. The hydrolyzed polymers were recovered by lyophilization.

The hydrolysis of poly(NVF-*co*-NVIBA) hydrogel (NVF content; 30 mol %) was carried out under 2 N HCl solution at 30 °C for 12 h. After being neutralized, the hydrolyzed gel membranes were then soaked in distilled water for 1 week at room temperature with the water changed every day.

Characterization. The molecular weights of poly(NVF) were determined via aqueous size exclusion chromatography (SEC) on a TSK guard column PWXL with one column each of TSK gel G4000PWXL and G6000PWXL at 40 °C with aqueous 0.1 M NaCl eluent at a flow rate of 1.0 mL min^{-1}. The molecular weights of poly(NVIBA) and poly(NVF-*co*-NVIBA) were characterized using gel permeation chromatography (GPC). GPC analysis was performed on a TOSOH HLC-8120GPC with a TSK Super H-L as the guard column, and one column each of TSK gel Super H3000 and Super H4000. DMF (included 10 mM LiBr) was used as eluent at a flow rate of 0.6 mL min^{-1} at 40 °C. Calibration was performed with commercial poly(ethylene oxide) (TSK standard TOSOH CO.).

^{1}H NMR spectra were recorded on a JEOL GSX-400 (400 MHz). 3-(Trimethylsilyl)propanesulfonic acid sodium salt (DSS) was added as an internal reference in D_2O. The composition ratios of the copolymers and the proportion of hydrolytic cleavages were determined by comparing the signal intensity of the side chain aldehyde protons (7.9−8.2 ppm) in the poly(NVF) and poly(NVF-*co*-NVIBA) and the side chain methyne protons (2.4−2.6 ppm) in the poly(NVIBA) and poly(NVF-*co*-NVIBA).

Thermosensitive Properties. The LCSTs of 0.2 wt % polymer solutions were observed using a Jasco Model V-550 spectrophotometer at 500 nm, using a Peltier type thermostatic cell holder coupled with a controller ETC-505T to determine the turbidity. The rates of heating and cooling of the sample cells were adjusted to 1.0 °C min^{-1}. Temperature was controlled by PID constants using a computer. The LCST was defined as 50% transmittance of polymer solution during the heating process. Hydration of the polymer solution, which varied in NVF components, was observed by differential scanning calorimetry (DSC). DSC was done on a Seiko Instruments Inc. DSC 6100 at a heating rate of 2 °C min^{-1}. Transition temperatures were determined from the intersection point of the baseline and the edge of the endotherm. Polymer solutions were prepared with Milli-Q (Millipore, Bedford, Warrington, PA) grade water (pH 5.5), and alkaline conditions were prepared with 0.01 N NaOH solution.

The swelling weight for the given hydrogels in water was gravimetrically measured. The swelling ratio was defined as $Wt/W_{20} \times 100$ (%), where Wt is the swollen weight of a gel in pure water at t (°C) and W_{20} the swollen weight of a gel in pure water at 20 °C.

Results and Discussion

Copolymerization of Poly(NVF) and Poly(NVIBA). Table 1 shows the results of copolymerization of NVF and NVIBA. The number-average molecular weights (M_n) were around 3×10^4 g mol^{-1}, polydispersities around 3, and conversions approximately 90%. The copolymer composition ratios were similar to the monomer concentration ratios in the feed. The monomer reactivity ratios r_1 and r_2 values were 1.08 and 0.92 (M_1 = NVF, M_2 = NVIBA), as reported before,[9] indicating that the reactivity of NVIBA vinyl groups was nearly the same as that of NVF. These results suggest that NVIBA can also be classified as a nonconjugative monomer, as is NVF. Therefore, the comonomers were definitely converted to random copolymers. The feed ratios of the monomers and the copolymer compositions were very similar, as is expected in a random copolymer. As well, the observed absence of a compositional drift between the low and high conversion samples is also characteristic of random copolymers.

Table 1. Copolymerization of NVF with NVIBA at 60 °C for 24 h[a]

run	in feed (mol %) NVF	NVIBA	$M_n^b \times 10^{-4}$	M_w/M_n^b	yield (%)	in copolymer (mol %)[c] NVF content
1	10	90	2.8	3.4	78	8
2	20	80	3.4	2.8	89	18
3	25	75	3.1	2.9	94	24
4	30	70	3.3	2.7	89	26
5	40	60	3.1	2.5	95	39

[a] Polymerization was carrid out in methanol using AIBN (1.0 mol %) as an initiator. [b] Estimated by GPC (standard; PEO). [c] Determined by ^{1}H NMR(400 MHz); D_2O.

Table 2. Preparation of Hydrogels by Copolymerization[a]

run	in feed (mol %) NVF	NVIBA	conversion (%)[b]
1	0	100	92
2	10	90	91
3	20	80	88
4	30	70	90

[a] Polymerization was carried out in methanol using AIBN (1 mol %). [b] Calculated by the weight of dried gel.

Hydrogel Synthesis. In the preparation of hydrogels, the nonconjugated divinyl compound, Bis-NVA, as cross-linker was synthesized in advance to achieve the suitable copolymerizability with NVF and NVIBA. Hydrogels were prepared by radical copolymerization with various mixtures of NVF with NVIBA in methanol at 60 °C for 24 h in a sealed tube using AIBN as initiator, as shown in Scheme 2. Table 2 shows the monomers and poly(NVF-*co*-NVIBA) content of gel yields. The conversion of hydrogels was over 90%, suggesting that the polymerizabilities of both monomer (NVF, NVIBA) and cross-linker (Bis-NVA) were fairly good under the experimental conditions employed here.

Hydrolysis of Homopolymer and Copolymer. Poly(NVF) was completely hydrolyzed at 80 °C after 100 min under both acidic and basic conditions, as illustrated in a previous paper,[9] while poly(NVIBA) did not cleave under 2 N HCl acidic conditions or in 2N NaOH basic conditions at 140 °C after 100 min. In the hydrolysis of homopolymers, after 3 weeks in a 2N HCl acidic conditions at 30 °C in a transparent homogeneous solution system below its LCST, poly(NVIBA)'s chemical structure was not affected, and it completely retained its side chains, as shown in Figure 1. The poly(NVF) was completely hydrolyzed after 2 weeks at 30 °C. Hydrolytic cleavage depends on the hydrophobicity of the substituent [H < $CH(CH_3)_2$]. These results have facilitated selective hydrolysis of poly(NVF-*co*-NVIBA), and it has thus become feasible to make poly(VAm-*co*-NVIBA). In the hydrolysis of copolymers, approximately 2 weeks after, only the poly(NVF) units in poly(NVF-*co*-NVIBA) were almost entirely hydrolyzed. Under these conditions, copolymer hydrolysis was affected somewhat by interference from completely retained poly(NVIBA)'s side chains.

Stimuli Responsiveness of Linear Polymers. The hydrolyzed copolymers were dissolved in Milli-Q grade water of pH 5.5 in these runs, and the side chain amino groups existed in the cationic charged form. According

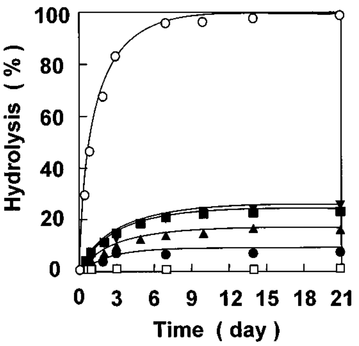


Figure 1. Time–conversion for hydrolysis of 2 wt % aqueous poly(NVF) and poly(NVIBA) solutions in 2 N HCl at 30 °C: (○) poly(NVF), $M_n = 2.6 \times 10^4$; (□) poly(NVIBA), $M_n = 2.2 \times 10^4$. Poly(NVF-*co*-NVIBA), NVF content (●) 8, (▲) 18, (■) 24, and (▼) 26 mol %.

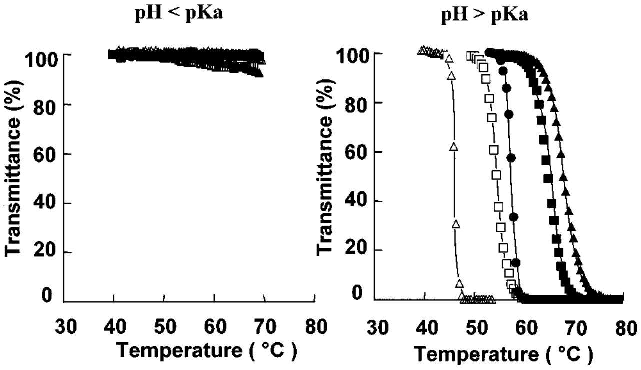


Figure 2. Temperature dependence of light transmittance of 0.2 wt % aqueous solution of hydrolyzed poly(NVF-*co*-NVIBA) on heating processes at pH 6.8–8.8, below the p*K* of amino groups 10.0, and pH 12.0–12.2, above the p*K* of amino groups 10.0. Hydrolysis conditions: 2 N HCl, 30 °C. Poly(VAm) content: (△) 8, (□) 18, (●) 24, (▲) 26, and (■) 39 mol %.

to the results of previous experiments of characterizing protonation of aqueous poly(VAm) solutions, the intrinsic pK_a of the amino group is 10.0.[34] Figure 2 shows the temperature dependence of light transmittance of 0.2 wt % aqueous hydrolyzed copolymer solutions in the pH range 6.8–8.8 (below pK_a). The NVF units of sample copolymers used were completely hydrolyzed. None of the samples showed LCSTs, though they became slightly turbid, whereas in the pH range 12.0–12.2 (above pK_a), the copolymers clearly displayed the LCSTs.

To further clarify the thermosensitive phenomena of linear copolymer solutions, a DSC study was performed. As NVF content increased, the endothermic peak corresponding to copolymer's LCST shifted to a higher temperature, and the transition enthalpy for poly(NVF-*co*-NVIBA) decreased. Figure 3 shows the relationship between the hydrophilic unit content and the LCST or the transition enthalpy. When the pH value of the solution was kept above the pK_a, we confirmed a peak shift for poly(VAm-*co*-NVIBA) aqueous solution similar to that of poly(NVF-*co*-NVIBA). Under conditions where pH > pK_a, as VAm content increased, the transition enthalpy also decreased for poly(VAm-*co*-NVIBA). These two copolymers appear to share that there is a relationship between hydrophilic unit content and the LCST as well as the transition enthalpy. In the pH range 12.0–12.2, the LCST temperatures increased successively, and this increase was dependent on the poly(VAm) content.

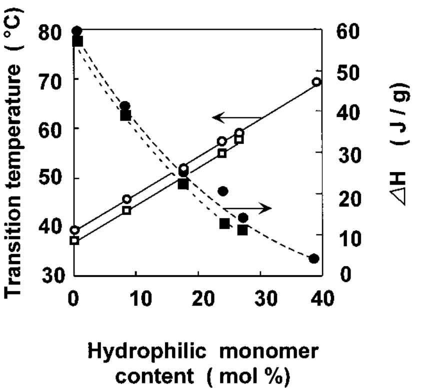


Figure 3. Relationship between the hydrophilic monomer content (mol %) and transition temperature (°C) or the transition enthalpy (J/g). Conditions: (○, ●) poly(NVF-*co*-NVIBA); (□, ■) poly(VAm-*co*-NVIBA).

A similar behavior can be expected from some other aqueous polyelectrolyte solutions. The LCSTs of a graft copolymer between NIPAAm and acrylic acid (AAc) [poly(NIPAAm-*g*-AAc)] appear at different temperatures as the pH increases from 4.0 to 7.4, that is, above and below the p*K* of AAc, respectively.[32] Distinct phase transitions are observed at pH levels that are below the pK_a of the poly(AAc), following neutralization of the $-COOH$. As the pH is raised above the pK_a of the acid groups, ionizing them to $-COO^-$, the LCST increases and the sharpness of the phase transition profile decreases. 4-Pentenoic acid (PAc) is more hydrophobic than NIPAAm in the acid form; on the other hand, PAc is more hydrophilic than NIPAAm in the ionized state. The random copolymers of NIPAAm and PAc [poly(NIPAAm-*co*-PAc)] have a LCST below 32 °C at low pH levels and a LCST above 32 °C at high pH levels. At pH 4.0, the LCSTs of poly(NIPAAm-*co*-PAc) decrease with an increase in the number of PAc units in the copolymer, and the phase transitions of the copolymer solutions become very sharp. At pH 7.5, the LCSTs of poly(NIPAAm-*co*-PAc) increase with an increase in PAc content, and the phase transitions of the copolymer solutions are not as sharp as those at low pH.[33]

Stimuli Responsiveness of Hydrogels. The resulting poly(NVF-*co*-NVIBA) gels, which had a 0–30 mol % NVF content, was amphiphilic and swelled readily in cold water, methanol, ethanol, and DMF. The swelling behavior was reflected in the solubility profile of linear poly(NVF-*co*-NVIBA)s.

The actual shrinking of poly(NVF-*co*-NVIBA) hydrogels (NVF content; 0, 10, 20, 30 mol %) in pure water was demonstrated in the series of photographs, shown in Figure 4. Figure 5 shows the shrinking curves of these hydrogels as a function of temperature. The hydrogels became opaque after stepwise temperature increases from 20 to 65 °C. This indicates that the polymer networks became heterogeneous after the temperature jumps. A similar behavior has been reported in other hydrogels. The poly(NIPAAm) hydrogel was reported to form skin layers, and this process of skin formation was mediated by diffusion of the collapsing polymer network at the interface.[35,36] Figure 6 shows the relationship between the hydrophilic NVF unit content and the LCST or the transition enthalpy. As NVF content in the hydrogels increased, the phase transition temperature shifted to a higher temperature, and the transition enthalpy for linear poly(NVF-*co*-NVIBA) decreased. As shown in Figures 5 and 6, the

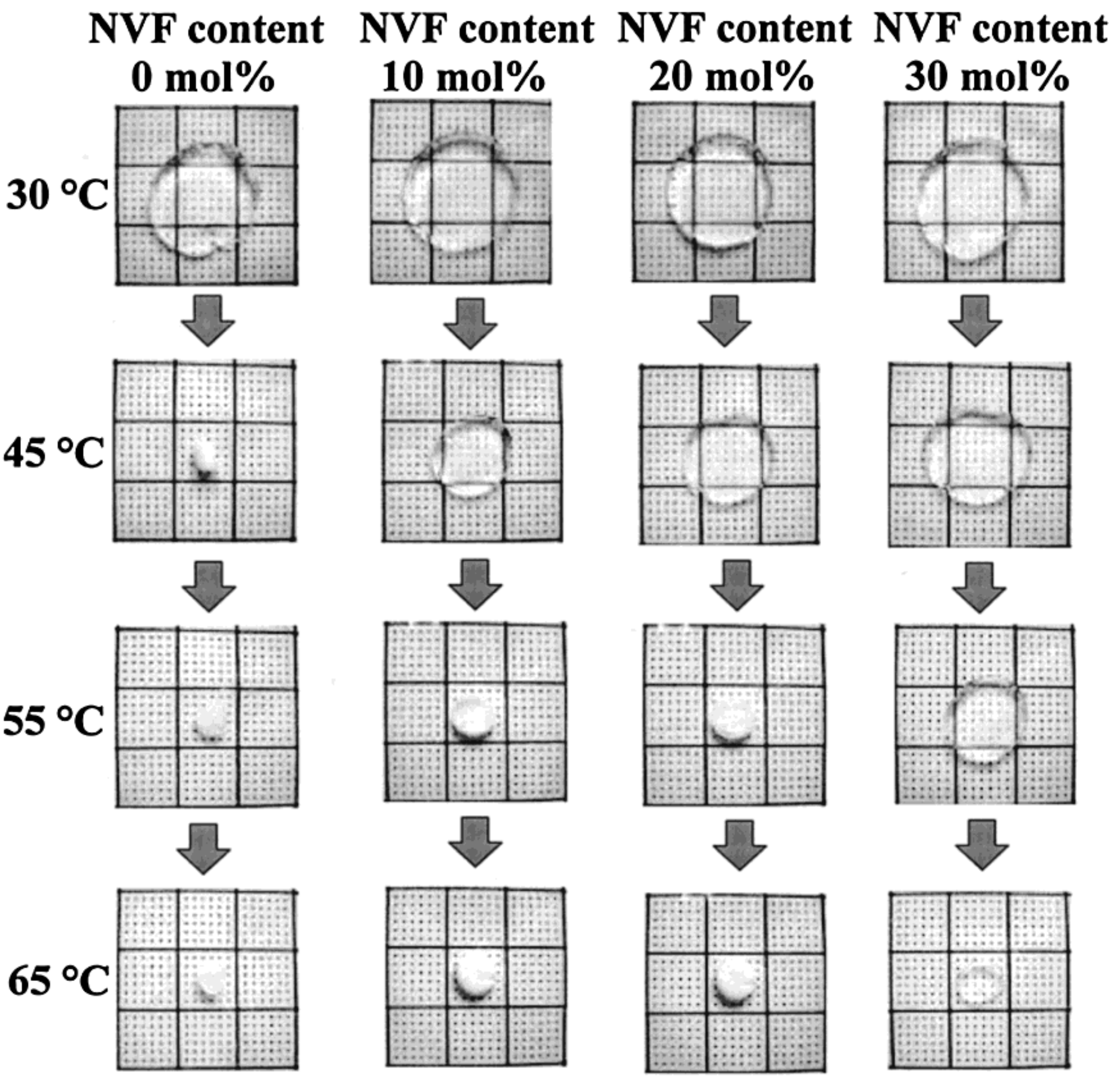


Figure 4. Swelling–shrinking behaviors of poly(NVF-*co*-NVIBA) hydrogels NVF content: (○) 0, (△) 10, (□) 20, and (▽) 30 mol %.

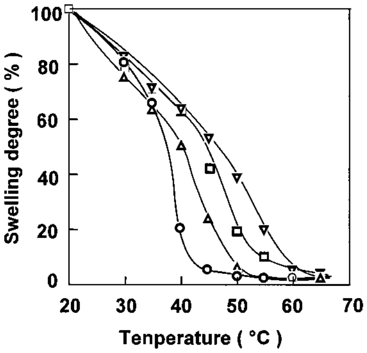


Figure 5. Shrinking curves of poly(NVF-*co*-NVIBA) hydrogel as a function of temperature. NVF content: (○) 0 , (△) 10, (□) 20, and (▽) 30 mol %.

phase transition temperature of the hydrogels increased with an increase in the NVF content of the gel network chains. The transition temperature of the hydrogels was almost the same as that for linear copolymers of NVF with NVIBA.

Finally, we report on the thermal and pH responsiveness of primary amine-containing hydrogel. Figure 7 shows the swelling–shrinking behaviors of hydrolyzed copolymer hydrogels. At pH 5.5, the resulting hydrogels did not show volume phase transitions. At pH values above the pK_a, the hydrogels showed volume phase transitions. The side chain amino groups existed in the free base form at pH 12.0; therefore, they were neutral and their hydrophilicity was weaker than that of cationic salts. The hydrolyzed hydrogels have been found to exhibit both thermal and pH responsiveness. Therefore, the primary amine-containing hydrogels are intelligent polymers and can act as a chemical modifier.

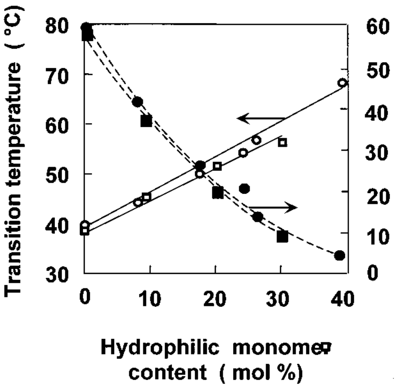


Figure 6. Relationship between the hydrophilic monomer content (mol %) and transition temperature (°C) or the transition enthalpy (J/g). Conditions: (○, ●) linear poly(NVF-*co*-NVIBA); (□, ■) poly(NVF-*co*-NVIBA) hydrogel.

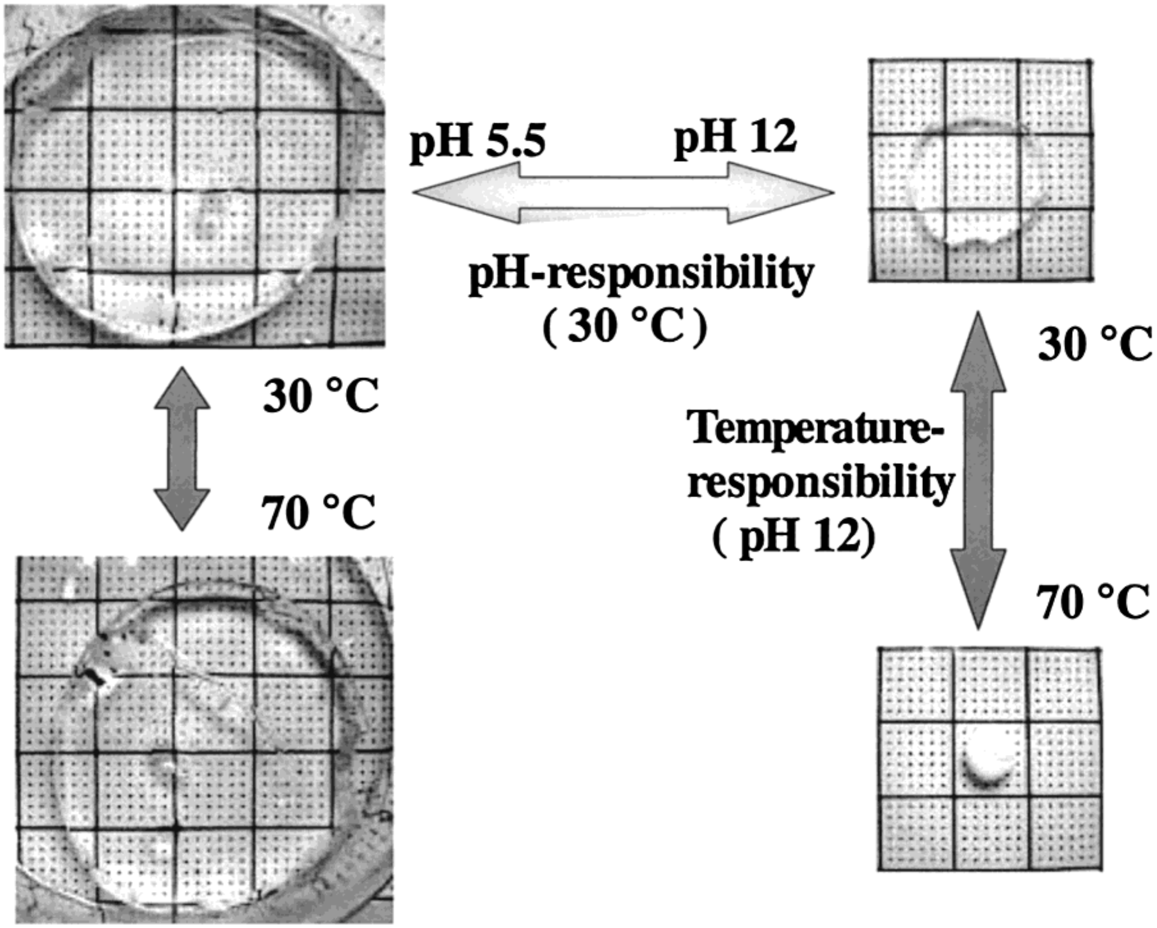


Figure 7. Swelling−shrinking behaviors of hydrolyzed copolymer hydrogels.

Conclusion

The results of this study show that the polymerizabilities of NVF and NVIBA and their respective copolymerizabilities were fairly good under the experimental conditions employed. Poly(NVF) and poly(NVIBA) were hydrolyzed under acidic conditions at 30 °C, in a transparent homogeneous solution system below the poly(NVIBA)'s LCST temperature. After 3 weeks in 2 N HCl acidic conditions, the chemical structure of poly(NVIBA) was not affected, with complete retention of the side chains, whereas poly(NVF) was completely hydrolyzed after 2 weeks. Under these conditions, poly(NVF-*co*-NVIBA) could be selectively hydrolyzed, and it is feasible to make poly(VAm-*co*-NVIBA). The poly(VAm-*co*-NVIBA) solutions (0.2 wt %) in the pH range 6.8−8.8 (below $pK_a = 10.0$) did not show a LCST, although they became slightly turbid, whereas in the pH range 12.0−12.2 (above pK_a), the copolymers clearly exhibited the LCSTs in water. At pH values above the pK_a, the LCST increased successively depending on the poly(VAm) content of copolymers. The side chain amino groups existed in the free base form at the pH values; therefore, they were neutral and their hydrophilicity was weaker than that of cationic salts at pH levels below pK_a. The primary amine-containing polymers have been found to exhibit thermal and pH responsiveness. The primary amine-containing hydrogels with thermal and pH responsiveness were successfully prepared by using a suitable cross-linker. It is considered that poly(*N*-vinylamide) derivatives are intelligent polymers and can act as chemical modifiers.

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