Synthesis and Solution Properties of Single-Chain Microgels from Poly(*N*-isopropylacrylamide) Copolymer

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ABSTRACT: "Single-chain" microgels were synthesized successfully from the cross-linkable poly(*N*-isopropylacrylamide) (PNIPAM) copolymer. This type of microgel has the exact chemical structure, molecular weight and molecular weight distribution of its precursor. It provides a direct way to compare the properties of linear polymers with those of their networks. The viscosity properties show that the microgels have lower critical solution temperatures (LCST) that are even higher than those of the corresponding linear copolymers. This can be attributed to the crosslinking points, which retard the change of the conformation of the network chains. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2179–2183, 2003

Key words: polyamides; transitions; microgels

INTRODUCTION

The relationship between polymer network properties and their structure is a basic topic in polymer physics and its applications. Owing to the fact that the polymer network cannot be dissolved or melted, there are only limited experimental ways to carry out structure characterization. This greatly retards the development of the network theory. It is well known that the properties of a polymer network are related to the corresponding linear polymer very closely. However, there are two major differences between them. First, a great difference appears in the molecular weight and molecular weight distribution. Second, the chemical composition is also different due to the introduction of the crosslinking agent. It will be helpful to study the effect of the crosslinking points from the network samples without these difficulties.

Poly(*N*-isopropylacrylamide) (PNIPAM) has an interesting coil-to-globule transition in water around room temperature. Much attention has been devoted to the study of the transition mechanism, the effects of the environment and the possible applications of the transition, especially in the development of controlled release drugs in the last three decades.[1–4] The solution behavior with the addition of surfactant [such as sodium n-dodecyl sulfate (SDS)] is interesting.[5–7] There is no visible phase separation of PNIPAM aqueous solution when the temperature is higher than its lower critical solution temperature (LCST). The surfactant is adsorbed onto the globule surface, which prevents association among the spheres during the coil-to-globule transition. With sufficient SDS molecules, the globules can be reduced to only one PNIPAM chain in each emulsion like particle. This indicates that the microgels should be prepared with both the molecular weight and the chemical constitution exactly as same as those of the precursor linear polymer if the crosslinking reaction is to take place in this special system. In this article, the single-chain microgels are prepared and their properties are studied. The difference between the microgels and their precursors can be attributed to the effects of the crosslinking points.

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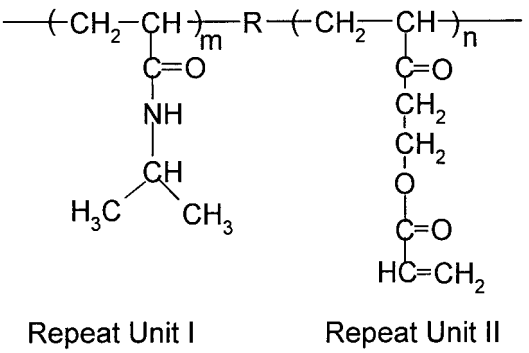
EXPERIMENTAL

Preparation of macro-monomer

N-isopropylacrylaminde was purchased from Acros Company, USA and was re-crystallized three times before use. The monomer was dissolved in methanol with a 5% molar ratio of hydroxyehtylacrylate. The mixture was polymerized for 7 h at 65°C under nitrogen protection with 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator. The product was dissolved in acetone after the removal of methanol. Then the solution was dropped into n-hexane, and the precipitate was collected and dried in vacuum. The un-reacted monomer was removed by immersing the solid sample in ether for 24 h. The copolymer was dissolved in fresh distilled pyridine over CaH_2, and freshly prepared acryloyl chloride was dropped in slowly. (The final ratio was about 10 : 1 for acryloyl chloride :

hydroxyl groups). The reaction system was maintained at room temperature for 12 h. The macro-monomer was precipitated in n-hexane after the pyridine salt had been removed by centrifugation. The product was further purified by dissolving it in acetone and precipitating it in n-hexane twice. The chemical structure of the prepared macro-monomer was drawn as follows:



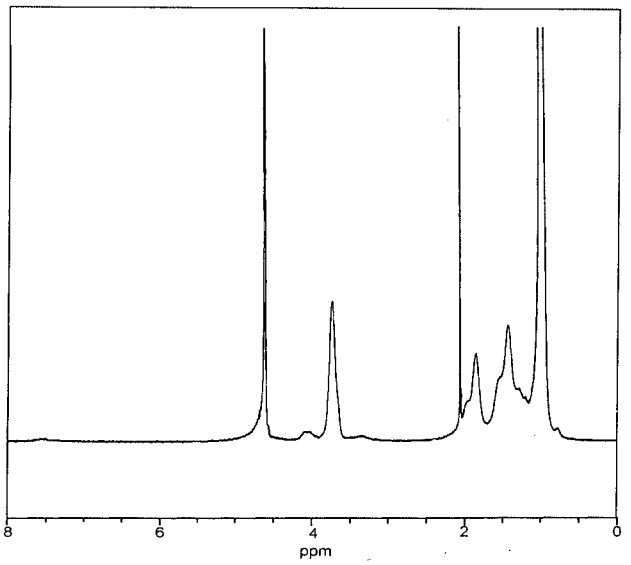


Figure 1 H-NMR spectrum of the crosslinkable poly(*N*-isopropylacrylamide) macro-monomer.

Synthesis of single-chain microgels

The synthesis of the microgels involved mixing 0.1 g macro-monomer and 0.5 g sodium n-dodecyl sulfate with 1 L deionized water and holding it at 70°C for one hour with bubbling nitrogen gas. The initiator, ammonium peroxysulfate, was added and the crosslinking reaction ran for 4 h. The reacted solution was concentrated to 100 mL and then transferred into a dialysis bag. The bag was placed in a water bath, and dialysis was accelerated by placing the bag under an electrostatic field to remove the surfactant (SDS) for several days. The endpoint of dialysis was tested by a saturated $BaCl_2$ and water solution. Finally, the single-chain microgel sample was collected from the precipitate in n-hexane.

Characterization

Three types of characterization were employed: size exclusion chromatography (SEC), differential scanning calorimetry (DSC), and viscometry. In SEC, a WATERS Model 244 GPC-LC chromatograph was connected to 500 Å, 10^3 Å and 10^4 Å μ-Styragel columns in series. The flow rate was kept at 1.0 mL/min with tetrahydrofuran (THF) as the eluent at room temperature using a WATERS Model R401 differential refractometer as the detector. The injection volume was 200 μL and the detection response was collected and recorded by computer automatically. The column set was calibrated by standard polystyrene samples.

A micro DSC "batch & flow" calorimeter (SETARAM Company, France) was employed to measure the heat effect during the volume-phase transition of the microgel in water, using pure water or the SDS solution as a reference.

A Ubbelodhe viscometer was used to measure the change in the relative viscosity of the solution with temperature. The experimental temperature range was 25 to 52°C, with steps of 1 to 5 degrees.

RESULTS AND DISCUSSION

Characterization of the macro-monomer

Figure 1 is the H-NMR spectrum of the prepared macro-monomer. It proves that the macro-monomer has the expected chemical structure. The molar ratio of Repeated Unit II is about 5.4% of the Repeated Unit I from the spectrum, which is very close to the expected value. The average molecular weight is about 73,000, and the polydispersity is about 1.8.

Solution properties of the microgel

It is well known that PNIPAM will undergo coil-to-globule transition and phase separation when the temperature rises from room temperature to about 32°C. If a surfactant (such as SDS) is added to the solution, there will be no phase separation even though the coil-to-globule transition is taking place. With the help of these phenomena, Yan et al.[8] studied the inter- and intra-molecular entanglement interaction of PNIPAM. The existence of the surfactant makes the properties of the solution more complicated. One of the obvious changes is the rise of the LCST. The higher the concentration of SDS, the higher the LCST will be. Curve c in Figure 2 shows the change in relative viscosity of

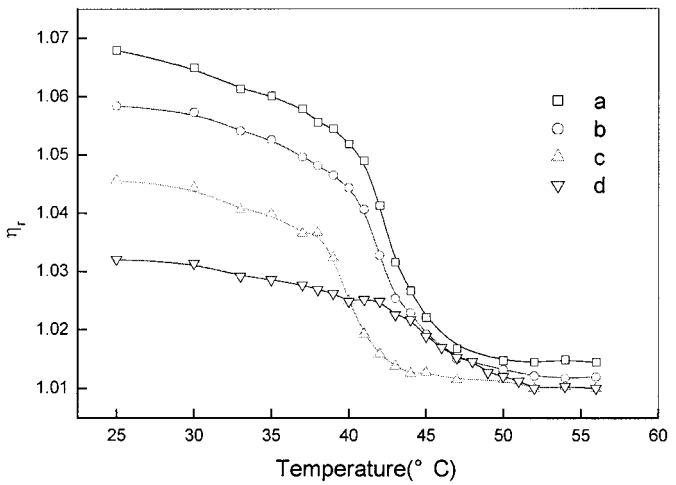


Figure 2 The dependence of η_r on temperature for monomers prepared in different ratios of copolymer to SDS (a) copolymer : SDS = 1 : 1.5, (b) copolymer : SDS = 1 : 2.5, (c) pure copolymer, (d) copolymer : SDS = 1 : 5.

the macro-monomer aqueous solution at a definite concentration of SDS with increasing temperature. As the viscosity measures the hydrodynamic volume of the polymer, there is obviously a coil-to-globule transition at about 40°C. The shape of the curve is similar to that of the homo-PNIPAM. The LCST is located in a higher position; this may be attributed to the surfactant SDS and the comonomer. The viscosity is almost constant above 45°C, which means the polymer takes the compact globule conformation.

The prepared microgels can be dissolved to form the real solution in water as its precursor. Curves a, b, and d in Figure 2 give the relative viscosity variation of these three microgel samples with temperature. These three curves have shapes similar to their precursors, but there are two differences. First, all of the coil-to-globule transitions occur at an even higher temperature, as shown in Table I. As the concentration of the surfactant, SDS, is the same in all of the experimental solutions, the higher LCST should come from the crosslinking points and can be explained with the theory proposed by Wu.[9] The Gibbs free energy of the gel during the swelling and contraction consists of two parts: the normal mixing free energy, ΔG_m, and the elastic free energy of the polymer network, ΔGel.

$$\Delta G_{el} = 3k_B T\phi[\alpha^2 - 1 - \ln\alpha]/(2N) \qquad (1)$$

Here k_B is the Boltzmann constant, $\alpha = (V/V_0)^{\frac{1}{3}} = (\phi_T/\phi_\theta)^{\frac{1}{3}}$, and ϕ_T and ϕ_θ are the volume fractions of the polymer network at temperatures T and θ respectively. N is the average degree of polymerization between two crosslinking points. Eq. 1 indicates that the elastic free energy retards the swelling and contraction of the network chain, or that the coil-to-globule transition takes place at higher temperatures in the microgels than in the linear macro-monomer.

The three microgel samples have different relative viscosities. These three samples were synthesized in different molar ratios of macro-monomer to SDS, as listed in Table I. The conclusion can be reached that samples M1 and M2 are not the real single-chain microgels or the multi-chain microgels, and only sample M3 is the expected microgel. The conclusion comes from the fact that viscosity is determined only by molecular weight when the polymer is at a fully compact globule status and the system temperature is well above the LCST. The sample M3 has the exact same viscosity values as the macro-monomer after the temperature is higher than 52°C. Within the lower temperature range, the viscosity of M1 and M2 multichain microgels is higher than that of their precursor, as the microgel samples have higher molecular weight. For the single-chain microgel sample, its viscosity is lower than that of macro-monomer, because they have the same molecular weight but different hydrodynamic volumes due to crosslinking points in the microgel that restrict its volume. This conclusion is also supported by SEC. Figure 3 compares the chromatograms from samples M1, M3 and the macromonomer. The retention volume of sample M1 is smaller than that of the macro-monomer, but sample

TABLE I
Experimental Data from Viscosity Measurement

Sample	R[1]	LCST (°C)[2] (C_{SDS} = 5.1×10^{-4} g/ml)	LCST (°C)[2]	M_g/M_m[3]
M1	1:1.5	43	35	1.4
M2	1:2.5	43	35	1.2
M3	1:5	46	35.5	1
Macro-monomer	—	40	33	—

[1] The ratio of the macro-monomer concentration to the concentration of SDS when prepared the microgel crosslinking.
[2] LCST data are determined at a concentration 7.6 × 10^{-4} g/ml of the microgel samples or macro-monomer
[3] The molecular weight ratio of the microgel to the macro-monomer

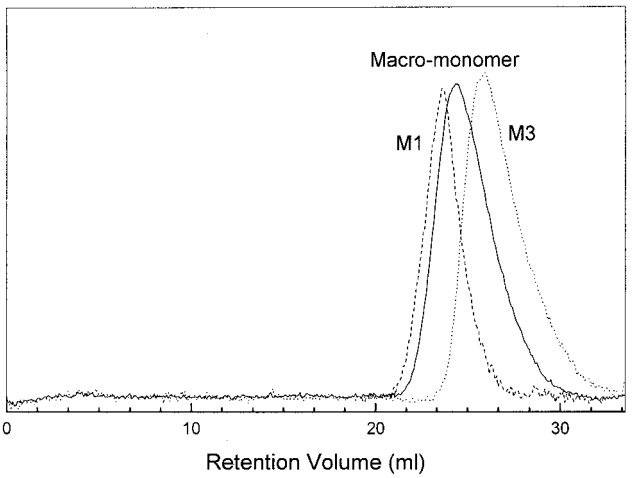


Figure 3 SEC chromatograms of the multi-chain microgel sample (M1), the single-chain microgel sample (M3), and the macro-monomer sample.

M3, the single-chain microgel, has the largest the retention volume.

When the system temperature is well above the LCST, the macro-monomer and the microgels will be in a compact and the uniform density globule form. Thus the intrinsic viscosity should be the measurement of the effective volume (ν) of the solute:

$$[\eta] \propto \nu \tag{2}$$

Also, the effective volume of the solute is proportional to the ratio of the molecular weight of the solute to its density (M/ρ), so

$$[\eta] \propto M/\rho \tag{3}$$

The density, ρ, should be the same if the compact globule has the same chemical composition at the uniform density state:

$$[\eta] \propto M \tag{4}$$

or

$$\frac{M_g}{M_l} \propto \frac{[\eta]_g}{[\eta]_l} \tag{5}$$

It should be noted that the above equation cannot be applied to the coil polymer. The calculated data are also listed in Table I, which shows that there are 1.4 macro-monomers within one microgel for sample M1 and 1.2 for sample M2.

Comparing the LCST data listed in Table I with SDS and without SDS in the solution, it can be found that the LCST values of the microgel samples are always higher than that of their precursor. Still, the single-chain microgel has the highest LCST. This means the degree of crosslinking is higher for the single-chain microgel sample. This can be proved further from the results of DSC experiments. The relevant experimental data are listed in Table II. The LCST values are very close to those determined from viscosity experiments. There the change of the enthalpy during the coil-to-globule transition follows the same order. The endothermic phenomena result from breaking the water molecules bound to the polymer chain accompanied by the conformation change.[10,11] The crosslinking points should decrease the solvated water molecules, which results in less endothermic effect. All of the experimental results support the idea that the higher crosslinking reaction can be achieved within a confined small volume during the preparation of the single-chain microgels.

CONCLUSIONS

Single-chain microgels have been prepared from the crosslinkable poly(*N*-isopropylacrylamide) copolymer. Three conclusions can be drawn directly from the comparison of the properties of the microgel to those of its precursor, as both of them have the same molecular weight and chemical composition: (1) the microgel samples have higher LCST values than their linear precursor, because crosslinking points retard the conformation transformation during the coil-to-globule transition; (2) the microgel samples have smaller enthalpy changes during the coil-to-globule transition, because the crosslinking points decrease solvated water molecules; and (3) the crosslinking possibility is higher within a smaller confined volume, as the LCST of the single-chain microgel is higher that that of the multi-chain microgel and less endothermic heat is observed in DSC.

TABLE II
LCST and ΔH Data from DSC in Pure Aqueous Solution

Sample	Heating rate (°C/min)	C (g/ml)	LCST (°C)	ΔH (J/g)
M2	0.3	7.6×10^{-4}	35.6	5.98×10^{-2}
M3	0.3	7.6×10^{-4}	35.8	4.86×10^{-2}
Macro-monomer	0.3	7.6×10^{-4}	33.9	6.56×10^{-2}

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