

Intrinsic Viscosity–Molecular Weight Relationships for Poly(*N*-isopropylacrylamide) Solutions

Shoei FUJISHIGE

*Research Institute for Polymers & Textiles,
Yatabe-Higashi 1-1-4, Tsukuba 305, Japan*

(Received September 1, 1986)

ABSTRACT: Poly(*N*-isopropylacrylamide) prepared by free radical polymerization was successfully fractionated into several fractions by using a carefully water-freed acetone as solvent and *n*-hexane as non-solvent. Based on the viscometric and osmometric studies of these fractions, the intrinsic viscosity–molecular weight relationships were determined as:

$$[\eta] = 9.59 \times 10^{-3} \bar{M}_n^{0.65} \text{ (in tetrahydrofuran at } 27^\circ\text{C)}$$

and

$$[\eta] = 14.5 \times 10^{-2} \bar{M}_n^{0.50} \text{ (in aqueous solution at } 20^\circ\text{C)}$$

These relationships imply that the statistical segment of poly(*N*-isopropylacrylamide) takes a considerably extended form in water than it does in tetrahydrofuran. It was also found that the aqueous solution exhibited an abnormal concentration dependence of viscosity at temperatures higher than 25°C and the phase separation at 30°C.

KEY WORDS Fractionation / Intrinsic Viscosity / Osmometry /

In order to shed more light on the roles of water molecules in denaturation of biological polymers, various solution properties of aqueous synthetic polymers have been studied by many investigators. Aqueous solutions of synthetic polymers which undergo phase separation at about 30–40°C on heating have attracted particular attention because of a certain similarity with the denaturation of proteins in aqueous solutions.

Klotz¹ has found that an aqueous solution of poly(vinylmethyloxazolidine) exhibits phase separation on heating at about 40°C. According to Horne *et al.*,² an aqueous atactic-poly(vinyl methyl ether) solution also exhibits a phase transition on heating at about 34°C. Some interesting phenomena were presented in these papers, but their detailed analysis has not fully been developed because of a lack of knowledge of the molecular characteristics of the polymer samples

used.

A more detailed but still qualitative study on such an aqueous solution exhibiting the phase transition on heating was conducted on poly(*N*-isopropylacrylamide) by Heskins *et al.*³ by using various methods of polymer characterization. They clarified some details of the thermal properties of the aqueous polymer solution but conducted their study using only one unfractionated polymer sample.

Thus, it seems worthwhile to reexamine the solution properties of poly(*N*-isopropylacrylamide) experimentally for obtaining a more quantitative picture of the thermal behavior of this polymer in water. In this paper, we first establish an effective procedure for molecular weight fractionation of poly(*N*-isopropylacrylamide) and then determine the intrinsic viscosity–molecular weight relationships by using the fractionated samples. A specific conformation of this polymer in aqueous

solution will then be noted.

EXPERIMENTAL

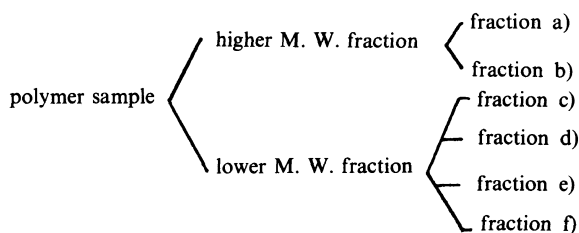
Polymerization

N-Isopropylacrylamide monomer (Eastman Kodak Co.) was recrystallized twice from a benzene/*n*-hexane mixture. It was polymerized in a benzene/acetone mixture with azobisisobutyronitrile as the initiator at 60°C. The

polymer was separated from the reaction medium as a suspension.

Fractionation

The molecular weight fractionation of the polymer thus prepared was performed by the phase separation in a carefully water-freed acetone/*n*-hexane mixture at room temperatures according to the following scheme:



Viscometry

A modified (dilution type) Ubbelohde type viscometer⁴ was used to measure the wide spread flow time at different temperatures.

Osmometry

A High Speed Membrane Osmometer, Model 501 of Hewlett Packard was used at 37°C. The procedure and technique were calibrated by using a standard polystyrene sample with a molecular weight, $\bar{M}_w = 200,000$, and molecular weight distribution index, $\bar{M}_w/\bar{M}_n \leq 1.06$. *p*-Dioxane was selected as the solvent of the osmometry because it could be easily used at 310 K.

RESULTS AND DISCUSSION

Poly(*N*-isopropylacrylamide) is soluble in acetone, methyl ethyl ketone, chloroform, *p*-dioxane, ethyl alcohol, methyl alcohol, tetrahydrofuran, cold water and some other solvents which are capable of forming reasonably strong hydrogen bonds with the polymer. It was found that the molecular weight fractionation was not achieved by the phase separation induced by heating the aqueous

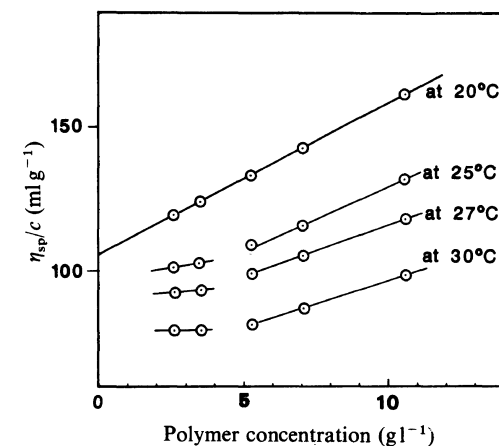


Figure 1. Effects of temperature on the reduced viscosity of poly(*N*-isopropylacrylamide) (fraction 3-b) in aqueous solution.

polymer solution. The phase separation of the polymer from a carefully water-freed acetone/*n*-hexane mixture successfully gave polymer fractions whose molecular weights were in order of the composition of solvent/non-solvent mixtures.

As shown in Figure 1, the reduced viscosity obtained at 20°C of the aqueous polymer

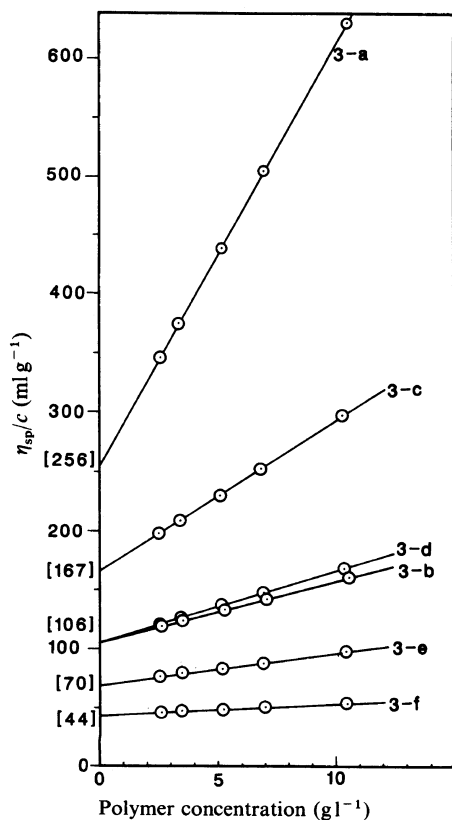


Figure 2. Determination of the intrinsic viscosity of poly(*N*-isopropylacrylamide) fractions in aqueous solutions at 20°C.

solutions gave a straight linear correlation as a function of polymer concentration, while the other data obtained at 25°C or above gave complicated correlations depending on the temperatures. Above 30°C, a capillary flow of the viscometer induces formation of tiny fibrillar suspension which disturbs viscosity measurements of the aqueous polymer solutions. It was thus found that 20°C corresponds approximately to the critical temperature for the viscometry of aqueous poly(*N*-isopropylacrylamide) solutions. Figures 2 and 3 show the viscosity data of the aqueous solutions and of the tetrahydrofuran solutions, respectively. The intrinsic viscosity of each polymer fraction is shown in the square bracket along the left ordinate. Fraction b) and fraction d) have

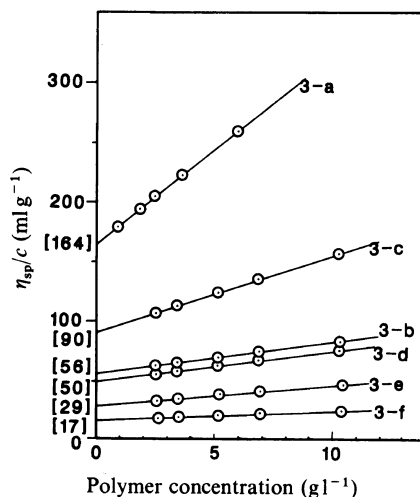


Figure 3. Determination of the intrinsic viscosity of poly(*N*-isopropylacrylamide) fractions in THF solution at 27°C.

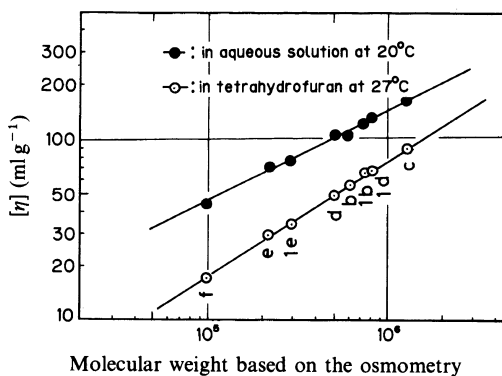


Figure 4. Determination of parameters for Mark-Houwink-Sakurada equation.

different slopes but give the same intrinsic viscosity in aqueous solution.

In contrast to the aqueous solutions, no abnormal concentration dependence of the reduced viscosity was observed in tetrahydrofuran nor in other organic solvents, such as acetone, alcohols and *p*-dioxane.

The intrinsic viscosities of fractions b, c, d, e, f, and l-b, l-d, l-e in water at 20°C and in tetrahydrofuran at 27°C are shown in Figure 4, from which Mark-Houwink-Sakurada equations were determined as:

$$[\eta] = 9.59 \times 10^{-3} \bar{M}_n^{0.65}$$

(in tetrahydrofuran at 27°C) (1)

and

$$[\eta] = 14.5 \times 10^{-2} \bar{M}_n^{0.50}$$

(in aqueous solution at 20°C) (2)

The molecular weight of fraction a) was too large to be determined by osmometry, and it was estimated by eq 1 to be $\bar{M}_v = 3.1 \times 10^6$.

The exponents in eq 1 and 2 indicate that tetrahydrofuran is a good solvent for poly-(*N*-isopropylacrylamide) and water is approximately the theta solvent. Nevertheless, the values of $[\eta]$ in water are considerably larger than those in tetrahydrofuran. This strongly

suggests that the unperturbed dimension of this polymer, hence the statistical segment diameter, is about $5^{1/3}$ times larger in water than in tetrahydrofuran. This difference in segment size may be ascribed to the stabilization of a local elongated structure of the polymer backbone by hydrogen bonding.

REFERENCES

1. I. M. Klotz, *Fed. Proc.*, **24**, Suppl. No. 15, S-24 (1965).
2. R. A. Horne, J. P. Almeida, A. F. Day, and N-T. Yu, *J. Colloid Interface Sci.*, **35**, 77 (1977).
3. M. Heskins and J. E. Guillet, *J. Macromol. Sci.-Chem.*, **A2**, 1441 (1968).
4. S. Fujishige, J. Kuwana, and M. Shibayama, *J. Polym. Sci., B*, **1**, 355 (1963).