Pergamon

PII: S0014-3057(97)00013-X

Eur. Polym. J. Vol. 33, No. 9, pp. 1553–1556, 1997

0014-3057/97 $17.00 + 0.00

SHORT COMMUNICATION

DIFFERENCES IN VIBRATIONAL SPECTRA OF POLY(*N*-ISOPROPYL ACRYLAMIDE) FROM WATER SOLUTION BEFORE AND AFTER PHASE SEPARATION

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(Received 20 February 1996; accepted in final form 23 October 1996)

Abstract—Two poly(*N*-isopropyl acrylamide) (PNIPA) samples were prepared by drying the 5 wt% water solution of PNIPA either at 25°C without phase separation (referred to as **I-B**) or at 38°C after phase separation (**I-C**). PNIPA sample **I-A** was directly cast from its acetone solution. The IR absorbance of CH_3 asymmetric stretch related to the CH_2 symmetric stretch is higher for the samples **I-C** and **I-A** when compared with the same absorbance ratio for the sample **I-B**. At the same time, the vibration frequencies of amide **I** and **II** for **I-C** are similar to those for **I-A**, but obviously different from those for **I-B**. Raman scattering intensities corresponding to the CH_3 and CH_2 vibrations also depend on the sample preparation methods. A simple model simulation suggests that the above observations would be attributed to the configuration change in the side chain of the amide group. The *trans* isomer is dominant in sample **I-B** and *cis* isomer dominant in samples **I-A** and **I-C**. © 1997 Elsevier Science Ltd

INTRODUCTION

Aqueous solution of poly(*N*-isopropyl acrylamide) (PNIPA) exhibits a lower critical solution temperature (LCST) around 32°C [1]. Many methods, including cloud point measurement [2], light scattering [3, 4], differential scanning calorimetry [5, 6], viscometry [7, 8] and fluorescence [9] have been used to reveal the essential mechanism of the phase separation. A two-step process has been proposed for this LCST phenomenon [4], which is a collapse of single PNIPA chains followed by the aggregation into larger particles suspended in the water-rich phase.

Therefore, the conformation of PNIPA chains in water should be different before and after the phase separation. Light scattering results given by Fujishige *et al.* [2, 10] and by Wu and Zhou [11, 12] indicate the existence of thermodynamically stable collapsed chain globules for narrowly distributed PNIPA in very dilute water solutions as the temperature rised just above the LCST. The driving force inducing the chain collapse and aggregation in the PNIPA/water solution is considered to be the hydrophobic effect, which should be the combination effect of both the hydrogen bond and the van der Waals interactions as described by Nemethy and Scheraga [13–15].

The specific conformation of side chain and main chain induced by the phase separation may lead to a specific conformation in the PNIPA solid samples prepared by a specific method as stated hereafter. As the first attempt, we measured the IR and Raman spectra of PNIPA solid samples obtained from PNIPA/water solution with and without surviving the phase separation to reveal the conformational changes.

EXPERIMENTAL

Polymerization of PNIPA

The recrystallized monomer *N*-isopropyl acrylamide (Kohjin Co., Japan) was radically polymerized in water at 25°C initiated by ammonium persulfate and $Na_2S_2O_5$ mixture. The reaction solution thus obtained was precipitated into benzene to gather PNIPA. After that the polymer was carefully purified and dried.

The weight average molecular weight M_w of our PNIPA sample measured by gel permeation chromatography (GPC) on a Waters-150C is 129,000 and $M_w/M_n = 1.80$, when polystyrene was taken as the standard.

IR and Raman measurements

A water solution of 5 wt% PNIPA was divided into two parts. One was simply dried at 25°C under vacuum to produce a transparent and brittle sample of PNIPA assigned as **I-B**. The other was kept at 38°C in an air thermostat to induce phase separation, then dried at the same temperature

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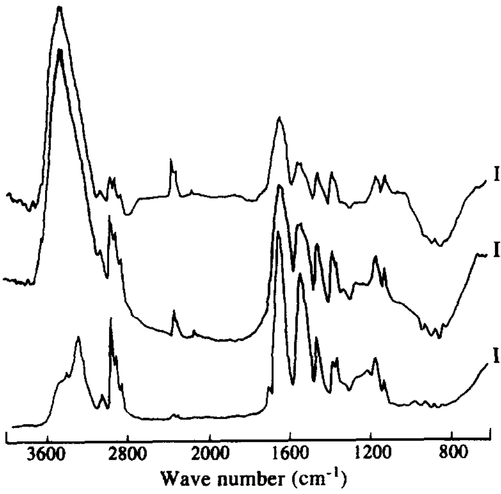


Fig. 1. IR spectra of three poly(*N*-isopropyl acrylamide) samples, from top: **I-B**, dried from 5 wt% water solution at 25°C without phase separation; **I-C**, dried from 5 wt% water solution at 38°C after phase separation; **I-A**, directly casted from acetone solution.

after removing the light phase by a syringe. Consequently, a transparent brittle pellet of PNIPA was also obtained as sample **I-C**. Sample **I-A** was obtained after being cast directly from PNIPA/acetone solution.

The Fourier-transform IR (FT–IR) spectra of these PNIPA samples were recorded on an Analect RFX-65 FT–IR spectrometer at room temperature. The Raman spectra of the polymer samples **I-B** and **I-C** were measured with a SPEX1403 Raman spectrometer using the incident light of 514.5 nm in wavelength.

RESULTS AND DISCUSSION

Vibrational spectra

The FT–IR spectra of three PNIPA samples are illustrated in Fig. 1. The main absorbance bands of sample **I-A** can be assigned as follows: amide **I**, 1647 cm^{-1}; amide **II**, 1541 cm^{-1}; N—H stretch, 3300–3434 cm^{-1}, C—H stretch, 2875, 2933 and 2972 cm^{-1}; asymmetrical CH_3 bending, 1460 cm^{-1}; twin methyl group, 1385 and 1365 cm^{-1}. The band at 3068 cm^{-1} is the overtone of 1541 cm^{-1} resonance. The broad absorbance in the region 3200–3600 cm^{-1} may be related to the presence of residual solvents water and/or methanol from the sample preparation.

An important difference between samples **I-B** and **I-C** exists in the relative intensity of the absorbance corresponding to the methyl group in the isopropyl group. In the region of 2875 to 2972 cm^{-1}, there are four bands for the C—H stretch as CH_3: asymmetric at 2972 cm^{-1} and symmetric at 2933 cm^{-1}; CH_2: asymmetric at a wavenumber little higher than 2933 cm^{-1} and symmetric at 2875 cm^{-1}, respectively. Despite the sloping baseline in this region affected by the residual solvent, the absorbance at 2972 cm^{-1} related to the band at 2875 cm^{-1}, A_{2972}/A_{2875} is obviously higher for the sample **I-C** obtained via solution phase separation, whereas the same relative absorbance is lower for the sample **I-B** directly dried from PNIPA/water solution. Other absorbance bands for the twin methyl group at 1385 and 1365 cm^{-1} also exhibit difference in relative intensities.

In order to overcome the disturbance on the FT–IR baseline by the residual water in the PNIPA samples, Raman spectra of **I-B** and **I-C** samples were determined in the region 2850–3100 cm^{-1}. Figure 2 shows the results in which three peaks can be recognized at 2875, 2924 and 2975 cm^{-1}, respectively, just like those in the IR spectra. Also, significant differences in the relative intensity can be seen between these two samples. The scattering intensities of the peaks at 2975 and 2924 cm^{-1} relative to that at 2875 cm^{-1}, I_{2975}/I_{2875} and I_{2924}/I_{2875} are 1.05 and 1.71, respectively for the sample **I-B**. In contrast, those for the sample **I-C** are 0.99 and 1.48, respectively. Therefore, the above differences in the IR and Raman spectra for the samples **I-B** and **I-C** seem to be caused by sample-preparing process other than the residual water. However, owing to different mechanism of IR and Raman spectrum the A_{2972}/A_{2875} may be inconsistent with the I_{2975}/I_{2875} for a given sample.

These results strongly suggest that the condensed state of PNIPA sample **I-C** from its water solution after the phase transition is close to that of PNIPA

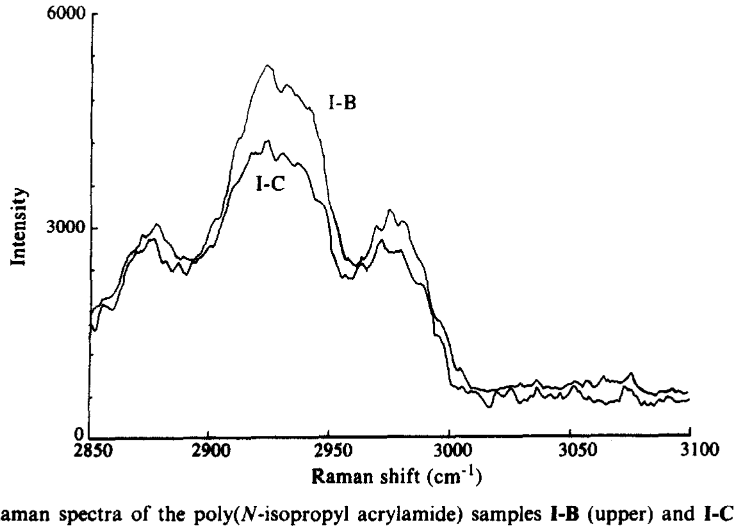
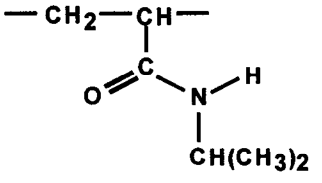


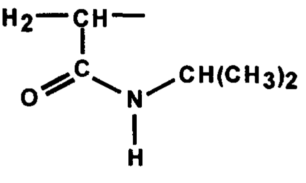
Fig. 2. Raman spectra of the poly(*N*-isopropyl acrylamide) samples **I-B** (upper) and **I-C** (lower).

sample **I-A** directly casted from its organic solution and differs from PNIPA sample **I-B** also from water solution but without phase separation.

Conformation of amide group

The amide group has a flat conjugated plane in which there are four atoms of carbonyl carbon, oxygen, nitrogen and one main chain carbon directly attached by the carbonyl carbon, while two covalent bonds of N—H and N—$CH(CH_3)_2$ define another plane adjacent to the carbonyl carbon. The rotation round the C—N bond in amide group is greatly restricted by the requirement of forming a more effective conjugate bond. As a result, there are two most preference conformations for side chain on PNIPA molecules [16, 17], referred to as *trans* and *cis* conformations according to the position of the lone hydrogen atom attaching the nitrogen related to the oxygen atom as follows:


trans-conformation


cis-conformation

Russell and Thompson [16] found from small molecules of *N*-monosubstituted amides R—CONH—R′ that the *trans* isomer would be predominant if the skeleton group R is of sterically small one, while the amides of phenyl acetic acid had excess of the *cis* form. Accompanying the flip motion of the substitution to the amide groups round C—N bond, there appear to be two types of N—H bonds and two sorts of isopropyl groups corresponding to these two isomers. The FT–IR and Raman spectra mentioned above seems to reflect these characters.

We calculated the absorbances of CH_3 and CH_2 stretches for these two conformations using the derivatives of the dipolar moment with respect to the normal coordinates [18] in an attempt to ascertain which isomer is corresponding to either of these two sample-preparing procedures. The calculation was carried out only on one repeat unit, regarding two sections of the chain attaching this unit as two mass points and taking the hydrogen bond effect into account. Figure 3 shows the results in which the wavenumber of each absorbance only means the relative position. The ratio of the absorbance intensity of asymmetric stretch for CH_3 to that of symmetric stretch for CH_2, i.e., $A_{as}^{CH_3}/A_s^{CH_2}$ for the *trans* conformation is much lower than the ratio for the *cis* conformation, indicating two limit cases of IR spectra for PNIPA.

Since the PNIPA solid is in its glass state [19], it should be an aggregate of various possible conformations and the vibrational spectrum will reflect the averaged state but not a special conformation as those selected in the simulation. Comparing with the calculated spectra, one can find that in the samples **I-A** (cast from acetone solution) and **I-C** (via phase separation) the cis conformation appears to be dominant in the side chain, while in the sample **I-B** (dried from water solution without phase separation) the *trans* isomer may be the main conformation.

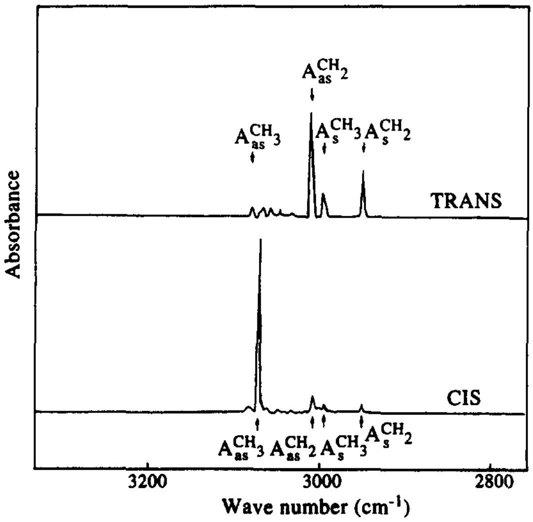


Fig. 3. Model simulations of IR absorptance corresponding to the asymmetric and symmetric stretches of CH_3 at the side chain and CH_2 in the backbone for poly(*N*-isopropyl acrylamide) with selected side chain conformation: *trans* (upper) and *cis* (lower) isomers.

Acknowledgements—This work was jointly supported by the National Basic Research Project "Macromolecular Condensed State" of China, the "Trans-Century Training Program Foundation for the Talents" by the State Education Commission of China and the fund of Higher Education Bureau, Guangdong Province.

REFERENCES

1. Schild, H. G., *Prog. Polym. Sci.*, 1992, **17**, 163.
2. Fujishige, S., Kubota, K. and Ando, I., *J. Phys. Chem.*, 1989, **93**, 3311.
3. Kubota, K., Fujishige, S. and Ando, I., *Polym. J.*, 1990, **22**, 15.
4. Yamamoto, I., Iwasaki, K. and Hirotsu, S., *J. Phys. Soc. Jpn*, 1989, **58**, 210.
5. Schild, H. G. and Tirrell, D. A., *J. Phys. Chem.*, 1990, **94**, 4352.
6. Otake, K., Inomata, H., Konno, M. and Saito, S., *Macromolecules*, 1990, **23**, 283.
7. Heskins, M. and Guillet, J. E., *J. Macromol. Sci.-Chem.*, 1968, **A2**(8), 1441.
8. Fujishige, S., *Polym. J.*, 1987, **19**, 297.

9. Winnik, F. M., *Macromolecules*, 1990, **23**, 233.
10. Kubota, K., Fujishige, S. and Ando, I., *J. Phys. Chem.*, 1990, **94**, 5154.
11. Wu, C. and Zhou, S., *Macromolecules*, 1995, **28**, 5388.
12. Wu, C. and Zhou, S., *Macromolecules*, 1995, **28**, 8381.
13. Nemethy, G. and Scheraga, H. A., *J. Chem. Phys.*, 1962, **36**, 3382.
14. Nemethy, G. and Scheraga, H. A., *J. Chem. Phys.*, 1962, **36**, 3401.
15. Nemethy, G. and Scheraga, H. A., *J. Phys. Chem.*, 1962, **66**, 1773.
16. Russell, R. A. and Thompson, H. W., *Specochim. Acta*, 1956, **8**, 138.
17. Socrates, G., *Infrared Characteristic Group Frequencies*. John Wiley & Sons, Chichester, 1980.
18. Wilson, E. B. Jr, Decius, J. C. and Cross, P. C., *Molecular Vibrations—The Theory of Infrared and Raman Vibrational Spectra*. Dover, 1980.
19. Zeng, F. and Tong, Z., *J. South China Univ. Tech.* (in Chinese), 1994, **22**(6), 8.