Determination of PEG Concentration in Its Aqueous Solution Using Differential Scanning Calorimetry

T. YAMAUCHI* and A. HASEGAWA

Department of Wood Science and Technology, Faculty of Agriculture, Kyoto University, Sakyo-ku Kyoto 606-01, Japan

SYNOPSIS

The Freezing and melting behavior of aqueous poly(ethylene glycol) (PEG) solutions up to a concentration of 10% was examined using DSC. So long as the molecular weight of PEG is over 1000, the cooling and heating DSC curves have two peaks, which are attributed to freezable bound water and free water. The amounts of freezable bound water and nonfreezing water linearly increase with an increase of PEG concentration. Therefore, a method using DSC was proposed for determining the concentration of aqueous PEG solutions. Although PEG concentration can be determined by the heat of freezable bound water, the ratio of heat of freezable bound water to heat of free water is a better way to determine the concentration. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyethlene glycol (PEG) is a water-soluble polymer that has been used in various fields such as detergents, medicines, cosmetics, and textiles. PEG also has been used as a standard solute in the solute extrusion method to characterize the swelling of pulp fibers[1] and has been employed in a study on polymer adsorption.[2] Because its molecular conformation in aqueous solution is random and simulates a sphere, PEG samples of different molecular weights are commercially available.[3] In analytical uses, the determination of its concentration in an aqueous solution is extremely important. The concentration has been determined using an interferometer[4] or by the orthodox method, i.e., the mass change of the solution before and after evaporation of water. The former method requires expensive instruments and the latter method is tedious. Further, both require a fairly large amount of the solution.

Recently, polymer gels and their hydration have been extensively studied using differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and some other methods.[5,6] The results from all of these methods suggested that three kinds of water exist in hydrogels. Among these methods, DSC is the most popular one, and the amounts of free water, freezable bound water, and nonfreezing bound water have been determined by DSC.[7] Taking into consideration the facts that polymer gels are a kind of concentrated solution of polymer and that the freezable bound water is based on the existence of polymer in the aqueous solution, DSC could be applied to determine the amount of polymer in the solution, i.e., its concentration. In the present study, DSC curves of aqueous PEG solutions at different concentrations were examined to establish the determination method of PEG concentration using DSC.

EXPERIMENTAL

Diffential Scanning Calorimetry

A Rigaku heat-flux-type differential scanning calorimeter 8240B, equipped with a cooling cell, was used to determine the cooling and heating DSC curves.[8] Based on preliminary experiments, the following procedure was found to give reproducible results: A given amount of sample, about 10 μL, was quantitatively transferred in a micropipette to the DSC aluminum sample pan. The aluminum lid was put on the sample to cover it. After weighing quickly,

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 49, 1653–1658 (1993)
 CCC 0021-8995/93/091653-06

the pan was placed in the DSC chamber and was promptly cooled below 0°C to minimize the evaporation of water from the sample. Further cooling to −50°C was carried out at a scanning rate of 3°C/min. The sample was then heated at a scanning rate of 2°C/min toward room temperature. Heat (entalpy) determination from the DSC peak area was calibrated using a series of distilled water samples of different weights, assuming that the heat of fusion for water is 333 J/g.[9]

Polyethylene Glycol (PEG)

All PEG samples were supplied by Sanyo Kasei Co. The molecular weights given are those reported by the supplier. It is well known that commercially available PEG has a fairly narrow molecular weight distribution.[3] Except for the experiment on the effect of molecular weight, the term "PEG" in this study means the PEG of molecular weight 20,000.

The PEG concentration was determined by the weight difference before and after removal of water from the solution, i.e., about 10 mL of the solution in a weighing bottle was first air-dried at least 2 days in a throughly ventilated box and was further vacuum-dried at room temperature to avoid decomposition of PEG by heat.

RESULTS AND DISCUSSION

Cooling and Heating DSC curves

Figure 1 shows the DSC curves for cooling and heating a 10% PEG solution. When the PEG solution was cooled from room temperature, a sharp peak at about −15°C (peak I) and, further, a small broad peak at about −25°C (peak II) were observed. On the other hand, on heating from below −50°C, a small broad peak at about −10°C (peak II) and, further, a large peak at about 0°C (peak I) were observed. The cooling curve of the PEG solution was similar to those of some kinds of cellulose that had adsorbed water[7] and the heating curve was similar to that of a hydrogel.[6] According to Lee et al.,[6] the peak at the lower temperature side in each curve should be attributed to the freezable bound water, and the peak at the higher temperature side in each curve, to the free water in hydrogels. The peaks of the PEG solution must be identified in analogy with those of the hydrogels. There should be three kinds of water: free water, freezable bound water, and nonfreezing water. It is most plausible that the water tightly bound to polymer molecules, the water enclosed by the entangled polymer chains, and the other water should be assigned to nonfreezing water, freezable bound water, and free water, respectively.

Effect of Molecular Weight on DSC Curve

The origin of the secondary peak at the lower temperature side (peak II) in the DSC curves can be further clarified by taking into account the results of PEG with various molecular weights. Figure 2 shows a series of heating curves of PEG solutions with molecular weights of 1000, 4000, and 20,000. With decreasing molecular weight, the peak temperature shifted toward the lower temperature side and the peak area decreased. The change with mo-

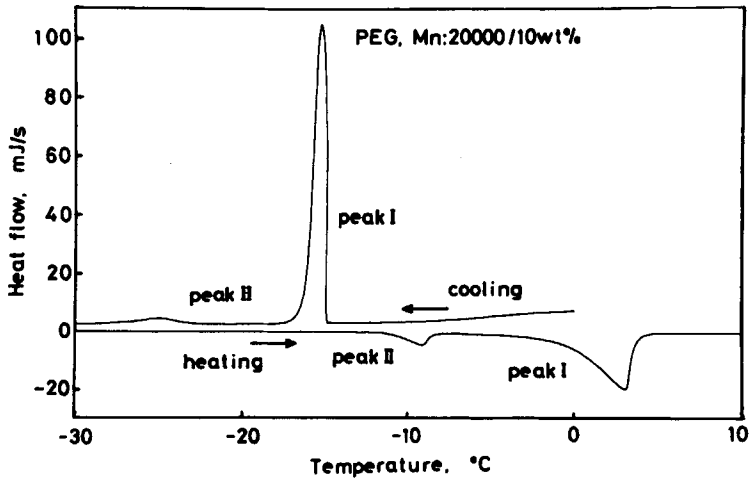

Figure 1 Cooling and heating DSC curves of aqueous PEG solution.

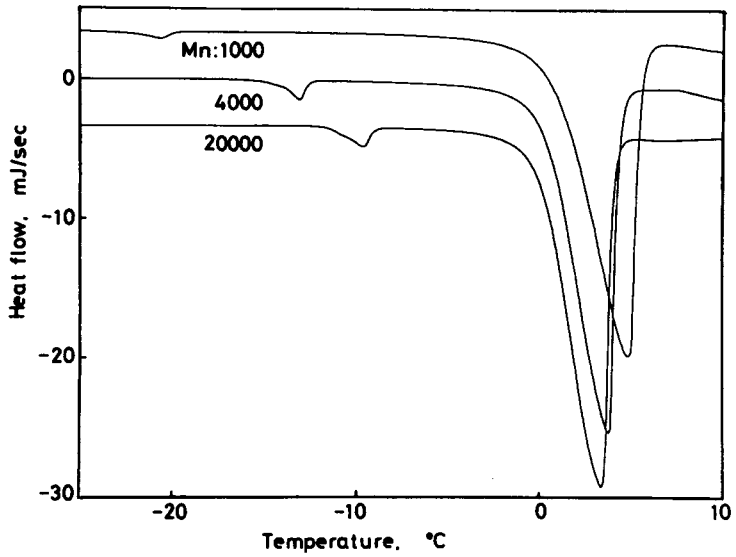

Figure 2 Effect of molecular weight of PEG on DSC heating curve.

lecular weight was greater with lower molecular weight. Incidentally, PEG of molecular weight 500 did not manifest the secondary peak and displayed only the main peak at about 0°C. PEG is well known to be a very flexible polymer and has a tendency to show a random coiled conformation in its aqueous solution. A molecular weight of 500 or 1000 means that the degree of polymerization (DP) is about 9 or 18, respectively. These results show that the water enclosed by the PEG molecular chain begins to appear at a DP between 9 and 18 and the amount of the enclosed water increases with increase of molecular weight. The shift of the peak temperature for peak II with molecular weight could suggest some changes in molecular conformation in the solution.

Change of Heat of Fusion with Concentration

The heat of peak I and the total amount of heat from peaks I and II for PEG solutions ranging from

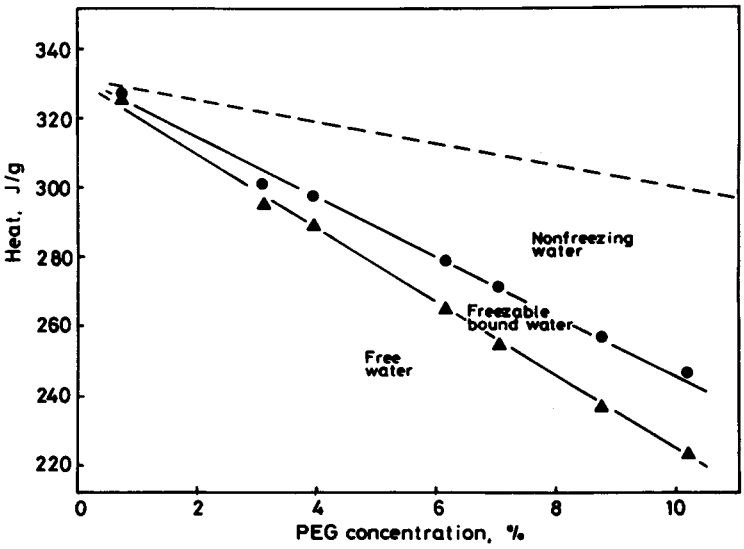

Figure 3 Relationship between PEG concentration and the amounts of nonfreezing water and freezable bound water.

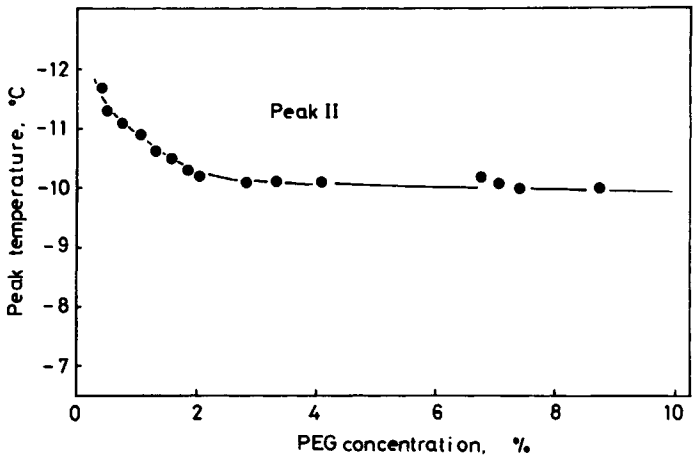

Figure 4 Effect of PEG concentration on the peak temperature of peak II.

0 to 10% are shown in Figure 3 as the two solid lines. The calculated relationship between heat and PEG concentration is also provided in Figure 3 as a broken line, assuming that all water in the solution was freezable and that its heat of fusion is 333 J/g. The difference between the two solid lines gave the heat from peak II and that between the broken line and the upper solid line gave the heat corresponding to the nonfreezing water. The heat from peak I decreased with an increase in concentration. Concurrently, the heat of peak II and the heat corresponding to the nonfreezing water increased proportionally with the concentration. This means that the amounts of freezable bound water and nonfreezing water linearly increase with a decrease in the amount of free water, as concentration increased within the range of PEG concentrations tested, i.e., the amount of water tightly bound to the polymer chain and that enclosed by the entangled polymer chain linearly increase with increase of the concentration. Figure 4 shows the change of peak temperature of peak II with concentration, suggesting that the polymer conformation also changes with the concentration.

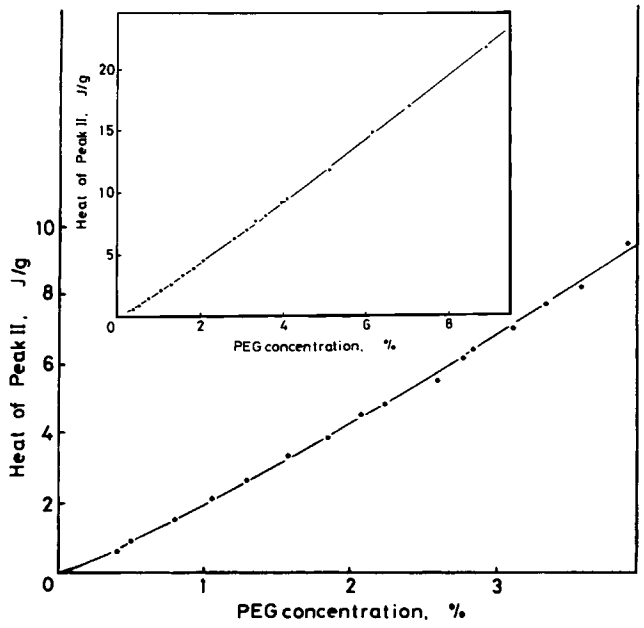

Figure 5 Relationship between PEG concentration and heat of freezable bound water.

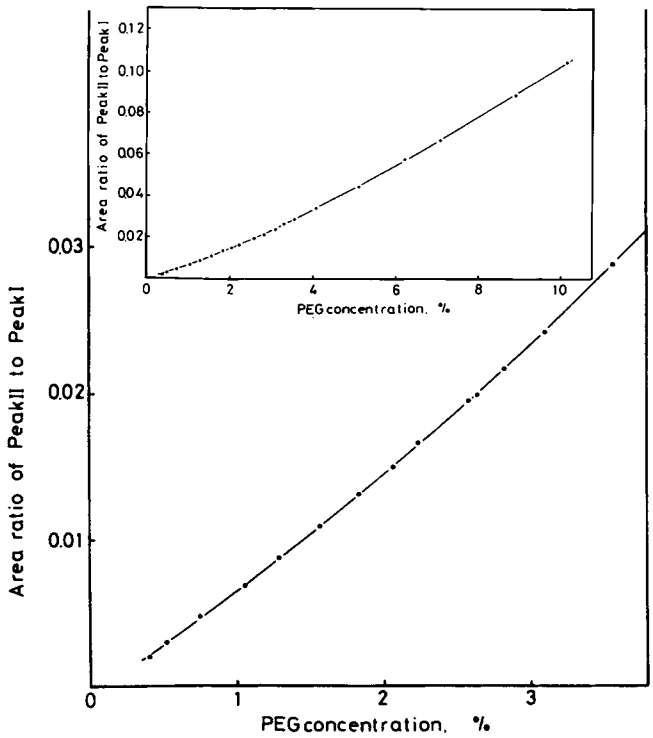

Figure 6 Relationship between PEG concentration and the ratio of heat of freezable bound water to that of free water.

Determination of PEG Concentration

Utilizing the proportional relationship between PEG concentration and heat of peak II detectable using DSC, the concentration conversely should be determined by the heat of peak II. Figure 5 shows the relationship between heat of peak II and PEG concentration. A nearly linear relationship was obtained. The bottom enlarged figure shows that the relationship is slightly concave downward within the concentration range 0–3.5%. Further, some scatter of the data was found in the enlarged figure. The scatter is too large to use the relationship for determining the concentration precisely.

The main cause for the scatter, i.e., experimental error, must be the mass determination using a semimicrobalance. Error in mass determination is to some extent unavoidable in the use of DSC. Consequently, the heat of peak II relative to the heat of peak I is considered instead of the heat of peak II itself, i.e., the ratio of heat from peak II to that from peak I was plotted against the concentration in Figure 6. The relationship was nearly linear and faintly concave downward. As shown in the bottom enlarged figure, scatter of the data was not observed. These results showed that the relative value of the heat of peak II to that of peak I was better than the heat of peak II for the purpose of concentration determination.

CONCLUSIONS

DSC cooling and heating curves of aqueous PEG solution have two distinctive peaks, which are attributed to the free water and freezable bound water, respectively. The freezable bound water, which might consist of the water enclosed by the entangled PEG molecular chains, begins to appear at a DP between 9 and 18. The amounts of freezable bound water and nonfreezing water linearly increase with an increase in concentration. The measurement of peak area for a PEG solution can give the value of the concentration. The ratio of the heat of freezable bound water (secondary peak) to that of free water (main peak) is better for the purpose of PEG concentration determination.

The authors wish to thank Dr. J. L. Davis, Department of Engineering Professional Development, University of Wisconsin-Madison, for his critical reading of the manuscript and Prof. K. Murakami for his continuous interest and encouragement.

REFERENCES

1. L. G. Aggebrandt and O. Samuelson, *J. Appl. Polym. Sci.*, **8**, 2801 (1964).
2. Y. Kitani, J. Osawa, and K. Nakato, *Mokuzai Gakkaishi*, **16**, 326 (1970).
3. H. Tatkow, W. C. Feist, and C. F. Southerland, *Forest Prod. J.*, **16**(10), 61 (1966).
4. J. E. Stone, A. M. Scallan, and B. Abrahamson, *Svensk Papperstidn*, **71**, 687 (1968).
5. H. Hatakeyama, H. Yoshida, and T. Hatakeyama, *Cellulose & Its Derivatives, Chemistry, Biochemistry & Applications*, J. F. Kennedy, G. O. Phillips, D. J. Wedlock, and P. A. Williams, Eds., Ellis Horwood, Chichester, 1985, p. 255.
6. H. B. Lee, M. S. Jhon, and J. D. Andrade, *J. Colloid Interface Sci.*, **51**, 225 (1975).
7. K. Nakamura, T. Hatakeyama, and H. Hatakeyama, *Text. Res. J.*, **51**, 607 (1971).
8. T. Yamauchi and K. Murakami, *J. Pulp Paper Sci.*, **17**, J223 (1991).
9. E. Berlin, P. G. Kliman, and M. J. Pallansch, *J. Colloid Interface Sci.*, **34**, 488 (1970).

Received December 8, 1992
Accepted December 23, 1992