

Poly(ethylene oxide)-물, Poly(ethylene oxide)-요소 수용액에 대한 고유점도의 온도의존

全相一* · 張貴重

강릉대학교 자연과학대학 화학과

(1996. 9. 9 접수)

Temperature Dependence of the Intrinsic Viscosities for Poly(ethylene oxide)-Water and -Aqueous Urea Systems

Sang Il Jeon* and Gue Dong Chang

Department of Chemistry, Kangnung National University, Kangnung 210-702, Korea

(Received September 9, 1996)

요약. 물과 요소 수용액에서 Poly(ethylene oxide) (PEO)의 구조 성질에 대한 온도의 효과를 보고한다. 물과 요소/물 혼합물(요소 농도는 각각 0.2, 1, 2 M)에서 PEO에 대한 고유점도와 Huggins 계수의 값은 점도측정 방법에 의해 얻어졌으며, 이것을 물 구조 변화 관점에서 논의했다. 낮은 온도(22 °C 이하)에서 PEO-물간 상호작용은 우세해 사슬은 펼쳐져 있는 반면, 높은 온도(24 °C 이상)에서는 상호작용이 우세하지 못하고 사슬은 소수성 수화에 의해 엉켜있게 된다. 즉, 온도가 상승함에 따라 PEO-물 상호작용은 우세하지 못하게 된다. 요소가 계에 가해짐에 따라 PEO 사슬은, 우세하지 못한 PEO-물 상호작용으로부터 유발된 구조화된 물의 동요에 의해, 더 펼쳐지거나 거대해지게 된다. 고유점도 값에 대한 온도의 효과는 Arrhenius 행동을 나타낸다. 따라서 점성 흐름에 대한 활성화 에너지를 구해 논의하였다.

ABSTRACT. The effects of temperature on the conformational properties of poly(ethylene oxide) (PEO) in aqueous and aqueous urea solutions are reported. The values of intrinsic viscosity and Huggins coefficients for the PEO dissolved in water and urea/water mixtures (urea concentration 0.2, 1, and 2 M) were obtained using a viscometry method and discussed with respect to the change of water structure. At low temperatures (below 22 °C), the PEO-water interaction is favorable and the chain can be extended, whereas at higher temperatures (above 24 °C), it is less favorable and the chain can be contracted by a hydrophobic hydration, i.e., the PEO-water interaction becomes to be unfavorable with the increase in temperature. As the urea is added to the system, the PEO chain can be more extended and huged by the perturbation of the structured water originating from the unfavorable PEO-water interaction. The effect of temperature on the intrinsic viscosity values shows an Arrhenius behavior. The activation energies of the viscous flow were obtained and discussed.

INTRODUCTION

Poly(ethylene oxide) (PEO) is a unique member of the polyepoxides, with the general formula $[(CH_2)_xO]_n$, in that it is soluble in both organic and aqueous solvents.¹ The characteristic feature of it contains both nonpolar ($-CH_2-CH_2-$) and polar ($-O-$) sites in a chain. Its properties have made

it a polymer of considerable commercial and fundamental importance as evidenced by the extensive literature that exists regarding this polymer, especially in aqueous solution.²⁻⁵ The amphiphilic character of it opens the possibility for particularly interesting hydrophobic and hydrophilic interactions of the PEO chain in the solvent. The nega-

tive change of entropy is recorded upon the addition of PEO to water.⁶ This phenomena is due to a reduction in entropy of the water (i.e., the structuring of the neighboring water molecules) at the hydrophobic interface.^{7,8} This is commonly referred to as the hydrophobic hydration,⁹⁻¹¹ which promotes the hydrophobic interaction between the hydrophobic groups. Such hydrophobic interactions are often believed to contribute to the stability of ordered macromolecular structures.^{12,13} There has also been a hypothesis that PEO, which is known to be helical in the solid state, remains some of its helicity even in dilute aqueous solution.^{4,14,15} PEO is reported to have the lowest characteristic ratio of 4.0 of all the linear flexible polymer chains studied, i.e., PEO is an unusually flexible polymer.¹⁵ Also PEO has the inverse solubility-temperature behavior,¹ i.e., the polymer is soluble at ambient temperature and separates from solution on heating, exhibiting a θ temperature of 97 ± 3 °C.¹⁶

Specifically, Raman,¹⁷ NMR,¹⁸ and other methods¹⁹ have been used to study the conformational changes induced by changing the solvent or the temperature. It is theoretically²⁰ and empirically^{5,15,18,21} found that the conformations of EO segments are divided into two classes, one being polar, having a low energy but a low statistical weight, and one being less polar, or nonpolar, having a higher energy but a higher statistical weight. At low temperatures, the former class of states dominates and the polymer-water interaction is favorable, whereas at higher temperatures, the latter states become increasingly populated, rendering the polymer-water interaction less favorable.

The addition of electrolytes, such as simple salts, or nonelectrolytes, such as urea, is a common method for altering the solvent properties of water.²² Urea, $[(\text{NH}_2)_2\text{CO}]$, a well-known protein denaturant, has been found to be an efficient modifier of the properties of aqueous solutions. Two different mechanisms have been proposed to explain the action of urea in aqueous solutions: (i) an indirect mechanism,²³ according to which urea acts as a "structure-breaker" and thus facilitates the hydration of nonpolar solutes, and (ii) a direct

mechanism,^{24,25} whereby urea has almost no effect on the water structure, replaces some of the water molecules in the hydration shell of the solute, and self-associates. The indirect mechanism has received the most attention and is widely accepted,²⁶ many experimental results seem to support the idea that the addition of urea to water does destroy the solvent structure.^{27,28} In this study, the temperature effects on the conformational properties of PEO in aqueous and aqueous urea solutions are studied by viscometry with respect to the change of water structure, and experiments for the amounts of urea are also performed.

EXPERIMENTAL

PEO was obtained from Aldrich Chemical Co. with average molecular weight of 1.0×10^5 . The urea of A.C.S. reagent grade was also received from Aldrich Co. Aqueous urea solutions were always prepared just prior to use. The apparatus and procedures for the measurements of the intrinsic viscosity of PEO in aqueous urea solutions have been described in the previous paper.²⁹ Experiments were performed at regular 2 °C temperature intervals over the range 10~32 °C. The temperature was kept constant to ± 0.01 °C.

RESULTS AND DISCUSSION

The experiments were performed to determine the intrinsic viscosities (η) and Huggins coefficients (k_H) of PEO in aqueous solutions, and the results are shown in Table 1. The Huggins coefficients meaning the measure of the polymer-solvent interaction are obtained from the following Huggins equation.³⁰

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \quad (1)$$

where η_{sp} is the specific viscosity and c is the concentration of dissolved polymer denoted by g/dL. The value of k_H is often near 0.35 and approximately 2.0 for flexible random coil polymer molecules in good solvents and for uncharged spherical molecules,³¹ respectively, and increases as the solvent power to polymer molecules decreases.^{31,32}

Table 1. The values of intrinsic viscosity and Huggins coefficient of PEO with average molecular weight of 1.0×10^5 in water at various temperatures

Temperature ^a (°C)	$[\eta]$ (dL/g)	k_H
10.16	0.9825	0.6331
12.08	0.9625	0.6858
14.07	0.9495	0.6683
16.10	0.9360	0.6379
18.07	0.9141	0.7128
20.05	0.8979	0.7236
22.05	0.8797	0.7708
24.04	0.8492	0.8664
26.02	0.8296	0.8907
28.02	0.8108	0.9287
30.01	0.7923	0.9288
31.98	0.7746	0.9670

^aTemperature was controlled to be ± 0.01 °C.

From the estimation of Huggins coefficients in Table 1, they are not less than 0.6 in all cases at any observed temperatures and increase with temperature. The water is not a very good solvent for PEO with average molecular weight of 1.0×10^5 in this investigated temperature range and its role as a solvent is diminished with the increase in temperature, which is agreed with the fact that PEO has the inverse solubility-temperature behavior.¹ The Huggins coefficient of PEO is abruptly increased during the change of temperature from 22 to 24 °C, which means that the capability of water as a solvent on PEO changes largely.

The intrinsic viscosity is a measure of the hydrodynamic volume of the macromolecules dissolved in solvents.^{31,33} If the polymer-solvent interaction is favorable, the polymer is more expanded to a large volume space and has a value of higher intrinsic viscosities. The intrinsic viscosities of PEO in aqueous solutions at various temperatures are presented in Table 1, and it shows a decrease in intrinsic viscosity with temperature. As the temperature increases, the power of water as a solvent decreases, the PEO chain in water contracts in a small volume space, and it also has a higher value of Huggins coefficients. The diminution of solvent power of water to PEO and the contraction of PEO chain in water are recorded with the in-

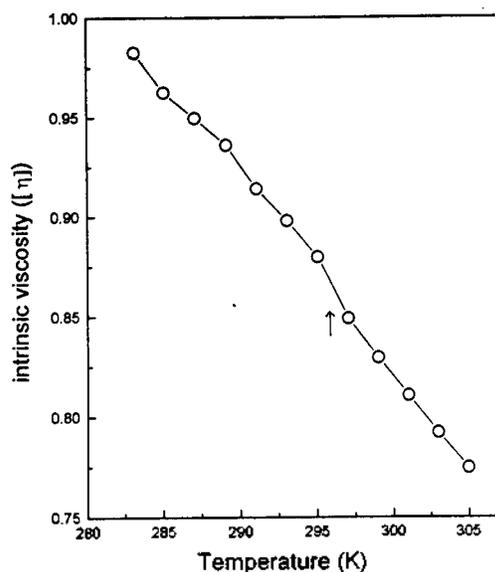


Fig. 1. Temperature dependence of the intrinsic viscosity for PEO in water. The arrow means the breaking region of the curve.

crease in temperature, which mean that the water surrounding the hydrophobic groups of PEO is more structured by the hydrophobic hydration^{9,10,11} and the PEO chain can be more contracted by the hydrophobic interaction^{29,34} between the intra-chain hydrophobic groups.

To see more clearly the effects of temperature on the conformation of PEO in water, the intrinsic viscosity vs temperature are plotted and given in Fig. 1. The decrease in intrinsic viscosity with temperature is clearly observed, and the unique interesting one is the break down the smooth decreasing curve of it in the temperature range of 22~24 °C, which is a similar result as one of Huggins coefficients. The hydrodynamic volume of the PEO chain in water is decreased more sharply in this temperature range. The polymer-water interaction becomes to be unfavorable due to the decreasing of the solvent power of water, which promotes the hydrophobic interaction. The plots of $[\eta]$ vs. T can be described by the following empirical equation³⁵ to understand further the temperature effect on the changes of intrinsic viscosity.

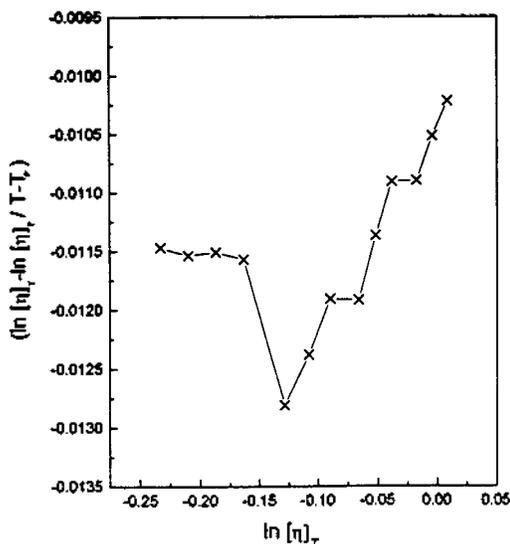


Fig. 2. Treatment of the intrinsic viscosity according to eq. 2.

$$\ln[\eta]_T = \{\ln[\eta]_r + k_1(T - T_r)\} / \{1 - k_2(T - T_r)\} \quad (2)$$

where $[\eta]_T$ and $[\eta]_r$ are the intrinsic viscosities at a temperature T and an arbitrary reference temperature T_r , respectively. The parameters k_1 and k_2 are determined from the intercept and slope of the plot of $(\ln[\eta]_T - \ln[\eta]_r)/(T - T_r)$ vs. $\ln[\eta]_r$.³⁵ In this study the form of the plot of $(\ln[\eta]_T - \ln[\eta]_r)/(T - T_r)$ vs. $\ln[\eta]_r$ are meaningful and given in Fig. 2. The reference temperature (T_r) was chosen 32 °C (any chosen reference temperatures between 10 and 32 °C do not affect the form of the plot in Fig. 2). If we follow the $\ln[\eta]_r$ value corresponding to the temperature T through the axis of abscissa, the steep increase in $(\ln[\eta]_T - \ln[\eta]_r)/(T - T_r)$ is obviously observed at the value of $\ln[\eta]_r$ corresponding to 22 °C. It is clearly said that the changes of conformation of aqueous PEO solutions occur at this temperature. As mentioned in the introduction part, the PEO chain has a conformation being polar due to the favorable polymer-water interaction at low temperatures and it has a conformation being nonpolar due to the unfavorable polymer-water interaction at higher temperatures. This is manifested in the contraction of PEO coils by the hydrophobic interaction with increasing temperature. One says that decreasing the

temperature or increasing the polarity (or hydrogen bonding capacity) of the solvent favors the gauche conformers representing the helical form.¹⁸ From this study, we can see that the temperatures below 22 °C corresponds to the low ones, the PEO chain has the more extended partially helical conformation owing to the favorable PEO-water interaction, and the temperatures above 24 °C corresponds to the higher ones, it has the more contracted conformation in a relatively small volume space by the unfavorable PEO-water interaction inducing a hydrophobic hydration.

Urea is a well-known effective protein denaturant by altering the solvent properties of water.^{22,29,36-39} The aqueous solutions of it is prepared by the addition of urea into water and the concentrations of them are controlled to maintain 0.2, 1, and 2 mole/L. The weighed amount of PEO is dissolved in them and the intrinsic viscosities of PEO in aqueous urea solutions are determined by the aforementioned method to see the urea effect of the temperature dependence on the conformation of PEO. The intrinsic viscosities and Huggins coefficients of PEO in 0.2, 1, and 2 M aqueous urea solutions at various temperatures are presented in Table 2. The values of Huggins coefficient of PEO in aqueous urea solutions are generally lower than that in water in all investigated temperature ranges, and this tendency is growing with the increase in the concentration of urea. It means that the polymer-solvent (aqueous urea solution) interaction is more favorable by the addition of urea, i.e., the perturbation of the structured water inducing the unfavorable polymer-solvent interaction and the solvent becomes to be better. From the estimation of the Huggins coefficients, the aqueous urea solution is a better solvent than water for PEO. The concentrated aqueous urea solution has a smaller Huggins coefficients and a larger intrinsic viscosities than the diluted one means that the polymer-solvent interaction is more favorable and the PEO chain can have larger hydrodynamic volume, which may be due to the perturbation of the structured water by urea. The Huggins coefficients continuously increase with the increase in temperature in 0.2 M aqueous urea

Table 2. The values of intrinsic viscosity and Huggins coefficient of PEO in 0.2, 1, and 2 M aqueous urea solutions at various temperatures

0.2 M			1 M			2 M		
Temp. (°C)	$[\eta]$ (dL/g)	k_H	Temp. (°C)	$[\eta]$ (dL/g)	k_H	Temp. (°C)	$[\eta]$ (dL/g)	k_H
10.17	0.9710	0.5284	10.17	1.0383	0.5245	10.18	1.1156	0.4264
12.10	0.9507	0.5233	12.11	1.0269	0.5062	12.10	1.1004	0.4286
14.08	0.9365	0.5551	14.08	1.0053	0.5441	14.08	1.0880	0.4223
16.11	0.9209	0.5565	16.11	0.9890	0.5567	16.12	1.0681	0.4526
18.09	0.8978	0.5995	18.08	0.9719	0.5688	18.10	1.0509	0.4693
20.07	0.8922	0.5656	20.06	0.9652	0.5352	20.07	1.0431	0.4639
22.06	0.8756	0.6105	22.06	0.9511	0.5314	22.07	1.0244	0.4780
24.04	0.8600	0.6357	24.05	0.9362	0.5307	24.06	1.0088	0.4837
26.04	0.8454	0.7082	26.03	0.9185	0.5517	26.05	0.9932	0.4736
28.03	0.8297	0.7191	28.02	0.9048	0.5537	28.04	0.9770	0.5129
30.02	0.8159	0.7206	30.02	0.8897	0.5602	30.03	0.9677	0.4794
32.00	0.8001	0.7205	32.00	0.8792	0.5448	32.01	0.9553	0.4740

solution, but the increasing tendency of them is slight in 1 and 2 M aqueous urea solutions. As the amount of urea is increased, the urea greatly perturbs the structured water originating from the hydrophobic hydration. So the existence of structured water being due to the increase in temperature may be reduced in the concentrated urea conditions. The intrinsic viscosities representing the hydrodynamic volume of PEO in aqueous urea solutions vs temperature are plotted to get the information of the temperature effect on the conformation of PEO in them, which are given in Fig. 3. From Fig. 3, we can see that the hydrodynamic volume of the PEO chain in aqueous urea solutions also decreases with temperature meaning the contracted polymer chain due to a unfavorable polymer-solvent interaction, which is the same result as water and corresponds well to the above explanation of Huggins coefficients. The form of each curve is similar to that of aqueous PEO solutions. It is also broken at the point corresponding to any other temperature, but the breaking degree is minute. The breaking point is appeared in the temperature range of 18~20 °C which is slightly different from the result of the aqueous PEO solutions. The form of breaking of the curve is also different from that. It is worth to compare and see the conformation of PEO in both aqueous and

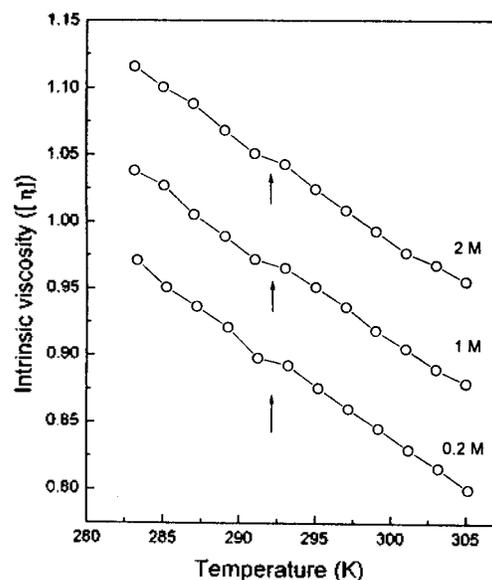


Fig. 3. Temperature dependence of the intrinsic viscosity for PEO in 0.2, 1, and 2 M aqueous urea solutions. The arrow means the breaking region of the curve.

aqueous urea solutions with the variation of temperature. The results of them are collected in Fig. 4. While the curve in water is steeply down, it in aqueous urea solutions is gently down. Comparing the curves in water and 0.2 M aqueous urea solution, the curve in 0.2 M aqueous urea solution

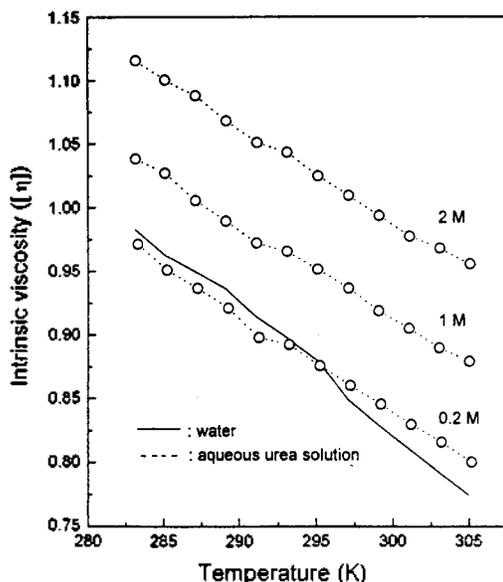


Fig. 4. Temperature dependence of the intrinsic viscosity for PEO in water and urea/water mixtures (urea concentration 0.2, 1, and 2 M).

are situated in the lower position at low temperatures and in the upper position at higher temperatures, respectively. As mentioned above, the chain is contracted with the increase in temperature, which is partly due to the hydrophobic interaction and is also supported by the fact of the solvent becoming a poorer solvent at higher temperatures. If the small amount of urea (0.2 M) is added to the system, the structured water inducing the hydrophobic interaction is destroyed and the chain is extended, which is noticeable in the high temperature region owing to the more existence of the structured water. This situation may not be dominant at low temperatures, which is mainly due to the following facts; as the polymer-water interaction is favorable at low temperatures, the structured water exists a little and the destruction of it by urea is little.

As the more amounts of urea is added (i.e., 1 and 2 M aqueous urea solutions), all of the intrinsic viscosity values of PEO in aqueous urea solutions lies above that in water for the corresponding investigated temperature ranges. More amounts of urea has a strong ability to break the structured water not being completely unperturbed by the

small amounts of urea, so the Huggins coefficients decrease and the intrinsic viscosities increase. If the concept of water structure perturbing capability of urea is only applied to the explanation of the experimental results, the increase in intrinsic viscosity and decrease in Huggins coefficients must no further continue at some amounts of urea (the limited quantity of structured water can be nearly vanished by some amounts of urea). But the increase in intrinsic viscosity continues with the increase in urea amounts. So we must introduce a concept of PEO-urea interaction, in which the urea replaces the structured water originating from the hydrophobic hydration, interacts directly³⁶ with PEO, and promotes the larger hydrodynamic volume of polymer chain due to the binding of urea³⁶ to PEO. The increase in intrinsic viscosity may be continued until the addition of urea has stopped. Our experimental results are clearly explained with the aid of these two different concepts (the water-structure breaking by urea and PEO-urea interaction), both of which increase the hydrodynamic volume and the degree of polymer-solvent interaction.

The form of intrinsic viscosity versus temperature curves at the breaking point in both two cases (water and aqueous urea solutions) are slightly different. They are steeply and slowly down in water and aqueous urea solutions, respectively. The temperature greatly affects the conformation of PEO in water (in this case, the increase of temperature induces the unfavorable PEO-solvent interaction and contracts the PEO chain by the hydrophobic hydration). If some amounts of structured water is already destroyed by the addition of urea, then the conformation is a little changed at the breaking point with the increase in temperature.

The effect of temperature on the intrinsic viscosity values shows an Arrhenius behavior.⁴⁰ The variations of $\ln[\eta]$ with $1/T$ are plotted in Fig. 5 and used to calculate the activation energy (E_{av}) of the viscous flow by equation 3,^{40,41} which is based on the concept that the flow of molecules is hindered by a barrier of some kind related to the quasi-lattice structure of the liquid, and given

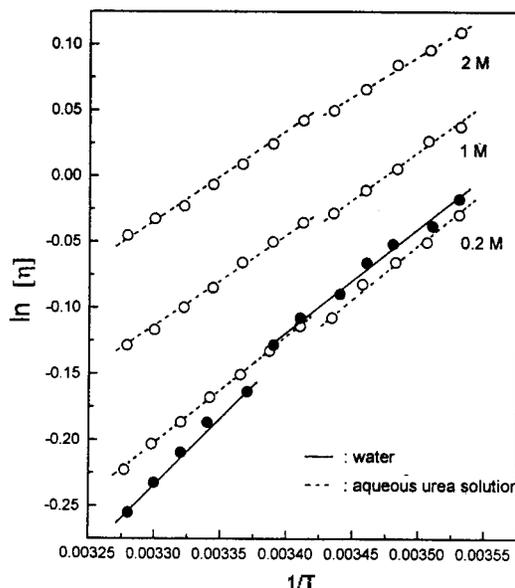


Fig. 5. Plots of $\ln [\eta]$ vs. $1/T$ for PEO in water and aqueous urea solutions.

in Table 3.

$$[\eta] \propto e^{E_{a\eta}/RT} \quad (3)$$

The activation energies in the range of low temperatures have a smaller value than that in high temperatures, which may also be explained by the concept of superior water-polymer interactions at low temperatures and the contracted conformation due to the hydrophobic hydration (poor water-polymer interactions) at higher temperatures. The hydrophobic hydration promotes the structuring of water surrounding the hydrophobic groups of PEO, which resists the flow of polymer chain in the sea of solvent and induces the higher activation energies to the viscous flow. As the urea is added to the aqueous PEO solutions, some of the structured water surrounding the hydrophobic groups is perturbed, which lowers the activation energy, and the tendency is greater in the high temperature region, which is caused by the more existence of the structured water. There is a growing tendency to the lowering the activation energies with the increase in the concentration of urea, resulting from the destruction of more amounts of structuring water by the more amounts of urea

Table 3. The calculated activation energies (kJ/mol) of the viscous flow of PEO in water and aqueous urea solutions

	Water	Aqueous urea solution		
		0.2 M	1 M	2 M
low temperature region ^a	6.38	6.50	5.89	5.15
high temperature region ^b	8.62	6.73	5.99	5.49

^aLow temperature region means the lower temperature parts on the breaking point base of the curve in Fig. 1 and Fig. 2, i.e., 10–22 °C in water and 10–18 °C in aqueous urea solutions. ^bHigh temperature region means the upper temperature parts on the breaking point base of the curve in Fig. 1 and Fig. 2, i.e., 24–32 °C in water and 20–32 °C in aqueous urea solutions.

and the easier flow of PEO with decreasing barrier.

CONCLUSIONS

The experimental results from the investigation of the temperature effects on the conformational properties of aqueous PEO solutions with respect to the change of water structure are following.

1. The PEO-water interaction is decreased with the increase in temperature, which induces the hydrophobic hydration and contracts the PEO chain by the intrachain hydrophobic interaction.

2. The conformation of PEO chain in water can be greatly changed at the temperature range of 22–24 °C, from the extended partially helical structure to the contracted random coiled one.

3. If the urea is added to the aqueous PEO solution, it would destroy the structured water resulting from the hydrophobic hydration and interact directly with PEO by replacing the structured water. So the chain can be more extended and huged, inducing the increase in intrinsic viscosity and the decrease in Huggins coefficients.

4. There is a tendency to the lowering the activation energy to the viscous flow with the decrease in temperature and increase in the concentration of urea, resulting from the perturbation of

the structured water inducing a barrier to the viscous flow.

Acknowledgment. This paper was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation.

REFERENCES

- Molyneux, P., Ed. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC Press: Boca Raton, Florida, 1983; Vol. 1 and 2.
- Andrade, J. D. *Surface and Interfacial Aspects of Biomedical Polymers*; Plenum Press: N. Y., 1985.
- Liu, K. J.; Parsons, J. L. *Macromolecules* **1969**, *2*, 529.
- Koenig, J. L.; Angood, A. C. *J. Polym. Sci., Polym. Phys.* **1970**, *8*, 1787.
- Fuson, M. M.; Miller, J. B. *Macromolecules* **1993**, *26*, 3218.
- Kjellander, R.; Florin, E. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2023.
- Bieze, T. W. N.; Barnes, A. C.; Huige, C. J. M.; Enderby, J. E.; Leyte, J. C. *J. Phys. Chem.* **1994**, *98*, 6568.
- Barnes, A. C.; Bieze, T. W. N.; Enderby, J. E.; Leyte, J. C. *J. Phys. Chem.* **1994**, *98*, 11527.
- Franks, F. *Water A Comprehensive Treatise*; Plenum: N. Y., 1975; Vol. 4.
- Mancera, R. L.; Buckingham, A. D. *J. Phys. Chem.* **1995**, *99*, 14632.
- Head-Gordon, T. *J. Am. Chem. Soc.* **1995**, *117*, 501.
- Hammes, G. G.; Roberts, P. B. *J. Am. Chem. Soc.* **1968**, *90*, 7119.
- Hammes, G. G.; Schimmel, P. R. *J. Am. Chem. Soc.* **1967**, *89*, 442.
- Maxfield, J.; Shepherd, I. W. *Polymer* **1975**, *16*, 505.
- Devanand K.; Selser, J. C. *Macromolecules* **1991**, *24*, 5943.
- Brandrup, J.; Immergut, E. H. (Eds.), *Polymer Handbook*, 3rd ed.; Wiley-Interscience: New York, 1989.
- Bartlett, J. R.; Cooney, R. P. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 597.
- Bjorling, M.; Karlstrom, G.; Linse, P. *J. Phys. Chem.* **1991**, *95*, 6706.
- Andersson, M.; Karlstrom, G. *J. Phys. Chem.* **1985**, *17*, 883.
- Karlstrom, G. *J. Phys. Chem.* **1985**, *89*, 4962.
- Malmsten, M.; Linse, P.; Zhang, K.-W. *Macromolecules* **1993**, *26*, 2905.
- Alexandridis, P.; Athanassiou, V.; Hatton, T. A. *Langmuir* **1995**, *11*, 2442.
- Frank, H. S.; Franks, F. *J. Chem. Phys.* **1968**, *48*, 4746.
- Roseman, M.; Jencks, W. P. *J. Am. Chem. Soc.* **1975**, *97*, 631.
- Muller, N. *J. Phys. Chem.* **1990**, *94*, 3856.
- Kresheck, G. C. In *Water-A Comprehensive Treatise, Vol 4: Aqueous Solutions of Amphiphiles and Macromolecules*; Franks, F., Ed.; Plenum Press: New York, 1975.
- Baglioni, P.; Ferroni, E.; Kevan, L. *J. Phys. Chem.* **1990**, *94*, 4296.
- Baglioni, P.; Rivara-Minten, E.; Dei, L.; Ferroni, E. *J. Phys. Chem.* **1990**, *94*, 8218.
- Jeon, S. I.; Choi, H.-K.; Ra, S. C.; Yoon, B. J. *Bull. Korean Chem. Soc.* **1994**, *15*, 748.
- Rabek, J. F. *Experimental Methods in Polymer Chemistry*; Wiley: New York, 1980.
- Tanford, C. *Physical Chemistry of Macromolecules*; Wiley: New York, 1969.
- Loffler, R.; Richtering, W. H.; Finkelmann, H.; Burchard, W. *J. Phys. Chem.* **1992**, *96*, 3883.
- Van Krevelen, D. W. *Properties of Polymers*; Elsevier: New York, 1976.
- Jeon, S. I.; Jhon, M. S. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3555.
- Bohdanecky, M.; Petrus, V.; Horsky, J. *Macromolecules* **1995**, *28*, 8344.
- Bonner, O. D.; Bednarek, J. M.; Arisman, P. K. *J. Am. Chem. Soc.* **1977**, *99*, 2898.
- Freifelder, D. *Physical Biochemistry*; W. H. Freeman & Co.: San Francisco, 1982.
- Jeon, S. I.; Jhon, M. S. *J. Polym. Sci. Part A, Polym. Chem.* **1989**, *27*, 237.
- Erdey-Gruz, T. *Transport Phenomena in Aqueous Solutions*; Wiley: New York, 1974.
- Mortimer, R. G. *Physical Chemistry*; Benjamin: New York, 1993.