수용액에서 점도계법에 의한 폴리에틸렌 옥사이드의 구조성질에 대한 요소 용질들의 효과

羅承昌 · 尹炳集 · 全相一*
강릉대학교 자연과학대학 화학과
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Effect of Ureas on the Conformational Properties of Poly(ethylene oxide) in Aqueous Solutions by Viscometry

Seung Chang Ra, Byoung Jip Yoon, and Sang Il Jeon*
Department of Chemistry, Kangnung National University, Kangnung 210-702, Korea
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요 약. 수용액에서 폴리에틸렌 옥사이드(PEO)의 구조성질이 일련의 요소용질들의 물 구조 간섭 정도 관점에서, 16℃에서 점도계법으로 연구되어졌으며, 또한 16℃와 25℃의 두 온도에서 PEO에 대한 요소와 메틸요소의 양 변화가 마찬가지로 행해졌다. 결과는 16℃에서 분자량이 1.0×10^5인 PEO의 요소들에 의한 사슬 퍼짐은 25℃에서 분자량이 8.0×10^3인 PEO의 경우와 비슷한데, 이것은 요소들의 물 구조 간섭 정도가 두 경우에 비슷하기 때문이라 설명했다. 요소는 PEO 주위 물 구조를 간섭함으로써, 그리고 메틸요소는 메틸요소와 PEO간 소수성 상호인력을 함으로써, PEO 사슬을 펴지게 한다. 분자량이 1.0×10^5인 PEO는 그 자체내에 소수성 부분을 가지는데, 이것은 다음과 같이 대략 두 부분으로 분류할 수 있다. 하나는 16℃에서 많이 나타나며, 분자내 소수성 상호인력을 할 수 있는 내부 소수성기와, 다른 하나는 25℃에서 많이 나타나며, 외부에서 가해진 소수성 용질들과 분자간 소수성 상호인력을 할 수 있는 바깥쪽으로 노출된 소수성기이다.

ABSTRACT. The conformational properties of poly(ethylene oxide) (PEO) in aqueous solutions are studied by viscometry with respect to the water structure perturbing capabilities of a series of urea solutes at 16℃, and experiments for the effect of amounts of urea and methylurea on PEO at 16 and 25℃ are also performed. The results show that the chain expansion, by ureas, of PEO of 1.0×10^5 molecular weight at 16℃ is similar to that of PEO of 8.0×10^3 molecular weight at 25℃ with respect to the water structure perturbation. Urea and methylurea make the PEO chain expand by the perturbation of water structure around PEO and by the hydrophobic interaction between methylurea and PEO, respectively. PEO of 1.0×10^5 molecular weight has hydrophobic sites on it, which are roughly classified into two parts; one is the inner hydrophobic groups which can interact between themselves (intramolecular hydrophobic interaction) and prevails at 16℃, and the other is the outer, exposed hydrophobic groups which can interact with the added hydrophobic solute (intermolecular hydrophobic interaction) and prevails at 25℃.

INTRODUCTION

Poly(ethylene oxide) (PEO) is one of simple water-soluble synthetic polymers and its properties in aqueous solutions have been extensively studied from the scientific viewpoint.[1~5] The characteristic feature of it contains both nonpolar ($-CH_2-CH_2-$) and polar ($-O-$) sites in a chain. The amphiphilic character of it opens the possibility for particularly interesting hydrophobic and hydrophilic interactions of the PEO chain in the solvent.[6,7] The

negative change of entropy is recorded upon the addition of PEO to water.[1] This phenomenon is due to a reduction in entropy of the water (i.e., the structuring of the neighboring water molecules) at the hydrophobic interface.[8,9] This is commonly referred to as hydrophobic hydration, which promotes the hydrophobic interaction[10] between the hydrophobic groups. Such hydrophobic interactions are often believed to contribute to the stability of ordered macromolecular structures.[6,7] There has also been a hyphothesis that PEO, which is known to have a helical structure in the solid state, retains some of its helicity even in dilute aqueous solutions.[5,11,12]

Cooperative processes are frequently observed in biological macromolecules.[13] Protein denaturation[13] is a particularly well-studied example in which macromolecules are transformed from their native state to a disordered random coil-like state by the variation of temperature or urea-guanidine concentration. Aqueous solutions of urea and substituted ureas are found to be effective denaturants of proteins.[13,14] Denaturation may alter the solvent structure so as to weaken the intramolecular hydrophobic interactions.[6,7] The change of water structure takes place upon addition of water structure-breaking and -making of solutes.[15~18] The concept of water structure perturbing effect of solutes has been used as a powerful indirect tool for interpreting solute-water interactions in aqueous solutions.[18,19] In this study, the conformational properties of aqueous PEO solutions are studied by viscometry with respect to the water structure perturbing capabilities of a series of urea solutes at 16 ℃, and experiments for the effect of amounts of urea and methylurea on PEO at 16 and 25 ℃ are also performed.

EXPERIMENTAL

PEO was obtained from Aldrich Chemical Co. with average molecular weight of 1.0×10^5. The A.C.S. reagent grade, urea(U), thiourea(TU), methylurea(MU), 1,3-dimethylurea(DMU), ethylurea(EU), and tetramethylurea(TMU) were used as received from Aldrich Co. Aqueous ureas solutions were always prepared just prior to use.

The apparatus and procedures for the measurement of the intrinsic viscosity of PEO in aqueous ureas solutions have been described in the previous paper.[20] Experiments were performed at 16 and 25 ℃ (± 0.01).

RESULTS AND DISCUSSION

PEO in water has both upper and lower critical solution temperatures of -9 and $+103$ ℃, respectively.[21,22] In aqueous solution, PEO chain retains to a large degree the trans, gauche, and trans sequence.[13,14] The gauche conformers indicating a helical arrangement are favored at low temperatures,[13,14] which may be partly due to the intramolecular hydrophobic interactions of PEO in water.[7,20] To investigate the conformational properties of PEO at low temperature, an experimentally available temperature of 16 ℃ is chosen and the effect of ureas is investigated with respect to the perturbation of water structure around PEO.

Aqueous solutions of ureas are effective denaturants, whose function has been explained in terms of water structure perturbability.[6,7,20,23] The water structure perturbing capability is closely related to the excess apparent molal heat capacities, ϕC_p^0 (excess) (cal deg^{-1} mol^{-1}) by Bonner et al.[24] and is given in Table 1. The smaller the quantity of ϕC_p^0 (excess) is, the larger the water structure breaking effect is. In order to see the effect of ureas on PEO in water, the intrinsic viscosity ratios,[20,23] $[\eta]_u/[\eta]_w$ are calculated from the obtained intrinsic viscosities of PEO in water and of PEO in 0.2 M aqueous ureas solutions, $[\eta]_w$ and $[\eta]_u$, respectively. The results are summarized in Table 1 and plotted in Fig. 1. The more hydrophobic solutes than U except TMU induce the intrinsic viscosity ratio to increase, i.e., increase the hydrodynamic volume of PEO (Fig. 1). It may be explained by the hydrophobic interaction[20,23,25] between the hydrophobic groups of the hydrophobic solute and PEO. These hydrophobic interactions between the solute and PEO seem to happen only for the small sizes of ureas solutes(methylurea, ethylurea, and 1,3-dimethylurea) (Fig. 1). The

Table 1. The Excess apparent molal heat capacities, ϕC_p^0 (excess), of ureas, and intrinsic viscosity ratios, $[\eta]_u/[\eta]_w{}^c$, of PEO[b] in 0.2 M aqueous ureas solutions at 16 ℃

Ureas solutes	ϕC_p^0 (excess)[c]	$[\eta]_u/[\eta]_w$
Thiourea(TU)	−17.4	1.011
Urea(U)	−5.8	1.057
Methylurea(MU)	10.7	1.087
Ethylurea(EU)	20.7	1.074
1,3-Dimethylurea(DMU)	25.6	1.075
Tetramethylurea(TMU)	50.1	1.052

[a] $[\eta]_w$ is the intrinsic viscosity of PEO in water at 16 ℃ and has a value of 0.950 dL/g. [b] 1.0×10^5 average molecular weight of PEO used. [c] obtained from reference (24) and unit in cal deg^{-1} mol^{-1}.

unexpected low value of intrinsic viscosity ratio is found for the large hydrophobic solute such as tetramethylurea (TMU), which must be interpreted as the chain contraction[20,23] by the induced water structure (hydrophobic hydration) instead of the hydrophobic interaction between TMU and PEO.

Thiourea(TU) and urea(U) have the lower value of ϕC_p^0 (excess) than other solutes studied, *i.e.*, stronger water structure breaker. They are supposed to break the structured water efficiently around the hydrophobic groups of PEO and reduce the strength of hydrophobic interaction, and the chain would get more expanded. But the result in *Fig.* 1 is not consistent with the simple expectation. The less expansion of the PEO chain by this stronger water structure breaking solutes than other ones is observed in *Fig.* 1. This is a peculiar phenomenon. From the light scattering study by Devanand and Selser,[26] the unusual large second virial coefficient (A_2) values for aqueous solutions of PEO are obtained. They interpreted them as a result of a particularly strong and unique interaction between PEO and water. The structured water around PEO may not be easily disturbed by the small amounts of U and TU (0.2 M) because of these strong interactions. The similar phenomenon like this was also observed in our previous study for PEO of 8.0×10^3 at 25 ℃.[20] One can say
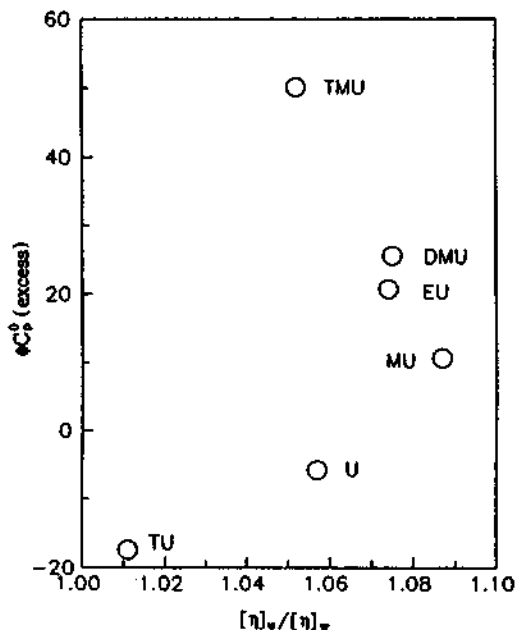

Fig. 1. The relation between excess apparent molal heat capacities, ϕC_p^0 (excess) (cal deg^{-1} mol^{-1}) of ureas, and intrinsic viscosity ratios, $[\eta]_u/[\eta]_w$, of PEO of 1.0×10^5 average molecular weight in 0.2 M aqueous solutions of ureas at 16 ℃.

that the chain expansion, by ureas, of PEO of 1.0×10^5 molecular weight(named poly(ethylene oxide)[21]) at 16 ℃ is similar to that of PEO of 8.0×10^3 molecular weight (named poly(ethylene glycol) (PEG)[21]) at 25 ℃[20] with respect to the water structure perturbation.

Varying the amounts of water structure perturbants, the chain can be profoundly affected. The effect of variation of amounts of perturbants on PEO is examined. The perturbants of U and MU are only chosen to investigate the respective effects of water structure-breaking and -making around PEO. The results are shown in *Table* 2 at two different temperatures. The coiled PEO chain is more expanded with the increase of the concentration of perturbants, and the tendency is greater for MU. In order to see the systematic dependence of the conformation of PEO chain on the concentration of perturbants at two different temperatures, the intrinsic viscosity ratios are plotted against the molar concentrations of U and
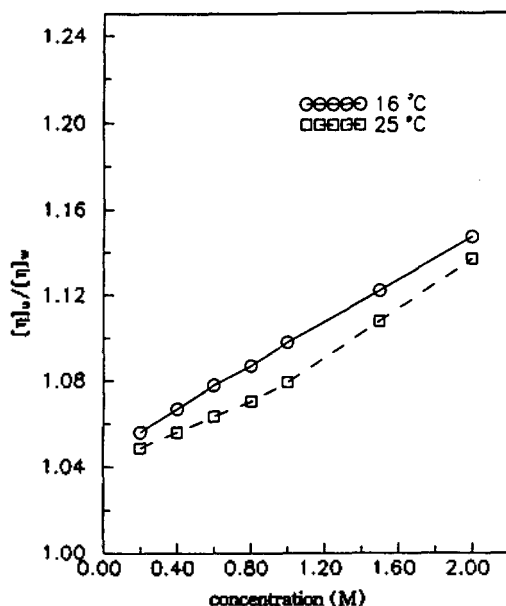
Fig. 2. The relation between intrinsic viscosity ratios, $[\eta]_u/[\eta]_w$, of PEO of 1.0×10^5 average molecular weight and molar concentrations of urea at two different temperatures.
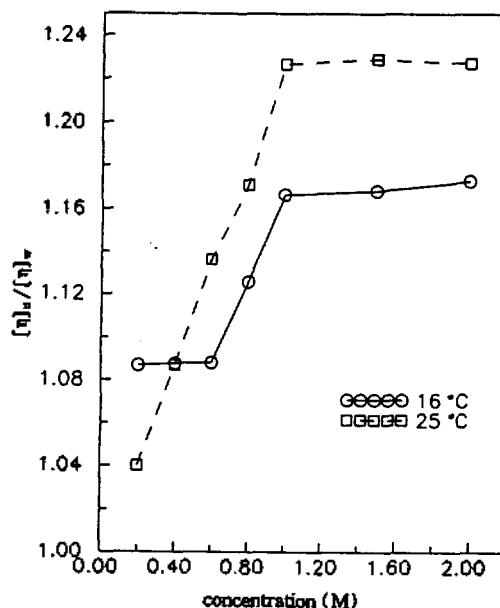

Fig. 3. The relation between intrinsic viscosity ratios, $[\eta]_u/[\eta]_w$, of PEO of 1.0×10^5 average molecular weight and molar concentrations of methylurea at two different temperatures.

MU in *Figs.* 2 and 3, respectively. From *Fig.* 2, one can see that the water structure around PEO is more perturbed and the chain is more expanded by the increasing amount of urea. The strong interaction between PEO and water is gradually lessened as the amount of urea increases. The gradual expansion of the PEO chain by the increasing addition of urea at 16 ℃ is more remarkable than that at 25 ℃. This means that the chain is more expanded by the gradual breakdown of the hydrophobic interaction with the increasing addition of urea because the conformation of PEO at 16 ℃ is coiled by strong and large hydrophobic interaction between the hydrophobic groups of PEO. A rise in perturbation trends of MU (*Fig.* 3) is entirely different from that of U (*Fig.* 2). The water structure making MU solute can promote the intramolecular hydrophobic interactions in PEO by the hydrophobic hydration, and the chain should have been more or less contracted.[20,23] This type of behavior is common for any other synthetic water soluble polymers with hydrophobic groups[23]

and is also observed in our study for PEO of 1.0×10^5 molecular weight in 0.2 M aqueous solutions of MU at 25 ℃ (*Table* 2 and *Fig.* 3). If more amounts of MU is added to the aqueous solutions of PEO, the chain is expected to be more contracted by the increase of hydrophobic interaction. But the opposite trend was found. The PEO chain is expanded in spite of the increasing addition of MU (*Fig.* 3). PEO chain can have the exposed hydrophobic groups which do not participate in the intramolecular hydrophobic interaction. MU has one hydrophobic, methyl, group in the molecule, and can participate in the hydrophobic interaction. The exposed hydrophobic groups of PEO take part in the intermolecular hydrophobic interaction between them and MU. This invokes the large hydrodynamic volume of PEO and thus the intrinsic viscosity ratio to increase, which is shown in *Fig.* 3. The increase of the hydrodynamic volume of the chain by MU is reduced at low temperatures. This means that PEO itself at 16 ℃ has the small amounts of exposed hydrophobic groups.

Table 2. Intrinsic Viscosity ratios, $[\eta]_u/[\eta]_w{}^a$, of PEO[b] with the variation of concentrations of urea and methylurea at two different temperatures

Temperature(°C)	Solutes	Molar concentrations (M)						
		0.2	0.4	0.6	0.8	1.0	1.5	2.0
16	U	1.057	1.067	1.078	1.087	1.098	1.122	1.145
	MU	1.087	1.088	1.088	1.126	1.167	1.168	1.173
25	U	1.049	1.056	1.064	1.070	1.079	1.108	1.137
	MU	1.040	1.087	1.136	1.179	1.226	1.229	1.230

$^a[\eta]_w$ is 0.950 and 0.900^{20} dL/g at 16 and 25 °C, respectively. [b]1.0×10^5 average molecular weight of PEO used.

The PEO chain at 16 °C has large amounts of inner hydrophobic groups participating in the strong intramolecular hydrophobic interaction (maintaining the helices) and the small amounts of exposed outer hydrophobic groups that can take part in the intermolecular hydrophobic interaction. The situation at 25 °C is different from that at 16 °C. The PEO chain at 25 °C has the small amounts of inner and the large amounts of exposed outer hydrophobic groups. The large or small amounts of inner or outer hydrophobic groups of PEO will be relative and can vary with the environmental conditions.

The exposed hydrophobic groups of PEO to added methylurea solute results in a hydrophobic interaction between them. This makes the chain have a large hydrodynamic volume and increases the intrinsic viscosity ratio. However the increase persists only upto 1.0 molar concentrations of MU (*Fig.* 3). This can be explained by the exhaustion of the exposed hydrophobic groups of PEO which are available to participate in the hydrophobic interaction with MU.

CONCLUSIONS

The experimental data from the investigation on conformational properties of PEO in aqueous solution by adding ureas at two different temperatures result in the following five conclusions.

1. The chain expansion, by ureas, of PEO of 1.0×10^5 molecular weight at 16 °C is similar to that of PEO of 8.0×10^3 molecular weight at 25 °C with respect to the water structure perturbation.

2. The perturbation of the water structure around PEO by ureas is small, which can be partly explained as a strong unique interaction between PEO and water.

3. The increase of addition of urea makes PEO expand its hydrodynamic volume by the perturbation of the water structure around PEO.

4. The increase of addition of methylurea makes PEO greatly expand its hydrodynamic volume by the hydrophobic interaction between the hydrophobic groups of MU and PEO, but the expansion stops at some amounts of added MU.

5. PEO (of 1.0×10^5 molecular weight) at 16 °C is coiled by large amounts of intramolecular hydrophobic interaction between the hydrophobic groups of PEO, which can induce the strong interaction between PEO and water. And it has small amounts of exposed hydrophobic groups, which can participate in the intermolecular hydrophobic interaction with the added hydrophobic solute.

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