19. C. T. Hung and R. B. Taylor, *J. Chromatogr.*, **209**, 175 (1981).
20. J. C. Kraak, C. X. Ahn, and J. Fraanje, *J. Chromatogr.*, **209**, 369 (1981).
21. J. H. Knox and R. A. Hartwick, *J. Chromatogr.*, **204**, 3 (1981).
22. D. W. Armstrong and S. J. Henry, *J. Liq. Chromatogr.*, **3**, 657 (1980).
23. R. Weinberger, P. Yarmchuck, and L. J. Cline Love, *Anal. Chem.*, **54**, 1552 (1982).
24. J. G. Dorsey, M. T. De Echegaray, and J. S. Landy, *Anal. Chem.*, **55**, 924 (1983).
25. R. A. Barford and B. J. Sliwinski, *Anal. Chem.*, **56**, 1554 (1984).
26. A. Berthod, I. Girard, and C. Gonnet, *Anal. Chem.*, **58**, 1359 (1986).
27. A. Berthod, I. Girard, and C. Gonnet, *Anal. Chem.*, **58**, 1362 (1986).
28. A. Kasturi and R. K. Gillpin, *J. Chromatogr. Sci.*, **25**, 29 (1987).
29. Y. N. Kim and P. R. Brown, *J. Chromatogr.*, **384**, 209 (1987).
30. A. Berthod, J. M. Asensio, and J. J. Laserna, *J. Liq. Chromatogr.*, **12**, 2621 (1989).
31. D. Bentrop, F. V. Warren, Jr., S. Schmitz, and B. A. Bidlingmeyer, *J. Chromatogr.*, **535**, 293 (1990).
32. B. K. Lavine, A. J. White, and J. H. Han, *J. Chromatogr.*, **542**, 29 (1991).
33. H. Wada, H. Ozaki, K. Makino, T. Takeuchi, and H. Hatano, *Anal. Lett.*, **16**, 1537 (1983).
34. H. Wada, *Chromatographia*, **18**, 550 (1984).
35. K. Yasukawa, M. Kasai, Y. Yanagihara, and N. Noguchi, *Nucleic Acids Res.*, **15**, 109 (1984).
36. H. Wada, *J. Chromatogr.*, **332**, 255 (1985).
37. P. Mukerjee and K. J. Mysels, *Critical Micelle Concentrations of Aqueous Surfactants Systems*, NSRDS-NBS 36, National Breau of Standards, Washington, D.C., 1971.

The Steric Repulsion Properties of Polyethylene Oxide

Sang Il Jeon* and Joseph D. Andrade†

**Department of Chemistry, Kangnung National University, Kangnung 210-702*
†Departments of Bioengineering and Materials Science, University of Utah, Salt Lake City, Utah 84112, U.S.A.

Received October 29, 1991

Polyethylene oxide (PEO) surfaces are recognized as having an effective steric stabilization character. A theoretical scaling analysis involves the osmotic and elastic coefficients of the polymer as a function of molecular weight, in a good solvent. The calculated results show that PEO in water may exhibit the greatest flexibility among water soluble polymers, probably due to its lowest elastic contribution.

Introduction

Polymers adsorbed on solid surfaces immersed in a liquid medium are considerably protected against aggregation, a phenomenon termed steric stabilization. There exist long-range repulsion forces between two surfaces bearing such adsorbed layers, and these repulsive forces overcome the attractive van der Waals forces acting between the bare surfaces.

Polyethylene oxide (PEO) adsorbed surfaces are recognized as effective in minimizing protein adsorption[1-5], probably due to a steric stabilization effect[6,7]. Direct force measurements[8-10] between two adsorbed PEO surfaces onto mica in a good aqueous 0.1 M KNO_3 solvent by the Israelachvili force method[11] show that the repulsion forces develop at certain separation distances due to the steric repulsion phenomenon.

A scaling model of chains adsorbed onto a surface in a good solvent was proposed by Alexander[12] and further extended by de Gennes[13] to give a form for the sterc repulsion force profile. The force is analyzed in terms of a repulsive osmotic term, which comes from the increased polymer concentration in the intersurface gap as the surfaces approach, and an elastic term in which the reduction in free energy, on compression of the over-extended chains, is taken into account. The Alexander-de Gennes model has been developed into a theory of the forces between two such adsorbed layers by Patel *et al*[14]. Their result is that the force *vs* separation distance between two adsorbed surfaces can be expressed as a universal dimensionless function which contains two unknown proportionality constants resulting from the osmotic and elastic contributions.

In this paper, the more effective character of PEO for protein-resistant surfaces was studied by comparison of the osmotic and elastic coefficients of PEO of several molecular weights in good aqueous electrolyte and toluene solvents. The osmotic and elastic coefficients of PEO in aqueous electrolyte and toluene solvents were estimated by the universal curve-fitting method of Patel *et al.*[14] adsorbed on mica surfaces in 0.1 M aqueous KNO_3[8,9,15,16] and toluene solvents[10,16,17], using a least-squares curve fitting method. The data for polystyrene (PS) adsorbed on mica surface in toluene[7,18] is also

Table 1. The Calculated Osmotic and Elastic Coefficients of PEO and PS in Aqueous 0.1 M KNO_3 and Toluene Solvents with the Variation of Molecular Weight of Polymer

	PEO in aq. KNO_3		PEO in toluene			PS in toluene		
M_w	3.1×10^5	4.0×10^4	3.1×10^5	1.6×10^5	4.0×10^4	3.75×10^5	1.81×10^5	1.41×10^5
Γ ($mg \cdot m^{-2}$)	4.0	4.0	2.0	1.5	1.0	3.0	1.6	3.0
L_0 (exp) (Å)	400	225	750	550	280	1100	750	650
k_1	0.004	0.002	0.12	0.23	0.18	0.64	11.44	1.50
k_2	0.12	0.025	1.08	0.68	0.24	0.07	0.75	0.16
L_0 (Å)	397	218	705	640	270	1170	690	616

considered for comparison.

Method

The universal dimensionless function relating the dimensionless energy (ε) and dimensionless separation distance (∂) in a good solvent was obtained by Patel *et al.*[14] as follows:

$$\varepsilon=4\pi k_1 x^{5/4}\{[(x\partial)^{-5/4}-1]+(5/7)[(x\partial)^{7/4}-1]\} \quad (1)$$

where,

$$x^3=(7/5)(k_2/k_1),\quad \partial=D/(2aN\sigma^{1/3}),$$

and

$$\varepsilon=(F/R)(a^2/k_BT)(1/N\sigma^{11/6})$$

In these formulas, two unknown proportionality coefficients, k_1 and k_2, are referred to as the osmotic and elastic contributions to the force, respectively, D is the separation distance between the two adsorbed surfaces, a is the size of a segment of the polymer chain (2.78 Å for PEO and 2.22 Å for PS from crystallographic data[19-21]), N is the number of segments in the nonadsorbing part of the chain, k_BT is the thermal energy, F/R is the force between crossed cylinders having radius R, which is 2π times the energy per unit area of interaction between parallel plates[22], and σ is a dimensionless surface density of chains emanating from the surface, $\sigma=a^2/\delta^2$, where δ is the average spacing between chains on the surface.

The surface density (σ) can be calculated from the data of adsorbed amounts by assuming hexagonal packing of spheres of polymer[15]. D and F/R are given by the published experimentally determined force *vs* separation distance plots, which are reduced to the dimensionless distance (∂) and dimensionless energy (ε) based on σ. The coefficients k_1 and x are then calculated from Eq. (1) by using the least-squares curve fitting method, giving the final k_1 and k_2 values for PEO and PS of several molecular weights in good aqueous electrolyte and toluene solvents.

Force *vs* separation profiles[7-10,15-18] represent the onset of repulsions as a function of separation distance, which is the basis of the experimentally determined effective layer thickness of the adsorbed chains, L_0 (exp), as measured by half the range for onset of repulsive interactions. The theoretically effective single layer thickness of the adsorbed chains, L_0, is given by consideration of the osmotic and elastic contributions, $L_0=[(5/7)\cdot(k_1/k_2)]^{1/3}\cdot Na\sigma^{1/3}$, which is also compared with the L_0 (exp).

Results and Discussion

The calculated results from the published data[7-10,15-18] are given in Table 1. To some extent, a consistency of experimental and theoretical layer thickness values of adsorbed chains (L_0 (exp) and L_0) tells that the theory is about correct and suitable to study the steric repulsion properties of PEO in water. The remaining data except L_0 are inconsistent and are not easily comparable with each other, which may be largely due to the lack of certainties of experimentally determined adsorbed amounts (the adsorbed amounts affect the degree of osmotic and elastic contributions to the force). The adsorbed amounts in the literature are rough values, which is verified by the experimental fact[8,9,15,16] that all direct force measurements between two adsorbed polymer surfaces show different force values, even for measurements at the same molecular weight and solvent conditions, i.e., different measurements for the same sample produce the different results (in part due to difference in the adsorbed amounts of polymer on the surface).

The repulsive osmotic coefficient is increased due to increased polymer concentration in the intersurface gap as the surfaces approach. The osmotic effect will dominate at very high compressions[7,15] and is expressed in Eq. (1). If Table 1 is looked at as a rough estimate, the osmotic coefficients (k_1) are nearly similar for each different polymer-solvent system in spite of the difference of molecular weight, which means that the osmotic pressure is about the same for the same polymer-solvent systems. The comparison of k_1 values for each different polymer-solvent system (about>1 for PS-toluene, 0.1-0.5 for PEO-toluene, and 0.002-0.01 for PEO-aqueous KNO_3) show that toluene is a good solvent for PS and PEO and the aqueous 0.1 M KNO_3 solution is a solvent (not good) for PEO. Toluene is a better solvent for PS than PEO, which is also supported by the experimental fact that the PEO block is adsorbed onto the mica and PS does not, for PS-PEO diblock copolymers in toluene[17]. To have approximately the same value of k_1 for different molecular weight PEO-water systems, it is necessary to control the adsorbed amounts. It is also a prior condition that the adsorbed amounts generally increase with adsorption of longer chains[10]. The same procedures are also applied for PEO-tolune and PS-toluene systems. The results are shown in Table 2. Comparing the L_0 values, PEO is less strectched in aqueous 0.1 M KNO_3 solevent than in toleuene, which could be due in part to a greater decrease in k_1 in aqueous solvent. The lower value of k_1 of PEO in aqueous electrolyte than in orga-

Table 2. The Revised Osmotic and Elastic Coefficients of PEO and PS in Good Solvents with the Correction of the Adsorbance

	PEO in aq. KNO_3		PEO in toluene			PS in toluene		
M_w	3.1×10^5	4.0×10^4	3.1×10^5	1.6×10^5	4.0×10^4	3.75×10^5	1.8×10^5	1.41×10^5
Γ (mg · m^{-2})	4.0	3.2	1.6	1.6	0.9	2.1	3.9	3.0
k_1	0.004	0.004	0.2	0.2	0.2	1.5	1.5	1.5
k_2	0.12	0.03	1.43	0.51	0.23	0.12	0.25	0.16
L_0/L_c (%)	3.95	8.6	3.6	6.3	10.7	14.6	17.9	20.5

nic solvent is also supported by the polymer-solvent interaction parameter, χ (0.39 and 0.48 for PEO-toluene[23] and PEO-0.1 M KNO_3[24], respectively). Values of χ up to 0.5 are found for systems showing complete miscibility, while for $\chi>0.5$ the systems are characterized by only limited miscibility, with higher values of χ corresponding to decreasing extent of interaction of the two components[4]. In our previous study[25], the osmotic contribution has the more effect on the chain extension than the elastic contribution. The variation of the k_1 value has the more effect on the change of the layer thickness of the chain in a good solvent.

The effects of k_1 and k_2 values on the steric force are opposite; the increase of osmotic contribution (k_1) gives rise to an increase of the spacing between chains in solvent, stretching them. On the other hand the elastic contribution (k_2) is a stiffness factor; its increase makes the chain more stiff and less flexible, and harder to stretch. PEO in water has lower k_1 and k_2 values than in other solvent systems. The lower the k_1 value, the less stretch (i.e., it is less effective for steric repulsion) of the chain. On the other hand, the lower the k_2 value, the more flexible the chain. The k_2 value of PEO in aqueous solvent is lower than in any other investigated polymer-solvent systems.

PEO is very flexible and movable. Long flexible PEO chains on the surface have been called "molecular cilia" by Nagaoka and coworkers[3]. Thus the prominent steric repulsion properties of PEO in water are mainly contributed by this flexibility, which is probably caused by the large decrease in k_2 in spite of the decrease of k_1. On the other hand, the remarkable stretching of the PS chain in toluene is mainly attributed to the large increase in the osmotic contribution in spite of the increase of the elastic contribution. Table 2 shows that change of molecular weight has great influence on the degree of the elastic contribution to the force and also on the layer thickness (L_0) (the osmotic contribution is assumed to be constant for the same polymer-solvent system, even if the molecular weight of polymer is varied). L_0 can be compared with the fully extended layer thickness (contour length)[26], $L_c=aN$. L_0/L_c values are shown in last row of Table 2. The chains are stretched to about 3 to 20% of their fully extended length according to their molecular weight. Considering the effect of solvent on PEO, for a given mass of polymer the L_0/L_c values are similar for each PEO-solvent systems in spite of the larger decrease in k_1 value in aqueous electrolyte, which could be due to a decrease in k_2 value and the difference in the conformation of the PEO in organic solvents and in water. PEO in organic solvents exists as a random coil, whereas in water its conformation is helical[4,27,28]. As the molecular weight of the polymer is decreased, the ratio, L_0/L_c, is increaesed, mainly due to the larger decrease of the elastic contribution. The chain is actually more flexible and stretched, as the chain is shortended. Thus the longest chain of PEO in water without any flexibility may not be effective for steric repulsion, which is supported experimentally[3] and theoretically[24,29] by some investigators. A suitable length of PEO with higher flexibility (higher L_0/L_c value) is appropriate for steric repulsion, i.e., protein-resistance.

Conclusion

We examined the main factors in the prominent steric repulsion properties of PEO adsorbed surfaces in water, considering the osmotic and elastic contributions to the steric repulsion force. As the elastic contribution of the polymer chain in a good solvent is lowered, the stiffness is lowered, and the flexibility is increased. PEO in water has the highest flexibility, probably caused by having the lowest elastic contribution. The prominent steric repulsion properties of PEO adsorbed surfaces in water may be mainly due to the greater contribution of an elastic factor than an osmotic one. Comparing the osmotic contributions of various polymer-solvent systems, water may not be a very good solvent for PEO, and toluene is a good solvent for both PEO and PS, but it is a better one for PS. The layer thickness of the chains is mainly controlled by the osmotic factor, so longer chains are observed in PS-toluene than in any other polymer-solvent system because of higher osmotic contribution to the steric repulsion force. As the molecular weight of the polymer is lowered, the chain is more stretched to its fully extended state and is more flexible. Thus a moderate length of PEO with higher flexibility should be more suitable for steric repulsion.

Acknowledgement. This work was supported by the research fund from the Kangnung National University, 1991.

References

1. D. E. Gregonis, D. E. Buerger, R. A. Van Wagenen, S. K. Hunter, and J. D. Andrade, *Biomaterials 84, Trans. Soc. Biomater.*, 7, 766 (1984).
2. J. D. Andrate (Ed.), "Surface and Interfacial Aspects of Biomedical Polymers", Ch. 1, Plenum Press, New York, 1985.
3. J. D. Andrate, S, Nagaoka, S. Cooper, T. Okano, and S. W. Kim, *ASAIO J.*, **10**, 75 (1987).
4. J. H. Lee, "Interactions of PEO-Containing Polymeric Surfactants with Hydrophobic Surfaces", Ph. D. Thesis,

University of Utah, 1988.

5. W. R. Gombotz, A. S. Hoffman, J. M. Harris, B. Hovanes, G. H. Wang, and A. Safranj, "IUPAC Macromolecules Symposium", Seoul, Korea, June, 1989.
6. P. G. de Gennes, *Ann. Chim.*, *77*, 389 (1987).
7. H. J. Taunton, C. Toprakcioglu, L. J. Fetters, and J. Klein, *Nature (London)*, **332**, 712 (1988).
8. J. Klein and P. Luckham, *Nature (London)*, **300**, 429 (1982).
9. J. Klein and P. Luckham, *Macromolecules*, **17**, 1041 (1984).
10. P. Luckham and J. Klein, *Macromolecules*, **18**, 721 (1985).
11. J. N. Israelachvili and G. J. Adams, *J. Chem. Soc., Faraday Trans. 1*, **79**, 975 (1978).
12. S. J. Alexander, *J. Phys. (Les Ulis, Fr.)*, **38**, 983 (1977).
13. P. G. de Gennes, *Acad. Sci. Paris*, **300**, 839 (1985).
14. S. Patel, M. Tirrell, and G. Hadziioannou, *Colloids Surf.*, **31**, 157 (1988).
15. P. F. Luckham and J. Klein, *J. Chem. Soc. Faraday Trans.*, **86**, 1363 (1990).
16. J. Klein and P. F. Luckham, *Macromolecules*, **19**, 2007 (1986).
17. H. J. Taunton, C. Toprakciglu, and J. Klein, *Macromolecules*, **21**, 3333 (1988).
18. H. J. Taunton, C. Topracioglu, L. J. Fetters, and J. Klein, *ACS: Div. of Polym. Chem. (Polym. Preprints)*, **30**, 368 (1989).
19. H. Tadokoro, Y. Chatani, T. Yoshihara, S. Tahara, and M. Murahashi, *Makromol. Chem.*, **73**, 109 (1964).
20. Y. Takahashi and H. Tadokoro, *Macromolecules*, **6**, 672 (1973).
21. J. Brandrup and E. H. Immergut (Eds.), "Polymer Handbook", 3rd ed., Willey-Interscience, New York, 1989.
22. J. N. Israelachvili, "Intermolecular and Surface Forces", Academic Press, New York, 1985.
23. F. J. Ansorena, M. J. Fernandez-Berridi, M. J. Barandiaran, G. M. Guzman, and J. J. Iruin, *Polym. Bull.*, **4**, 25 (1981).
24. B. Vincent, P. F. Luckham, and F. A. Waite, *J. Colloid Interface Sci.*, **73**, 508 (1980).
25. S. I. Jeon, J. H. Lee, J. D. Andrade, and P. G. de Gennes, *J. Colloid Interface Sci.*, **142**, 149 (1991).
26. G. Hadziioannou, S. Patel, S. Granick, and M. Tirrell, *J. Am. Chem. Soc.*, **108**, 2869 (1986).
27. S. H. Maron and F. E. Filisko, *J. Macromol. Sci.*, **B6**, 57 (1972).
28. S. H. Maron and F. E. Filisko, *J. Macromol. Sci.*, **B6**, 79 (1972).
29. S. I. Jeon and J. D. Andrate, *J. Colloid Interface Sci.*, **142**, 159 (1991).

Electrical Conductivity of the Solid Solutions X $ZrO_2+(1-X)$ Yb_2O_3; $0.01\le X\le 0.09$

Byoung Ki Choi, Joon Ho Jang, Seong Han Kim, Hong Seok Kim, Jong Sik Park, Yoo Young Kim, Don Kim, Sung Han Lee, Chul Hyun Yo, and Keu Hong Kim*

Department of Chemistry, Yonsei University, Seoul 120-749. *Received November 4, 1991*

ZrO_2-doped Yb_2O_3 solid solutions containing 1, 3, 5, 7 and 9 mol% ZrO_2 were synthesized from spectroscopically pure Yb_2O_3 and ZrO_2 powders and found to be rare earth *C*-type structure by XRD technique. Electrical conductivities were measured as a function of temperatures from 700 to 1050℃ and oxygen partial pressures from 1×10^{-5} to 2×10^{-1} atm. The electrical conductivities depend simply on temperature and the activation energies are determined to be 1.56-1.68 eV. The oxygen partial pressure dependence of the electrical conductivity shows that the conductivity increases with increasing oxygen partial pressure, indicating *p*-type semiconductor. The P_{O_2} dependence of the system is nearly power of 1/4. It is suggested from the linearity of the temperature dependence of electrical conductivity and only one value of $1/n$ that the solid solutions of the system have single conduction mechanism. From these results, it is concluded that the main defects of the system are negatively doubly charged oxygen interstitial in low ZrO_2 doping level and negatively triply charged cation vacancy in high doping level and the electrical conduction is due to the electronic hole formed by the defect structure.

Introduction

Oxides of the rare-earth elements generally have the rare-earth *C*-type structure when the ratio of the radius of oxygen anion to that of metal cation is between 0.60 to 0.89[1]. And the number of oxygen anions occupied on the lattice sites is six and two of eight lattice oxygen sites become vacancies[2]. Accordingly, the oxides of these rare-earth elements have similar physical properties. It was reported that Sm_2O_3, Gd_2O_3 and other oxides belonging to these rare-earth *C*-type oxides have mixed conduction mechanism that ionic conduction occurs predominantly over electronic conduction[3,4], whereas in the case of Yb_2O_3, there were few experimental data because of thermal instability.

Kang *et al.*[5] reported that above 700℃, pure Yb_2O_3 has the activation energy of from 1.92 to 1.95 eV and shows