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Polymer 42 (2001) 4773–4775

polymer

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Polymer Communication

Osmotic second virial coefficient for linear and star poly(ethylene oxide)

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Received 24 February 2000; received in revised form 13 April 2000; accepted 9 July 2000

Abstract

Experimental osmotic second virial coefficients are reported for linear and star poly(ethylene oxide) in water and 1-propanol in the temperature region 25–55°C. All measured osmotic second virial coefficients are positive.

At fixed temperature, the osmotic second virial coefficient for star poly(ethylene oxide) is lower than that for the linear polymer of comparable molecular weight. The osmotic second virial coefficient for star poly(ethylene oxide) decreases with rising temperature in both water and 1-propanol. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Osmotic second virial coefficient; Poly(ethylene oxide); Star polymer

1. Introduction

Poly(ethylene oxide) is a water-soluble, biodegradable polymer with a variety of interesting possible applications (see, for example, O'Connor et al. [1], or Tsuji et al. [2]). Poly(ethylene oxide) of low molecular weight, in the range 200–20,000 g/mol, is used in cosmetics, lubricants, pharmaceuticals and electronics [3]. Star poly(ethylene oxide) has characteristics that make it suitable as a carrier for bioactive molecules into the blood stream or as an enhancer of antibody/antigen reactions [4]. Regular star polymers are branched structures where equi-sized linear arms emanate from a central core. Because the core is usually limited in size, it does not significantly affect any thermodynamic property. Star polymers with up to 450 arms with desired chemical and molecular weight asymmetries can be synthesized [5–7]. Several articles report the effect of branching upon the thermodynamic properties of dilute polymer solutions; primary attention has been given to linear and star polystyrenes in organic solvents (see, for a review, Grest et al. [7]).

Only a few studies have considered dilute polymer solutions in polar solvents (see, for example, Nagahama et al. [8]).

Poly(ethylene oxide) is a peculiar polymer; it is soluble in most organic solvents, as well as in water, because the polymer backbone contains oxygen atoms in every third position. The electron-rich oxygen atom offers a site for coordination with a solvent's electron-poor groups. [For a simulation study of the effect of solvent and temperature on poly(ethylene oxide), see Ferreira et al. [9]]. Poly(ethylene oxide) is able to hydrogen bond with polar solvents, an important feature for its use in numerous applications.

Mio and Prausnitz [10] reported solvent activities for chloroform and acetone in concentrated poly(ethylene oxide) solutions. The polymers used were linear, 17-, and 20-arm star poly(ethylene oxide); branching slightly increases solvent sorption.

This work is concerned with dilute polymer solutions of linear and 7-arm star poly(ethylene oxide). Osmotic second virial coefficients for linear and 7-arm star poly(ethylene oxide) are reported in water and in 1-propanol.

Nagahama and coworkers [8] reported osmotic second virial coefficients for aqueous linear poly(ethylene oxide) with molecular weights 105,000 and 520,000 g/mol; the positive osmotic second virial coefficient decreases with rising temperature. For aqueous linear poly(ethylene oxide), molecular weight 105,000 g/mol, the theta temperature is near 50°C.

2. Experimental method and results

Osmotic pressures were measured with a membrane osmometer, model 231, from Jupiter Instrument Co., Jupiter, Florida (USA). Measurements were made for solutions of 7-arm star and linear poly(ethylene oxide) in nanopure water and in 1-propanol (Fisher Scientific, used as

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PII: S0032-3861(00)00649-2

Table 1
Polymer properties

Polymer	Acronym	Molecular weight (g/mol)	Polydispersity	Supplier
Linear poly(ethylene oxide)	LPEO1	53,500[a]	1.07	Polymer Source, Inc.
Linear poly(ethylene oxide)	LPEO2	77,600[a]	1.06	Polymer Source, Inc.
7-arm star poly(ethylene oxide)	SPEO	70,000	–	Shearwater Polymer, Inc.

[a] From size-exclusion chromatography.

received). Polymers were kept under vacuum anywhere from two to three days before measurement to ensure removal of low-molecular-weight impurities. Table 1 shows polymer characteristics. The cellulose acetate membranes were supplied by Jupiter Instrument Company. The molecular-weight-cut-off was 10,000 g/mol.

The osmotic pressure, Π, of a polymer solution can be expressed in a virial expansion [11]:

$$\frac{\Pi}{\mathrm{R}\cdot T} = \frac{1}{M_\mathrm{n}}\cdot c_2 + B_{22}\cdot c_2^2 + B_{222}\cdot c_2^3 + \dots, \qquad (1)$$

where R, M_n, B_{22}, B_{222} and c_2 are, respectively, the gas constant, the polymer's number average molecular weight [12], second and third virial coefficients and polymer mass concentration. At low polymer concentration, terms of order higher than second can be neglected, and Eq. (1) reduces to:

$$\frac{\Pi}{\mathrm{R}\cdot T}\cdot\frac{1}{c_2} = \frac{1}{M_\mathrm{n}} + B_{22}\cdot c_2 \qquad (2)$$

The results reported for B_{22} and M_n are obtained by fitting experimental data to Eq. (2). B_{22} provides information about interactions between a pair of molecules in solution. When B_{22} is positive, the molecules repeal each other and the solvent is considered a 'good' solvent. When B_{22} is negative, the molecules attract each other and the solvent is considered a 'poor' solvent. For a polymer-solvent system, B_{22} is a function of temperature. It can be positive at certain temperatures and negative at others. B_{22} equals zero at the theta temperature.

Table 2 shows experimental molecular weights and osmotic second virial coefficients. The molecular weight is generally comparable to that obtained from the supplier when the polydispersity is taken into account. All osmotic second virial coefficients are positive.

Fig. 1 shows experimental osmotic second virial coefficients as a function of temperature for linear and 7-arm star poly(ethylene oxide). At fixed temperature, B_{22} for a star polymer is lower than that for the linear homologue, in agreement with other reports for other branched polymers at good solvent conditions (see, for example, [7] and [13]). This result follows from the radius of gyration that is smaller for a star polymer than for a linear polymer with the same molecular weight. At good solvent conditions, the repulsion between two different molecules is of shorter range for star polymers than for linear homologues. B_{22} for 7-arm star poly(ethylene oxide) decreases with rising temperature in both polar solvents, as observed for linear poly(ethylene oxide) in water [8]. Extrapolating to the temperature where B_{22} equals zero for 7-arm star poly(ethylene oxide) in water, we obtain a theta temperature near 55–60°C, slightly higher than the 50°C reported for linear poly(ethylene oxide) [8]. In agreement with results reported by Mio and Prausnitz [10] and with results for linear and star polymers in non-polar solvents, branching appears to increase solubility. This result is probably due to the compact structure of star polymers which, at poor solvent conditions, does not allow them easily to penetrate into each other. Therefore a 'steric repulsion' may be responsible for increased solubility. The theta temperature for 7-arm star poly(ethylene oxide) in 1-propanol is near 52°C.

3. Conclusions

Osmotic second virial coefficients are reported for linear and 7-arm star poly(ethylene oxide) in water and in 1-propanol. These results confirm that branching lowers the osmotic second virial coefficient for polymers in good solvents,

Table 2
Osmotic second virial coefficients for poly(ethylene oxide), linear and 7-arm star

Polymer	Solvent	Temperature (°C)	M_n (10^{+3} g/mol)	B_{22} (10^{-7} l mol/g^2)
LPEO1	water	33.8	72 ± 8	9.0 ± 0.2
SPEO	water	28.9	73 ± 2	8.15 ± 0.1
SPEO	water	33.8	110 ± 5	5.85 ± 0.1
SPEO	water	43.4	60.6 ± 1.4	5.10 ± 0.15
LPEO1	1-propanol	49.6	55.3 ± 0.3	4.34 ± 0.02
LPEO2	1-propanol	49.6	67.2 ± 0.3	7.8 ± 0.1
SPEO	1-propanol	44.5	75 ± 4	5.3 ± 0.4
SPEO	1-propanol	49.0	71.5 ± 2.5	2.3 ± 0.3

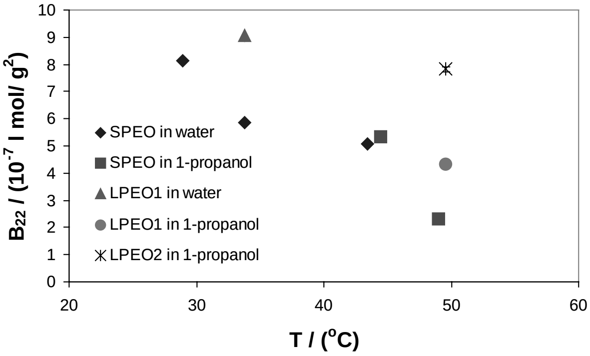

Fig. 1. Osmotic second virial coefficient of poly(ethylene oxide), linear and 7-arm star, in water and 1-propanol. B_{22} decreased with rising temperature for star poly(ethylene oxide) in both solvents. B_{22} for the star polymer is lower than that for the linear polymer at the same experimental conditions. Symbols are larger than the experimental uncertainty.

probably because of the smaller radius of gyration that characterizes star polymers when compared to linear polymers of the same molecular weight.

For 7-arm star poly(ethylene oxide), the osmotic second virial coefficient decreases with rising temperature in both polar solvents. The estimated theta temperatures are near 57°C in water and 52°C in 1-propanol. The theta temperature in water is higher than that reported for linear poly(ethylene oxide), indicating that branching, because of the repulsion generated by the high segment density around the center of mass, increases solubility also in hydrogen-bond-forming solvents.

Acknowledgements

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences Chemical Science Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

References

[1] O'Connor SM, Gehrke SH, Retzinger GS. Langmuir 1999;15:2580.
[2] Tsuji H, Smith R, Bonfield W, Ikada Y. J Appl Polym Sci 2000;75:629.
[3] Clinton N, Matlock P. Encyclopedia of polymers, 6. New York: Wiley, 1986. p. 225.
[4] Merrill EW. J Biomater Sci Polym Edn 1993;5:1.
[5] Hadjichristidis N. J Polym Sci, Part A: Polym Chem 1999;37:857.
[6] Cloutet E, Fillaut J-L, Astruc D, Gnanou Y. Macromolecules 1998;31:6748.
[7] Grest GS, Fettres LJ, Huang JS, Richter D. Prigogine I, Rice SA, editors. Adv Chem Phys 1996;94:67.
[8] Nagahama K, Inomata H, Saito S. Fluid Phase Equilib 1994;96:203.
[9] Ferreira BA, Dos Santos HF, Bernardes AT, Silva GG, De Almeida WB. Chem Phys Lett 1999;307:95.
[10] Mio C, Prausnitz JM. Polymer 1998;39:25.
[11] Tombs MP, Peacocke AR. The osmotic pressure of biological macromolecules. Oxford: Clarendon, 1974.
[12] Young RJ, Lovell PA. Introduction to polymers. 2nd ed. London: Chapman and Hall, 1991.
[13] Gauthier M, Chung J, Choi L, Nguyen TT. J Phys Chem B 1998;102:3138.