Lawrence Berkeley National Laboratory

Recent Work

Title

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

Permalink

<https://escholarship.org/uc/item/7c33n9fp>

Author

Striolo, A.

Publication Date

2000-03-01

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Osmotic Second Virial Coefficient for Linear and Star Poly(ethylene oxide)

Alberto Striolo and John M. Prausnitz

Chemical Sciences Division

March 2000

Submitted to
Polymer Communications

Lawrence Berkeley National Laboratory

REFERENCE COPY
Does Not
Circulate

Bldg. 50 Library - Ref.

Copy 1

LBNL-45300

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

**Osmotic Second Virial Coefficient for Linear
and Star Poly(ethylene oxide)**

Alberto Striolo and John M. Prausnitz

Department of Chemical Engineering

University of California

and

Chemical Sciences Division

Lawrence Berkeley National Laboratory

University of California

Berkeley, CA 94720, U.S.A.

March 2000

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

Osmotic Second Virial Coefficient for Linear and Star Poly(ethylene oxide)

Alberto Striolo and John M. Prausnitz*

Chemical Engineering Department

University of California, Berkeley
and

Chemical Sciences Division

Lawrence Berkeley National Laboratory

Berkeley, CA 94720

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 to 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.

Key words: Osmotic Second Virial Coefficient, Poly(ethylene oxide), Star Polymer

* to whom correspondence should be addressed

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/mole, 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/mole; the positive osmotic second virial coefficient decreases with rising temperature. For

aqueous linear poly(ethylene oxide), molecular weight 105000 g/mole, the theta temperature is near 50°C.

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. 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 and Table 2 shows solvents characteristics. Solvents were used as received. The cellulose acetate membranes were supplied by Jupiter Instrument Company. The molecular-weight-cut-off was 10,000 g/mole.

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

$$\frac{\Pi}{R \cdot T} = \frac{1}{M_n} \cdot c_2 + B_{22} \cdot c_2^2 + B_{222} \cdot c_2^3 + \dots \quad (1)$$

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 Equation 1 reduces to:

$$\frac{\Pi}{R \cdot T} \cdot \frac{1}{c_2} = \frac{1}{M_n} + B_{22} \cdot c_2 \quad (2)$$

The results reported for B_{22} and M_n are obtained by fitting experimental data to Equation 2.

Tables 3 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.

Figure 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 star polymer is lower than that for the linear homolog, in agreement other reports for

other branched polymers at good solvent conditions (see, for example, [7] and [13]). 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. The theta temperature for 7-arm star poly(ethylene oxide) in 1-propanol is near 52°C.

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.

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 increases solubility in hydrogen-bond-forming solvents.

Acknowledgments

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, S.M.; Gehrke, S.H.; Retzinger, G.S., *Langmuir* 1999; 15,: 2580.
- 2 Tsuji, H.; Smith, R.; Bonfield, W.; Ikada, Y.; *J. Applied Polymer Science* 2000; 75: 629.
- 3 Clinton, N.; Matlock, P. *Encyclopedia of Polymers*, Vol. 6, John Wiley & Sons, New York, 1986, p.225.
- 4 Merrill, E.W., *J. Biomater. Sci. Polymer Edn*, 1993; 5: 1.
- 5 Hadjichristidis, N., *J. Polym. Sci. A Polym. Chem.* 1999; 37: 857.
- 6 Cloutet, E.; Fillaut, J.-L.; Astruc, D.; Gnanou, Y.; *Macromolecules* 1998; 31: 6748.
- 7 Grest, G.S.; Fetters, L.J.; Huang, J.S.; Richter, D. In Prigogine, I.; Rice, S.A. editors, *Advances in Chemical Physics* 1996; 94, p.67.
- 8 Nagahama, K.; Inomata, H.; Saito, S., *Fluid Phase Equilibria* 1994; 96: 203.
- 9 Ferreira, B.A.; Dos Santos, H.F.; Bernardes, A.T.; Silva, G.G.; De Almeida, W.B., *Chemical Physics Letters* 1999; 307: 95.
- 10 Mio, C.; Prausnitz, J.M., *Polymer*, 1998; 39: 25.
- 11 Tombs, M.P.; Peacocke, A.R. *The osmotic pressure of biological macromolecules*, Clarendon Press, Oxford, 1974.
- 12 Young, R.J.; Lovell, P.A. *Introduction to polymers*, 2nd ed., Chapman & Hall, London, 1991.
- 13 Gauthier, M.; Chung, J.; Choi, L.; Nguyen, T.T., *J. Phys. Chem. B* 1998; 102: 3138.

Table 1 Polymer properties

Polymer	Acronym	Molecular weight (g/mole)	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.

Table 2 Solvent properties

Solvent	Supplier	Lot number
1-propanol	Fisher Scientific	992377

Table 3 Osmotic second virial coefficients for poly(ethylene oxide), linear and 7-arm star

Polymer	Solvent	Temperature (° C)	M_n (10^3 g/mole)	B_{22} (10^{-7} l mole/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} decreases 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.

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY
ONE CYCLOTRON ROAD : BERKELEY, CALIFORNIA 94720