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Solvent Activities in Solutions of Star and Linear Poly(ethylene oxide) and Polystyrene

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ABSTRACT

Solvent activities were measured using a gravimetric method in the range 48 to 70 °C.

The polymers were: 15-arm, 20-arm star and linear poly(ethylene oxide), and 8-arm star and linear polystyrene. The solvents were acetone, chloroform and cyclohexane. In the concentrated regime, to 0.5 solvent weight fraction, there is no significant effect of polymer structure on solvent activities.

Keywords: Vapor-liquid equilibrium, Star polymer, Gravimetric method, Poly(ethylene oxide), Polystyrene

INTRODUCTION

Star polymers are branched polymers with several arms of approximately equal lengths joined together at one end of each chain to a central core.

Poly(ethylene oxide) stars have received attention because of their potential biomedical applications (Merrill¹). Star polymers may also have industrial applications: they have been used as melt-strength improvers; because their solution viscosity is lower than that of a linear polymer, they have better processibility than their linear homologues (Guo et al.², Shalaby et al.³); and, they are useful in coatings to improve the balance of hardness and flexibility (Simms⁴, Simms and Spinelli⁵).

This work compares solvent activities in linear and star polymers.

MATERIALS AND EXPERIMENTAL PROCEDURE

Solvents were used after degassing by a freeze/thaw procedure described by Panayiotou and Vera⁶. Solvent properties are given in Table I.

Two types of star polymers were studied: Star Polystyrene (PS) and Star Poly(ethylene oxide) (PEO).

The octafunctional linking agent used for the synthesis of 8-arm PS is the end product of tetravinylsilane with methyl dichlorosilane: $\text{Si}-(\text{CH}=\text{CH}_2)_4 + \text{SiCH}_3\text{Cl}_2\text{H}$.

Star PEO is made by polymerization of ethylene oxide from a cross-linked divinyl benzene core (Gnanou et al.⁷, Rein et al.⁸). The arms have hydroxyl (OH) groups as chain ends.

Polymer properties are given in Tables II and III.

For measuring solvent activities, the experimental method is based on the gravimetric-sorption technique. The amount of solvent absorbed by a polymer is measured at increasing solvent pressure. The solvent pressure is read from a mercury manometer. The uncertainty in the pressure reading is 1 torr. The polymer is loaded onto calibrated quartz springs. By measuring the elongation of the springs due to solvent absorbed by the polymer, the solvent weight fraction (w_1) in the condensed phase is calculated. The uncertainty is about 2% in w_1 but it increases to 5-10 % for small w_1 (below 0.1).

Details of the apparatus and procedure are given by Panayiotou and Vera⁶ and by Gupta and Prausnitz⁹.

COMPARISON BETWEEN STAR AND LINEAR POLYMERS

The effect of branched structure on phase equilibria in polymer solutions has received some attention through liquid-liquid equilibria (LLE) experiments. Sato et al.¹⁰ and Kajiwara et al.¹¹ measured LLE for branched PS in solution as a function of molecular weight (MW) and compared their results with those for linear PS. They found that the upper critical-solution temperature is a few degrees lower for branched PS than for linear PS. Faust et al.¹² found differences between the cloud-point curve for the blend star PS/PVME (poly vinyl methyl ether) and linear PS/PVME: the former is shifted to the PS-rich side of the composition axis. Upper and lower critical-solution temperatures have been measured for star-branched polystyrene in cyclohexane by Cowie¹³ and by Yokoyama¹⁴. Their results show that branching effects are much more pronounced in the upper critical region; branching reduces the upper critical-solution temperature and enhances the solubility of the polymer. The differences in critical temperature are small, but increase as the molecular weight decreases.

This work reports solvent activities (vapor-liquid equilibria) for two kinds of star polymers: star PEO and star PS. Since the MW of the polymers is very high, and because the core weight is only 2-3% the total MW, the effect of the core is negligible.

Solvent activities were also obtained for linear PS and linear PEO with molecular weights similar to those of the stars.

Table IV presents the binary systems studied.

RESULTS

The vapor-liquid equilibrium data are given in Table V.

In Figures 1 to 5 the abscissa represents the solvent weight fraction (w_1) and the ordinate gives the solvent activity (a_1), equal to the ratio of the solvent pressure to the pure-solvent vapor pressure (P^s) at the temperature of the experiment. Values of P^s , calculated using the equations given by Daubert and Danner¹⁵, are given in Table VI.

The data show that there is only a small difference between the solution properties of star polymers and those of linear polymers. See for example the system chloroform-PS shown in Figure 1.

Star PS absorbs more cyclohexane than linear PS (Figure 2), especially if the molecular weight is low, i. e. if the arms of the stars are shorter. However, the data in Figure 2 are at very low solvent absorption (below 0.1 solvent weight fraction) where the experimental uncertainty is higher.

Figures 3, 4 and 5 show results for star and linear PEO in chloroform at 70 and 48.2°C, and in acetone at 48.2°C. For these three systems, solvent absorption increases from linear to 20-arm-star, to 15-arm-star PEO. This trend corresponds to the decrease in polymer molecular weight (MW=200000, 170000, 130000) but the difference in MW should not be significant enough to determine a difference in VLE data. At constant solvent activity, the difference in solvent weight fraction in the liquid phase is not large, only slightly higher than the experimental uncertainty.

These results confirm that branching increases the solubility of the polymer. However, the star samples used here have only a few arms (8, 15 or 20) where each arm is a long chain of

repeating units. Therefore, it is not surprising that limited branching has only a small effect on phase behavior.

Because the star polymers have a polydispersity index equal to 1.2-1.4, some stars with a lower number of arms may be present in the polymer sample.

Figures 4 and 5 present results for two star-PEO polymers and for a linear-PEO polymer in chloroform and in acetone at 48.2 °C. The three polymers are semicrystalline at the temperature of the experiment (the melting temperature of PEO is 65 °C). The effect of polymer crystallinity on the solvent absorption curve has been studied previously. (See, for example, Allen et al.¹⁶).

We expect that the star PEO has a smaller degree of crystallinity because it is more difficult to align the branches of a star in an ordered way and also because the presence of more chain ends introduces more defects in the solid crystalline structure. Both the degree of crystallinity and the melting point of the star polymer should be lower than those of the linear polymer. Therefore, when the polymers are in the solid state (left part of the plot, corresponding to the steep rise of solvent activity) the stars should absorb more solvent and they should have a narrower flat region compared to the linear polymers, consistent with the observed results shown in Figures 4 and 5.

CONCLUSIONS

Vapor-liquid equilibrium data were obtained for concentrated solutions of linear and star polystyrene and for linear and star poly(ethylene oxide).

There is no significant difference in solvent activities in concentrated solutions of linear

and star polymers; however, the stars seem to be slightly more soluble in the solvent. Crystallinity in the polymer has an important effect on the swelling of a polymer at temperatures below its melting point. Because linear polymers are more easily crystallized than star polymers, they have a relatively lower capacity to absorb solvent.

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REFERENCES

1. Merrill E. W., *J. Biomater. Sci. Polymer Edn.*, 1993, **5**, 1.
2. Guo A., Liu G., Tao J., *Macromolecules*, 1996, **29**, 2487.
3. Shalaby S. W., McCormick C. L., Butler G. B., 'Water Soluble Polymers.' 1991, ACS Symposium Series No.467; American Chemical Society: Washington DC.
4. Simms J. A., *Progr. Org. Coatings*, 1993, **22**, 367.
5. Simms J. A., Spinelli H. J., *J. of Coatings Techn.*, 1987, **59**, 125.
6. Panayiotou C. P., Vera J. H., *Polym. J.* 1984, **16**, 89.
7. Gnanou Y., Lutz P., Rempp P., *Makromol. Chem.*, 1988, **189**, 2885.
8. Rein D., Lamps J. P., Rempp P., Lutz P., Papanagopoulos D., Tsitsilianis C., *Acta*

- Polymer.*, 1993, **44**, 225.
9. Gupta R. B., Prausnitz J. M., *Fluid Phase Equil.*, 1996, **117**, 77.
 10. Sato S., Okada M., Nose T., *Polymer Bulletin*, 1985, **13**, 277.
 11. Kajiwaru K., Burchard W., Kleintjens L. A., Koningsveld R., *Polymer Bulletin*, 1982, **7**, 191.
 12. Faust A. B., Sremcich P. S., Gilmer J. W., Mays J. W., *Macromolecules*, 1989, **22**, 1250.
 13. Cowie J. M. G., Horta A., McEwen I. J., Prochazka K., *Polymer Bulletin*, 1979, **1**, 329.
 14. Yokoyama H., Takano A., Okada M., Nose T., *Polymer*, 1991, **32**, 3218.
 15. Daubert T. E., Danner R. P., 'Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation.' 1989, Hemisphere Pub. Corp., New York.
 16. Allen G., Booth C., Gee G., Jones M. N., *Polymer*, 1965, **5**, 367.

Table I. Solvents Properties

Solvent	Supplier	Lot number	Purity
Acetone	Fisher Scientific, Pittsburgh, PA	952818	99.6%
Chloroform	Fisher Scientific, Pittsburgh, PA	952629	99.9%
Cyclohexane	Fisher Scientific, Pittsburgh, PA	902968	99.+%

Table II: Star-Polymer Properties

Star Polymer	Supplier	Catalog No.	Number of arms	Total molecular weight (Mw [*])	Arm molecular weight (Mn ^{**})
PS	Polymer Source, Inc., Dorvall, Quebec, Canada	P296-St8	7.6	74,000	9,800
PS	Polymer Source, Inc., Dorvall, Quebec, Canada	P332-St8	8.3	391,000	46,700
PEO	Shearwater Polymers, Inc. Huntsville, AL	Star-130	15	130,000	
PEO	Shearwater Polymers, Inc. Huntsville, AL	Star-170	19-20	170,000	

* = weight-average molecular weight

**= number-average molecular weight

Table III. Linear-Polymer Properties

Polymer	Supplier	Catalog No.	Molecular weight	Mw/Mn
PS	Pressure Chemical Comp., Pittsburgh, Philadelphia	50124	233,000 (Mn)	1.06
PS	Scientific Polymer Products, Inc.,Ontario, NY	542	18,700 (Mw)	1.04
PS	Scientific Polymer Products, Inc.,Ontario, NY	543	75,700 (Mw)	1.17
PEO	Scientific Polymer Products, Inc.,Ontario, NY	136B	200,000 (Mw)	

Table IV. Binary Systems Studied

Polymer	Catalog No.	Solvent	Temperature (°C)
Linear PS	50124	Chloroform	50
Linear PS	542	Acetone Chloroform	48.2
Linear PS	543	Cyclohexane	48.2
Star PS	P296-St8	Cyclohexane Chloroform	48.2
Star PS	P332-St8	Cyclohexane	48.2
Linear PEO Star-PEO	136B Star-130 Star-170	Acetone	48.2
Linear PEO Star-PEO	136B Star-130 Star-170	Chloroform	48.2 70

Table V. Experimental Vapor-Liquid Equilibrium Data. P is the total pressure and w_1 is the weight fraction of solvent

Polystyrene ($M_n=233000$); Solvent: Chloroform; $T=50^\circ\text{C}$

w_1	P (torr)
0.129	144.5
0.193	205.5
0.286	281.0
0.371	341.5
0.434	383.5
0.514	437.0
0.551	456.0

Polystyrene (Mw=18700); Solvent: Acetone; T=48.2°C

w ₁	P (torr)
0.020	111.0
0.030	197.0
0.050	285.0
0.059	309.0
0.064	321.0
0.080	351.0
0.104	374.0
0.112	400.5
0.125	423.0
0.143	444.5
0.174	468.0

Polystyrene ($M_w=18700$); Solvent: Chloroform; $T=48.2^\circ\text{C}$

w_1	P (torr)
0.158	162.0
0.237	219.0
0.313	276.0
0.412	346.0
0.458	387.0
0.522	414.0
0.569	448.5
0.587	458.0

Star polystyrene ($M_w=74000$); Solvent: Chloroform; $T=48.2^\circ\text{C}$

w_1	P (torr)
0.075	90.0
0.105	122.0
0.142	160.0
0.184	191.5
0.226	221.0
0.280	255.0
0.316	286.5
0.383	321.0
0.445	353.5
0.502	391.0
0.564	429.5
0.619	443.5

Star-PS (Mw=74000, Mw=391000); Linear-PS (Mw=75700)

Solvent: Cyclohexane; T=48.2°C

w ₁ (MW=74000)	w ₁ (Mw=391000)	w ₁ (Mw=75700)	P (torr)
0.002	0.010	0.008	49.5
0.003	0.019	0.020	68.0
0.009	0.037	0.030	95.0
0.009	0.054	0.037	115.5
0.019	0.085	0.063	138.0
0.045	0.119	0.102	158.5

Star-PEO (Mw=130000, Mw=170000); Linear-PEO (Mw=75700)

Solvent: Acetone; T=48.2°C

w ₁ (Mw=130000)	w ₁ (Mw=170000)	w ₁ (Mw=75700)	P (torr)
0.004	0.008	0.007	130.0
0.007	0.011	0.006	174.5
0.009	0.017	0.012	224.5
0.011	0.024	0.014	276.0
0.025	0.037	0.021	322.5
0.061	0.077	0.037	388.0
0.170	0.149	0.053	437.5

Star-PEO (Mw=130000, Mw=170000); Linear-PEO (Mw=200000)

Solvent: Acetone; T=48.2°C

w ₁ (Mw=130000)	w ₁ (Mw=170000)	w ₁ (Mw=200000)	P (torr)
0.012	0.008	0.005	115.0
0.015	0.008	0.007	160.0
0.017	0.012	0.008	195.5
0.021	0.018	0.013	240.5
0.023	0.023	0.019	276.5
0.033	0.038	0.023	320.0
0.050	0.059	0.029	358.0
0.077	0.086	0.045	396.5
0.154	0.141	0.059	431.0
0.292	0.268	0.098	465.0
0.354	0.338	0.205	492.5
0.385	0.367	0.287	506.0
0.418	0.398	0.355	522.0

Star-PEO (Mw=130000, Mw=170000); Linear-PEO (Mw=200000)

Solvent: Chloroform; T=48.2°C

w ₁ (Mw=130000)	w ₁ (Mw=170000)	w ₁ (Mw=200000)	P (torr)
0.011	0.015	0.007	25.5
0.022	0.026	0.016	45.0
0.034	0.039	0.023	64.0
0.057	0.074	0.045	88.0
0.131	0.153	0.066	109.5
0.184	0.174	0.082	126.5
0.339	0.330	0.168	143.5
0.364	0.354	0.345	158.5
0.399	0.388	0.384	177.0
0.439	0.428	0.420	200.0
0.526	0.516	0.506	260.5
0.602	0.589	0.580	313.5
0.672	0.660	0.652	367.5
0.720	0.705	0.695	404.0

Star-PEO (Mw=130000, Mw=170000); Linear-PEO (Mw=200000)

Solvent: Chloroform; T=70°C

w ₁ (Mw=130000)	w ₁ (Mw=170000)	w ₁ (Mw=200000)	P (torr)
0.093	0.098	0.094	77.0
0.159	0.151	0.143	124.5
0.225	0.224	0.216	189.5
0.310	0.307	0.290	268.5
0.387	0.374	0.367	354.5
0.457	0.438	0.430	431.5
0.527	0.504	0.494	514.5
0.595	0.566	0.554	612.5
0.671	0.642	0.623	707.0

Table VI. Vapor Pressures (P^s) of the Pure Solvents

Solvent	T (°C)	P^s (torr)
Acetone	48.2	574
Chloroform	48.2	493
	50	526
	70	1022
Cyclohexane	48.2	255

Figure Captions

Figure 1. Activity of chloroform in 8-arm star PS ($M_w=74000$ (•)) at 48.2 °C and in linear PS ($M_n=233000$ (Δ)) at 50 °C

Figure 2. Activity of cyclohexane in 8-arm star PS ($M_w=74000$ (•) and $M_w=391000$ (+)) and in linear PS ($M_w=75700$ (Δ)) at 48.2 °C

Figure 3. Activity of chloroform in 15-arm star PEO ($M_w=130000$ (•)), in 20-arm star PEO ($M_w=170000$ (+)) and in linear PEO ($M_w=200000$ (Δ)) at 70 °C

Figure 4. Activity of chloroform in 15-arm star PEO ($M_w=130000$ (•)), in 20-arm star PEO ($M_w=170000$ (+)) and in linear PEO ($M_w=200000$ (Δ)) at 48.2 °C

Figure 5. Activity of acetone in 15-arm star PEO ($M_w=130000$ (•)), in 20-arm star PEO ($M_w=170000$ (+)) and in linear PEO ($M_w=200000$ (Δ)) at 48.2 °C

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

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