

# Solvent activities in solutions of star and linear poly(ethylene oxide) and polystyrene

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Solvent activities were measured using a gravimetric method in the range 48–70°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. © 1998 Elsevier Science Ltd. All rights reserved.

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## 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<sup>1</sup>. 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<sup>2,3</sup>; and they are useful in coatings to improve the balance of hardness and flexibility<sup>4,5</sup>.

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 Vera<sup>6</sup>. Solvent properties are given in *Table 1*.

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<sup>7,8</sup>. The arms have hydroxyl (OH) groups as chain ends. Polymer properties are given in *Tables 2* and *3*.

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 Panayotou and Vera<sup>6</sup> and Gupta and Prausnitz<sup>9</sup>.

## 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.*<sup>10</sup> and Kajiwara *et al.*<sup>11</sup> measured LLE for branched PS in solution as a function of molecular weight ( $M_w$ ) 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.*<sup>12</sup> 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 Cowie<sup>13</sup> and Yokoyama<sup>14</sup>. 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 (vapour–liquid equilibria) for two kinds of star polymers: star PEO and star PS. Since the  $M_w$  of the polymers is very high and because the core weight is only 2–3% the total  $M_w$  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 4* presents the binary systems studied.

## RESULTS

The vapour–liquid equilibrium data are given in *Table 5*. In *Figures 1–5* the abscissa represents the solvent weight fraction ( $w_1$ ) and the ordinate gives the solvent activity ( $a_1$ ),

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**Table 1** Properties of the solvents

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	99.0 + %

**Table 2** Star polymer properties

Star polymer	Supplier	Catalogue No.	Number of arms	Total molecular weight ( $M_w^*$ )	Arm molecular weight ( $M_n^{**}$ )
PS	Polymer Source, Inc., Dorvall, Quebec, Canada	P296-St8	7.6	74 000	9800
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 3** Linear polymer properties

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

**Table 4** Binary systems studied

Polymer	Catalogue No.	Solvent	Temperature (°C)
Linear PS	50124	Chloroform	50.0
Linear PS	542	Acetone	48.2
Linear PS	543	Cyclohexane	48.2
Star PS	P296-St8	Cyclohexane	48.2
Star PS	P332-St8	Cyclohexane	48.2
Linear PEO	136B		
Star-PEO	Star 130	Acetone	48.2
Star-PEO	Star-170		
Linear PEO	136B		48.2
Star-PEO	Star-130	Chloroform	70.0
Star-PEO	Star-170		

**Table 5** Experimental vapour–liquid equilibrium data. P is the total pressure and  $w_1$  is the weight fraction of solvent

Polystyrene ( $M_n = 233\ 000$ ); Solvent: Chloroform; Temp. = 50°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 ( $M_w = 18\ 700$ ); Solvent: Acetone; Temp. = 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 ( $M_w = 18\ 700$ ); Solvent: Chloroform; Temp. = 48.2°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 ( $M_w = 74\ 000$ ); Solvent: Chloroform; Temp. = 48.2°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 ( $M_w = 74\ 000$ , $M_n = 391\ 000$ ); Linear-PS ( $M_w = 75\ 700$ ); Solvent: Cyclohexane; Temp. = 48.2°C			
$w_1$ ( $M_w = 75\ 700$ )	$w_1$ ( $M_w = 391\ 000$ )	$w_1$ ( $M_w = 74\ 000$ )	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 ( $M_w = 130\ 000$ , $M_n = 170\ 000$ ); Linear-PEO ( $M_w = 200\ 000$ ); Solvent: Acetone; Temp. = 48.2°C			
$w_1$ ( $M_w = 130\ 000$ )	$w_1$ ( $M_w = 170\ 000$ )	$w_1$ ( $M_w = 200\ 000$ )	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

**Table 5** continuedStar-PEO ( $M_w = 130\,000$ ,  $M_w = 170\,000$ ); Linear-PEO ( $M_w = 200\,000$ ); Solvent: Acetone; Temp. = 48.2°C

$w_1$ ( $M_w = 130\,000$ )	$w_1$ ( $M_w = 170\,000$ )	$w_1$ ( $M_w = 200\,000$ )	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 ( $M_w = 130\,000$ ,  $M_w = 170\,000$ ); Linear-PEO ( $M_w = 200\,000$ ); Solvent: Chloroform; Temp. = 48.2°C

$w_1$ ( $M_w = 130\,000$ )	$w_1$ ( $M_w = 170\,000$ )	$w_1$ ( $M_w = 200\,000$ )	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 ( $M_w = 130\,000$ ,  $M_w = 170\,000$ ); Linear-PEO ( $M_w = 200\,000$ ); Solvent: Chloroform; Temp. = 70°C

$w_1$ ( $M_w = 130\,000$ )	$w_1$ ( $M_w = 170\,000$ )	$w_1$ ( $M_w = 200\,000$ )	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

equal to the ratio of the solvent pressure to the pure-solvent vapour pressure ( $P^S$ ) at the temperature of the experiment. Values of  $P^S$ , calculated using the equations given by Daubert and Danner<sup>15</sup>, are given in *Table 6*.

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 3–5* 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

**Table 6** Vapour pressures ( $P^S$ ) of the pure solvents

Solvent	Temperature (°C)	$P^S$ (torr)
Acetone	48.2	574
	48.2	493
Chloroform	50	526
	70	1022
Cyclohexane	48.2	255

weight ( $M_w = 200\,000$ , 170 000, 130 000) but the difference in  $M_w$  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 behaviour.

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, Ref. <sup>16</sup>).

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

Vapour–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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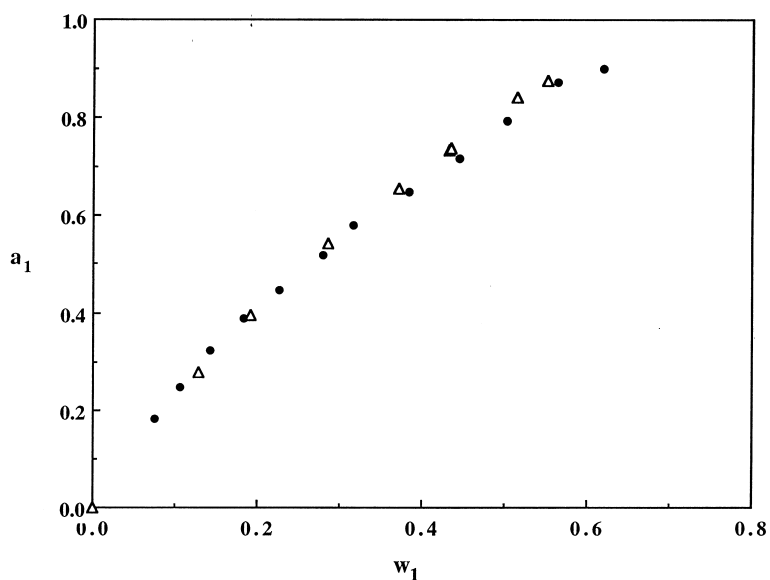


Figure 1 Activity of chloroform in 8-arm star PS [ $M_w = 74\,000$  (●)] at 48.2°C and in linear PS [ $M_w = 233\,000$  (Δ)] at 50°C

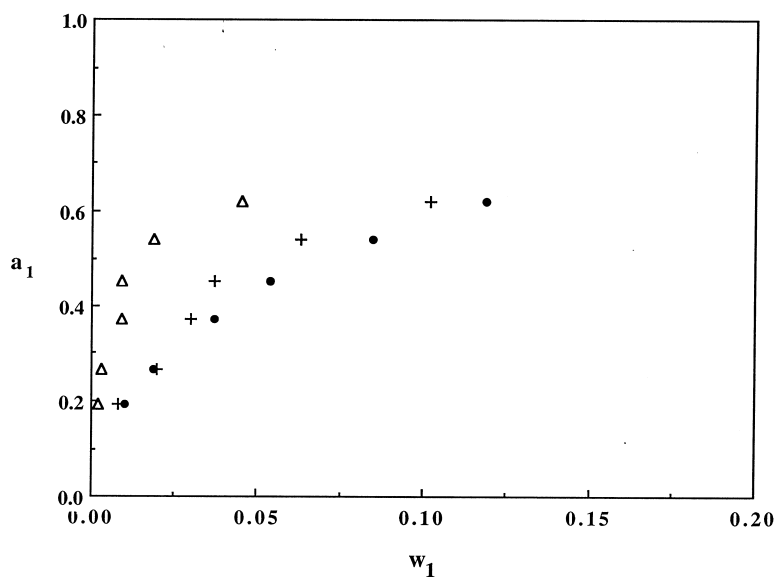


Figure 2 Activity of cyclohexane in 8-arm star PS [ $M_w = 74\,000$  (●) and  $M_w = 391\,000$  (+)] and in linear PS [ $M_w = 75\,700$  (Δ)] at 48.2°C

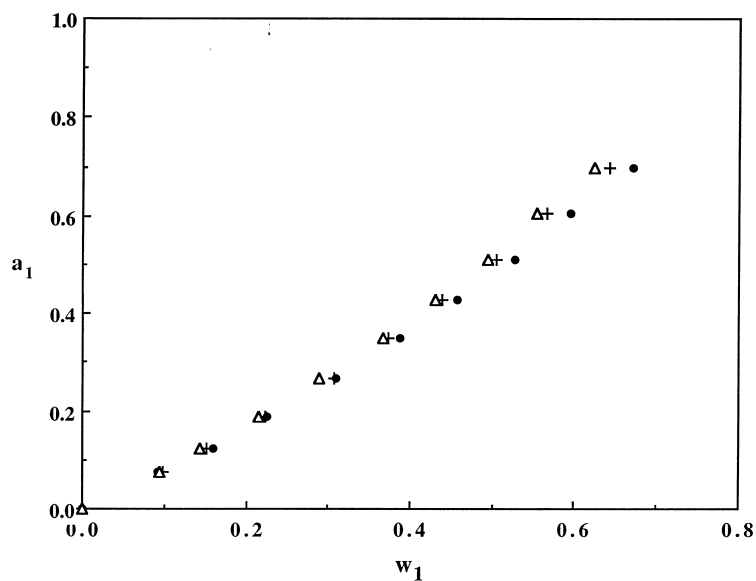
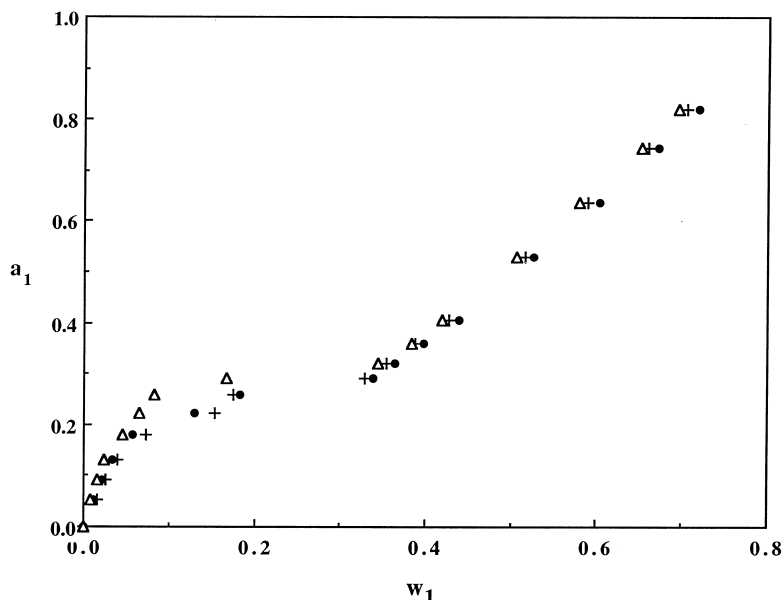
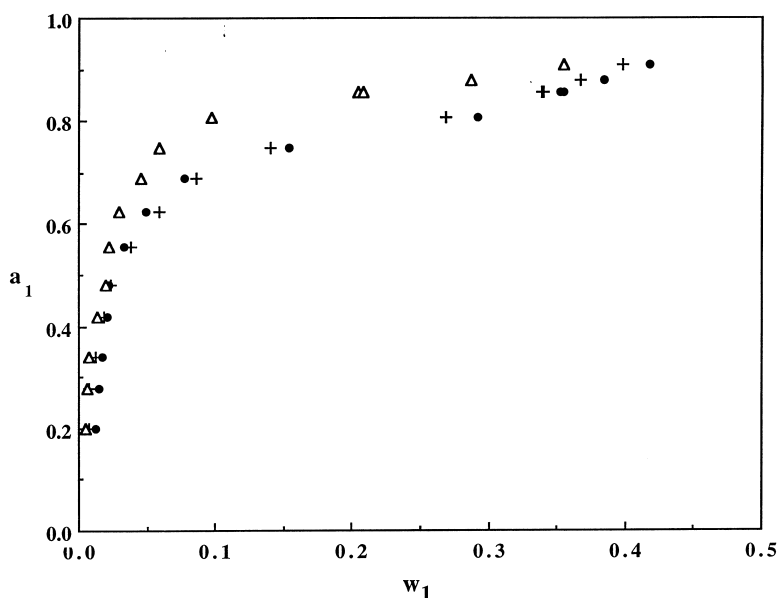


Figure 3 Activity of chloroform in 15-arm star PEO [ $M_w = 130\,000$  (●)], in 20-arm star PEO [ $M_w = 170\,000$  (+)] and in linear PEO [ $M_w = 200\,000$  (Δ)] at 70°C



**Figure 4** Activity of chloroform in 15-arm star PEO [ $M_w = 130\,000$  (●)], in 20-arm star PEO [ $M_w = 170\,000$  (+)] and in linear PEO [ $M_w = 200\,000$  (Δ)] at 48.2°C



**Figure 5** Activity of acetone in 15-arm star PEO [ $M_w = 130\,000$  (●)], in 20-arm star PEO [ $M_w = 170\,000$  (+)] and in linear PEO [ $M_w = 200\,000$  (Δ)] at 48.2°C

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