Temperature and solvent effects on the intrinsic viscosities of a star-shaped polystyrene

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The excluded-volume effect on the solution behaviour of a star-shaped polystyrene has been studied by measuring intrinsic viscosities over the temperature range 25–55°C. Two good solvents (benzene, dioxane) were selected together with two poor solvents (cyclohexane, 71.4% dioxane–28.6% methanol). The viscosity–temperature coefficients and apparent activation energies were compared. Other parameters investigated were: α (the expansion factor), θ (the theta or Flory temperature), ψ_1 (the entropy parameter of the solvent) and κ_1 (the enthalpy parameter of the solvent). Since measurements were carried out in dilute solutions, the Kirkwood approximation was assumed, namely that polymers behave hydrodynamically like spheres. The classical method developed by Flory and Fox was used for analysis. The theory of Flory and Fox modified by Benoit and coworkers is discussed.

(Keywords: star-shaped polystyrene; intrinsic viscosity; equivalent hydrodynamic volume; good solvent and poor solvent; temperature coefficient; expansion factor; thermodynamic parameters)

INTRODUCTION

Investigations[1] on short-range interactions and polymer chain dimensions of a star-shaped polystyrene demonstrate that the g factor, which generally has been known to be dependent on the number of arms attached to the molecule, is also dependent on the temperature of the solution. The mean square radius of gyration of the star-shaped polystyrene changes much faster with temperature than that of linear polystyrene of the same molecular weight. The present paper is concerned with long-range intramolecular interactions of the same star-shaped polystyrene. Intrinsic viscosities have been determined in two good solvents (benzene, dioxane) and two poor solvents (cyclohexane, 71.4% dioxane–28.6% methanol) in the temperature range 25–55°C. Data were treated by two classical methods: the Kirkwood approximation that polymer molecules in dilute solution behave hydrodynamically like hard spheres[2]; and the Flory and Fox equations[3] for the calculation of thermodynamic parameters θ, ψ_1 and κ_1.

EXPERIMENTAL

Materials

The star-shaped polystyrene was the same one as used for the determination of unperturbed dimensions[1]. It was a gift from Dr J.-G. Zilliox. The polymer carries 13 side monodisperse branches and its molecular weight is 2.5×10^6.

Benzene was purified by being shaken with concentrated sulphuric acid, washed twice with water, dried with sodium sulphate and then distilled.

Cyclohexane was purified by the method described before[1]. Dioxane and methanol were spectroquality reagent obtained from Matheson, Coleman and Bell Company, and were used without further purification.

Preparation of solutions and viscosity measurements

These were the same as described before[1].

Because of the uncertainty in the flow time, measurements for each solution were run as many as 10 to 11 times, often consecutively, until reasonable reproducibility was reached.

RESULTS AND DISCUSSION

Intrinsic viscosities

Intrinsic viscosities of the star-shaped polystyrene are given in *Table 1*, and for convenience of inspection the data are plotted in *Figure 1* in the form of $[\eta]$ *versus* temperature. The intrinsic viscosity values of the star-shaped polystyrene in good solvents (benzene and dioxane) decrease linearly as temperature increases, whereas in poor solvents (cyclohexane, 71.4% dioxane–28.6% methanol) they increase linearly with temperature.

No such contrast has been observed with respect to 'goodness' of solvent on the intrinsic viscosity of linear polystyrene. For a linear polystyrene[4] with molecular weight 9.75×10^4, there is a very small change in intrinsic viscosity over the temperature range between 25 and 65°C regardless of whether the polymer was dissolved in a good solvent such as benzene ($[\eta]$, 2.54–2.57) or dioxane ($[\eta]$, 2.11–2.14) or in a poor solvent such as cyclohexanone ($[\eta]$, 1.97–1.98). It is believed that only when the molecular weight exceeds one million, e.g. 1.3×10^6, does the intrinsic viscosity of linear polystyrene increase rapidly with temperature; however, whether in good solvent (benzene) or poor solvent (cyclohexane), the change of linear polystyrene is in the same direction[3].

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Table 1 Intrinsic viscosities $[\eta]$ (dl g^{-1}) of the star-shaped polystyrene

Temp. (°C)	Solvent			
	Benzene	Dioxane	Cyclohexane	71.4% Dioxane–28.6% Methanol
25	1.369	1.200	–	0.560
30	1.339	1.148	–	0.597
35	1.320	1.119	0.476	0.639
40	1.281	1.068	0.502	0.661
45	1.290	1.010	0.555	0.685
50	1.222	0.967	0.608	0.682
55	1.202	0.923	0.661	0.725

Equivalent hydrodynamic volume

Along with the Kirkwood approximation[2], Flory has shown that in dilute solution the coils of polymer molecules behave essentially like hard spheres[5]. This is particularly the case in 'good' solvents. De Gennes answers the question why the coils behave as hard spheres by theorizing that 'the coils refuse to interpenetrate'[2]. Since a star-shaped polystyrene has high segment density near the centre of the molecule, we may reasonably assume that it is in the form of a sphere even in 'poor' solvents. We can thus compare the equivalent hydrodynamic volume of the molecule in four different solvents and at different temperatures. Viscosity data seem to be appropriate for this estimation[6]. The following is a simple derivation of the method that we used for the calculation of V_e (the equivalent hydrodynamic volume).

Einstein's viscosity equation introduces a shape parameter ν in the form:

$$\eta = \eta_0(1 + \nu\phi)$$

where η is the viscosity of the solute, η_0 that of the solvent and ϕ is the volume fraction of the solute. If the polymer molecule is in the form of a sphere, $\nu = 2.5$ and

$$\phi = \frac{NC}{M} V_e$$

where N is Avogadro's number (unit: number of particles mol^{-1}), C is the concentration of the solute (unit: g cm^{-3}), M is the molecular weight of the solute (unit: g mol^{-1}) and V_e is the equivalent hydrodynamic volume (unit: cm^3/particle). Substituting the equation for ϕ into the Einstein equation, we obtain:

$$\frac{\eta - \eta_0}{\eta_0 C} = \frac{\nu N}{M} V_e$$

In a very dilute solution:

$$[\eta] = \lim_{C \to 0} \frac{\eta - \eta_0}{\eta_0 C}$$

and we have:

$$[\eta] = \frac{\nu N}{M} V_e$$

Hence we obtain the following expression for the calculation of equivalent hydrodynamic volume

$$V_e = \frac{M[\eta](10^2)}{(2.5)(6.02 \times 10^{23})}$$

where the factor 10^2 is introduced in the numerator to convert the unit of intrinsic viscosity from dl g^{-1} to $cm^3\ g^{-1}$.

In *Table 2* we give the calculated values of equivalent hydrodynamic volume. As temperature increases, the equivalent hydrodynamic volume decreases in good solvents, but increases in poor solvents. From 25 to 55°C, it decreases 12% in benzene and 23% in dioxane, but increases 29% in 71.4% dioxane–28.6% methanol. In cyclohexane it increases 39% from 35 to 55°C.

However, in comparison with the equivalent hydrodynamic volume in poor solvents at 25°C, the polymer molecule is 2.5 times larger in benzene and 2.0 times larger in dioxane.

Temperature coefficient and the apparent activation energy of flow

The star-shaped polystyrene exhibits a linear relationship between $[\eta]$ and T and between $\log[\eta]$ and $1/T$ respectively, within, of course, experimental error. This indicates that no phase transition occurred within this temperature range. In *Table 3* the viscosity temperature coefficient $d[\eta]/dT$ and the apparent activation energy of flow, E_a, are listed. The values of E_a were calculated from the slope of the plot using the relationship:

$$E_a = 2.3R[d \ln[\eta]/d(1/T)]$$

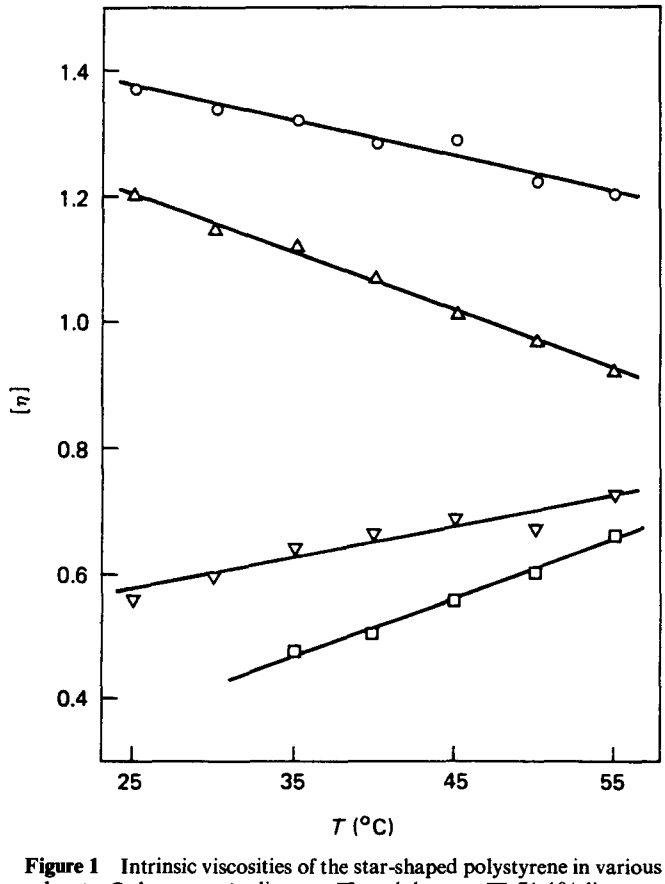

Figure 1 Intrinsic viscosities of the star-shaped polystyrene in various solvents: ○, benzene; △, dioxane; □, cyclohexane; ▽, 71.4% dioxane–28.6% methanol

Table 2 Equivalent hydrodynamic volume $V_e \times 10^{16}$ (cm^3/molecule) of the star-shaped polystyrene as a function of environment and temperature

Temp. (°C)	Solvent			
	Benzene	Dioxane	Cyclohexane	71.4% Dioxane–28.6% Methanol
25	2.27	1.99	–	0.930
30	2.22	1.91	–	0.991
35	2.19	1.86	0.790	1.06
40	2.13	1.77	0.833	1.10
45	2.14	1.68	0.921	1.14
50	2.03	1.61	1.01	1.13
55	2.00	1.53	1.10	1.20

Table 3 The viscosity temperature coefficient and the apparent activation energy of flow

Solvent	$d[\eta]/dT$ (dl g^{-1} K^{-1}) $\times 10^3$	E_a (kcal mol^{-1})
Benzene	−5.46	0.825
Dioxane	−9.30	1.71
Cyclohexane	9.52	−3.40
71.4% Dioxane–28.6% Methanol	5.08	−1.32

The viscosity temperature coefficient is negative for good solvents and positive for poor solvents. This is the opposite of the apparent activation energy. It is believed that the apparent activation energy of flow is related to the free rotation of the chain segments. The positive sign is normal with macromolecular compounds, whereas the negative sign has been observed with aqueous solutions of poly(methacrylic acid). The star-shaped polystyrene does not behave normally in comparison with other macromolecular compounds.

The expansion factor α

Using the equation derived by Flory and Fox[3]:

$$[\eta] = KM^{1/2}\alpha^3$$

we calculated the values of α as a function of temperature and they are listed in *Table 4*. All polymers are known to show coil expansion with temperature. Here, we see no exception with the star-shaped polystyrene. The value of α increases with temperature no matter whether the solvent is good or poor, but the extent of expansion varies. In good solvents the expansion is 11–16% from 25 to 55°C, whereas in poor solvents the expansion is 22–26% from the θ temperature to 55°C.

Thermodynamic parameters

Attempts have been made for more than two decades to correlate the expansion factor α with an interaction parameter z which involves the binary cluster integral β. However, it is difficult to determine the potential $u(r)$ in β, and hence a value of z. We made use of the original set of equations developed by Flory to calculate $\psi_1(1-\theta/T)$, which is equivalent to β. The uncertainty in ψ_1 is neither greater nor less than in β, but it is much easier and requires less guessing to estimate the magnitude of ψ_1 than that of β.

Our calculation of thermodynamic parameters is based upon the following equation derived by Flory[3,5]:

$$\alpha^5 - \alpha^3 = 2C_M\psi_1(1-\theta/T)M^{1/2}$$

$$C_M = \left(\frac{27}{2^{5/2}\pi^{3/2}}\right)\left(\frac{\bar{v}^2}{NV_1}\right)\left(\frac{M}{\langle r^2\rangle}\right)^{1/2}$$

$$= 1.4\times 10^{-24}\frac{\bar{v}^2}{V_1}\frac{\Phi}{K}$$

In the above equations, ψ_1 is an entropic parameter, θ is the temperature at which the chemical potential due to polymer segment–solvent interaction is zero, $\bar{v}$ is the partial specific volume of the polymer and V_1 is the molar volume of the solvent. The partial specific volume of the star-shaped polystyrene under study was calculated using the data published in the previous paper[7]: $\bar{v}=0.932$ (benzene, 25°C), 0.938 (dioxane, 25°C), 0.923 (cyclohexane, 35°C), and 0.883 (71.4% dioxane–28.6% methanol, 25°C). All the values of $\bar{v}$ are a little higher than those reported in the literature (e.g. 0.927 for linear polystyrene in cyclohexane at 35°C). The molar volume of solvent is calculated using the equation:

$$V_1 = \frac{1}{\rho}\text{(mol. wt)}$$

for a single solvent and the equation:

$$V_{12} = \rho_{12}^{-1} = \left(\frac{x\rho_2 + (100-x)\rho_1}{x+(100-x)}\right)^{-1}$$

for a solvent mixture[8]. The density (ρ) data were obtained from 'International Critical Tables'[9]. The calculated values of molar volume of solvent (in ml) are: 88.89 (benzene), 85.25 (dioxane), 105.4 (cyclohexane) and 74.66 (71.4% dioxane–28.6% methanol), all at 25°C. This might introduce an error to the cyclohexane (which was used for study at 35°C), but the error is again believed to be not significant. The value of Φ was taken to be 2.9×10^{21} (ref. 1).

In *Figure 2* the data are plotted in the form of

$$\frac{K_T}{K_{25}M^{1/2}}(\alpha^5-\alpha^3)$$

versus $1/T$. Four straight lines are obtained for the four different solvent systems. The factor K_T/K_{25} is introduced for correction of C_M values, the temperature

Table 4 The temperature dependence of molecular expansion factor α_η

Temp. (°C)	Solvent			
	Benzene	Dioxane	Cyclohexane	71.4% Dioxane–28.6% Methanol
25	1.35	1.29	–	–
30	1.37	1.31	–	1.05
35	1.40	1.33	–	1.10
40	1.43	1.35	1.05	1.15
45	1.49	1.37	1.12	1.21
50	1.52	1.40	1.20	1.25
55	1.57	1.44	1.29	1.33

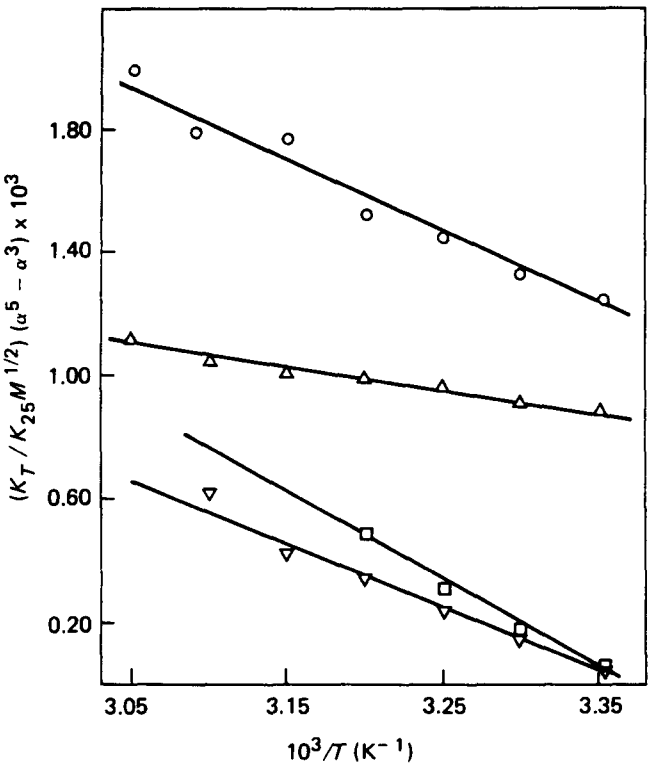

Figure 2 Plot of $(K_T/K_{25}M^{1/2})(\alpha^5-\alpha^3)$ *versus* $1/T$ for the star-shaped polystyrene in various solvents: ○, benzene; △, dioxane; □, cyclohexane; ▽, 71.4% dioxane–28.6% methanol

25°C being chosen as our reference. From the intercept we calculated ψ_1, and from the equation derived by Flory:

$$\kappa_1/\psi_1=\theta/T$$

we obtained κ_1, an enthalpy parameter. The ratio of slope over intercept gives the value of θ. In *Table 5* the three thermodynamic parameters θ, ψ_1 and κ_1 of the star-shaped polystyrene are listed. These can only be considered as provisional values as in the case of linear polystyrene[3]. The uncertainties in K_T values are being inherited in the determination of the thermodynamic parameters. The values of ψ_1 and κ_1 are lower than expected. In cyclohexane the value of ψ_1 for linear polystyrene[3] is 0.13, for star-shaped 0.062; that of κ_1 for linear[3] is 0.13, for star-shaped 0.065. In both cases the difference is of the order of a factor 2. In benzene, ψ_1 is 0.09 for linear[3], 0.06 for star-shaped; κ_1 is 0.03 for linear[3], and 0.05 for star-shaped.

While all these values of θ, ψ_1 and κ_1 are not as accurate as we would wish them to be, they provide a qualitative observation about the thermodynamic behaviour of the star-shaped polystyrene. As the temperature increases, the coil of the star-shaped polymer expands. According to Flory[5] the sign of $\delta(\Delta G_a)$ (the change in free energy to bring the segment k from infinity to the distance a) depends on the value of $\psi_1-\kappa_1$. If so, we see that the value of $\delta(\Delta G_a)$ is positive for the star-shaped polystyrene in good solvents, meaning that the process to bring the chain segment together is not favourable. On the other hand, the value of $\delta(\Delta G_a)$ is negative for the same star-shaped polystyrene in poor solvents, meaning that the process of bringing together is favourable.

Because of the multiple contacts of the polymer segments with solvent and between polymer segments themselves, the thermodynamics of a branched polymer may not be as simple as expected. This is particularly the case with the θ temperature. Benoit and coworkers[10] suggested that there are virtually three θ temperatures: θ_α, the temperature at which $\alpha=1$; θ_{A_2}, the temperature at which the second virial coefficient $A_2=0$; and θ, the Flory temperature at which $\alpha=1$ and $A_2=0$ simultaneously. For a linear polystyrene $\theta_\alpha=\theta_{A_2}=\theta$; for a branched polystyrene the three θ values are not necessarily equal to each other. According to Vrij[11] and Casassa[12], θ_{A_2} is always larger than θ; but, according to Benoit and coworkers, if the coefficient A_2 includes a third term in the series expansion of free energy parameter, then χ is small and positive, and $\theta_\alpha<\theta_{A_2}<\theta$ (ref. 10).

We followed the suggestion by Benoit and coworkers by plotting $\alpha^8-\alpha^6$ vs. $\alpha^3(1-\theta/T)10^2$ or $(\alpha^8-\alpha^6)g^3/M^{1/2}$ vs. $\alpha^3g^{3/2}(1/T)$, where g is the geometric factor (i.e. $\langle R^2\rangle_{branch}/\langle R^2\rangle_{linear}$). Each gives a straight line, but the correction of θ is either very small or shows greater uncertainty. For example, the plot of $\alpha^8-\alpha^6$ vs. $\alpha^3(1-\theta/T)10^2$ for the star-shaped polystyrene in benzene gives $\theta_\alpha=155$°C (in comparison with our value 159°C); the plot of $(\alpha^8-\alpha^6)g^3/M^{1/2}$ vs. $\alpha^3g^{3/2}(1/T)$ for the star-shaped polystyrene in cyclohexane gives the following data: x intercept $=1.32\times10^{-3}$, y intercept $=0.491\times10^{-3}$, and slope $=0.372$. The ratio

$$\frac{\text{slope}}{y\text{ intercept}}=0.758\times10^3=\frac{\theta}{\alpha^3g^{3/2}}$$

It is difficult to select the value of g for calculation. If we select $g_\eta=g_s^{3/2}=0.381$, then $\theta_\alpha=289$ K, too low in comparison with θ (=304 K). On the other hand, if we select $g_{th}=0.219$, then $\theta_\alpha=320$, too high in comparison with θ.

It has been reported in the literature[13,14] that θ_{A_2} is not a constant for branched polymers. Its value depends on molecular weight as well as number of branches. Given that this is the case, there does not seem to be any accurate method as yet for the determination of θ temperature from experimental data (light scattering as well as intrinsic viscosity).

However, even though the accuracy remains to be improved for the determination of θ temperature and other thermodynamic parameters to characterize the excluded-volume effect on the molecular interaction between polymer segment and solvent, the classical method developed by Flory and Fox still seems to provide a means to obtain reasonable magnitudes. It is believed that the calculated data we obtained correctly describe the solution behaviour of the star-shaped polystyrene at various temperatures, even though their accuracy could be much improved.

Table 5 Thermodynamic parameters of the star-shaped polystyrene at 25°C

Solvent	θ (K)	ψ_1	κ_1
Benzene	159	0.0572	0.0497
Dioxane	216	0.0188	0.0136
Cyclohexane	304	0.0619	0.0650
71.4% Dioxane–28.6% Methanol	298	0.0405	0.0409

CONCLUSIONS

The intrinsic viscosity of the star-shaped polystyrene in good solvents decreases linearly as temperature increases, whereas in poor solvents it increases linearly with temperature.

As temperature increases, the equivalent hydrodynamic volume decreases in good solvents, but increases in poor solvents.

The viscosity temperature coefficient is negative for good solvents and positive for poor solvents. This is the opposite of the apparent activation energy of flow.

The value of $\delta(\Delta G_a)$ is positive in good solvents but negative in poor solvents. This means that the process to bring the chain segment together is not favourable in good solvents, but favourable in poor solvents.

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