Unperturbed dimensions and the *g* factor of a star-shaped polystyrene

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Unperturbed dimensions of a star-shaped polystyrene near the θ temperatures, 25°C, 35°C and 45°C were determined by the measurement of intrinsic viscosity of the polymer in poor solvents. It was found that the inferred mean square radius of gyration of the star-shaped polystyrene, while much smaller than that of the linear polystyrene, as expected, changes much faster with the increase of temperature. The geometric factor g of the star-shaped polystyrene was found to be temperature-dependent.

(Keywords: unperturbed dimension; star-shaped polystyrene; intrinsic viscosity; θ temperature; the g-factor)

INTRODUCTION

In the previous paper[1] on the differential refractive indices of star-shaped and linear polystyrenes, we presented a set of data which suggests that there is a difference in the polarizability of the two polymers under the same conditions. The polarizability of the linear polystyrene is constraint free, while that of the star-shaped polystyrene is constrained. In this paper our work is extended to investigate the unperturbed dimensions of the same star-shaped polystyrene near the θ temperatures, 25°C, 35°C and 45°C by the measurement of intrinsic viscosity of the polymer in poor solvent. In order to determine the g factor, experiments were carried out on the same linear polystyrene in the same solvents and temperature. The objective is to ascertain the effect of temperature on the two parameters, the unperturbed dimension and the g factor.

EXPERIMENTAL

Materials

The star-shaped polystyrene M2C sample was obtained as a gift from Dr Jean-George Zilliox of CNRS Centre de Recherches sur les Macromolecules, Strasbourg, France. The polymer carries 13 side monodisperse branches. It was synthesized[2] by anionic block copolymerization of styrene and divinylbenzene (DVB) under high vacuum, using sec-butyllithium as initiator. The molecular weight was determined with light scattering and was found to be 2.5×10^6. The linear polystyrene sample was obtained from Waters Associates sold as a standard for HPLC. Analysis of the HPLC data with a method recently developed[3] shows that the polydispersity for both linear and star-shaped polystyrene is <1.1. This supports the contention that for the star-shaped polystyrene sample, the polydispersity originating from fluctuations in the length of arms is negligible[4]. The molecular weight of the linear polystyrene was found to be 2.5×10^6. Cyclohexane was treated with concentrated sulphuric acid and nitric acid, and with a concentrated solution of potassium permanganate in 10% sulphuric acid. It was then washed with water, dried and distilled. *p*-Dioxane, toluene and methanol were of spectroquality, obtained from Matheson, Coleman and Bell Company and used without further purification.

Preparation of solutions

Approximately 0.2–0.5 g (weighed to ±0.1 mg) of polymer was dissolved in a solvent to make 50 ml of solution. This was the stock solution and labelled as 1 CM (concentration maximale). The solution was then diluted to 3/4 CM, 1/2 CM and 1/4 CM. Viscosity measurements were taken with all four solutions.

Viscosity measurements

Flow time of each solvent and each solution was measured with a Ubbelhode viscometer. No kinetic energy corrections were made with this viscometer, because the flow time of the solvent was at least 100 s. Temperature was controlled by a Forma water bath or Lauda control unit accurate to ±0.1°. Since the intrinsic viscosities of most samples are less than 3.000 dl g^{-1}, the effect of the rate of shear is small. No correction was made to zero rate of shear[5]. Measurements for each solution were run as many as ten to eleven times. The criteria for the selection of the data reported in this paper were reproducibility and linearity of the plot.

Critical miscibility measurements

0.3 g (weighed to ±0.1 mg) of each sample (linear as well as star-shaped polystyrene) was mixed with 40 ml of solvent in a long test tube equipped with a tight glass stopper. The test tube was submerged in a water bath at 70°C for about two hours and shaken from time to time to make sure that the solution was clear. The temperature of the water bath was then cooled down slowly; the water was kept stirring constantly. The temperature at which the polymer solution became cloudy was recorded and this temperature is labelled as critical temperature, T_c.

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Table 1 Miscibility measurements

	Star-shaped	Linear	
	T_c (°C)	T_c (°C)	θ (°C)
71.4% Dioxane 28.6% Methanol	23	23	25
Cyclohexane	32	33	35
72.8% Toluene 27.2% Methanol	43	44	45

RESULTS AND DISCUSSION

Critical temperature

We chose the three particular solvents because their θ temperatures for linear polystyrene are known[6] (25°C, 35°C and 45°C respectively). We were aware of three pertinent questions. First, with the molecular weight as high as 2.5×10^6, the θ temperature for linear polystyrene may not be exactly the same as that in the low molecular weight range[7]. Second, the θ temperature for star-shaped polystyrene is not necessarily the same as for linear polystyrene. It was suggested that the θ temperature is lower for star-shaped than for linear[8]. Third, and most seriously, the definition of θ temperature is not as clear as we thought[9,10]. Worse than that is the multiple definition of θ for star-shaped polymer[11], θ_{A2} and θ_α. They are not identical. For this reason we judiciously accepted the experimental definition of θ, reported in literature, such that θ is the temperature at which $a = 0.5$ in the equation

$$[\eta] = KM^a \tag{1}$$

To ascertain how close the θ temperature of a star-shaped polystyrene is to the linear polystyrene, we rely on the measurement of phase equilibrium. Since we used only one sample of star-shaped polystyrene, we cannot determine the θ temperature directly from the T_c measurements[12].

Table 1 gives the critical temperature of linear and star-shaped polystyrenes in three different poor solvents. It is seen that $T_c \hat{=} \theta - 2°C$ for the linear polystyrene and T_c is lowered by approximately 1 to 2 degrees for the star-shaped than for the linear polymer. In view of the large discrepancy reported in literature concerning the θ temperature of star-shaped polystyrenes, we feel justified in choosing the three temperatures, 25°C, 35°C and 45°C, in three different solvents for comparison. They are 'near' the θ temperatures and the conformation of the star-shaped polystyrene under these conditions (θ temperatures) is 'near' the unperturbed state.

It should be pointed out that the phase equilibrium measurement can only be used to investigate the average bulk property of the polymer solution; it cannot detect the subtlety of whether there is any preferential adsorption of one solvent over another onto the polymer molecule[13].

Intrinsic viscosities

Intrinsic viscosities of the star-shaped and linear polystyrenes at the three different temperatures each near θ are given in *Table 2*.

As expected, bulk viscosities and solution viscosities can be lower for branched polymers than for linear polymers of equivalent weight[8]. What is unexpected is that the decrease in the value of intrinsic viscosity of linear polystyrene is approximately 1% for the interval of 10°C. We repeated the experiment 10 times and the 1% decrease persisted. We believe that this is not an artifact.

The decrease in the intrinsic viscosity of star-shaped polystyrene is more than 15%. This indicates the effect of temperature on the segment density in the core of the molecule. The decrease in both polystyrenes is linear, but the negative slope of the star-shaped polystyrene is much greater than that of the linear polystyrene as demonstrated in *Figure 1*. The plot is in the form of K vs. T, where K was converted from $[\eta]$, using equation (1).

Unperturbed dimensions of the star-shaped and linear polystyrenes

For several decades, the random flight model has been used for the analysis of experimental data including intrinsic viscosity leading to the calculations of dimen-

Table 2 Intrinsic viscosities of star-shaped and linear polystyrenes at three temperatures, each near θ

		$[\eta]$ (dl g^{-1})	
Temp. (°C)	Solvent	Star-shaped (MW 2.5×10^6)	Linear (MW 2.5×10^6)
25	71.4% Dioxane 28.6% Methanol	0.560	1.264
35	Cyclohexane	0.476	1.248
45	72.8% Toluene 27.2% Methanol	0.392	1.240

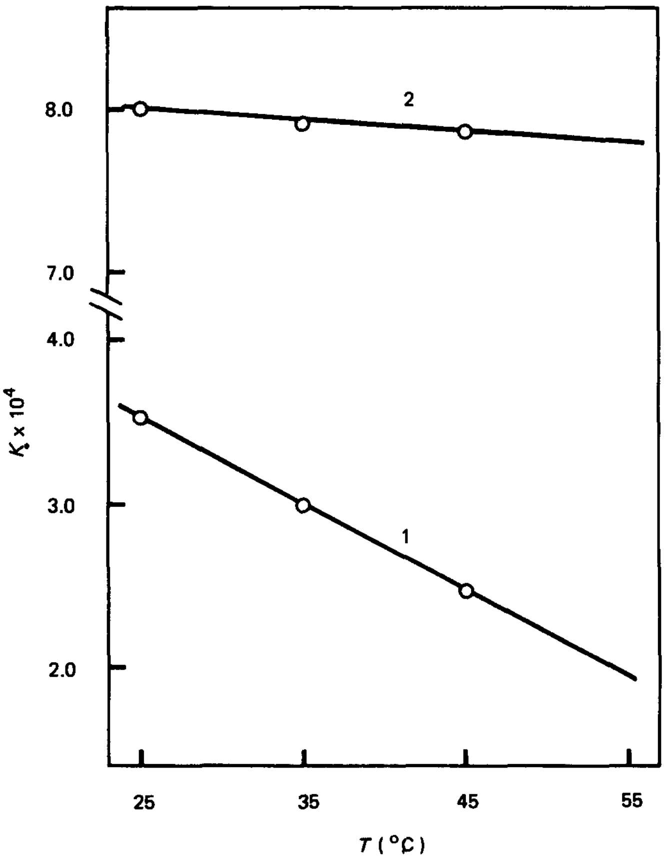

Figure 1 K as a function of temperature. (1) star-shaped polystyrene; (2) linear polystyrene

Table 3 Temperature dependence of the inferred unperturbed dimensions and the g factor

T (°C)	$\times 10^{12}$ cm^2 $\langle s^2\rangle_{\mathrm{ob}}$	$\times 10^{12}$ cm^2 $\langle s^2\rangle_{\mathrm{ol}}$	$\times 10^{18}$ $\langle s^2\rangle_{\mathrm{ob}}/M$	$\times 10^{18}$ $\langle s^2\rangle_{\mathrm{ol}}/M$	g_η
25	10.3	17.7	4.12	7.08	0.443
35	9.21	17.5	3.68	7.00	0.381
45	8.10	17.4	3.24	6.96	0.316

sions of polymer molecules. Criticisms have been numerous with respect to the oversimplification of the model and attempts have been made to make the model more realistic in interpreting the observed results[10]. But so far there is no simple theory that does not contain some flaws. For this reason we still use the simplest equation which has been known to investigators for several decades to calculate the mean square radius of gyration, $\langle s^2\rangle$, of both the star-shaped and linear polystyrenes. The calculation is based on the equation:

$$K=\Phi\left(6\langle s^2\rangle/M\right)^{3/2}$$

The value of Φ, a universal constant, poses another problem. Three well-known theories[14–16] give three different ways of calculation, leading to the different values of Φ. So far no exact evaluation of Φ is as yet achieved[17]. For star-shaped polystyrene the value varies from 2.1×10^{21} to 3.2×10^{21}. Since an observed average value[18] was proposed to be 2.9×10^{21}, we used 2.9×10^{21} in our calculations and assumed that Φ does not vary with temperature in the range between 25°C and 55°C[19]. The results are given in *Table 3*.

As expected (from *Figure 1*) the mean square radius of gyration decreases with temperature much faster for the star-shaped polystyrene than for the linear polystyrene. From 25°C to 55°C the decrease in dimension is 37% for the star-shaped polystyrene but less than 2% for the linear polystyrene.

The geometric factor g

The effect of branching on the dimension of the polymer molecule is often described in terms of the geometric factor g which is defined by:

$$g=\frac{\langle s^2\rangle_{\mathrm{ob}}}{\langle s^2\rangle_{\mathrm{ol}}}=g_s$$

or

$$g=\frac{[\eta]_{\mathrm{ob}}}{[\eta]_{\mathrm{ol}}}=g_\eta$$

where subscript o refers to θ temperature, b to branch and l to linear.

In *Table 3* we list the values of g_η as a function of temperature. Inspection of *Table 3* reveals that our experimental data are in good agreement with the results reported by Noda and coworkers[18] who used the light scattering method to estimate $\langle s^2\rangle$.

An important point that emerges from *Table 3* is that g_η is a function of θ temperature. As θ temperature increases, g_η factor decreases. This is consistent with the observation that the change in the radius of gyration with temperature is much faster for the star-shaped polystyrene than for the equivalent linear polystyrene.

CONCLUSION

(1) The unperturbed dimension of the linear polystyrene is not, as was reported, temperature-independent[20]. The effect of temperature on the unperturbed dimension of the star-shaped polystyrene, however, is much more pronounced than that on the linear polystyrene. This is because the star-shaped polystyrene has high segment density which is sensitive to temperature.

(2) Since the unperturbed dimension in one θ temperature is not the same as in another θ temperature and since the sensitivity to temperature of the star-shaped polystyrene is not the same as that of the linear polystyrene, the geometric factor g_η must take temperature into consideration, i.e. temperature as an independent variable. g_η is not a function of the number of branches alone, as was originally thought[21].

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