Examination of the Temperature Coefficient of Polystyrene.   Effect of Solvent, Temperature, and Molecular Weight

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Synopsis

The temperature coefficient of polystyrene was examined in three Θ solvents by several different methods.   Four homogeneous samples were employed, having molecular weights of 51,000, 97,200, 160,000, and 392,000.   It was found that the linear expansion factor α and the temperature coefficient were dependent upon the solvent, temperature range and molecular weight of the polymer.

Introduction

A number of conflicting results and concepts have recently appeared in the literature concerning the temperature coefficient of the unperturbed dimensions of polystyrene in solution.[1-5]   The diversity of the data even includes a difference in sign.   There have been several reports on carefully performed experiments that fall into two major classes.   The first group has studied several low molecular weight polystyrene samples assuming that the linear expansion factor α is small enough to be ignored.[2,4]   The second group has used a single, higher molecular weight sample and has confined the study to the region of the Θ temperature.[1,3,5]

In the present work, four homogeneous polystyrene samples were used in five different Θ solvents and one good solvent.   With this choice of polymer molecular weight range, it was possible to combine the most advantageous features of both groups without being solely dependent on either one.   It was also possible to investigate areas that were unattainable in previous studies.

Experimental

Four samples of polystyrene were used.   This polymer was obtained from Arro Labs of Joliet, Illinois.   The molecular weight data were supplied by the manufacturer.   The polystyrene was prepared in the manner given by Wyman and Altares[6] and had a maximum heterogeneity ratio

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$(\bar{M}_w/\bar{M}_n)$ of less than 1.10. In all cases, the molecular weights were determined by osmometry in two solvents at three different temperatures. Our molecular weight determinations were in fine agreement with the manufacturer's data. The four fractions used had number-average molecular weights of 51,000, 97,200, 160,000, and 392,000. The weight-average molecular weights were not determined.

All the solvents were C.P. grade except toluene, which was reagent grade. The toluene was triply distilled before using.

The viscosity measurements were made in Cannon-Ubbelohde semimicro calibrated dilution viscometers. The flow times for the solvents were long enough in order to neglect any kinetic energy corrections. The viscometers were suspended in water or oil baths that could easily be controlled to better than ±0.01°C.

All solutions and dilutions were made at the Θ temperature of the solvent–polymer system. In the temperature study, the densities were determined and suitable corrections were made for the solvent expansion. In the case of toluene, all solutions and dilutions were made at 25°C. The values for the variation of density of the toluene with temperature were taken from the literature.[7]

Treatment of the Data

Two recent papers by Orofino[1,5] in which the intrinsic viscosity of polystyrene was determined in Θ solvents, noticeable curvature appeared in the graphs for η_{sp}/c and ln η_r/c. In order to eliminate the use of curved lines in the extrapolation to infinite dilution to obtain $[\eta]$, we employed the following technique. Normally one writes

$$\eta_{sp}/c = [\eta](1 + k'[\eta]c + k''[\eta]^2c^2 + \ldots) \qquad (1)$$

and

$$\ln \eta_r/c = [\eta](1 - \beta'[\eta]c + \beta''[\eta]^2 c^2 - \ldots) \qquad (2)$$

with $\beta' + k' = \frac{1}{2}$.

However, if eq. (2) is subtracted from eq. (1) and one divides by the concentration c, one obtains

$$\frac{\eta_{sp} - \ln \eta_r}{c^2} = \frac{[\eta]^2}{2} + (k'' - \beta'')[\eta]^3c + \ldots \qquad (3)$$

Thus a graph of $(\eta_{sp} - \ln \eta_r)/c^2$ versus c is a single straight line with an intercept $[\eta]^2/2$. This basic technique was used throughout and no difficulties were encountered.

Recently there has again been considerable concern about the determination of unperturbed polymer dimensions from viscosity measurements in non-ideal solvents.[8,9] At Θ conditions

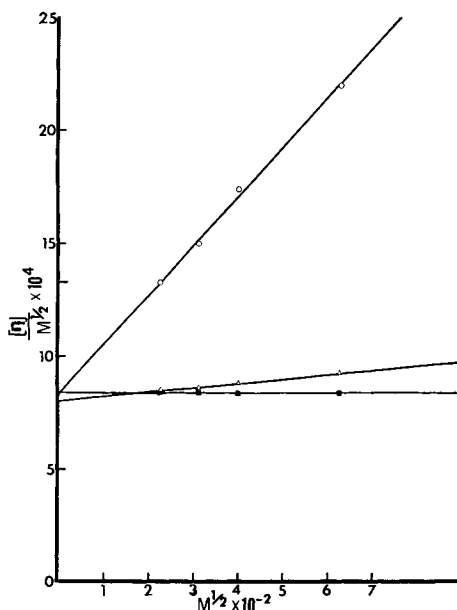$$K = [\eta]/_{\Theta}m^{1/2} \qquad (4)$$

Fig. 1. Test of eq. (5): (O) toluene at 34.8°C.; (■) chlorodecane at 6.6°C.; (Δ) chloro-
decane at 34.8°C.

but to obtain K under other conditions presents a problem. Various extrapolation techniques have been suggested, and these are summarized by Cowie.[8] However, in agreement with Cowie, it was finally decided to use the expression given by Stockmayer and Fixman.[10] This equation seems to be the most versatile form.

They suggest that

$$[\eta]/M^{1/2} = K_\Theta + 0.51\Phi B \, M^{1/2} \tag{5}$$

that is, a graph of $[\eta]/M^{1/2}$ versus $M^{1/2}$ should be a straight line with an intercept equal to K_Θ and a slope related to B, the polymer–solvent interaction parameter. An application of eq. (5) is shown in Figure 1 for toluene at 34.8°C. and chlorodecane at 34.8°C. and 6.6°C. The straight-line relationship is followed as predicted.

Results and Discussion

The present study was undertaken to help clarify some of the problems that have arisen in both the absolute value as well as the sign of $d \ln \langle r_0^2 \rangle / dT$ for polystyrene. Basically two different approaches have been reported. Bianchi and co-workers[2,4] have reported several studies using several very low molecular weight samples in good solvents like toluene and benzene, while Orofino[1,3,5] in his work employs one high molecular weight polystyrene in several Θ solvents. Here we have used several molecular weights in a number of Θ solvents at varying temperatures.

It appears that several methods to obtain the temperature coefficient (TC) $d \ln \langle r_0^2 \rangle / dT$ of the mean-square unperturbed dimension of a macromolecule are possible.   First, one could measure $[\eta]_\Theta$ in various Θ solvents with Θ temperatures along a certain temperature range and calculate the TC directly as

$$\frac{d \, d \ln [\eta]_\Theta}{dT} = \frac{3}{2} \frac{d \ln \langle r_0^2 \rangle}{dT} \tag{6}$$

A second technique allows one to measure $[\eta]$ over a large temperature range and if the variation of α, the expansion factor, is known as a function of the temperature, then

$$\frac{d \ln [\eta]}{dT} - b \frac{d \ln \alpha}{dT} = \frac{3}{2} \frac{d \ln \langle r_0^2 \rangle}{dT} \tag{7}$$

with b either 3 or 2.5.[11]

A third method would be to use an equation such as that of Stockmayer and Fixman[10] and obtain the K_Θ values in the same solvent as a function of the temperature, thus evaluating $d \ln K_\Theta / dT$ directly.   Apparently the advantage of this last method is the fact that it involves a pure thermal effect, since the same solvent is used throughout.

One further advantage that is presented here is the fact that it should be possible to examine the effect of molecular weight on all of the parameters involved.

The summary of all the intrinsic viscosity results is presented in Table I. Also included in the table is the value $K_\Theta = [\eta]_\Theta / M^{1/2}$ for each of the solvents used.

In an attempt to evaluate an average value for TC, a plot of $\ln K$ versus T was made and is shown in Figure 2 for three solvents.   In all cases the slopes of these lines are negative, thus reflecting the sign of TC.   The values of the TC by this method are presented in Table II.   This approach, however, does not lend itself to examine any dependence of molecular weight upon TC.   One can re-examine the data using eq. (7) for each molecular weight.   In this work $d \ln ([\eta]/[\eta]_\Theta)/dT$ was substituted for $b \, d \ln \alpha/dT$, that is, no choice was made for b.   The summary of these results is given in Table III.

In evaluating the linear expansion factor α at a given temperature, normally one would use the well-known relationship

$$\alpha^3 = [\eta]/[\eta]_\Theta \tag{8}$$

where $[\eta]$ represents the intrinsic viscosity of a polymer–solvent system determined at the Θ temperature and $[\eta]_\Theta$ is the intrinsic viscosity in the Θ solvent at the same temperature.   However, it appears that an alternative method would be to use the same solvent and merely change the temperature.   This α would then be a measure of the thermal expansion only.   Since, for polystyrene, the most widely known and used Θ system

TABLE I
Summary of Intrinsic Viscosity Data

Solvent	$\bar{M}_n$	$[\eta]$, dl./g.						$K_\Theta \times 10^4$
		6.6°C.	34.8°C.	35.9°C.	58.6°C.	70°C.	85°C.	
Chlorodecane	51,000	0.190[a]	0.192		0.193	0.195		8.41
	97,200	0.262[a]	0.267		0.274	0.281		8.39
	160,000	0.336[a]	0.354		0.362	0.376		8.43
	392,000	0.526[a]	0.580		0.622	0.650		8.39
Diethyl malonate	51,000			0.172[a]	0.177	0.182	0.180	7.61
	97,200			0.237[a]	0.250	0.258	0.252	7.60
	160,000			0.303[a]	0.330	0.334	0.330	7.58
	392,000			0.476[a]	0.553	0.578	0.577	7.60
Chlorododecane	51,000				0.176[a]	0.172	0.171	7.79
	97,200				0.246[a]	0.240	0.243	7.89
	160,000				0.312[a]	0.320	0.322	7.80
	392,000				0.491[a]	0.515	0.544	7.84
Cyclohexane	51,000		0.184[a]					8.14
	97,200		0.254[a]					8.14
	160,000		0.331[a]					8.28
	392,000		0.516[a]					8.24
Ethylcyclohexane	51,000					0.191[a]		8.45
	97,200					0.268[a]		8.59
	160,000					0.333[a]		8.33
	392,000					0.529[a]		8.45

[a] Θ temperature for his solvent.

TABLE II
Temperature Coefficient from K Data

Solvent	$d \ln \langle r_0^2 \rangle / dT \times 10^3$
Chlorodecane	-0.99
Diethyl malonate	-0.84
Chlorododecane	-3.18

TABLE III
Variation of the Intrinsic Viscosity with Temperature

Solvent	$\bar{M}_n$	$d \ln [\eta] / dT \times 10^3$	$d \ln ([\eta]/[\eta]\Theta)/$ $dT \times 10^3$
Chlorodecane	51,000	0.37	0.38
	97,200	1.06	0.80
	160,000	1.60	1.60
	392,000	3.31	3.31
Diethyl malonate	51,000	1.60	1.60
	97,200	2.47	2.48
	160,000	2.98	2.98
	392,000	5.82	5.82
Chlorododecane	51,000	-1.26	-1.26
	97,200	-2.52	-2.46
	160,000	0.95	0.93
	392,000	3.87	3.87

is cyclohexane at 34.8°C.,[12] it appears that the majority of the expansion factors measured could have both a thermal and solvent effect. The thermal effect is easy to define and determine. However, the environ-
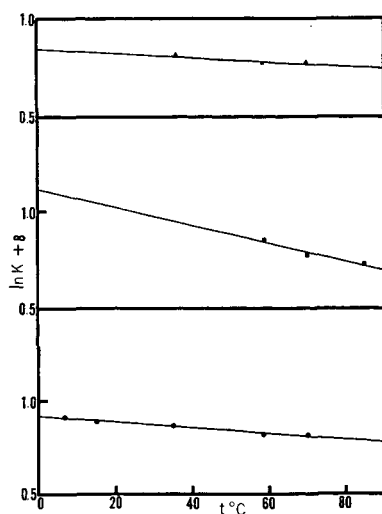

Fig. 2. An evaluation of TC from K: (●) chlorodecane; (▲) diethyl malonate; (■) chlorododecane.

mental parameter is more difficult. In a very detailed study, Orofino[1] suggests that the parameter τ be arbitrarily chosen. It is defined as

$$\left(\frac{d\Gamma_2}{dT}\right)_{\Theta} = M \left(\frac{\bar{v}^2}{V_1}\right) \frac{\psi_1}{\Theta} = \tau \tag{9}$$

Basically this is the temperature derivative of the second virial coefficient Γ_2 at $T = \Theta$. The quantity ψ_1 is characteristic of polymer–solvent conformation, $\bar{v}$ is the partial specific volume of the polymer, V_1 is the solvent molar volume, and M is the molecular weight. In another study, Abe and Fujita[13] were rather successful in using the arbitrary parameter, $\psi_1 \Theta$, which represents the heat of dilution.

Examining the pure thermal expansion seems rather straight-forward. In Figure 3 ln α^3 is graphed against the temperature. The expansion with temperature is apparent. This was done in chlorodecane.

A calculation of the expansion parameter α was also made in order to determine environmental effects. Besides the systems given by Orofino,[1] ethylcyclohexane,[12] decalin,[14] and dioctyl phthalate[15] were also used. At temperatures that were not examined directly, the intrinsic viscosities were obtained from a least square determination of the ln [η] against temperature. The values of the parameter ψ_1 were either calculated from eq. (9) by using Orofino's data or through the use of B as given by Berry.[15] This work was limited to the sample with molecular weight of 392,000. The results of this calculation are also shown graphically in Figure 3. Again, the data are for chlorodecane, since it had the greatest span of temperature.

A direct evaluation of TC from [η]$_\Theta$ by means of eq. (6) was not possible. In Figure 4 the data for all four fractions are shown along with Orofino's results.[1] The lines are drawn by the method of least squares. The results
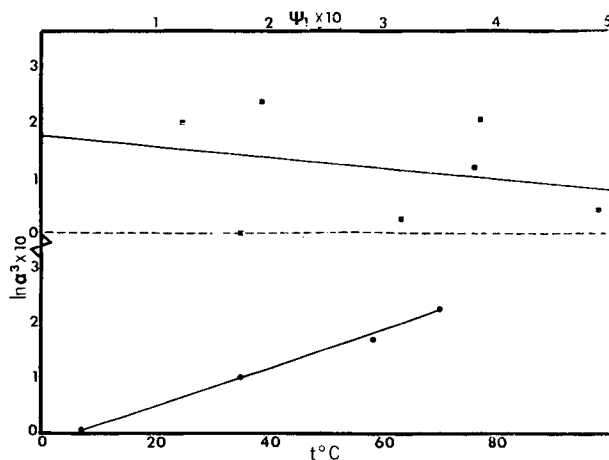

Fig. 3. Variation of (bottom) ln α^3 with temperature and (top) ln α^3 with the parameter ψ_1. In both cases, the lines are drawn by the best least-squares line through all the data.

did not fall into solvent types as reported by Chiang for linear polyethylene[16] using hydrocarbons and higher alcohols as solvents.

The dependence of $\ln [\eta]_\Theta$ and $\ln K_\Theta$ on ψ_1 and $\psi_1{}^\Theta$ is shown in Figures 5 and 6. No calculation attempting to separate the temperature and environmental effects was made.

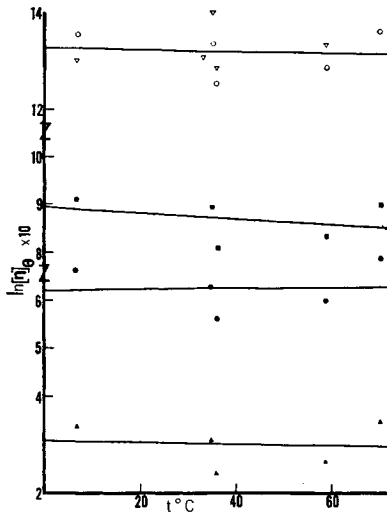Fig. 4. M_n = Variation of $\ln [\eta]_\Theta$ with Θ: (O) 392,000; (■) $\bar{M}_n$ = 160,000; (●) $\bar{M}_n$ = 97,200; (▲) $\bar{M}_n$ = 51,000; (▽) Orofino's data.
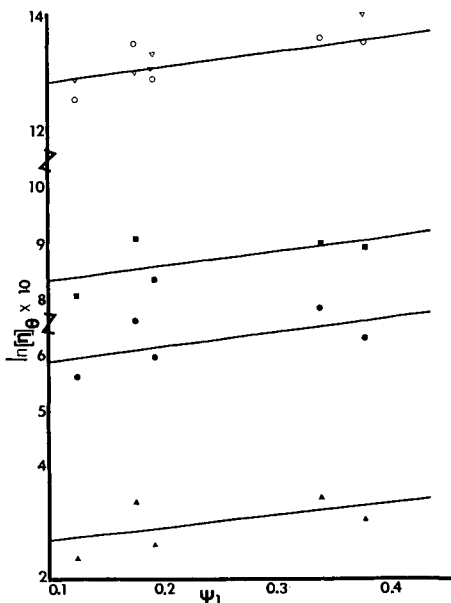

Fig. 5. Variation of $\ln [\eta]_\Theta$ with the parameter ψ_1: (O) $\bar{M}_n$ = 392,000; (■) $\bar{M}_n$ = 160,000; (●) $\bar{M}_n$ = 97,200; (▲) $\bar{M}_n$ = 51,000; (▽) Orofino's data. Least-square lines through all the points.
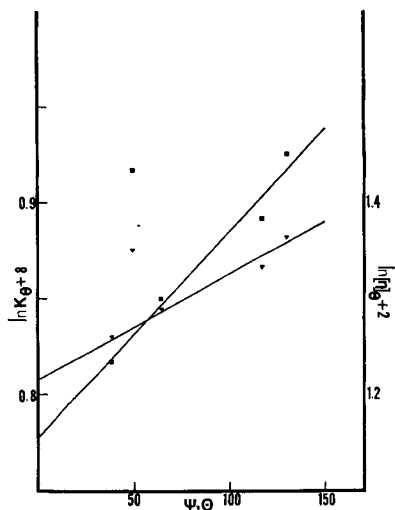
Fig. 6. The variation of ln K_Θ and ln $[\eta]_\Theta$ with the parameter $\psi_1{}^\Theta$: (■) ln K_Θ; (▼) ln $[\eta]_\Theta$. Lines shown omitting point at $\psi_1{}^\Theta = 49$.

TABLE IV

Intrinsic Viscosity of Toluene Solutions

Molecular weight	$[\eta]$, dl./g.						T_m, °C.
	6.6°C.	25°C.	34.8°C.	45°C.	58.6°C.	70°C.	
51,000	0.296	0.298	0.301	0.294	0.288	0.287	32.2
97,200	0.456	0.457	0.468	0.443	0.438	—	32.8
160,000	0.637	0.661	0.695	0.685	0.650	0.650	37.3
392,000	1.280	1.300	1.380	1.390	1.282	1.281	41.0

A detailed temperature study was made in toluene with the four poly-styrene fractions. The results are given in Table IV. These values are not in accord with Berry's statement that there was no temperature dependence of $[\eta]$ in toluene.[15] A careful study indicates that perhaps even a slight maximum appears as shown for the system poly(methyl meth-acrylate)–acetone.[17] The temperature of the maximum point is given in the 8th column of the table. An attempt to evaluate TC from these data was questionable but the results clearly point to what Bianchi states[11] and what Orofino and Ciferri[3] insinuate in the statement: "In addition, it is impor-tant to realize that temperature coefficients of polymer dimensions as expressed by $d \ln \langle r_0{}^2 \rangle / dT$ may not be constant over an extended interval of temperatures; there are already some indications of this effect, involving even a change in sign of TC over a range of temperatures. It is therefore necessary to refer the value of TC to the experimentally studied tempera-ture range." This change in sign of TC may be taking effect in some of the data shown in Table I at the higher temperatures and lower molecular weights.

With all the data, the quantity $(\alpha^5 - \alpha^3)/M^{1/2}$ was calculated. In no instance was this ever a constant, even in a Θ solvent above the Θ temperature. It was of interest however, to examine some recent excluded volume calculations of Flory and Fisk.[18] In chlorodecane, diethyl malonate, and chlorododecane, only the fraction with molecular weight 392,000 was used, the reason for this being that ψ_1 given by Orofino had a similar molecular weight. In treating the toluene data, the Θ temperature was taken to be
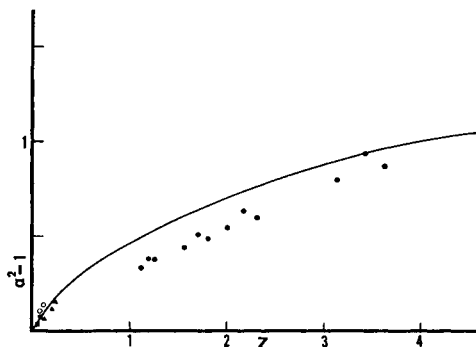

Fig. 7. Examination of eq. (12): (O) diethyl malonate; (▲) chlorodecane; (■) chlorododecane; (●) toluene.

137°K. (after Bianchi), basically because it was given to 5%.[19] The original value of 160°K. of Fox and Flory had an uncertainty of 50°K. The thermodynamic parameter ψ_1 was also used from Bianchi work for the same reason. However this value was adjusted to compare with similar values determined from the second virial coefficient. Krigbaum[20] has shown that the ψ_1 values from intrinsic viscosity are lower than those from the virial coefficient. The value of Z can be given by

$$Z = X^{1/2}\beta \left(\frac{X}{4\pi\langle S_0^2\rangle}\right)^{3/2} \tag{10}$$

where X is the number of chain segments, $\langle S_0^2\rangle$, the mean square radius of gyration, and β, the excluded volume. In terms of the parameters ψ_1 and Θ,

$$\beta = 2(V_s^2/V_1)\psi_1(1 - \Theta/T) \tag{11}$$

where V_s and V_1 are the molecular volumes of the segment and the solvent, respectively.

At 25°C., Berry,[14] using the osmotic pressure data of Bawn[21] on polystyrene in toluene, calculates that $Z = 5.3 \times 10^{-3}M^{1/2}$. By using this relationship, the ψ_1 value was adjusted to 0.45 from 0.15 as given by Bianchi. This threefold increase is in line with the values reported by Krigbaum in other systems.[20] The results of this calculation are shown graphically in Figure 7 with the line drawn from the theory

$$(\alpha^5 - \alpha^3)/z = 0.648h(z/\alpha^3) \tag{12}$$

with

$$h(\zeta) = 1 + 0.969/(1 + 10\zeta)^{2/3} \qquad (13)$$

The agreement is satisfactory.

In the work presented, an attempt was made to examine the various aspects and methods suggested for the determination of the temperature coefficient of polystyrene. It is believed that the results indicate a strong dependence upon molecular weight and the solvent and a smaller dependence upon the temperature range in which the measurements were made.

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