Thermal variation of the apparent specific volume of polystyrenes in solution

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A new approach to the polymer interactions inside and outside the coil is discussed and we explain the experimental variation of the apparent specific volume of polystyrene in good and in θ-solvents. In cyclohexane we define two very different regions above and below the θ-point. For the region above the θ point we calculate the thermal dilation coefficient, $\bar{\alpha}$, subtracting the intramolecular segment density effect. We relate $\bar{\alpha}$ to the external degrees of freedom of the chain starting from the Prigogine theory of polymer solutions. We first considered the intramolecular segment interactions of the coil in the dilute solution.

INTRODUCTION

Recent work[1,2] has provided new information on the apparent specific volume, ϕ_2, of polymers in solution and, in particular, has established the influence of molecular weight (above 2×10^4) and intramolecular segment density inside the macromolecular coil. A first hypothesis can explain these dependences by the modification of the packing of solvent molecules contained inside the coil when the intramolecular concentration of polymer increases with creation of free volume. But recently, Privalko *et al.*[3,4] assumed the existence of organized domains in macromolecular solutions.

In a previous paper[5], we have shown through the study of polystyrenes in mixed solvents, that the relation between the apparent specific volume of the polymer and the intramolecular segment density depends on the molar volume of the solvent. This result allows us to complete the description of the phenomenon. In fact, we can predict that the packing of the solvent molecules inside the coil varies with their shape and size.

In the present paper, concerned with the thermal variation of ϕ_2, we provide further information which confirms our interpretation.

It is generally assumed[6] that the thermal dilation coefficient $\bar{\alpha}$ [$\bar{\alpha} = (1/\phi_2)\mathrm{d}\phi_2/\mathrm{d}T$] of a polymer in solution is equal to that of the pure liquid polymer; the number of macromolecular external degrees of freedom being considered as similar in the both states. Nevertheless, we know some examples for which this assumption is not verified. For example, in the case of polystyrenes, data in the literature provide values of $\bar{\alpha}$ equal to $5 \times 10^{-4}\,\mathrm{d}^{-1}$ [7,8], $2.5 \times 10^{-4}\,\mathrm{d}^{-1}$ [9] and $18 \times 10^{-4}\,\mathrm{d}^{-1}$ [10] for pure liquid polystyrenes, for polystyrenes in benzene and for polystyrenes in a mixture of benzene–methanol, respectively. This problem, in fact, has not been studied a great deal.

The first results of François *et al.*[1,2] allow us to expect an influence of the change in the polymer configuration with temperature on the thermal dilation coefficient. It is well known[11] that for a polymer dissolved in a good solvent, the macromolecular dimensions do not vary with temperature.

The first aim of the present work is to compare the variation of apparent specific volume of polystyrenes of different molecular weight against temperature for solvents of different thermodynamic quality. We have explained the observed differences by taking into account the intramolecular segment density variation. The second part will be a discussion about the $\bar{\alpha}$ values.

EXPERIMENTAL

The polystyrene samples were prepared by anionic polymerization. The molecular weights of these samples as well as the nature of the initiator used for their polymerization are reported in *Table 1*.

The polymer concentrations ranged between 0.5 and 1.5×10^{-2} g/g. The corresponding accuracy in the determination of ϕ_2 was $\pm 2 \times 10^{-4}$ cm^3/g.

All the density measurements were carried out with a Kratky densimeter[12] improved in our laboratory[13]. The experimental details of measurements at variable temperatures have been given in a previous paper[13]. *Figure 1* gives some results of the variation of the density of cyclohexane and benzene *versus* temperature in comparison with the literature data. We can remark on the reproducibility of our different experimental investigations and the good agreement with literature data.

Figure 2 represents the variation of ϕ_2 *versus* temperature for PS 1 obtained with two different experiments and shows the good reproducibility of the measurements.

Table 1 Characteristics of the polymers studied

Polymer No.	Initiator	M_n	M_w
PS 1749	Butyllithium	–	1.4×10^6
PS 3	Cumylpotassium	6.6×10^5	7×10^5
PS 1	Cumylpotassium	1.35×10^5	1.4×10^5
PS 1278	α-Methylstyrene tetramer	53 000	74 000
PS 31	α-Methylstyrene tetramer	73 000	–
PS 1903	α-Methylstyrene tetramer	4150	4990

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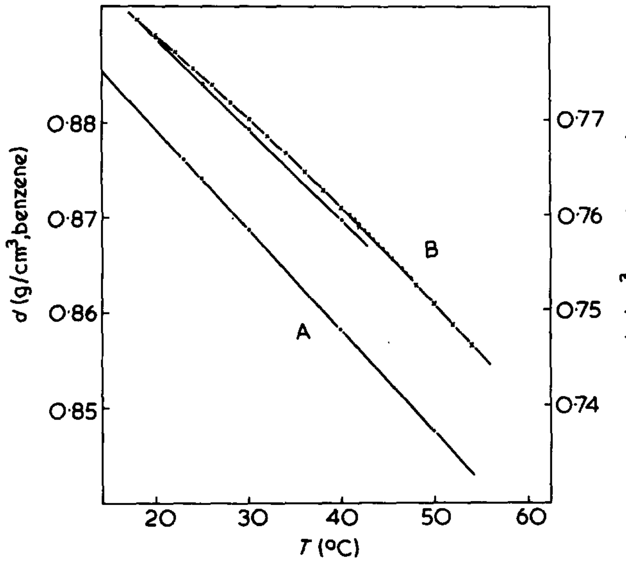

Figure 1 Variations of the density of benzene A, and cyclohexane B, with temperature determined by our measurements and compared with literature data. +, x, our results; ●, literature data[21]

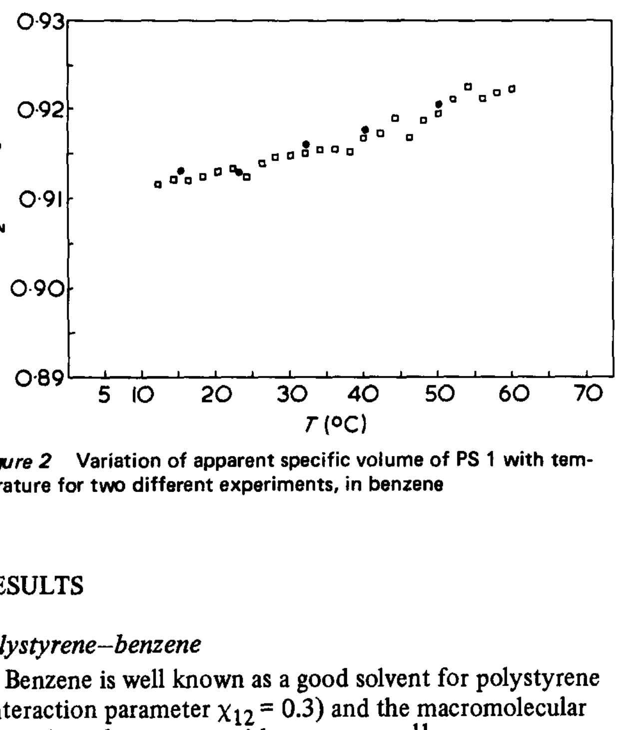

Figure 2 Variation of apparent specific volume of PS 1 with temperature for two different experiments, in benzene

RESULTS

Polystyrene–benzene

Benzene is well known as a good solvent for polystyrene (interaction parameter $\chi_{12} = 0.3$) and the macromolecular dimensions do not vary with temperature[11].

For each of the studied polystyrenes, a linear variation of ϕ_2 as a function of T is observed (*Figure 3*). $\bar{\alpha}$ can be considered as constant in this range of temperature and its value does not depend on the molecular weight of the samples, which appear in *Table 2*. The mean value, $2.7 \times 10^{-4}\ \mathrm{d}^{-1}$, of $\bar{\alpha}$ is in good agreement with the value of $2.5 \times 10^{-4}\ \mathrm{d}^{-1}$, given by Boyer and Spencer[9] for polystyrene dissolved in toluene, a solvent of thermodynamic quality similar to that of benzene, and with values of $2.9 \times 10^{-4}\ \mathrm{d}^{-1}$, calculated by Hert and Strazielle[10] starting from measurements of refractive index increments for polystyrenes in benzene. Eskin *et al.*[4] have obtained $5 \times 10^{-4}\ \mathrm{d}^{-1}$ for $\bar{\alpha}$ for a polystyrene of 3×10^5 molecular weight, in toluene. If we compare these results to the data given by Fox and Flory[7] and Ueberreiter and Kaning[8], we find that the $\bar{\alpha}$ value of polystyrene in a such solvent is near to that of the amorphous polymer below T_g, we obtain $\bar{\alpha} = 2.5 \times 10^{-4}\ \mathrm{d}^{-1}$, which is quite different to that obtained for liquid polymer ($6 \times 10^{-4}\mathrm{d}^{-1}$). This fact is not consistent with the Bondi's[6] assertion, giving, for the polymers in solution, an $\bar{\alpha}$ value equal to 9/10 of that obtained for liquid polymers.

As a conclusion of this first study: (a) the variation of ϕ_2 for polystyrenes in a good solvent *versus* T is linear over the whole range of temperature; (b) $\bar{\alpha}$ does not depend on molecular weight; (c) $\bar{\alpha}$ is different from that of liquid polymers.

Polystyrene–butanone

For the second study, MEC was chosen for the following reasons.

The solvent–polymer interaction parameter, χ_{12}, is rather high ($\chi_{12} = 0.47$ at 25°C). The macromolecular coil is not as expanded as in benzene but its expansion remains constant with temperature. MEC is an athermic solvent and its molar volume is 90 cm^3, similar to that of benzene = 80 cm^3.

The results, obtained with the samples PS 1 and PS 1770, which are reported in *Table 2*, show a linear variation, $\phi_2 = f(T)$ and $\bar{\alpha} = 2.6 \times 10^{-4}\ \mathrm{d}^{-1}$, as for benzene.

Polystyrene–cyclohexane

Figure 4 gives the values of ϕ_2 as a function of T for five samples of polystyrenes PS 1903, PS 1770, PS 1, PS 3, PS 1749, of which characteristics are given in *Table 1*.

In comparison with the results obtained for the two preceeding solvents, the curves are more complex in this case and we can distinguish two different regions of temperature.

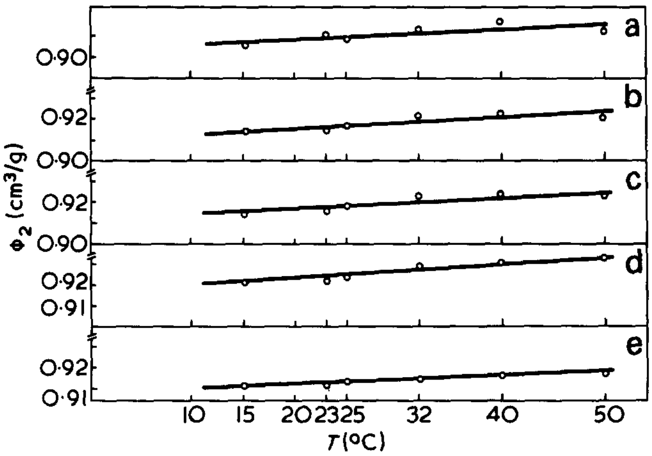

Figure 3 Variations of apparent specific volume of polystyrenes with temperature, in benzene. (a) PS 1749; (b) PS 1278; (c) PS 31; (d) PS 1903; (e) PS 1

Table 2 Values of $\bar{\alpha}$ for polystyrenes dissolved in benzene, butanone and cyclohexane. The values for cyclohexane have been calculated from: $\bar{\alpha} = (1/\phi_{20})(\mathrm{d}\phi_{20}/\mathrm{d}T)$

Polymer No.	α calc. (d^{-1})		
	Benzene	Butanone	Cyclohexane
PS 1749	2.6×10^{-4}	–	8.8×10^{-4}
PS 3	–	–	8.6×10^{-4}
PS 1	2.5×10^{-4}	2.61×10^{-4}	7.9×10^{-4}
PS 1278	2.6×10^{-4}	–	–
PS 1770	–	2.73×10^{-4}	8.6×10^{-4}
PS 31	2.7×10^{-4}	–	–
PS 1903	2.9×10^{-4}	–	8.7×10^{-4}

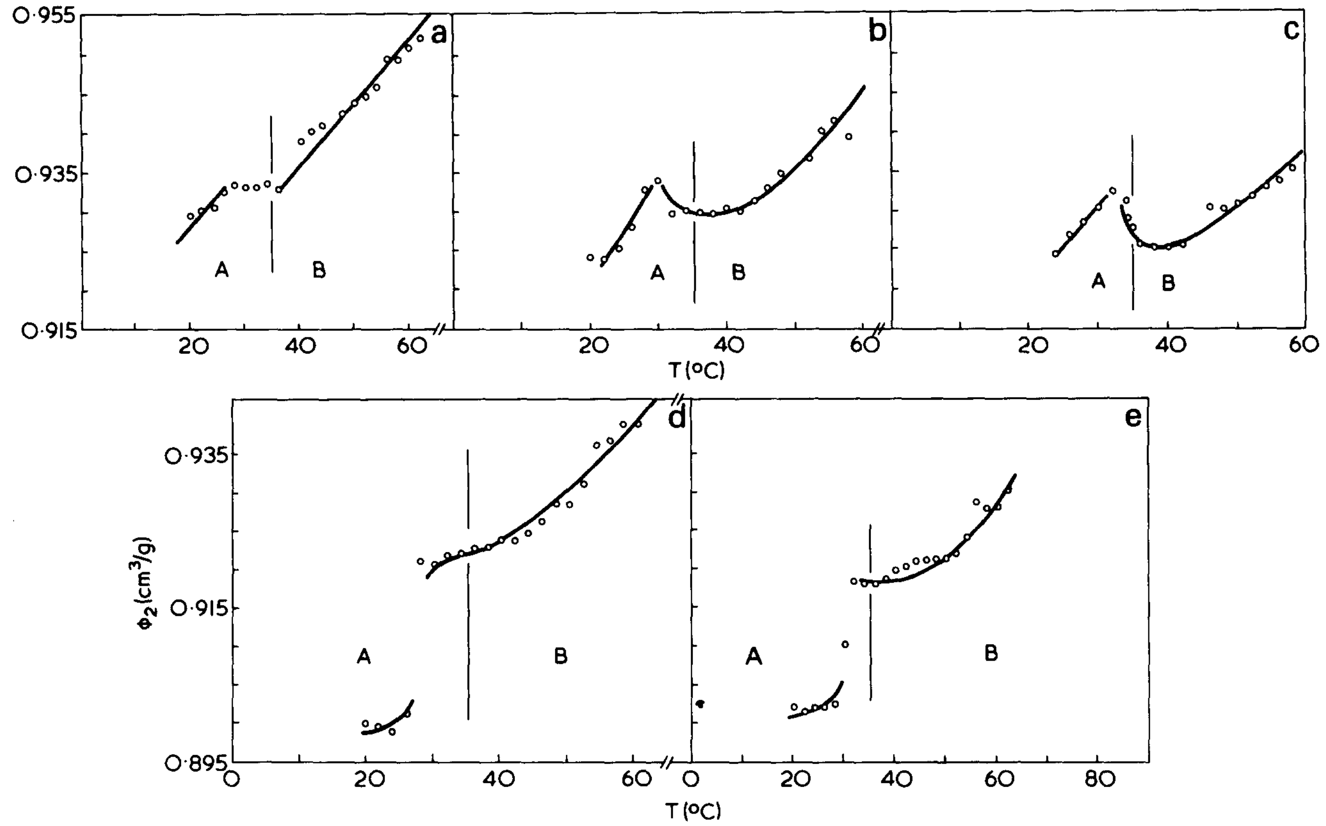

Figure 4 Variation of apparent specific volume of polystyrenes 1–5 with temperature, in cyclohexane (a) PS 1903 + cyclohexane; (b) PS 1770 + cyclohexane; (c) PS 1 + cyclohexane (d) PS 3 cyclohexane (e) PS 1749 + cyclohexane

(1) A region A, above the θ-point, where ϕ_2 increases with temperature, the observed variations depending on molecular weight. The function $\phi_2 = f(T)$ is linear for polymers 1903 and 1770 of molecular weights equal to 4.5×10^3 and 1.4×10^4, respectively.

When the molecular weight of the samples increases, the curves become different from straight lines, $d\phi_2/dT$ being low for T near θ and increasing with T to attain an asymptotic value for 50°C. This effect is more pronounced for the higher molecular weight.

(2) A region B, below the θ-point. The curves present different features according to the molecular weight.

For high molecular weight (1.4×10^6 and 7×10^5), the polymer precipitates at temperatures slightly lower than the θ-point (32°C from Flory) and we observe, just below θ, a strong decrease of ϕ_2 which reaches low values varying slightly with temperature.

For intermediate molecular weight, as PS 1 ($M_w = 1.4 \times 10^5$), the critical miscibility temperature is given by Flory as 21°C, and we observe, when T decreases, starting from θ-point, successively, an increase of ϕ_2 and a decrease, with a slope lower than that observed for a high molecular weight sample.

For low molecular weights, below θ, we don't observe an increase of ϕ_2 with decreasing temperature but a plateau followed by a decrease of ϕ_2.

DISCUSSION

Influence of intramolecular segments density. Difference between a good and a θ- solvent

In the preceeding paper, we have been able to relate quantitatively the variations of ϕ_2 with simultaneous variations of the intramolecular segment density and of the molar volume of the solvent. The present results can be interpreted in the same way.

Generally, the variation of ϕ_2 of a given compound with T is due to the increase of the free volume of the molecule corresponding to its external degrees of freedom[6] and is approximately linear. It appears necessary for polymers to take into account the variations of the chain conformation and of the molar volume of the solvent, according to the empirical equation established by François *et al.*[2]:

$$\phi_2 = \phi_{20} + DV - B\exp(-C\langle v_3\rangle)$$

where V is the molar volume of the solvent, $\langle v_3\rangle$ the volume fraction of the polymer inside the macromolecular coil and D, B and C constants equal to: 7.2×10^{-4}, 1.4×10^2 and 1.02×10^2 g^{-1}, respectively.

$\phi_{21} = (\phi_{20} + DV)$ corresponds to the apparent specific volume of polymers in a given solvent of low molecular weight ($M < 2 \times 10^4$) for which the effect of segment density vanishes[2].

The thermal dilation of non-polar liquids being 12×10^{-4} cm^3/d for benzene, MEC or cyclohexane, we can neglect the influence of the variation of the solvent molar volume.

The term $-B\exp(-C\langle v_3\rangle)$ in this equation does not vary with temperature for benzene and MEC as solvents and the variation of ϕ_2 with T, not perturbed by the intramolecular concentration effect, should be linear as shown by experimental results. In the case of cyclohexane, the increase of the radius of gyration R_G with T leads to a decrease of the term $-B\exp(-C\langle v_3\rangle)$, an effect which is in opposition to the normal increase of volume of the polymer. Thus, according

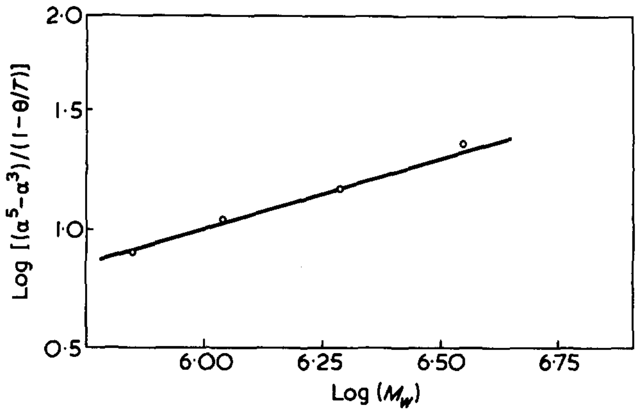

Figure 5 Plot of the Flory term $\alpha^5 - \alpha^3/1 - \theta/T$ *versus* log M_w, from experimental results of Decker[16], Candau[17] and Carpenter *et al.*[19]

to this relation, we can expect a non-linear variation of $\phi_2 = f(T)$, the discrepancies from straight lines depending on the temperature range and on the molecular weight of the polymer.

Region A

We have attempted to calculate, starting from equation (1) the effect of intramolecular concentration variation assuming that: (a) the A and B constants do not depend on temperature; (b) the discrepancies in the variation of $\phi_2 = f(T)$ from linearity are only due to the variation of the term $-B\exp(-C\langle v_3\rangle)$ and the variation of $\phi_{20} = f(T)$ should be linear, corresponding to the polymer properties independent of the segment density effect.

We consider that our hypothesis will be confirmed if this calculation allows us to determine a linear variation of ϕ_{20} against T. This approach is justified by the linear variation $\phi_2 = f(T)$ determined experimentally for good solvents with all the samples and for θ-solvent with samples of low molecular weight. In this last case, the variation $\langle v_3\rangle = f(T)$ is negligible.

The volume fraction of polymer inside the coil can be calculated by the following equation:

$$\langle v_3\rangle = 2C_M V/\phi_2 M^{0.5}\alpha^3$$

where M is the molecular weight and α the expansion factor of the macromolecular coil. C_M is the Flory constant:

$$C_M = 27\phi_2^2/[2^{2.5}(6\pi)^{1.5}N_A V(R_G^2/M)^{1.5}]$$

R_G is the radius of gyration. Its determination needs a good knowledge of the radius of gyration of the polymer at each temperature.

Theoretical. A Flory expression[11] can lead us to calculate $R_G = f(T)$ variations:

$$\alpha^5 - \alpha^3 = 2C_M\psi\left(1 - \frac{\theta}{T}\right)M^{0.5} \tag{2}$$

ψ is the entropic parameter for polystyrene diluted in cyclohexane (0.13 from Flory).

More recently, Daoud and Jannink[15] have established a phase diagram for polymers in solution and calculated different scaling laws for each domain, relating R_G to the molecular weight and the reduced temperature, $\tau = T - \theta/\theta$.

In our case, above θ-point, the radius of gyration of a polymer in dilute solution varies as $\tau^{2/5}$.

Experimental. The functions $R_G = f(T)$ have been determined from light scattering measurements for polystyrenes in cyclohexane by Decker[16], Candau[17], Zillox[18] and Carpentier *et al.*[19], the experimental results of these different authors being in good agreement.

In *Figure 5* we have plotted the Flory expression:

$$\log\left[\frac{\alpha^5 - \alpha^3}{1 - \left(\frac{\theta}{T}\right)}\right]$$

as a function of log$M$. The slope of 0.625 is different from the 0.5 value predicted by this theory.

The plot log $R_G = f(\log\tau)$ provides an exponent of the law $R_G = f(\tau)$ equal to 0.1 instead of 0.2 suggested by Daoud and Janninck[15] (*Figure 6*). Nevertheless, the same authors have verified the validity of their theory in the semidilute region by neutron scattering experiments.

We have preferred to determine an empirical law able to take into account the experimental data with an accuracy better than 4%:

$$\alpha^5 - \alpha^3 = 1.797 \times 10^{-3}M^{0.625}\left(1 - \frac{\theta}{T}\right) \tag{3}$$

Starting from equations (1) and (3), we have determined, for each temperature and each polymer studied, the values of ϕ_{20}. The results are reported in *Figures 7a–7e* in which we have also given the experimental data $\phi_2 = f(T)$. Whatever the molecular weight of the sample we obtain a linear variation $\phi_{20} = f(T)$. The slopes of the straight lines obtained do not depend on molecular weight as for the case of benzene. The calculated values (8.54×10^{-4} d^{-1}) of $\bar{\alpha}$ are reported in *Table 2*. We note a great difference with respect to the $\bar{\alpha}$ value in benzene.

We conclude that our interpretation of the apparent specific volume of polymer in solution is quantitatively able to explain some discrepancies in behaviour, taking into account the effects of intramolecular segment density, for $T > \theta$.

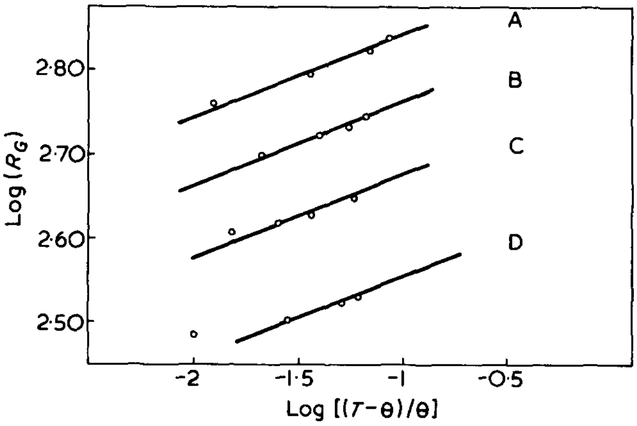

Figure 6 Plot of the logarithm of the radius of gyration *versus* the reduced temperature according to the expression of Daoud *et al.*[15]. A, $M_w = 3.2 \times 10^6$; B, $M_w = 1.95 \times 10^6$; C, $M_w = 1.1 \times 10^6$; D, M_w = 700 000

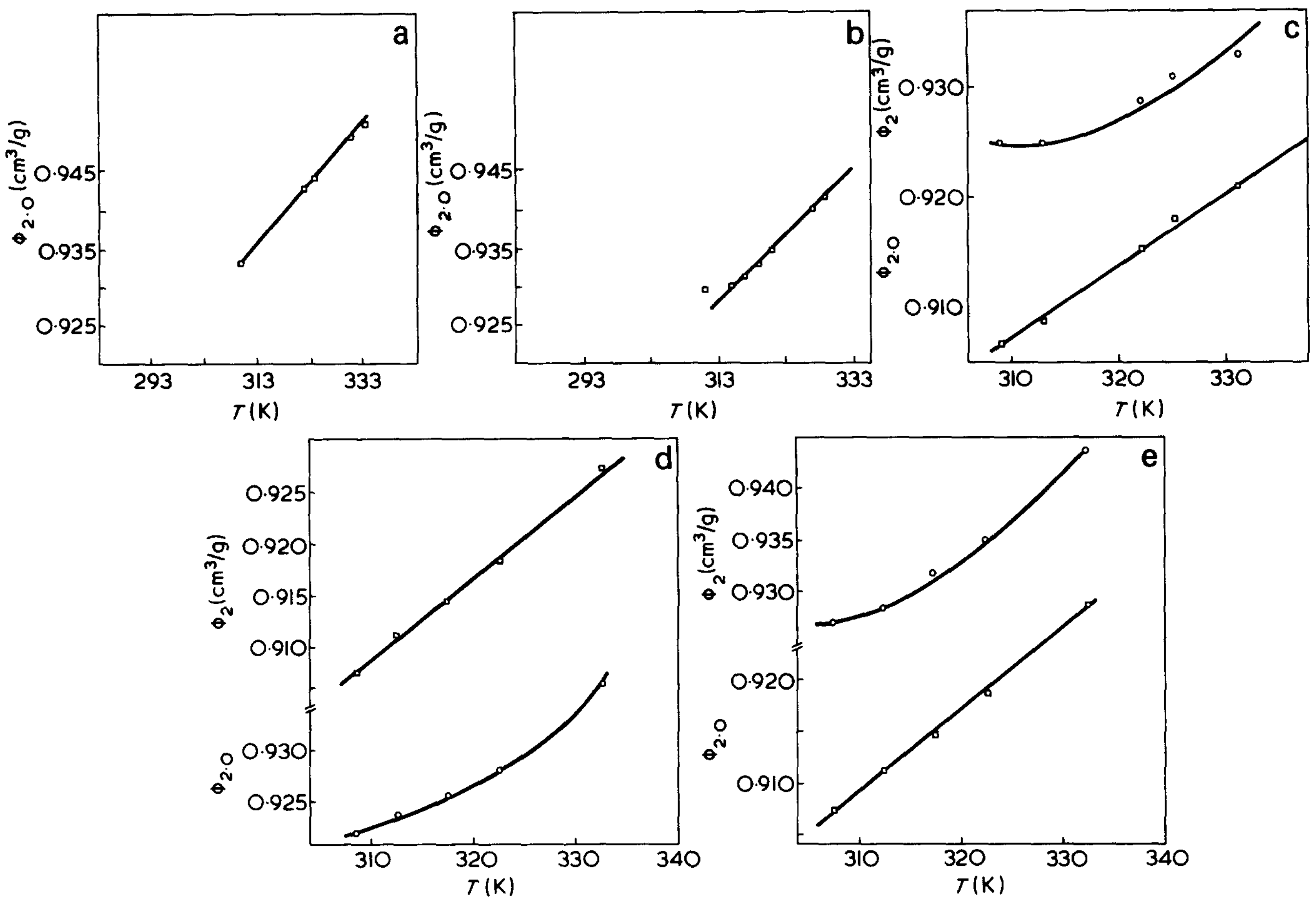

Figure 7 Comparison for all the polystyrenes studied of the variation of the apparent specific volume, ϕ_2, *versus* temperature with the variation of the corrected value ϕ_{20} *versus* temperature. (a) PS 1903; (b) PS 1770; (c) PSI, $\bar{\alpha} = 7.9 \times 10^{-4}$ d^{-1}; (d) PS 3, $\bar{\alpha} = 8.6 \times 10^{-4}$ d^{-1}; (e) PS 1749, $\bar{\alpha} = 8.8 \times 10^{-4}$

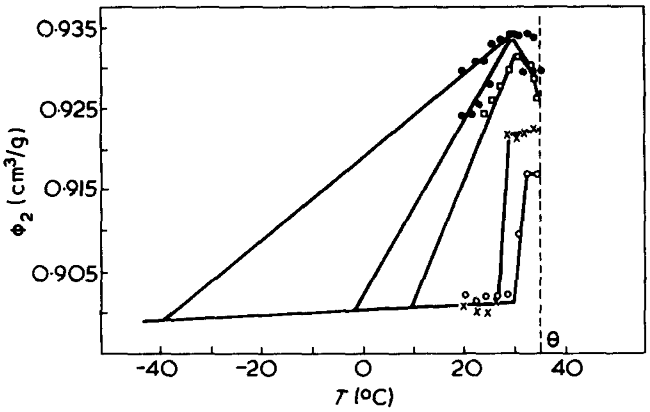

Figure 8 Variations of apparent specific volume of polystyrenes with temperature below the θ-point; ○, PS 1749; x, PS 3; □, PSA; ●, PS 1770

Region B

Below the θ-point, the variations with T of the macromolecular dimensions are not well known. It was thus difficult to use the same method of calculation in this case and we can only try to understand the experimental results following the same scheme.

On the same *Figure 8* we have plotted the variations of $\phi_2 = f(T)$ for all polymers studied. This Figure suggests these remarks.

For the samples PS 1749 and PS 3, we note a net change in this variation for temperatures equal to 30°C and 28°C respectively. These values correspond quite well to the precipitation temperatures, determined by Schulz and Flory[20], for the considered concentration of the solution.

The values of ϕ_2 obtained under these precipitation temperatures are similar for the two samples, 0.901 cm^3/g and lower than values 0.925 cm^3/g measured by Fox and Flory for amorphous polystyrenes. The precipitating polymer probably adopts a more compact configuration than a Gaussian coil in the amorphous state and we can assume that this ϕ_2 value corresponds to collapsed molecules. If this assumption is correct, the radius of gyration is proportional to $M^{1/3}$ and we could not expect a variation of ϕ_2 with molecular weight.

To verify this fact, we have determined by extrapolation (*Figure 8*) the temperatures at which ϕ_2 attains the curve corresponding to collapsed molecules for low molecular weight samples and compare them to the T_p temperatures of Schulz and Flory. *Table 3* reveals a correct agreement between the two series of values, except for the sample PS 1. We have only defined a tendency and it is clear that further experimental information is necessary for a valuable interpretation of the variation of ϕ_2 below the θ-point.

In this first part of our discussion, we have attempted to explain, following a scheme used to take into account the variations $\phi_2 = f(M)$ and $\phi_2 = f(\langle v_3 \rangle)$, the discrepancies between the thermal variations observed in a good solvent and a θ-solvent. We have been able to calculate values of $\bar{\alpha}$ which do not vary with molecular weight but are different depending on the solvent.

Table 3 Values of precipitation temperatures determined by Schultz and Flory[1] and from our density measurements for some polystyrenes in cyclohexane

Polymer	M_w	T_p (Flory–Schultz)[1] (°C)	T_p from density measurements[2] (°C)
1749	1.4×10^6	30.5	30
3	7×10^5	28.5	28
1	1.4×10^5	21	10
1770	1.4×10^4	7.8	−2
1903	5×10^3	−36	−40

Table 4 Number of external degrees of freedom, C

	C^1	C^2
Benzene[a]	1.27	1.43
Butanone[a]	1.40	1.37
Cyclohexane[a]	3.88	4.32
Toluene[b]	2.9	
Chloroform[b]	3.3	

[a] Our results C^1 obtained from Bondi's values of $\langle E_0\rangle$; C^2 obtained from $\langle E_0\rangle = \delta M\phi_2$; [b] Eskin's results[14]

External degrees of freedom

Eskin *et al.* have calculated the number of external degrees of freedom of the macromolecule from measurements of the thermal dilation coefficient of polymers in solution. The method, derived from Prigogine theory, has been established by Bondi and can be summarized as follows. The reduced temperature of polymers in solution, defined by Prigogine is expressed by $T^* = 5CRT/3\,\langle E_0\rangle$ as a function of temperature T, gas constant, R, the number of external degrees of freedom C, and $\langle E_0\rangle$ the average cohesion energy. The reduced thermal expansion coefficient, α^*, is then equal to $\alpha^* = 3\langle E_0\rangle\bar{\alpha}/5CR$.

It has been shown that in the range of temperatures studied $\alpha^* \sim 0.5$. We have then calculated the C values (reported in *Table 4*) for each solvent and for PSI, $\langle E_0\rangle$ being evaluated from Bondi's tables. Eskin has determined $\langle E_0\rangle$ as a function of δ where $\delta = (\delta_1\delta_2)^{1/2}$; δ_1 and δ_2 being the solubility parameters of polymer and solvent. $\langle E_0\rangle = \delta M\phi_2$. The C values obtained by this method are also reported in *Table 4*, with some values obtained by Eskin for PS ($M_w = 3.5 \times 10^5$) in other solvents.

The important value of $\bar{\alpha}$ obtained for cyclohexane through this calculation corresponds to an apparently greater number of degrees of freedom for the polymer in this solvent. On the other hand, the polymer in benzene solution seems to possess a slight freedom of motion. It is nevertheless difficult to bring concluding assertions about the relation existing between the thermodynamic quality of the solvent and the motional freedom of the polymer. Eskin have suggested, according to the hypothesis of Lange[21], that the adsorption of benzene molecules on the macromolecule can explain the diminution of $\bar{\alpha}$ and C observed.

CONCLUSION

This study of the temperature effect on the apparent specific volume ϕ_2 of polystyrene in solution allows us to make the following conclusions.

(1) The influence of the intramolecular segment density plays a part in the variation of $\phi_2 = f(T)$ as it does, at a given temperature, for the variation $\phi_2 = f(M)$.

(2) The partial thermal dilation coefficient, α, is independent of the polymer molecular weight. This indicates that the segment density is the same whatever the temperature considered. One can deduce that this effect is not directly related to a difference in the mobility of the chain related to its molecular weight or its structure but is only due to the phenomenon of statistical packing of solvent molecules around the chain.

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REFERENCES

1 François, J. and Candau, F. *Eur. Polym. J.* 1973, **9**, 1355

2 François J., Candau, F. and Benoit, H. *Polymer* 1974, **15**, 618, 625

3 Privalko, V. P. and Lipatov, Y. *Makromol. Chem.* 1974, **175**, 641

4 Privalko, V. P., Lipatov, Y. S. and Lobodina, A. P. *J. Macromol. Sci. (B)* 1974, **11**, 441

5 Sarazin, D. and François, J. to be published

6 Bondi, 'Physical Properties of Molecular Crystals, Liquids and Gases', Wiley, New York, 1968

7 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581

8 Ueberreiter, K. and Kanig, G. *Z. Naturforscher (A)* 1951, **6**, 651

9 Boyer, R. P. and Spencer, R. S. *J. Polym. Sci.* 1948, **3**, 1

10 Hert, M. and Strazielle, C. *Eur. Polym. J.* 1973, **9**, 543

11 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953, Ch 8

12 Stabinger, H., Leopold, H. and Kratky, O. 'Digital densimeter for Liquids and Gases', Anton Paar, Graz, Austria, 1966

13 Sarazin, D., Le Moigne, J. and François, J. *J. Appl. Polym. Sci.* to be published; Sarazin, D. *Thesis* University of Strasbourg

14 Eskin, V. Ye and Koratkina, O. Z. *Polym. Sci. USSR* 1972, **14**, 2310

15 Daoud M. and Jannink, G. *J. Phys. (Paris)* 1976, **37**, 973

16 Decker, D. *Thesis* University of Strasbourg (1968)

17 Candau, F. *Thesis* University of Strasbourg

18 Zilliox, J. G. *Thesis* University of Strasbourg (1970)

19 Carpenter, D. K. and Krigbaum, *J. Phys. Chem.* 1955, **59**, 1166

20 Shultz, A. R. and Flory, J. P. *J. Chem. Phys.* 1953, **74**, 4760

21 Koglin, Vandenhoeck and Ruprecht, 'Kurzes Handbuch au Chemie', Gottingen