alanine) for studying the effect of the sense of the helix.

It is therefore necessary to establish that the polypeptide is helical. The conformations determining whether the polypeptide is helical or not should be confirmed by other methods such as circular dichroism (c.d.) and nuclear magnetic resonance (n.m.r.) since helical poly(amino-acids) with opposite senses show, unfortunately, almost the same amide bands as found for the random coil polypeptides (at about 1660 and 1550 cm^{-1}).

C.d., n.m.r. and X-ray results can also give an indication of conformation. However, the c.d. spectra of aromatic polypeptides such as poly(Phe)[5], poly(Tyr)[6–8], poly(Trp)[9,10] and poly(Dopa)[11] are very anomalous and give little information about their helical sense since the $n-\pi^*$ peptide transition involves the contribution of the ^1L_a and ^1L_b transitions of the substituted benzenes in the Platt notation[12–14]. The n.m.r. spectrum is not always easy to measure in some solvents such as dioxane, dimethyl sulphoxide and trimethyl phosphate. X-ray analysis is elaborate and it is difficult to obtain information about the helical sense. The infra-red method has an advantage over c.d. in certain circumstances; that is, when the polypeptide has an aromatic side chain as described above and the c.d. spectrum of the polypeptide cannot be measured in the u.v. region owing to high absorption of the solvent. Because of the widespread use of infra-red techniques in the study of conformations of both polypeptides and proteins, we feel that the technique we have described here represents a facile method of characterization of the sense of helical conformation.

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Effect of concentration and temperature on the partial specific volume of a polystyrene sample in *trans*-decalin

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INTRODUCTION

The accuracy of molecular weight, frictional coefficient and other related data obtained from sedimentation velocity, diffusion and sedimentation equilibrium measurements on solutions of macromolecules is often restricted by a lack of accurate partial specific volume data, especially when studies are extended to higher concentrations. The partial specific volume, v_2, is not only a characteristic parameter of a certain macromolecule, it may also depend on solvent, concentration[1–5] and temperature[4,6,7].

Recently both the concentration and temperature dependence of the frictional coefficient obtained from sedimentation velocity measurements[8] were studied in wide ranges for the system polystyrene/*trans*-decalin[9]. In order to evaluate the frictional coefficient over the entire concentration and temperature interval in an unambiguous way, the concentration and temperature dependence of the partial specific volume of the solute was needed. Therefore specific volume measurements on solutions of a polystyrene sample in *trans*-decalin in the temperature range 20°–40°C and for mass fractions, w_2, ranging from 0.005 to 0.11 were performed.

Polystyrene in *trans*-decalin is a system with upper critical solution temperatures ranging from approximately 0° to 20°C; the actual temperature depending on the molecular weight of the sample[10]. From osmotic pressure measurements[11], it was observed that *trans*-decalin is a θ-solvent for polystyrene at 21°C (different θ-values have been reported in the temperature interval 20°–24°C[10,12–14]) and that it is considered to approach the good solvent region at about 40°C. Since the thermodynamic properties vary when going from θ- to good solvent conditions, it is plausible that this variation will affect the concentration dependence of the partial specific volume.

EXPERIMENTAL

A polystyrene sample with a narrow molecular weight distribution obtained from Pressure Chemical Company (M = 390 000, $\bar{M}_w/\bar{M}_n \leqslant 1.10$, manufacturer's data for lot No. 3b) was used without further purification.

The solvent *trans*-decalin was obtained by converting a commercial mixture of the *cis*- and *trans*-isomers into the *trans*-form by use of aluminium chloride. The product was washed thoroughly with water and dried over sodium metal. The final purification was made by fractional distillation under reduced pressure in an atmosphere of nitrogen. The purity of *trans*-decalin used was determined as 99.5% by gas chromatography.

Table 1 Results from specific volume measurements on the system polystyrene/*trans*-decalin

t(°C)	v_{10} (10^{-3} m^3/kg)	A_1 (10^{-3} m^3/kg)	A_2 (10^{-3} m^3/kg)	$(v_2)_{w_2=0}$ (10^{-3} m^3/kg)	$(\partial v_2/\partial w_2)_{w_2=0}$ (10^{-3} m^3/kg)
20.0	1.15009	−0.2242	−0.044	0.9259	−0.088
25.0	1.15523	−0.2270	−0.038	0.9282	−0.076
30.0	1.16027	−0.2295	−0.031	0.9308	−0.062
35.0	1.16545	−0.231[illegible]	−0.027	0.9336	−0.054
40.0	1.17067	−[illegible]50	−0.023	0.9357	−0.046

All the solutions were prepared by weighing. After addition of solvent the polymer was allowed to swell for two days before stirring was started after which the stirring was continued for several days to ensure homogeneity of the solutions.

The specific volume measurements were carried out using a Kratky[15,16] digital densitometer (Model DMA 60 with measuring unit, DMA 601A. Paar KG. Graz, Austria). The precision in the measured specific volume values was estimated to be ±3 x 10^{-8} m^3/kg. The measurements were made on solutions with polymer mass fractions between 0.005 and 0.11 at temperatures of 20°, 25°, 30°, 35° and 40°C.

RESULTS

The expression[17]:

$$v_2 = v + (1 - w_2)\frac{\partial v}{\partial w_2} \tag{1}$$

reveals that the partial specific volume of the solute, v_2, can be evaluated if the specific volume of the solution, v, is known as a function of the composition, w_2. If the dependence of v on w_2 can be written as:

$$v = v_{10} + A_1 w_2 + A_2 w_2^2 \tag{2}$$

where v_{10} is the specific volume of the solvent and A_1 and A_2 are coefficients to be determined, it follows that:

$$v_2 = v_{10} + A_1 + 2A_2 w_2 - A_2 w_2^2 \tag{3}$$

Here

$$v_{10} + A_1 \equiv (v_2)_{w_2=0}$$

and

$$2A_2 \equiv \left(\frac{\partial v_2}{\partial w_2}\right)_{w_2=0}$$

The specific volumes of *trans*-decalin, v_{10}, are given in *Table 1*. For the temperature interval 20°–40°C the following relation was found:

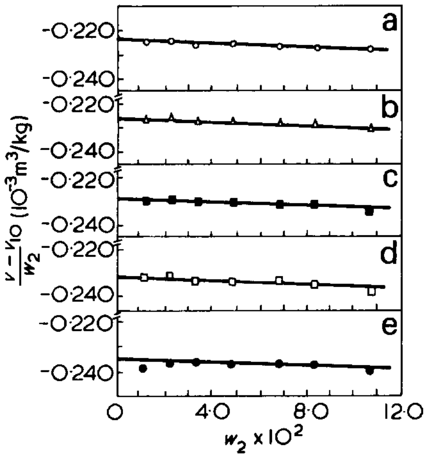

Figure 1 Reduced specific volume increment, $(v - v_{10})/w_2$, for solutions of polystyrene in *trans*-decalin *versus* mass fraction, w_2, at the temperatures: (a) 20°C (b) 25°C (c) 30°C (d) 35°C (e) 40°C

$$v_{10}(\text{m}^3/\text{kg}) = 1.15009 \times 10^{-3} + 1.027 \times 10^{-6}[t(°\text{C}) - 20.0]$$

In *Figure 1* the reduced specific volume increments, $(v - v_{10})/w_2$, are plotted *versus* w_2. The intercepts and slopes of the least squares fitted lines give the coefficients A_1 and A_2, respectively. The values are listed in *Table 1* together with the values of $(v_2)_{w_2=0}$ and $(\partial v_2/\partial w_2)_{w_2=0}$. From equation (3) calculated partial specific volumes of the solute are shown in *Figure 2*.

Figure 3 shows the temperature dependence of $(v_2)_{w_2=0}$ and $(\partial v_2/\partial w_2)_{w_2} = 0$.

DISCUSSION

As is evident from *Figure 2*, there is a small but significant concentration dependence of the partial specific volume of polystyrene in *trans*-decalin. A concentration dependence different from zero of the partial specific volume has for instance also been reported for polystyrene in toluene and in cyclohexane[4] and for some proteins in water[5]. On the other hand, there are also reports[18] where no concentration dependence has been observed. However, in the present study the partial specific volume decreases slightly with increasing w_2, whereas a contrary tendency was found for the systems polystyrene/toluene and polystyrene/cyclohexane[4]. This divergence could have its origin in the structural differences between the solvents studied. In connection with this it is interesting to mention that the refractive index increment for the present system also shows a significant concentration dependence[19]. Since the partial specific volume and the refractive index increment are quantities which are closely related[20–25], this supports a concentration dependence of the partial specific volume.

The partial specific volume at infinite dilution, $(v_2)_{w_2=0}$, increases with increasing temperature (see *Figure 3a*). The temperature derivative of $(v_2)_{w_2=0}$ is 5.0 x 10^{-7} m^3/kg K and this value is in agreement with those reported for other polymer–solvent systems[4,6].

Another interesting feature seen in *Figures 2* and *3b* is that the concentration dependence of the partial specific

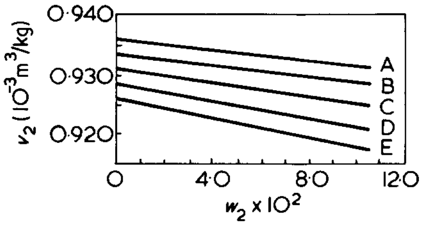

Figure 2 Partial specific volume, v_2, of polystyrene in *trans*-decalin *versus* mass fraction, w_2, according to the experimentally determined analytical relations (compare with the main text). A, 40°C; B, 35°C; C, 30°C, D, 25°C; E, 20°C

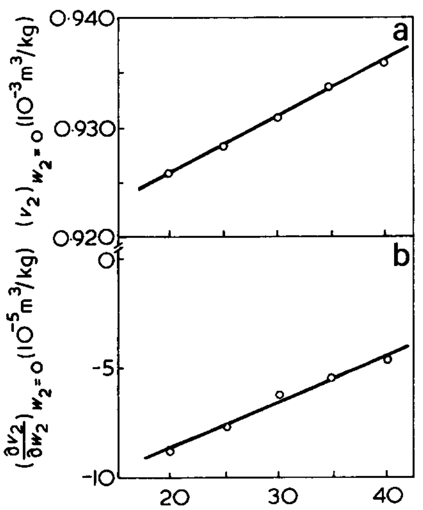

Figure 3 (a) Partial specific volume at infinite dilution, $(v_2)_{w_2=0}$, *versus* temperature, t, for the system polystyrene/*trans*-decalin. (b) $(\partial v_2/\partial w_2)_{w_2=0}$ *versus* temperature, t, for the system polystyrene/*trans*-decalin

volume decreases with increasing temperature. Since *trans*-decalin is a θ-solvent at about 20°C and could be considered as a thermodynamically good solvent at 40°C, this decrease could qualitatively be explained in the following way. The partial specific volume of the solute depends on both intra- and intermolecular segment–segment interactions and since these interactions are more pronounced in θ-solvents than in good solvents it is not unlikely that the concentration dependence of ν_2 should be stronger at θ-solvent conditions. For a more detailed analysis the nature of the solvent must also be taken into account.

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Apparatus for the manipulation of polymer-supported reagents

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There is now a considerable literature describing the preparation, purification and reactions of a wide variety of polymer-supported reagents[1]. The majority of these employ a bead form of polystyrene with a low crosslink ratio (1–2%) or of a macroporous nature, in order to minimize diffusional problems. Unfortunately such supports, particularly the latter type, can be somewhat mechanically unstable, and rapid magnetic stirring using a follower, or overhead stirring using a shafted impeller, can cause fragmentation of the spherical particles.

In order to overcome this problem we have produced two very simple devices for the rotation of flanged round-bottomed flasks, which produce highly efficient agitation, without mechanical damage. The first, *Figure 1*, is useful for reactions carried out at room temperature, and consists of a brass cage which can be mounted directly in the chuck of a standard geared-down laboratory stirrer motor. Two round brass plates, P, one having a central orifice, are connected by three long bolts, B, such that a flanged flask can be clamped firmly between them, within sections of a cork ring, R. The axis of rotation is adjusted to be ~25° to the vertical and a steady speed of ~50 rev/min maintained. The present device is suitable for 100 and 250 ml flasks, in which reactions involving up to ~30 g of polymer beads can be performed.

The second apparatus, *Figure 2*, consists of an early pulley-driven, P, rotary evaporator, adapted for a new role. Rotation takes place within concentric ground glass tubes, T, clamped at ~20° to the horizontal. Flanged flasks up to 1 litre can be employed, and heat applied using conventional baths if necessary. The reflux condenser is connected via an adaptor, A, which allows additions to be made to the flask while it is in motion.

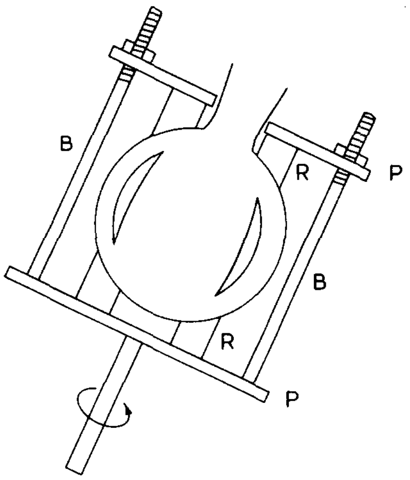

Figure 1 Rotating flask holder

Both devices can readily be used for air/moisture sensitive reactions.