Unperturbed dimensions of poly(β-hydroxybutyrate) in single and binary solvents

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Intrinsic viscosities $[\eta]$, mean-square radii of gyration $\langle S^2\rangle$ and weight-average molar masses $\bar{M}_w$ measured in 2,2,2-trifluoroethanol (TFE) at 298 K for several samples of poly(β-hydroxybutyrate) (PHB) have been used to derive the unperturbed dimensions $(\langle r^2\rangle_0/M)^{1/2}$ via different extrapolation procedures. Theta conditions, established turbidimetrically at 298 K in two binary solvents, viz. TFE/water (52.6/47.4 v/v) and chloroform/n-heptane (50.2/49.8 v/v), were confirmed by viscosity and light scattering, and enabled the unperturbed dimensions to be determined directly. The mean value of $(\langle r^2\rangle_0/M)^{1/2}$ by all procedures was 0.085 nm g$^{-1/2}$ mol$^{1/2}$, which, in conjunction with the corresponding quantity calculated on the basis of free rotation, affords a value of 1.67 for the steric factor σ. From values of $[\eta]$ in chloroform over the interval 280–318 K, a value of -1.5×10^{-4} K^{-1} was obtained for d ln $\langle r^2\rangle_0/\mathrm{d}T$. Differential refractometry and light scattering on solutions of PHB in the binary theta mixtures yielded high values for the coefficient of selective adsorption of the good solvent (TFE and chloroform) in each case.

(Keywords: poly(β-hydroxybutyrate); 2,2,2-trifluoroethanol; unperturbed dimensions; selective adsorption; theta conditions; radius of gyration; intrinsic viscosity)

INTRODUCTION

Poly(β-hydroxybutyrate) (PHB), an industrially useful polymer that can be produced by bacterial fermentation[1] and also by synthetic procedures[2], has the following repeating unit:

$$-\mathrm{O{-}CH(CH_3){-}CH_2{-}CO}-$$

It has been the subject of many investigations regarding its properties in the solid state. Of the few liquids that dissolve this polymer, 2,2,2-trifluoroethanol (TFE) is the best solvent thermodynamically, and dissolution in it occurs without degradation. Relatively few studies have been made on the behaviour of PHB in solution. The main findings of these have been summarized and discussed in relation to our recent investigations by light scattering and viscometry[3], which indicated that the conformation in solution is that of a random coil. As far as we can ascertain, the theta (θ) conditions have not been established for PHB. Moreover, although sufficient experimental data on PHB in good solvents have been obtained[4,5] to allow the unperturbed dimensions (*UD*) to be evaluated indirectly, this procedure has not in fact been implemented. *UD* is expressed as $(\langle r^2\rangle_0/M)^{1/2}$ where $\langle r^2\rangle_0$ is the mean-square end-to-end distance in the unperturbed state and M is the molar mass.

The major portion of the present communication is focused on the determinations of (a) *UD* indirectly from our previous data on PHB in TFE, (b) θ conditions and hence the *UD* directly and (c) the temperature coefficient of the *UD*, i.e. d ln$\langle r^2\rangle_0/\mathrm{d}T$.

Unless specifically indicated otherwise, the solvent and temperature are TFE and 298 K respectively and the wavelength of light *in vacuo* (λ_0) is 633 nm.

EXPERIMENTAL

Materials

The source and characterization of the eight PHB samples (designated S1–S8) have been reported in a previous communication[3] in which light scattering in TFE yielded values of the weight-average molar mass $\bar{M}_w$ ranging from 20.9 kg mol^{-1} for S1 to 929 kg mol^{-1} for S8, the corresponding values of the root-mean-square radius of gyration $\langle S^2\rangle_z^{1/2}$ increasing from 14 to 61 nm. Values of the second virial coefficient A_2, the polydispersity indices $\bar{M}_w/\bar{M}_n$ and the intrinsic viscosities $[\eta]$ in TFE were also given[3].

For studies in binary solvents the relevant liquids were dried and distilled and the water was doubly distilled.

Procedures

Light scattering and differential refractometry measurements were conducted on instruments modified for use at 633 nm as described previously[6,7]. The procedure for determining the specific refractive index increments in binary solvents at constant chemical potential of diffusible low-molar-mass components, $(\mathrm{d}n/\mathrm{d}c)_\mu$, has also been described in one of our earlier publications[8].

For each of the two binary solvent systems, TFE/water and chloroform/n-heptane, the method of Cornet and Ballegooijen[9] was employed to determine the volumetric θ composition. Essentially, the volume fraction of non-solvent ϕ_{ns} (water or n-heptane) at the onset of faint turbidity is noted for solutions of different concentration expressed as volume fraction of polymer ϕ_p, the apparatus[10] being maintained at 298 K. Normally the turbidity point can be taken as that at which the fine rulings on

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graph paper placed behind the tube are just indiscernible. However, detailed examination showed that this led to a marginally small overestimate of the required volume of non-solvent. Accordingly the turbidity point was recorded consistently at a very slightly smaller (ca. 1 drop) volume of non-solvent. The examination referred to consisted of adopting both the original and modified criteria of turbidity to obtain the relevant plots and resultant, possible θ compositions. Solutions were made up in each of these possible θ compositions and intrinsic viscosities were measured for all samples. Only the modified criterion of turbidity afforded finally a solvent composition for which $[\eta]/M^{1/2}$ was constant.

RESULTS AND DISCUSSION

Unperturbed dimensions in 2,2,2-trifluoroethanol

From the values of $[\eta]$ and $\bar{M}_w$ in TFE, the *UD* were derived via five different extrapolation procedures, viz. those of Stockmayer and Fixman[11] (SF), Ueda and Kajitani[12] (UK), Cowie[13] (C), Kurata and Stockmayer[14] (KS) and Flory and Fox[15] (FF). The relevant plots yielded values of K_θ from which $(\langle r^2\rangle_0/M)^{1/2}$ was calculated via equation (1), in which a value of 2.5×10^{23} mol^{-1} was taken for the Flory constant Φ:

$$K_\theta = \Phi(\langle r^2\rangle_0/M)^{3/2} \qquad (1)$$

An example of one of these plots is shown in *Figure 1*.

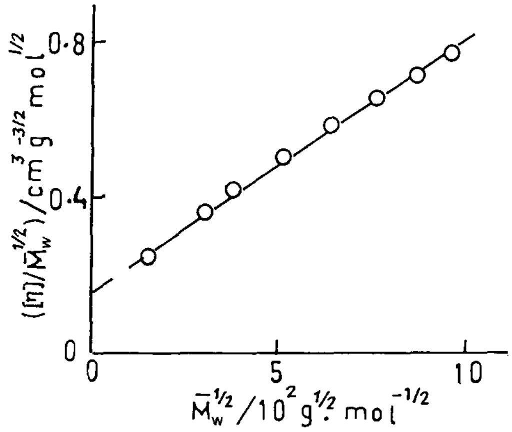

Figure 1 SF plot for PHB in TFE at 298 K

The values of K_θ and $(\langle r^2\rangle_0/M)^{1/2}$ listed in *Table 1* indicate that all these extrapolation procedures afforded good accord among the derived *UD*, the mean value being 0.085 nm g$^{-1/2}$ mol$^{1/2}$. Although four additional extrapolation plots were examined (Dondos and Benoit[16], Bohdanecký[17], Berry[18] and Inagaki *et al.*[19]), details are omitted here because they yielded widely discordant values of K_θ (and hence *UD*), which were all considerably smaller than those presented in *Table 1*.

Three extrapolation procedures utilizing values of $\bar{M}_w$ and the weight-average mean-square radius of gyration $\langle S^2\rangle_w$ in TFE were also employed. For this purpose the directly measured values of $\langle S^2\rangle_z$ were converted via equation (2) in which the polydispersity index h is defined[20] in equation (3):

$$\langle S^2\rangle_w = \langle S^2\rangle_z/[(h+2)/(h+1)] \qquad (2)$$

$$h = 1/[(\bar{M}_w/\bar{M}_n) - 1] \qquad (3)$$

The relevant equations for the plots were derived on the basis of the theories for the excluded-volume parameter Z as a function of the chain expansion factor α due to Kurata, Stockmayer and Roig[21] (KSR), Stockmayer's modification[22] of the expression of Flory[23] (Flo.), and Fixman[24] (Fix.). In the same sequence the forms of the extrapolation plots become:

$$\langle S^2\rangle_w/\bar{M}_w = \langle S^2\rangle_{0w}/\bar{M}_w + 0.0286Bg(\alpha)\bar{M}_w/\langle S^2\rangle_w^{1/2} \qquad (4)$$

where $g(\alpha) = 8\alpha^3/(1+3\alpha^2)^{3/2}$

$$\langle S^2\rangle_w/\bar{M}_w = \langle S^2\rangle_{0w}/\bar{M}_w + 0.056B(\langle S^2\rangle_{0w}/\bar{M}_w)(\bar{M}_w^2/\langle S^2\rangle_w^{3/2}) \qquad (5)$$

$$\langle S^2\rangle_w/\bar{M}_w = \langle S^2\rangle_{0w}/\bar{M}_w + 0.0299B(\langle S^2\rangle_{0w}/\bar{M}_w)^{-1/2}\bar{M}_w^{1/2} \qquad (6)$$

In equations (4)–(6) the quantity B contains, *inter alia*, the partial specific volume of polymer and the molar volume of solvent. All three plots afford $\langle S^2\rangle_{0w}/\bar{M}_w$ as the intercept. The plot according to equation (4) is actually an iterative procedure, which involves calculation of α (and hence $g(\alpha)$) after $\langle S^2\rangle_{0w}/\bar{M}_w$ has been obtained. In principle the procedure is repeated until no change is obtained in $\langle S^2\rangle_{0w}/\bar{M}_w$ after successive plots involving new values of $g(\alpha)$. In practice one iteration was sufficient in this case.

An example of one of the plots involving $\langle S^2\rangle_w$

Table 1 Unperturbed dimensions $(\langle r^2\rangle_0/M)^{1/2}$ of PHB derived from extrapolation procedures in TFE and directly in binary θ solvents at 298 K

Plot[a]	Extrapolation (E) or direct (D)	Relevant parameters	Solvent	K_θ (cm^3 g$^{-3/2}$ mol$^{1/2}$)	$(\langle S^2\rangle_0/M)$ (10^{-3} nm^2 g^{-1} mol)	$(\langle r^2\rangle_0/M)^{1/2}$ (nm g$^{-1/2}$ mol$^{1/2}$)
SF	E	$[\eta]$, $\bar{M}_w$	TFE	0.160	–	0.086
UK	E	$[\eta]$, $\bar{M}_w$	TFE	0.145	–	0.083
C	E	$[\eta]$, $\bar{M}_w$	TFE	0.146	–	0.084
KS	E	$[\eta]$, $\bar{M}_w$	TFE	0.160	–	0.086
FF	E	$[\eta]$, $\bar{M}_w$	TFE	0.149	–	0.084
KSR	E	$\langle S^2\rangle$, $\bar{M}_w$	TFE	–	1.52	0.096
Flo.	E	$\langle S^2\rangle$, $\bar{M}_w$	TFE	–	1.44	0.095
Fix.	E	$\langle S^2\rangle$, $\bar{M}_w$	TFE	–	1.55	0.093
MH	D	$[\eta]$, $\bar{M}_w$	TFE/water (52.6/47.4 vol/vol)	0.149	–	0.084
MH	D	$[\eta]$, $\bar{M}_w$	Chloroform/n-heptane (50.2/49.8 vol/vol)	0.157	–	0.086

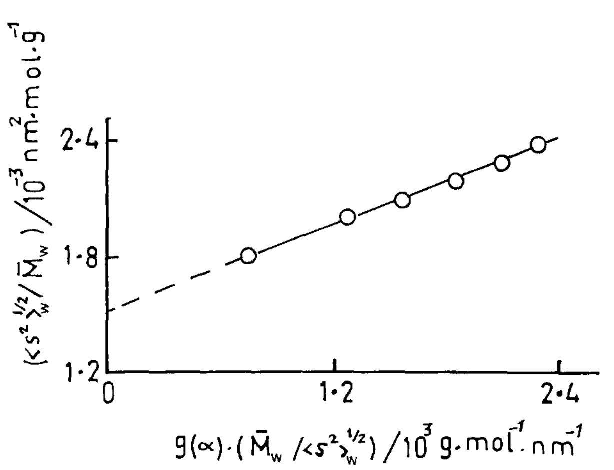

Figure 2 KSR plot for PHB in TFE at 298 K

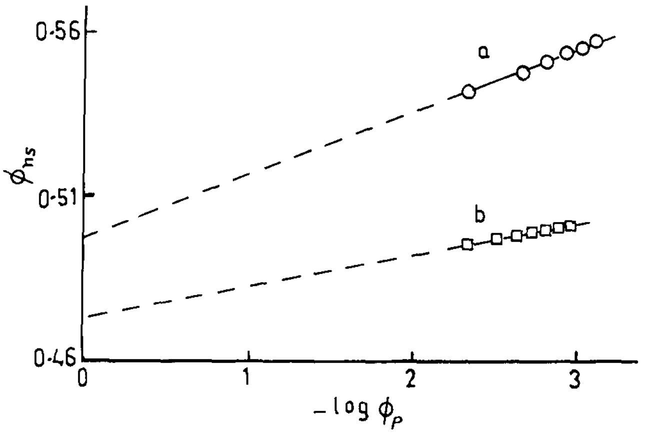

Figure 3 Determination of θ composition at 298 K according to method of Cornet and Ballegooijen: (a) binary solvent system chloroform/n-heptane (volume fraction ϕ_{ns}) and (b) binary solvent system TFE/water (volume fraction ϕ_{ns})

and $\bar{M}_w$ is shown in *Figure 2*. The derived values of $\langle S^2\rangle_{0w}/\bar{M}_w$ and resultant calculated values of $(\langle r^2\rangle_0/M)^{1/2}$ from all three plots are listed in *Table 1*, where it is seen that there is good accord, the mean value of $(\langle r^2\rangle_0/M)^{1/2}$ being 0.095 nm g$^{-1/2}$ mol$^{1/2}$. This is about 12% larger than the mean of the values obtained from plots involving $[\eta]$ and $\bar{M}_w$, the calculation of which entailed use of the constant Φ. If the lower value of $\Phi = 2.1\times10^{23}$ mol^{-1}, which is commonly found[25], is adopted here, there is closer agreement since the resultant mean value of $(\langle r^2\rangle_0/M)^{1/2}$ is increased thereby to 0.090 nm g$^{-1/2}$ mol$^{1/2}$.

Theta composition in binary solvents

The volume fraction of non-solvent (ϕ_{ns}) *versus* log ϕ_p displayed good linearity for both binary solvent systems (*Figure 3*). Extrapolation to pure polymer, i.e. to $\log \phi_p = 0$, yielded the following θ compositions: TFE/water (52.6/47.4 v/v) and chloroform/n-heptane (50.2/49.8 v/v).

Unperturbed dimensions in binary theta solvents

The exponent was exactly 0.50 in the Mark–Houwink plots for PHB in each of the two binary θ mixtures. An example of one of these plots is given in *Figure 4*. The values of K_θ and those of the *UD* calculated thereby via equation (1) are listed in *Table 1*. The mean value of 0.085 nm g$^{-1/2}$ mol$^{1/2}$ for $(\langle r^2\rangle_0/M)^{1/2}$ coincides with the average yielded from extrapolation plots involving $[\eta]$ in the single solvent, TFE.

In each of the two binary θ solvents light scattering measurements were made on sample S8 ($\bar{M}_w =$ 929 kg mol^{-1}). The plots in *Figure 5* verify that $A_2 = 0$. In the TFE/water system similar measurements were made on sample S5. The derived quantities, being apparent ones, are indicated as such by an asterisk (*) in *Table 2*, which also lists refractometric data and light scattering parameters derived from measurements in TFE. By means of equation (2) and the multiplicative factor $6^{1/2}$, values of $(\langle S^2\rangle_z^{1/2})^*$ (which in principle should be $\langle S^2\rangle_{0z}^{1/2}$) were converted to $(\langle r^2\rangle_0/M)^{1/2}$ in which the molar mass is $\bar{M}_w$, rather than $\bar{M}_w^*$. The resultant values of $(\langle r^2\rangle_0/M)^{1/2}$/nm g$^{-1/2}$ mol$^{1/2}$ were 0.065 and 0.074 for samples S5 and S8 respectively in TFE/water and 0.088 for sample S8 in chloroform/n-heptane. The last of these lies in fairly good accord with the *UD* obtained from viscosity in binary θ solvents as well as with the *UD* derived indirectly from viscometric and light scattering extrapolation plots. The other two values of $(\langle r^2\rangle_0/M)^{1/2}$ are considerably smaller and, even after considering possible uncertainties of ±5% in $(\langle S^2\rangle_z)^*$ and $\bar{M}_w$, they remain below the value of the *UD* that is indicated by the procedures already indicated in the text.

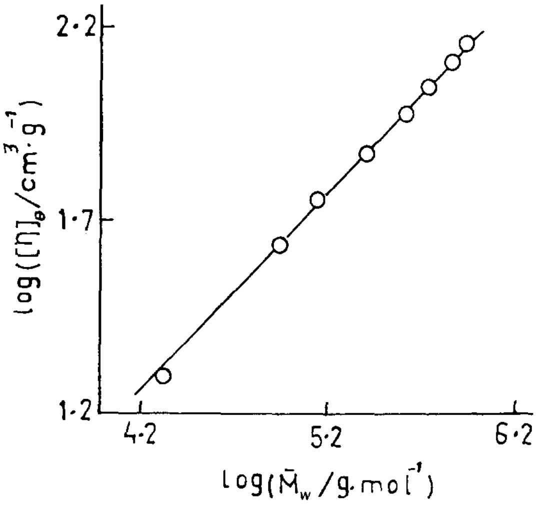

Figure 4 MH plot for PHB in TFE/water (52.6/47.4 v/v) at 298 K

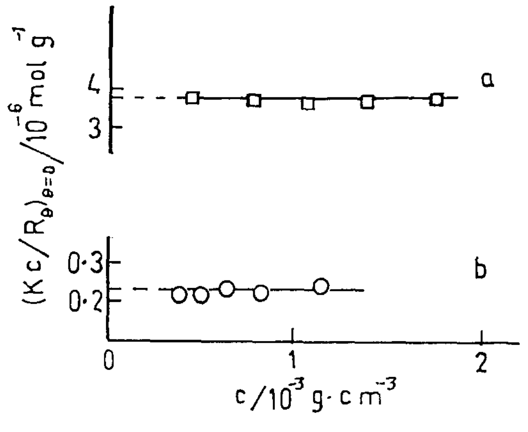

Figure 5 Dependence on concentration of light scattering data extrapolated to zero scattering angle θ at 298 K for sample S8 in (a) TFE/water (52.6/47.4 v/v) and (b) chloroform/n-heptane (50.2/49.8 v/v)

Table 2 Light scattering and refractometric data for PHB in two binary θ-mixtures and in TFE

	TFE		TFE/water		Chloroform/n-heptane
	Sample S5	Sample S8	Sample S5	Sample S8	Sample S8
$\bar{M}_w$ (kg mol^{-1})	413	929	–	–	–
$\bar{M}_w^*$ (kg mol^{-1})	–	–	100	266	4250
A_2 (10^{-4} m^3 kg^{-2} mol)	17.0	13.4	–	–	–
A_2^* (10^{-4} m^3 kg^{-2} mol)	–	–	0	0	0.1
$\langle S^2\rangle_z^{1/2}$ (nm)	39.4	61.0	–	–	–
$(\langle S^2\rangle_z^{1/2})^*$ (nm)	–	–	22.9	37.7	45.0
$(\mathrm{d}n/\mathrm{d}c)$ (dm^3 kg^{-1})	0.146		0.116		0.040
$(\mathrm{d}n/\mathrm{d}c)_\mu$ (dm^3 kg^{-1})	–		0.066		
$\mathrm{d}n_0/\mathrm{d}\phi_1$	–		−0.048		0.057

We are of the opinion that the good accord afforded by the value for sample S8 in chloroform/n-heptane is probably fortuitous and that it is not justifiable to identify the measured apparent value $(\langle S^2\rangle_z^{1/2})^*$ with the true root-mean-square radius of gyration in the unperturbed state. This assertion is made in view of the strong selective adsorption prevailing in these systems (*vide infra*). Yamakawa[26] has concluded that, in such circumstances, evidenced by a large difference between the actual $\bar{M}_w$ and the apparent value yielded by light scattering, coil dimensions cannot be obtained reliably. We have in fact observed previously for a different polymer binary θ mixture system[27] that differences do exist between *UD* obtained via viscosity and radius of gyration.

Another factor that we have considered in connection with $\langle S^2\rangle_z^*$ is also associated with selective adsorption. The light scattering plot extrapolated to zero concentration affords $\langle S^2\rangle_z^*$ from equation (7) in which λ_0 is the wavelength of light *in vacuo* and n_0 is the refractive index of the (binary) solvent, i.e. λ_0/n_0 represents the wavelength in the medium:

$$\langle S^2\rangle_z^* = (\text{slope/intercept})(3\lambda_0^2/16\pi^2 n_0^2) \tag{7}$$

In the immediate domain of the polymer coil, which is considerably adsorbed selectively by solvent 1, it might be reasonable to take n_0 as the refractive index (n_1) of pure liquid 1. Because $n_1 < n_0$ for the system TFE/water, the effect is to increase $\langle S^2\rangle_z^*$ (and hence the *UD*, which is the desired change). However, this explanation must be consistent in order to be tenable and for the other system, chloroform (solvent 1)/n-heptane, the reverse is true, i.e. $n_1 > n_0$. This would have the undesired effect of decreasing an already acceptable value of the *UD*.

Selective adsorption in binary theta solvents

Light scattering data (*Table 2*) were used to determine the coefficient of selective adsorption γ_1, where solvent component 1 is TFE in one binary θ mixture and chloroform in the other. In equation (8) $\bar{M}_w^*$ is the measured apparent molar mass of the polymer, $\bar{M}_w$ is the true value measured in TFE and $\mathrm{d}n_0/\mathrm{d}\phi_1$ represents the change in refractive index of binary solvent with volume fraction ϕ_1 of component 1 in it:

$$\gamma_1 = (\mathrm{d}n/\mathrm{d}c)[(\bar{M}_w^*/\bar{M}_w)^{1/2} - 1]/(\mathrm{d}n_0/\mathrm{d}\phi_1) \tag{8}$$

The listed values of $\mathrm{d}n_0/\mathrm{d}\phi_1$ were obtained by fitting measured values of n_0 over the whole composition range to a polynomial in ϕ_1, and relate to the differential at the specific composition used as the θ mixture[28]. For the system PHB/TFE/water, equation (8) yields $\gamma_1 = 1.2$ dm^{3}kg^{-1} for sample S5 and 1.1 dm^3 kg^{-1} for sample S8. For the system PHB/chloroform/n-heptane, $\gamma_1 = 0.80$ dm^3 kg^{-1} for sample S8.

An alternative determination[28] is from a comparison between dn/dc at constant composition with the corresponding quantity at constant chemical potential $(\mathrm{d}n/\mathrm{d}c)_\mu$, viz.:

$$\gamma_1 = [(\mathrm{d}n/\mathrm{d}c)_\mu - (\mathrm{d}n/\mathrm{d}c)]/(\mathrm{d}n_0/\mathrm{d}\phi_1) \tag{9}$$

As indicated in *Table 2*, this procedure was effected only in the TFE/water system (for which sample S8 was used). The resultant calculation via equation (9) yielded $\gamma_1 = 1.0$ dm^3 kg^{-1}, which is close to the value of selective adsorption of TFE yielded by equation (8).

Temperature coefficient of unperturbed dimensions

For two samples (S5 and S8) $[\eta]$ was measured in chloroform at five temperatures within the interval 280–318 K. Plots of $\ln[\eta]$ *versus* temperature (T) were linear in each case and of identical slope, -2.2×10^{-4} K^{-1}. The plot for sample S8 is given in *Figure 6a*. The slope, which is thus uninfluenced by molar mass, is expressible in the form of equation (11), which follows directly from equation (10):

$$[\eta] = K_\theta M^{1/2}\alpha^3 \tag{10}$$

$$\mathrm{d}\ln[\eta]/\mathrm{d}T = \tfrac{3}{2}\,\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T + 3\,\mathrm{d}\ln\alpha/\mathrm{d}T \tag{11}$$

Hence, because $\mathrm{d}\ln[\eta]/\mathrm{d}T$ is found to be constant, its value may be identified with the constant part[29] of the RHS of equation (11), i.e. $\tfrac{3}{2}\,\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$, whence the temperature coefficient of the unperturbed dimensions, $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$, has a value of -1.5×10^{-4} K^{-1}.

An alternative route to evaluation of this coefficient is via the procedure of Bohdanecký[30], whose analysis predicts linearity in a plot of $(P/Q)\,\mathrm{d}\ln[\eta]/\mathrm{d}T$ *versus* $(1/Q)$ and a slope equal to $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$. The quantities P and Q are defined as follows:

$$P = (5\alpha^2 - 3)/3\alpha^2 \tag{12}$$

$$Q = (\alpha^2 - 1)/\alpha^2 \tag{13}$$

The values of α were obtained from equation (14) in which $[\eta]_\theta$ is the intrinsic viscosity measured in the binary TFE/water θ mixture:

$$\alpha = ([\eta]/[\eta]_\theta)^{1/3} \tag{14}$$

The Bohdanecký plot for solutions of sample S8 is shown in *Figure 6b*. The value yielded for $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ is

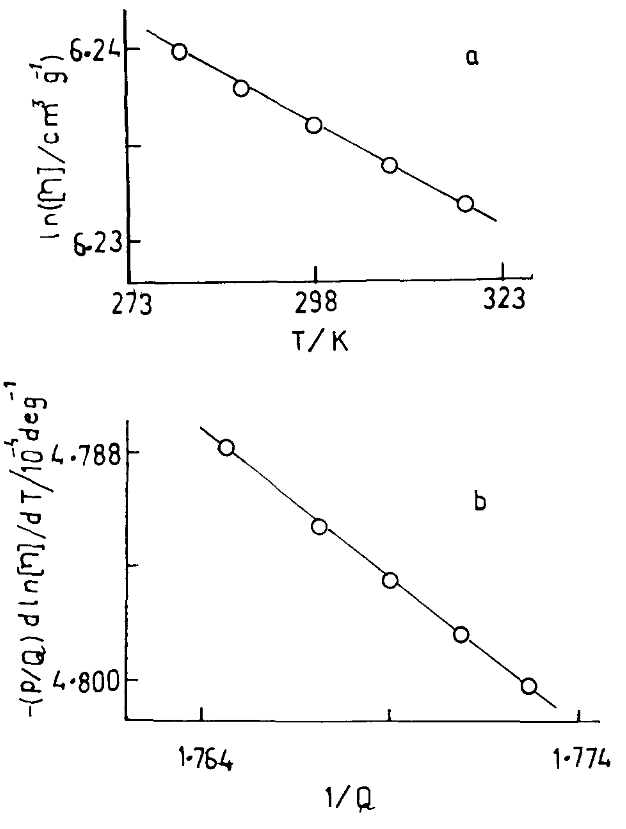

Figure 6 Determination of temperature coefficient of the unperturbed dimensions of PHB from (a) $\ln[\eta]$ in chloroform and (b) application of Bohdanecký's procedure to viscometric data in chloroform

identical in value ($-1.5 \times 10^{-4}\,\text{K}^{-1}$) with that obtained via the previously indicated procedure.

CONCLUSIONS

With regard to the viscometrically determined *UD* obtained both directly in the two binary θ mixtures and indirectly via extrapolation procedures in TFE, the findings are all self-consistent and yield a value of 0.085 (± 0.001) nm $\text{g}^{-1/2}$ $\text{mol}^{1/2}$. Because extrapolation procedures involving $\langle S^2 \rangle_w$ in TFE also yield consistency, the fact that the resultant *UD* from them is somewhat higher is unlikely to be attributable to errors in the radii of gyration. Although we have been unable to resolve this point satisfactorily, it is possible that it is associated with the polydispersity of the samples. As seen in equation (2), $\langle S^2 \rangle_w$ is obtained from $\langle S^2 \rangle_z$ by reducing the latter by a factor that is dependent on $\bar{M}_w/\bar{M}_n$. For example, this factor assumes values of 0.75, 0.67 and 0.60 at values of 1.5, 2 and 3 respectively for $\bar{M}_w/\bar{M}_n$. As indicated in our previous communication, the polydispersity indices were not derived by separate determinations of $\bar{M}_w$ and $\bar{M}_n$ but were obtained via g.p.c. in chloroform (courtesy of the suppliers of the samples) and may be subject to some uncertainty.

There do not appear to have been any previously published values of the *UD* or its temperature coefficient for PHB. The present value of 0.085 nm $\text{g}^{-1/2}$ $\text{mol}^{1/2}$ lies within the range of the relatively few reported values[31] of *UD* for aliphatic polyesters. A more meaningful basis for comparison is the steric factor σ:

$$\sigma = (\langle r^2 \rangle_0/M)^{1/2}/(\langle r^2 \rangle_{0f}/M)^{1/2} \qquad (15)$$

In equation (15) $\langle r^2 \rangle_{0f}$ is the mean-square end-to-end distance for a freely rotating chain. Using the relevant bond lengths and angles we have calculated[32] a value of 0.051 nm $\text{g}^{-1/2}$ $\text{mol}^{1/2}$ for $(\langle r^2 \rangle_{0f}/M)^{1/2}$ of PHB, whence $\sigma = 1.67$. This is of comparable magnitude to the value of σ for poly(oxyundecanoyl)[31], for example, since, although the *UD* is somewhat higher for this polyester, the effect is offset by the fact that its repeat unit has a high content of C–C bonds, which leads to a higher $(\langle r^2 \rangle_{0f}/M)^{1/2}$ (0.055 nm $\text{g}^{-1/2}$ $\text{mol}^{1/2}$) than for PHB. The overall effect is similar in origin but more pronounced in magnitude for the aromatic polyester poly(oxyethylene-oxyterephthaloyl)[31] ($\sigma \sim 1.3$–1.4) for which the *UD* is similar in value to that of PHB but for which the 1,4-phenylene group gives rise to a much higher value $(\langle r^2 \rangle_{0f}/M)^{1/2}$ (0.069 nm $\text{g}^{-1/2}$ $\text{mol}^{1/2}$). The small negative value of $d\ln\langle r^2 \rangle_0/dT$ is an effect purely of chain flexibility rather than being thermodynamic in origin. In this respect it is similar in magnitude and sign to the temperature coefficient observed for other polymers within the temperature region considerably displaced from the upper or lower critical solution temperature[29].

The coefficients of selective adsorption to PHB are large and simple calculation shows that the values of $\gamma_1/\text{dm}^3\,\text{kg}^{-1}$ happen to be very close to the corresponding number of molecules of TFE (and chloroform) adsorbed per monomer unit. In fact there are very few other liquids having sufficient affinity for PHB to dissolve this polymer. High selective adsorption, especially in binary solvents close to or at the θ composition, is not without precedent[27,33].

Because $dn_0/d\phi_1$ is negative for TFE/water and positive for chloroform/n-heptane, the values of $\bar{M}_w^*/\bar{M}_w$ are <1 and >1 respectively in these media. Correspondingly $(dn/dc)_\mu < dn/dc$ in TFE/water and, although $(dn/dc)_\mu$ was not measured in chloroform/n-heptane, the value of γ_1 measured by light scattering in the latter binary solvent allows one to estimate that $(dn/dc)_\mu \sim 0.086\,\text{dm}^3\,\text{kg}^{-1}$, i.e. $(dn/dc)_\mu > dn/dc$. Hence for both systems neither $(dn/dc)_\mu$ nor the difference between this quantity and dn/dc is especially large. Tuzar and Kratochvíl[33] deliberately sought conditions for attaining extremely high values of $(dn/dc)_\mu$ and found that this was possible for several polymers in mixtures of *m*-cresol with a precipitant, n-heptane. Details of their rationale are not reproduced here. In some respects their systems bear similarity to the present ones. However, there are sufficient important differences to indicate why the values of $(dn/dc)_\mu$ and γ_1 are not extremely high here. These include (1) similarity between the refractive indices of PHB and chloroform, (2) only small–medium values of $dn_0/d\phi_1$ and (3) some measure of affinity between the solvent components alone. Thus, unlike *m*-cresol/n-heptane, phase separation in chloroform/n-heptane (at $\phi_{ns} \sim 0.5$) was observed to occur at quite a low temperature (~ 255 K). Moreover, for TFE/water (at $\phi_{ns} \sim 0.5$) no phase separation occurred between 298 K and the temperature at which ice crystals formed (~ 269 K). Moreover, there is actually a strong affinity between TFE and water, which we have noted qualitatively from the maximum in absolute viscosity as a function of composition.

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