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Study of the poly(1,3,6,9-tetraoxacycloundecane) in aqueous solution. Comparison with other polyethers and poly(1,3-dioxolane)

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A sample of linear poly(1,3,6,9-tetraoxacycloundecane) ($[-CH_2-CH_2O)_3-CH_2O-]_n$, (PTGF)) of molecular weight 35000 was synthesized by cationic polymerization. The oligomeric cycles were eliminated by successive precipitations. This PTGF sample was studied at pure state by differential scanning calorimetry and dilatometry. In the amorphous state, the specific volume was found to be significantly lower than that of other polyethers [such as poly(ethylene oxide) (PEO)] and very close to that measured below the melting point. In aqueous solution, several properties are intermediate between those of PEO and PDXL [poly(dioxolane)], such as the cloud point and the excess mixing volume. Nevertheless, the chain flexibility of PTGF is unusually low. © 1997 Elsevier Science Ltd.

(Keywords: poly(1,3,6,9-tetraoxacycloundecane); density; melting temperature; aqueous solution; cloud point; excess mixing volume; viscosity)

INTRODUCTION

The polyethers constitute an interesting family of polymers, particularly with respect to their solubility and properties in aqueous media[1,2]. Much attention has been devoted to the case of poly(ethylene oxide) (PEO) whose solubility diagram exhibits a 'closed loop' form[3]. A phase separation is observed upon heating above 100°C and this behaviour is generally explained by the release of the hydration molecules which enhances the interactions between the hydrophobic parts of the polymer[4,5]. The phase diagram of PEO has also been interpreted by Karlström[6] by assuming that the increase of the χ Flory parameter upon heating is due to changes in the gauche–trans equilibrium in the chain. Each segment of the chain may exist in two forms due to the rotation around C–C and C–O bonds and a different hydration may be associated with these two forms. Saeki et al.[7] have proposed another alternative explanation which is based on the modified Flory–Huggins and Patterson theory[8,9].

Up to now, however, it seems difficult to explain how the solubility in water varies in the polyether series with the relative content of ethylene oxide and methylene oxide units. It is indeed well known that poly(methylene oxide) (PMO) is insoluble whereas it would be expected to be more soluble than PEO on the basis of

their solubility parameters. Such a difference can be understood by taking into account the greater ability of PMO to crystallize in bulk. In a recent work[10,12] we have studied the properties of poly(1,3-dioxolane) (PDXL) of the chemical formula:

$$[-(CH_2CH_2O)-CH_2O-]_n$$
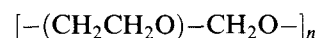
in bulk and in water. We have found that, while the melting temperature and enthalpy of fusion of PDXL are close to those of PEO, its solubility in water is much lower. The solubility domain is indeed limited at higher temperatures by the demixing curve (with a lower critical solution temperature (LCST) = 70°C to be compared to LCST = 110°C for PEO of the same molecular weight—35 000). Moreover, the solubility domain of PDXL does not extend beyond a polymer content of 50 wt%. It seems that the difference in solubility between PDXL and PEO cannot be explained by differences in their crystallinity and another phenomenon has to be invoked. The solubility parameter of PDXL calculated from Van Krevelen[12] ($\delta_{PDXL} = 25.4 J^{1/2} ml^{-1/2}$) is higher than that of PEO ($\delta_{PEO} = 22.8 J^{1/2} ml^{-1/2}$) which suggests that PDXL should be the more soluble in water.

In order to progress in the understanding of these complex behaviours, it is interesting to extend these studies to other polymers of this series, such as poly(1,3,6,9-tetraoxacycloundecane) (PTGF), whose chemical formula is:

$$[-(CH_2CH_2O)_3-CH_2O-]_n$$
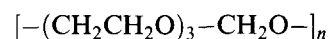
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We present in this paper the results of a physicochemical study of PTGF in bulk and in aqueous solution.

The aim of this paper is also to discuss the experimental results in comparison with those previously obtained with PEO, PDXL and PEO-PPO copolymers in the light of different recent theories.

EXPERIMENTAL

Samples

The PTGF sample was prepared by the cationic polymerization of the corresponding cyclic acetal 1,3,6,9-tetraoxacycloundecane, abbreviated as TGF (triethyleneglycol formal). This method allows the control of the molar mass and of the nature of chain end groups[13]. The polymerization was carried out under high vacuum conditions. Methylene chloride (CH_2Cl_2) was the solvent and methyl trifluoromethylsulfonate ($CF_3SO_3CH_3$) the initiator. The polymerization was terminated with sodium methanolate (CH_3ONa) to provide the chains with the following end groups:

$$CH_3O[-(CH_2CH_2O)_3-CH_2O-]_n-$$

and

$$CH_3O[-CH_2O-(CH_2CH_2O)_3-]_n-$$
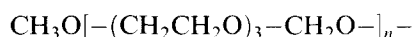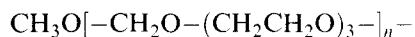
The preparation and purification of TGF and CH_2Cl_2 have been already described[14,15]. The initiator $CF_3SO_3CH_3$ was distilled under vacuum.

TGF (10 ml) and CH_2Cl_2 (28 ml) were distilled from the vacuum line into a reactor fitted with a Teflon stopcock. The solution was cooled to $-15°C$ and $30\,\mu l$ of initiator was added through a septum. After 16 h of reaction at $-15°C$ the reaction medium was deactivated by CH_3ONa.

The insoluble salts were eliminated by centrifugation followed by filtration on Millipore membranes. The crude sample was isolated by evaporation of the solvent. Its polymeric nature was checked by size exclusion chromatography (s.e.c.) in tetrahydrofuran (THF) which also shows the presence of oligomers. These oligomers represent 10 wt% of the crude sample and were quantitatively separated from the polymer by three successive precipitations using CH_2Cl_2 as a solvent and cyclohexane as a non solvent. They were identified as cyclic oligomers, from monomer to cyclic octamer, although a very small fraction of higher molecular weight species was also eliminated to which cyclic nature could not be determined using a s.e.c. calibration method[15]. The purified polymer was dried under vacuum at 40°C and kept in a desiccator in the presence of potassium hydroxide. Its chemical structure was checked by ^{1}H nuclear magnetic resonance (n.m.r.).

Size exclusion chromatography coupled with multiangle light scattering

We used a s.e.c. device working in aqueous medium and consisting of a Shimadzu pump, a degassing system, an automatic injector (liquid Chromatograph LC-10AD), a precolumn and three columns (TSK PW6, PW4 and PW2). Two detectors were used: a refractometer Waters 410 as concentration detector, and a Wyatt, multiangle light scattering apparatus allowing the determination of the molecular weight M_w and the radius of gyration of the macromolecules. The solvent

was water, containing 400 ppm of sodium azide as a bacteriostatic.

The solutions were always filtered on $0.22\,\mu m$ Millipore filters before injection.

Nuclear magnetic resonance

The [1]H n.m.r. spectra were obtained with a 200 MHz spectrometer (Brucker) using deuterated chloroform as solvent. The oxymethylene protons appear at 4.742 ppm (s, 2H) and the oxyethylene protons at 3.664 ppm (8H) and 3.65 ppm (4H).

Differential scanning calorimetry

A Perkin Elmer DSC 7 microcalorimeter equipped with a thermal analysis data station (TADS) was employed. The desired quantities of polymer sample and water were introduced into a sample pan, which was then tightly sealed. The pans were heated for 24 h at 80°C and then kept for 1 week at room temperature, to ensure thorough homogenization. The weight of each pan was determined prior to taking any data in order to obtain the concentration of the system in $g\,g^{-1}$. The sample was quenched at $-80°C$ and kept for 10 h at this temperature before measurements. Cooling and heating rates ranging between 2 and $10°C\,min^{-1}$ were used. The temperature interval was either $-50°C$ to $50°C$ or $-80°C$ to $0°C$ and the apparatus calibration was carried out with gallium. The melting temperatures were taken at the top of the peaks.

Turbidimetry

For the more dilute solutions (polymer concentration $C_p < 0.25\,g\,g^{-1}$), the cloud points (T_ps) were measured with a Mettler FP81 apparatus. The solutions contained in cylindrical cells (1 mm i.d. and 79 mm length) were heated at a rate of $2°C\,min^{-1}$. For the more concentrated solutions, the cloud points were determined by visual observations. The solutions contained in 10 mm diameter tubes were thermostatted at different temperatures.

Dilatometry

The density of the pure polymer sample was measured by classical dilatometry. The dilatometers have two parts: a reservoir of 1.7 ml and a capillary of 0.4 mm inner diameter and 400 mm length, connected by a spherical ground joint. The calibration of these dilatometers was made with mercury distilled under vacuum. The measurements were carried out with 500 mg of PTGF sample. The thermostat temperature (T) was controlled by a quartz thermometer. The stability is $\pm 2 \times 10^{-3}°C$ for $25°C \leq T \leq 44°C$, and $\pm 10^{-2}°C$ for $45°C \leq T \leq 70°C$. The reproducibility of the specific volume measurements is $6 \times 10^{-4}\,ml\,g^{-1}$.

The sample was submitted to several cycles of heating to 100°C and cooling to room temperature in order to eliminate traces of air.

Light scattering

Light scattering (LS) experiments were performed with an apparatus operating with a laser source of wavelength 6328 Å from Sematech (SEM-633). The scattered intensity was measured within a scattering angle θ ranging from 30 to 150° with increments of 5°. The cells were thermostatted at $\pm 0.1°C$. The solvent was water (distilled three times in a quartz apparatus) containing 0.05 N of NaCl and 200 ppm of sodium
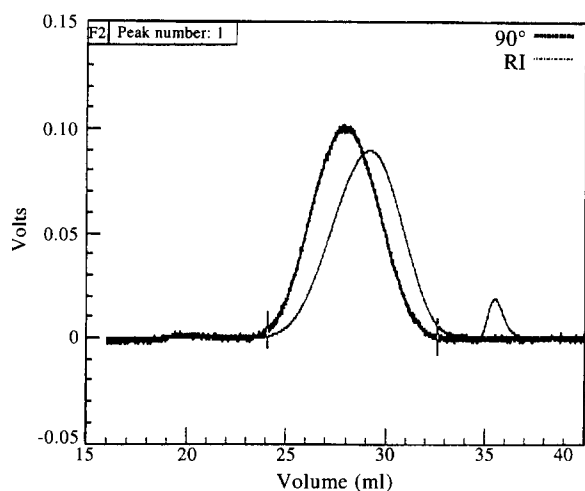
Figure 1 S.e.c. of the purified PTGF sample in aqueous solution: refractometric signal (————) and light scattering signal (———————)
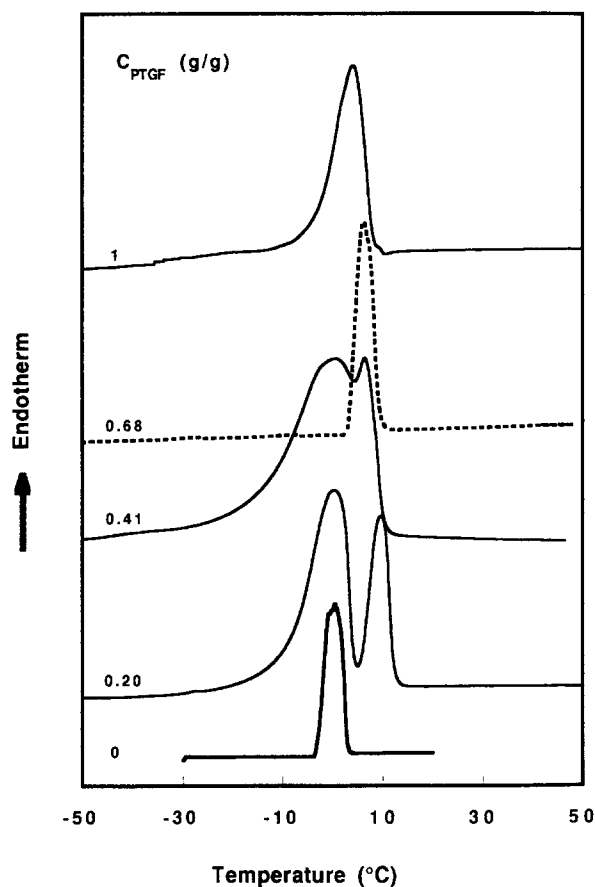

Figure 2 D.s.c. traces obtained by heating PTGF–water systems at different polymer concentrations, expressed in gg^{-1}

Table 1 Characterization of poly(1,3,6,9-tetraoxacycloundecane)

	M_w	Polydispersity
PTGF	38 000[a]	–
	32 000[b]	1.6
	37 000[c]	1.7

[a] From light scattering in water–0.05 N NaCl
[b] From s.e.c. in THF using a PEO calibration
[c] From s.e.c. coupled with multiangle light scattering in water– 0.1 N NaCl

azide as bacteriostatic. The stock solutions were prepared gravimetrically. They were heated for 2 h at 45°C and then gently stirred at room temperature for about 1 day. The optical clarification of the solutions was then obtained by filtration through hydrophilic $0.22\,\mu m$ Millipore filters.

Refractometry

The refractive index increments dn/dc of PTGF in aqueous solutions was measured on a home-built apparatus[16], using the Brice–Phoenix principle. This allows the measurements on solutions in the domain of low concentration used in light scattering experiments. The value found for 0.05 N NaCl at 25°C was 0.129 ml g^{-1}.

Viscosimetry

The viscosity measurements were made with an automatic capillary viscosimeter of high accuracy[17]. The capillary diameter was 0.7 mm and the water flow time was 33.700 ± 0.001 s at 25°C. The apparatus was thermostatted at ± 0.01°C. The data treatment automatically includes the kinetics energy corrections.

Densimetry

The density of aqueous polymer solutions was obtained with a Kratky densimeter DMAO2 equipped with a cell constructed in our laboratory[18].

RESULTS

Characterization of the purified PTGF sample

S.e.c. of PTGF in aqueous solution (*Figure 1*) shows a mononodal distribution ranging from a degree of polymerization of about 9 to one of about 620. The peak at elution volume around 35 ml is due to impurities in the solvent. To evaluate the amount of cycles still present in the purified PTGF, one has to consider that in the cationic polymerization of cyclic acetals linear species are formed in equilibrium with cycles. It was shown by Andrews *et al.*[20] that according to the Stockmayer–Jacobson theory[19], the absolute concentration of the unstrained rings can be expressed as $[cM_x] = A.x^{-2.5}$ where x is the degree of polymerization of the cyclic species, $[cM_x]$ its molar concentration and A is a constant depending on the chemical nature of the polymer, and expressed in mol l^{-1}. This has been confirmed experimentally and is well documented in the case of PTGF where this law is valid for cycles larger than tetramer[21,22] and where A was shown equal to 0.11 mol l^{-1} for polymerization run in methylene chloride solvent. This means that the lower the initial molar concentration of monomer, the higher the relative fraction of cyclic species compared to the linear ones formed after polymerization. In particular, when the initial concentration is low enough, only cyclic oligomers will be formed. The absolute concentration of unstrained ring can be converted in terms of monomer base units per litre incorporated into the ring

$$[cM_x]x = A\,x^{-1.5} \qquad (1)$$

Thus, it is possible to calculate the total amount of monomer units per litre incorporated in unstrained cycles for the whole sample. However, as mentioned in the experimental part, 10% per weight of the crude compound representing all the cycles from monomer to
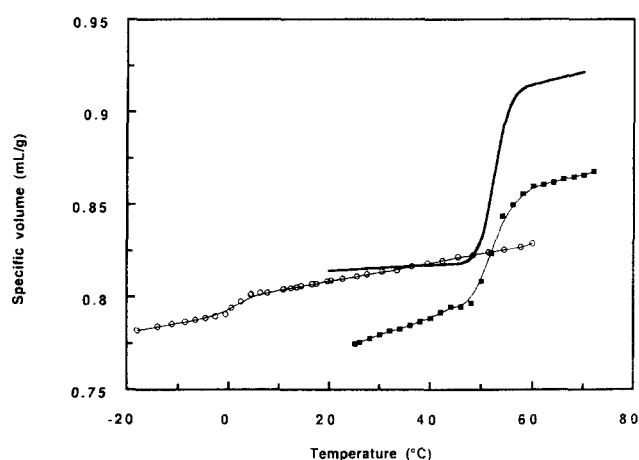
Figure 3 Specific volume of PTGF (O), PDXL (■, from ref. 10) and PEO (————, from ref. 25) as a function of temperature

octamer were eliminated, i.e. approximately $0.12 \, mol \, l^{-1}$ of monomer compared to the initial molar concentration (in the reaction medium) which is $1.17 \, mol \, l^{-1}$. Thus the purified polymer corresponding to 1.05 moles of monomer base units per litre still contains cycles which amount is calculated according to the equations:

$$\sum_{9}^{620}[cM_x]x = A\sum_{9}^{620}x^{-1.5} = 0.11 \times 0.6054 \qquad (2)$$

One finds 0.067 moles of monomer units per litre, which means that 6% of the purified polymer is made of rings containing 9–620 monomer units.

The molecular weight characteristics of the purified PTGF sample are reported in *Table 1*. The weight average molecular weights obtained from s.e.c. and light scattering are in very good agreement. No polymer retention on the chromatographic support could be observed.

Pure polymer in bulk

Differential scanning calorimetry measurements. *Figure 2* shows the differential scanning calorimetry (d.s.c.) endotherms obtained for various compositions of the system PTGF–water. For the pure polymer, the sample was cooled at $-0.2°C \, min^{-1}$ down to $-80°C$ and kept for 10 h at this temperature before measurements. The melting temperature T_{mp}, was found to be $4°C$ in agreement with previously published data[23], though a value of $-5°C$ was found by other authors[24]. The corresponding enthalpy ΔH_p is $30.2 \pm 0.5 \, J \, g^{-1}$. Interestingly enough, the presence of one methoxy group per three ethoxy groups has a more profound effect on the stability of the crystalline form (which decreases) than when the ratio is 1/1 as in PDXL. The ΔH_p values

for PEO and PDXL are 180 ± 5 and $107 \pm 3 \, J \, g^{-1}$ respectively for the same molecular weight as that of the PTGF sample under study. However, this comparison must be considered with caution, since the extent of crystallinity may be different for the three samples.

Dilatometry. In *Figure 3*, the temperature dependence of the specific volume of PTGF is presented. The sample was quenched at $-30°C$ and kept for 10 h at this temperature before measurements. The values were recorded upon heating at intervals of $3°C$, observing a 20 min stabilization period for each temperature of measurement. The transition corresponding to the polymer melting point occurs at $3 \pm 2°C$ in excellent agreement with the value obtained by d.s.c. measurements ($4°C$). The specific volume of PTGF can be written as:

$$V_{PC} = 0.7911 \pm 1.10^{-4} + (4.92 \pm 2.10^{-6})$$
$$\times 10^{-4} \times T(°C) \qquad (3)$$

and

$$V_{PC} = 0.7989 \pm 1.10^{-4} + (4.96 \pm 2.10^{-6})$$
$$\times 10^{-4} \times T(°C) \qquad (4)$$

where V_{PA} and V_{PC} correspond to the melt and the semicrystalline states respectively (T being expressed in $°C$).

In *Figure 3* are also reported previous results on PDXL[10] and PEO[25]. The curves differ not only with respect to the melting temperature but also in the discrepancy between the specific volumes of the crystalline and amorphous states. *Table 2* gives the values of several parameters *versus* the molar fraction of ethylene oxide units R, for PEO, PTGF and PDXL as obtained from our results and from other previous works.

In the series of polyethers $[-(CH_2CH_2O)_m-CH_2O-]_n$ where m ranges from 1 to $6^{23,24}$, the melting temperature and enthalpy are minimum for PTGF. Nekoomanesh *et al.*[24] have also observed an additional even–odd effect. For both T_{mp} and ΔH_{mp}, the lower values correspond to odd values of m. Such behaviour is generally explained in terms of differences in the crystallinity degree and in the packing of the crystal structure.

Concerning the volume properties of PTGF, the small difference between V_{pa} and V_{pc} at the melting point may also be interpreted through this qualitative explanation and it is clear that PTGF has a lower crystallinity degree than PEO and PDXL. What is puzzling, however, is the fact that in the amorphous state, the specific volume of PTGF is significantly lower than that of PEO and PDXL (*Table 2*). On the other hand, V_{pc} decreases monotonously with the ratio R. Moreover, the expansion coefficient $\alpha = 1/V(\partial V/\partial T)$ is 35% lower for PTGF than for PDXL. Up to now, we have no satisfactory

Table 2 Compared parameters for the polyethers series of approximately the same molecular weight

Polymers	$R = OE/(OE + OM)$	V_{PA} (ml g^{-1}) ($T = 25°C$)	α	T_m (°C)	V_{PC} (ml g^{-1}) ($T = 10°C$)	ΔH_p (J g^{-1})
PEO	1	0.8907	6.9×10^{-4}	70	0.80995	180
PTGF	0.75	0.81134	4.95×10^{-4}	5	0.78619	30.2
PDXL	0.5	0.83257	7.54×10^{-4}	55	0.7410	107.25
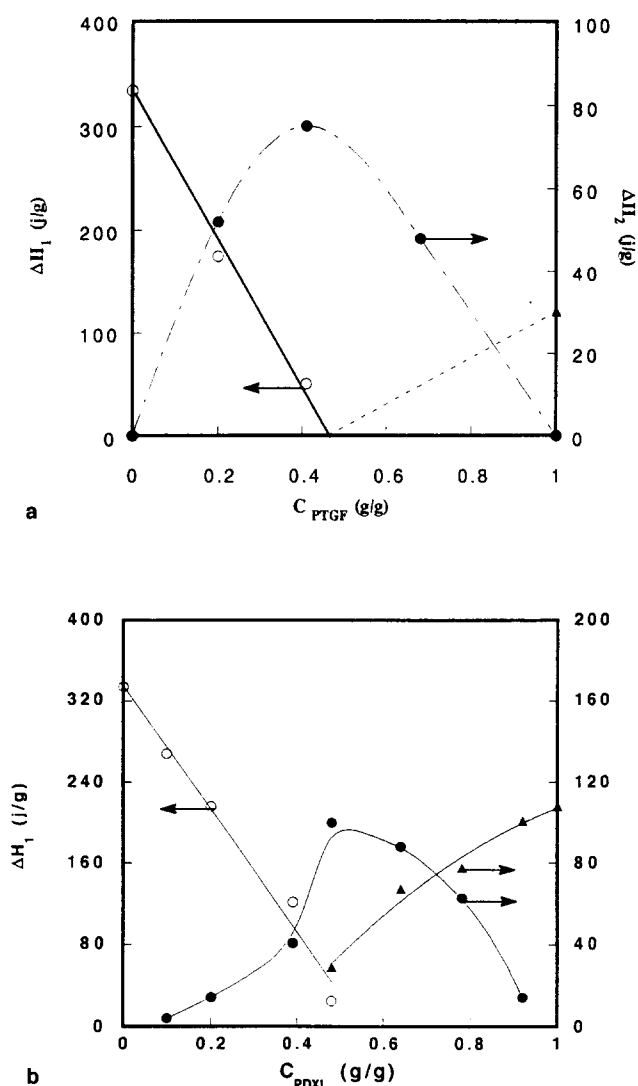
Figure 4 (a) Melting enthalpies of the free water (ΔH_1, O), the hydrate (ΔH_2, ●) and the polymer (ΔH_{mp}, ▲) vs polymer concentration, for PTGF. The point corresponding to the melting enthalpy of the pure polymer is also reported and in dotted lines are indicated the possible variations of ΔH_2 and of the PTGF melting enthalpy. (b) Melting enthalpies of the free water (ΔH_1, O), the hydrate (ΔH_2, ●) and the polymer (ΔH_{mp}, ▲) vs polymer concentration, for PDXL

explanation to propose for the evolution of the volume properties of PTGF. This polymer appears as peculiar and this is reminiscent of the other thermodynamic properties (T_{mp} and ΔH_m). However a higher specific volume should be expected if PTGF has a lower crystallinity. One may assume that a short distance organization between the three EO units belonging to neighbouring chains remains, even above the melting point of the polymer.

Polymer in water

D.s.c. measurements. D.s.c. experiments were carried out to determine the melting temperature of the polymer and of the water as a function of concentration. In the case of an aqueous solution of PEO[26,27], it has been shown that the d.s.c. traces exhibit an additional peak at about $-15°C$ which is generally attributed to an eutectic composition. For PDXL[10] three endothermic peaks have been observed, around 55, 13 and 0°C which correspond respectively to the melting of the polymer, of an hydrate

(with 3.3 water molecules per monomer) and of water. The hydrate was assumed to be a defined compound.

In the case of PTGF, only two peaks are apparently present in the traces (*Figure 2*).

For $C = 0.68$ g g^{-1}, only one peak of lower area than for the pure polymer is observed at a temperature slightly higher (7°C) and no peak at 0°C appears. This means that the water melting is not detectable at such a concentration. There is some controversy about the physical origin of this absence of a peak around 0°C[28] in the concentrated aqueous solutions of polymers. But, it is generally accepted that the water molecules are strongly bound to the polymer and cannot participate in the formation of ice. The presence of one peak only at this concentration also suggests that the melting temperature of the polymer is practically not shifted with respect to its value in the bulk. Moreover, the enthalpy associated with this peak is 48 J g^{-1}, which is much higher than that of pure PTGF (30.2 J g^{-1}). This suggests that it cannot be attributed to the polymer melting only, but that it corresponds to both the melting of the polymer and also of another species.

For the lower values of C (0.20 and 0.41 g g^{-1}), the endothermic peak of water melting appears, at 0°C, but for $C = 0.41$ g g^{-1}, it is not well separated from the second peak whose top lies at 10°C and 7°C, for $C = 0.20$ and 0.41 g g^{-1}, respectively. This makes more difficult the interpretation of the results than for PEO and PDXL, for which T_{mp}, T_{mw} (the water melting temperature), and T_{mh} (the hydrate melting temperature) are quite different. The main problem consists in assigning the second peak.

In *Figure 4a*, we have plotted the enthalpies associated with the peaks 1 and 2, after their manual deconvolution. It shows a variation of ΔH_1 similar to that already described for PEO or PDXL (see *Figure 4b*). This confirms the assignment of peak 1 to water melting. The melting enthalpy $\Delta H_1 = \Delta H_{mw}$ tends to zero for $C = 0.46$ g g^{-1}. This corresponds to 10 water molecules per monomer unit. The same analysis has given 3.3 and 3 water molecules for PDXL and PEO respectively. It was suggested that the ethyleneoxy groups are hydrated in the same way in both polymers, while the methyleneoxy groups are not hydrated and remain free in PDXL. In the case of PTGF, the number of approximately 10 water molecules per monomer corresponds to 3.3 water molecules per ethyleneoxy group and 2.5 water molecules per oxygen atom. This result seems to confirm that the ethoxy groups are the privileged sites of hydration in this polymer series. The same experiments already performed with EO-PO copolymers have led to 3 water molecules per ethyleneoxy, also[29].

The Flory–Huggins theory predicts the expression of the solvent melting point in a binary mixture and shows that the lower the interaction parameter χ_{12}, the higher the variations of T_{mw}, when composition changes. For aqueous solutions of PEO, T_{mp} was found to decrease from 55 to $-10°C$ when C_p changes from 1 to 0.5 g g^{-1}, while T_{mw} varies from 0 to $-10°C$ when C_p changes from 1 to 0.5 g g^{-1}. Hager and Macrury[26] have explained such variations through the Flory–Huggins theory, and have shown that a good agreement with the theoretical prediction can be found, at least for T_{mw} with a value of $\chi_{12} \approx 0.05$ which corresponds to good solvent conditions. The behaviour of PDXL and PTGF is completely different: T_{mw} slightly increases for PDXL and
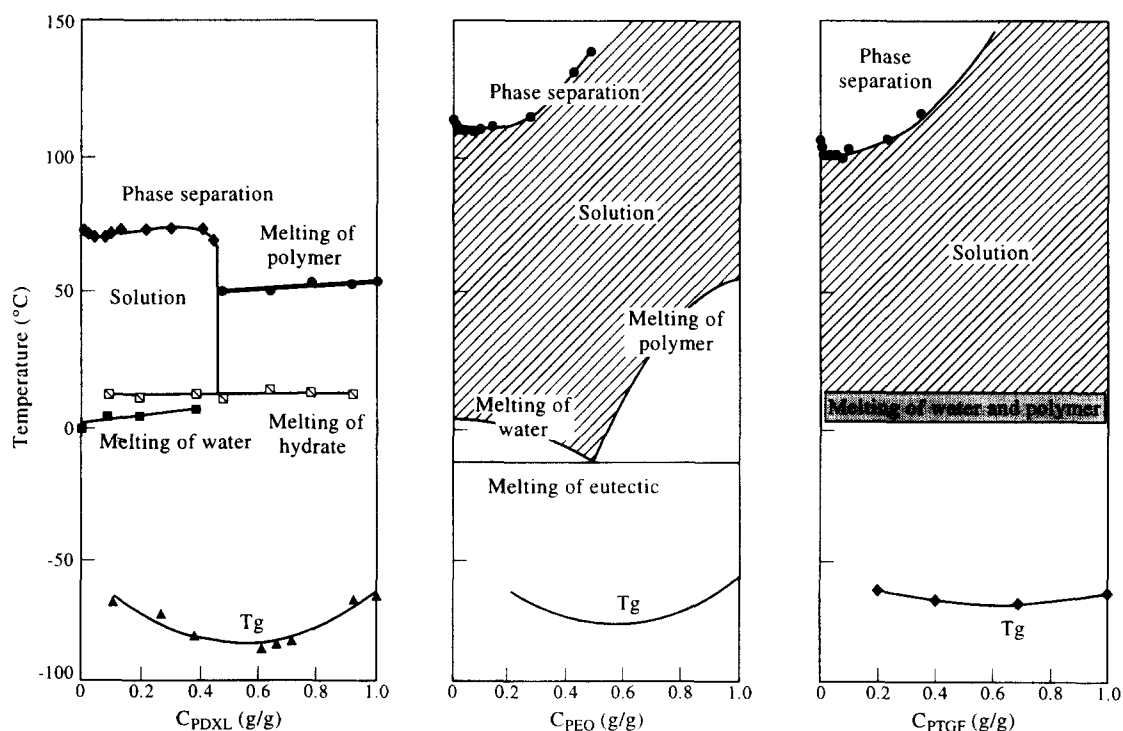
Figure 5 Phase diagrams of three polymers: from the left to the right: PDXL, PEO and PTGF
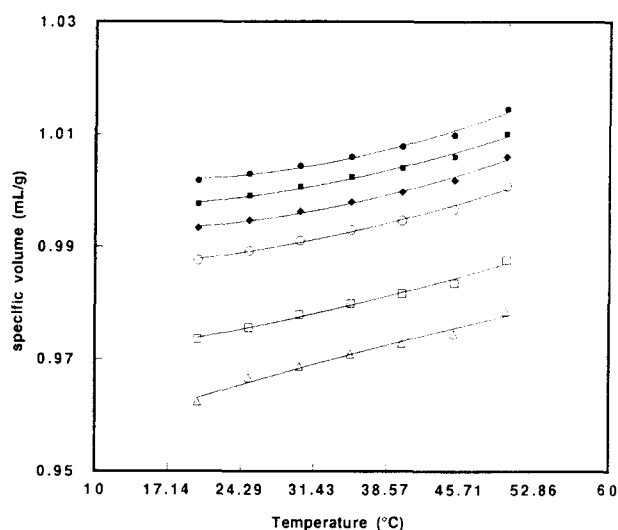

Figure 6 Variation of the specific volumes of the PTGF solutions vs temperature at different polymer concentrations (from the bottom to the top: C_{PTGF} $(g\,g^{-1})$ = 0.208, 0.155, 0.078, 0.05, 0.026, 0)

remains constant for PTGF when C_p increases up to $0.5\,g\,g^{-1}$. This result suggests that the value of χ_{12} of PDXL in water is higher than 0.5, and that of PTGF is close to 0.5.

The enthalpy associated with the higher temperature peak (from $T = 4°C$ to $10°C$) passes through a maximum when concentration varies. If this peak has to be attributed to the polymer melting, ΔH_2 should be expected to continuously decrease when C_p decreases. The variation of ΔH_2 resembles that obtained for PDXL (*Figure 4b*) or POE. Thus we can conclude that this second peak must be attributed at least partially to an hydrate melting for PTGF as well. By analogy with the cases of POE and PDXL, the contribution of the polymer melting to this peak can be assumed to be

negligible for $C_p = 0.21\,g\,g^{-1}$ and the melting temperature of the hydrate is $10°C$. For the higher concentration, $C_p = 0.68\,g\,g^{-1}$, the peak is due to both the polymer and hydrate melting but their respective contribution is difficult to distinguish.

Despite this problem of superimposition of the various d.s.c. peaks, we can deduce that PTGF in water exhibits a behaviour similar to that of PDXL but slightly different from that of PEO. Indeed, in the case of an eutectic composition, the T_{me} value is expected to be lower than those of the pure compounds, which is not the case here.

Finally, the d.s.c. measurements also give the glass transition temperature (T_g) as a function of the polymer concentration (*Figure 5*). $T_g = -63°C$ for the pure polymer, in accordance with the literature values of $-63°C$[23] and $-62°C$[24], and it slightly decreases when the system is diluted. The variation of $T_g = f(C)$ has the same general features as that of PEO and PDXL with a minimum at around $0.5\,g\,g^{-1}$. At this concentration, $T_g = -80°C$, $-80°C$ and $-70°C$ for PEO, PDXL and PTGF respectively. *Figure 5* allows us to compare the phase diagrams of the three polymers.

Turbidity measurements. It is well known that many aqueous solutions of polymer phase separate upon heating and the particular solubility diagram for the PEO–water system described as 'closed loop' is a typical and extensively investigated example[3].

The lower critical solution temperature (LCST) of PEO is 100°C for high molecular PEO and 110°C for $M_w = 35\,000$. In *Figure 5*, we have reported the demixing curves in the phase diagrams as obtained for three samples of PEO, PTGF and PDXL of approximately the same molecular weight (35 000).

The demixing line of PTGF is close to that of PEO, but with a lower value of LCST (98°C). The behaviour of PDXL is significantly different concerning the LCST
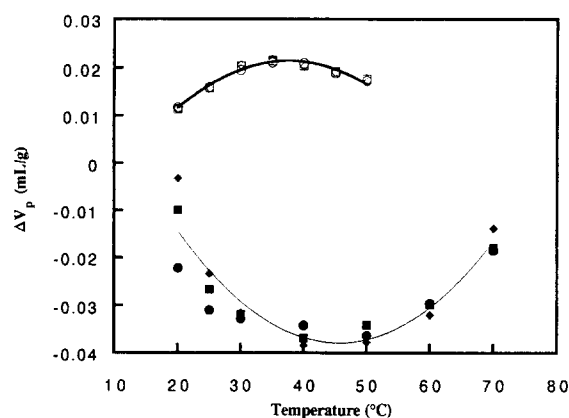
Figure 7 Variation of the mixing excess volume of PTGF (C_{PTGF} $(g\,g^{-1}) = 0.078$, $\Diamond$; 0.15, $\square$; 0.2, $\bigcirc$) and PDXL (C_{PDXL} $(g\,g^{-1}) = 0.07$, $\blacklozenge$; 0.1, $\blacksquare$; 0.2, $\bullet$) vs temperature
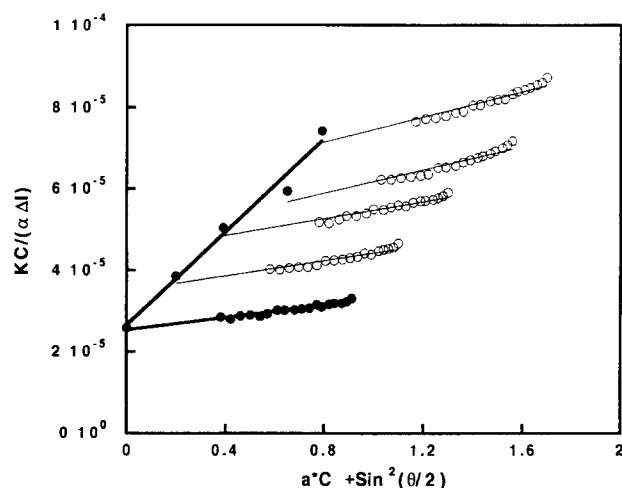

Figure 8 Zimm-plot of the PTGF sample in water, 0.05 N NaCl at 25°C; $KC/\Delta I$ is expressed in mol g^{-1}

value (74°C) as well as the shape of the line. Indeed, the cloud point increases when C increases for PEO and PTGF while the solubility of PDXL is limited in the low concentration range. Such a behaviour is not clearly understood. It may be explained by introducing in a theory of the Flory–Huggins type, applied to aqueous systems, an interaction parameter increasing strongly with concentration. It must be pointed out that we have recently observed that the solubility of PDXL of molecular weight between 10 000 and 30 000 strongly depends of the nature of the chains end groups: $-OCH_3$ or $-OH$. The behaviour of PDXL illustrated in *Figure 5* may be specific of $-OCH_3$ end groups which are able to decrease the solubility of the polymer in water. Nevertheless, it was observed that the value of LCST is the same with both end groups.

Figure 5 shows that the solubility domain of PTGF is limited by the demixing line at high temperatures, and by polymer and water crystallization at low temperatures.

Density measurements. We have measured by densimetry the specific volumes V_{12} of the solutions for $0 \leq C \leq 0.2\,g\,g^{-1}$ (*Figure 6*), in order to determine the sign and the amplitude of the excess mixing volume which constitutes an interesting information about the thermodynamic properties of the system.

The values of V_{12} increase normally with temperature.

The apparent specific volume of the polymer in solution V_2 is calculated from the classical law

$$V_2 = V_1 + \frac{V_{12} - V_1}{C} \tag{5}$$

V_1 and V_{12} being the specific volume of the solvent and of the solution respectively, and C being the weight concentration of polymer. For PTGF, we obtain $V_2 = 0.82685\,ml\,g^{-1}$ at 25°C. It is known that the partial molar volume, V_{m2}, of a large number of molecules, including non-ionic polymers, can be calculated from a simple law of additive partial molar volume group contributions[30–33]. For polymers, V_{m2} (with $V_{m2} = V_2 m_p$) represents the partial molar volume of the monomer unit. The V_{m2} value is 133.9 ml mol^{-1} for PTGF at 25°C.

By using for each constitutive group of PTGF the values given in ref. 32 for aqueous solutions ($V_{-CH} = 5.3$, $V_{-H} = 10.7$ and $V_{-O-} = 4.1\,ml\,mol^{-1}$), one finds $V_{m2} = 128\,ml\,mol^{-1}$, a value which differs by $-5.95\,ml\,mol^{-1}$ from the experimental one. Discrepancies of the same sign have already been observed between the calculated and experimental V_{m2} values in the case of PEO, PDXL[9] and ethylene oxide–propylene oxide copolymers (PEO–PPO) by Louai *et al.*[29]. These authors have proposed that the $-O-$ contribution could be 4.8 instead of 4.1 ml mol^{-1} at 25°C in water. By applying such a correction, the calculated value for PTGF becomes 131.2 ml mol^{-1}, which is closer to the experimental value. It must be pointed out that this usual additivity law does not take into account the specific solvation of the polymer according to its chemical structure.

Contrarily to the specific volume of the amorphous state, V_2 increases monotonously when R increases. This result is in agreement with calculated values.

Excess mixing volume

It is generally interesting to discuss the excess mixing volume (ΔV_P), which is expected to reflect water–polymer interactions. By using the measurements of the specific volume of PTGF in the amorphous state, we can calculate ΔV_P for different compositions and temperatures.

$$\Delta V_P = V_2 - V_{PA} \tag{6}$$

ΔV_P is the difference between the apparent specific volume in water and the specific volume of the pure polymer in the melt at the same temperature.

In *Figure 7*, the ΔV_P (ml g^{-1}) is plotted as a function of temperature for different polymer concentrations.

ΔV_P is always positive in the whole temperature range. This means that the solubilization of PTGF in water corresponds to a gain of volume with respect to the volumes of the polymer and water before mixing. This is an atypical behaviour, because ΔV_P for PEO, PDXL and PEO–PPO copolymers were found to be negative (*Figure 7*). In these latter cases, such variation is generally attributed to the formation of hydrogen bonds between ether oxygens and water molecules and the molar volume of the bound molecules is assumed to be lower than that of free water molecules[34,35]. Some authors have even proposed a structural model where PEO could be incorporated in the hexagonal water lattice[4,36]. In fact for PEO, the predicted molar excess volume is $-18\,ml\,mol^{-1}$, while the experimental value does not exceed $-4.4\,ml\,mol^{-1}$ at 25°C.
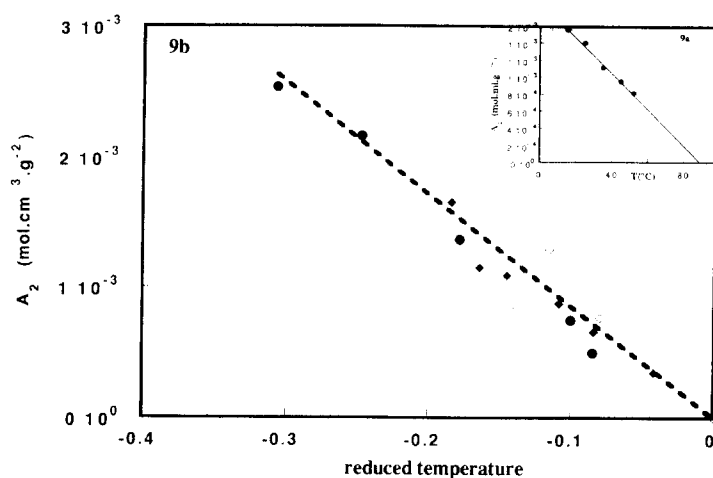
Figure 9 (a) Variation of the second virial coefficient of PTGF vs temperature. (b) Variation of the second virial coefficient vs the reduced temperature ((LCST-T)/T) for PTGF (O), PDXL (◆), PEO (●) and EO-PO copolymers (◇)
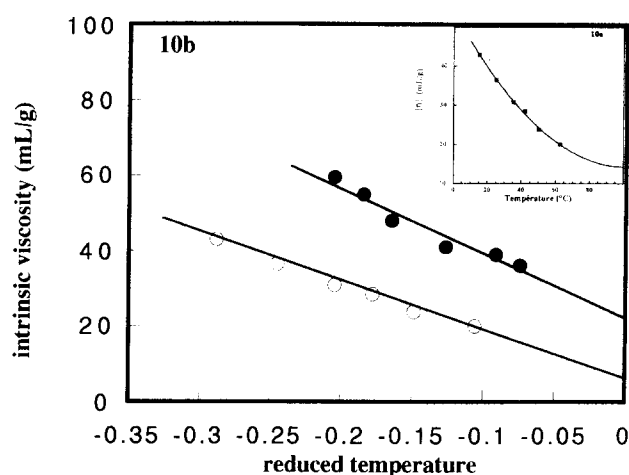

Figure 10 (a) Variation of the intrinsic viscosity of PTGF vs temperature. (b) Variation of the intrinsic viscosity vs the reduced temperature ((LCST-T)/T) for PTGF (O) and PDXL (●)

We cannot deduce that the PTGF is less hydrated in solution than the other polyethers, since the partial specific volume at infinite dilution monotonously changes with the polymer composition. What is in fact quite peculiar in the PTGF case, is the very low value of its specific volume in the amorphous state.

Light scattering and viscosity

Several previous works have been devoted to the problem of aggregation of PEO in water[37-39]. More recently, Selser and coworkers[40,41] have demonstrated that aggregate free solutions can be obtained by simple filtration using carefully purified water. We have also extensively studied the case of PDXL, and found that whatever the quality of the water used as solvent and porosity of the filters, it is very difficult to avoid aggregation in pure water and an excess of light scattered intensity is always observed[11] at low angle. In fact, it is not well understood if this phenomenon has a real physical significance, as proposed by de Gennes[42], or if it results from experimental artefacts. Nevertheless, we have shown that the addition of salt induces the disappearance of the low angle anomalies in the scattering curves[11].

We have made the light scattering study of PTGF

in the presence of salt (0.05 N NaCl) as a function of temperature. In *Figure 8*, is represented a classical Zimm plot obtained at 25°C. The angular dependence of the $KC_{pM}/\Delta I$ (where C_{pM} is the polymer concentration in g ml^{-1}, K is the optical constant and ΔI is the excess of scattered intensity of the solution with respect to the solvent (0.05 N NaCl)) is very linear. This confirms that under such salinity conditions, aggregation does occur. *Figure 9a* represents the temperature dependence of the second virial coefficient A_2. By extrapolation, at $A_2 = 0$, one finds a temperature of 90°C, which can be considered as the theta temperature of PTGF in water. Indeed, whatever the molecular weight, A2 is expected to tend to zero at $T = \theta$. This θ value is close to the LCST determined by turbidimetry for our sample of $M_w = 35000$ (see *Figure 5*). This is in agreement with the molecular weight dependence of LCST found by Saeki *et al.*[7] for PEO. The variations of A_2 as a function of the reduced temperature ($\tau = (\text{LCST} - \text{T})/\text{T}$) for PEO, PDXL and PTGF (compared at approximately the same molecular weight) are given in *Figure 9b*. The PTGF seems to have a different behaviour from both other polymers.

The intrinsic viscosity of PTGF was also measured as a function of temperature (see *Figure 10a*). This variation is plotted for PDXL and PTGF of approximately the same molecular weight using the reduced value τ. By extrapolation at $T = \theta = 90°C$ (as determined from the temperature dependence of A_2) or $\tau = 0$, one can obtain the intrinsic viscosity corresponding to the theta conditions. The value found for PTGF is surprisingly lower than that of PDXL: 7.5 ml g^{-1} and 22.9 ml g^{-1} respectively (*Figure 10b*). One can deduce the following Mark–Houwink laws for the intrinsic viscosity under the theta conditions, with a theoretical exponent 0.5 and obtain approximate values of the unperturbed dimensions of these polymers:

PTGF at LCST = 98°C $[\eta] = 0.04 \, M^{0.5}$ (7)

PDXL at LCST = 74°C $[\eta] = 0.11 \, M^{0.5}$ (8)

These power laws must be compared to those of:

PEO[1] at LCST = 110°C $[\eta] = 0.10 \, M^{0.5}$ (9)

or $[\eta] = 0.13 \, M^{0.5}$ (10)

and of an EO/PO copolymer:

$$0.8EO/0.2PO \quad \text{at LCST} = 65°C \quad [\eta] = 0.11\,M^{0.5}$$

$([\eta]$ is expressed in $ml\,g^{-1}$) \hfill (11)

Once again, the PTGF seems to exhibit a very peculiar behaviour with respect to the other polyethers, with a very low local rigidity of the chain. The length of the statistical segment, b, should be approximately 6.7 Å and 11 Å for PTGF and the other polymers respectively. The comparison may be more significant if we report the intrinsic viscosity to the number of chemical bonds n in the chain:

$$[\eta] = a\left[\frac{m_p}{n_p}\right]^{0.5}[n]^{0.5} = b[n]^{0.5} \tag{12}$$

where n_p is the number of chemical bonds per monomer units (C–C and C–O, $n_p = 3$ for PEO and EO/PO copolymers and 5, 11 for PDXL and PTGF respectively), a is the prefactor of the power laws (6 to 10) and m_p is the molecular weight of the monomer unit. The prefactor b of equation (12) is found equal to 0.44, 0.42, 0.15 and 0.44 for PEO, PDXL, PTGF and copolymer respectively. This suggests a much higher flexibility of PTGF as compared to the other polyethers. It has to be noted that this result is not in agreement with the determination of the characteristic ratios, C_∞, deduced from the fraction of cyclic polyacetals in PTGF and PDXL in methylene chloride solvent: 7.8[21] and 4.4[43], respectively.

DISCUSSION

If we try to summarize the results obtained for PTGF, and compare them with the data corresponding to the other polyethers, it appears that some of the measured parameters vary continuously with the fraction of EO units in the macromolecular chain, while other ones reflect a very peculiar behaviour for PTGF.

In the pure state, it had been already shown that the melting temperature of PTGF is much lower than that of PEO and PTGF. We report additional information concerning the volume properties. Indeed, the specific volume and the dilatation coefficient of PTGF in the amorphous state are surprisingly low. We have no explanation to propose at the molecular level. The problem is to understand why, in the absence of crystallinity, the sequence 3EO for 1MO induces such a compact packing. Further experiments able to give some information about the local arrangement of the monomer units are necessary.

In aqueous solution, the lower critical solution temperature monotonously decreases with the composition of the polymer. The apparent specific volume of all these polymers in water can be calculated from simple additivity laws of the apparent specific volume of each constituent of the chain. This means that nothing special occurs with PTGF, for these two quantities. Nevertheless, since its specific volume in the pure state is specially low, the mixing excess volume becomes positive while this parameter is generally believed to be strongly negative for the aqueous solutions of polymers. This may be understood by considering the following two antagonistic phenomena: firstly, PTGF is hydrated, as demonstrated by the d.s.c. experiments, and this effect

is accompanied by a loss of volume of water. Secondly, the compact packing found in the bulk disappears in aqueous solution and the average volume associated with the monomer unit increases. In PTGF the second effect dominates, while the first one is predominant for PEO and PDXL.

Another parameter varies continuously with the fraction of EO units in the polymer: the number of water molecules bound on the polymer as determined by d.s.c. at a temperature close to 0°C. We have concluded that this number corresponds, for PDXL, PTGF and PEO, to three molecules per EO unit, that we assume to be the only sites of water binding. It is interesting to note that, in other studies, we have also observed that the interactions with an anionic surfactant the sodium dodecyl sulfate regularly increase with the EO content in the chain.

The second virial coefficient of PTGF is intermediate between those of PEO and PDXL, but if it is plotted vs the reduced temperature, the straight line obtained has a slope significantly lower than those of the other polymers. Finally, the viscosity of PTGF is also surprisingly low in the whole range of temperature investigated and the unperturbed dimensions seem to indicate a high flexibility of the PTGF chain.

The phase separation behaviour of aqueous solutions of polymers has been interpreted from three concepts: the concept of free volume[7], the concept of hydration[5] and the concept of chain configuration[6]. It was interesting to question more or less quantitatively what approach may give the best account of the evolution of the polyethers properties in aqueous solution vs their composition.

Saeki *et al.*[7] have applied the Patterson theory[9] to the polar systems. The basis of these approaches is to introduce into the classical Flory theory[44] the dissimilarities of free volume between the polymer and the solvent. The Flory parameter χ is the sum of two terms:

$$\chi_{12} = \chi_{\text{(contact energy diss)}} + \chi_{\text{(free volume diss)}} \tag{13}$$

The first is the enthalpic term, related to the difference in the contact energies between solvent and polymer, and is a decreasing function of temperature. The second reflects the free volume effects and increases when temperature rises. For polar systems, this expression is rewritten by Saeki *et al.*[7]:

$$\chi_{12} = \left(\gamma_v \frac{V}{R}\right)\alpha^2 + \left(\frac{\gamma_v V T \alpha_p}{R}\right)\beta^2 + \left[VT\left(\frac{\left(\frac{\partial\gamma_v}{\partial T}\right)_p}{R}\right)\right]\sigma^2 \tag{14}$$

where γ_v and α_p are the thermal pressure and thermal expansion coefficients of the solvent, respectively. The parameter α^2 is related to the difference of cohesive energy and segmental size between solvent and polymer molecules. The parameter β^2 reflects the difference of the thermal expansion coefficient of the polymer and the solvent.

Starting from the classical Flory expressions for the chemical potentials of the solvent (1) and the polymer (2) which describe the phase separation in
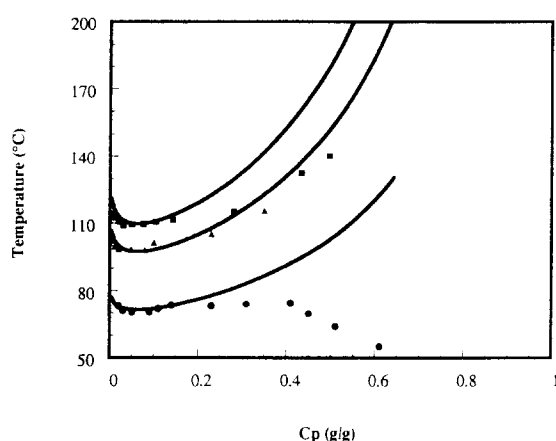
Figure 11 Experimental demixing lines for PEO (■), PTGF (▲) and PDXL (●); lines calculated with equation (14), ————

polymer solutions:

$$\mu_1 - \mu_1^0 = RT[\ln(1 - \phi_2) + (1 - 1/r)\phi_2 + \chi_{12}\phi_2^2] \quad (15)$$

$$\mu_2 - \mu_2^0 = RT[\ln(\phi_2) - (r - 1)(1 - \phi_2) + \chi_{12}r(1 - \phi_2)^2] \quad (16)$$

$$\text{with} \quad \mu_1 = \mu_1' \quad \text{and} \quad \mu_2 = \mu_2' \quad (17)$$

where ϕ_2 is the volume fraction the polymer and r is the ratio of the molar volume of polymer to that of solvent. It is possible from equations (15)–(17) to calculate the concentration dependence of χ_{12} at the phase separation, and by using expression (13), which gives the temperature dependence of χ_{12}, we have constructed the demixing lines for the three polymers, PEO, PTGF and PDXL. We have assumed that r was infinite for each polymer, and in expression (13), we have only varied the second term. Indeed, the solubility parameters δ_2 of PEO, PTGF and PDXL are respectively 22, 23 and 25.4 J$^{1/2}$ ml$^{-1/2}$, values calculated as described in ref. 10, and which can be compared with that of water $\delta_1 = 47.9$ J$^{1/2}$ ml$^{-1/2}$. By considering the proportionality between χ_{12} and $(\delta_2 - \delta_1)^2$, one can assume that the first enthalpic term in 14 does not vary much from a polymer to another. In *Figure 11* which shows that it is possible to get a good fit of the experimental demixing lines by taking for the terms $\alpha^2 = 0.1$ and $\gamma^2 = 0.1$ for the three samples and $\beta^2 = 0.15, 0.2$ and 0.4 for PEO, PTGF and PDXL respectively. The value of β^2 increases monotonously when the EO fraction in the chain decreases. Since (i) this parameter reflects the differences in the expansion coefficient of the polymer and the solvent and (ii) our density measurements have revealed a specially low value of α_p for PTGF, we expected also a non-regular variation of β^2 with the composition of the polymer. Thus, despite the fact that it is possible to fit the experimental data from the Saeki *et al.* approach[7], the parameters used for the fits do not reflect the true properties of the polymer. Thus, it seems that the concept of free volume is not appropriate in the case of the aqueous solutions of polymer. One may deduce that the free volume effects are only of marginal effect.

Let us consider now the theories based on a hydration effect. In the most recent approach of Matsuyama and Tanaka[5], the Flory theory is modified through the introduction of a binding equilibrium between water and the polymer. More precisely, a polymer chain containing

N segments possesses f sites of water binding. At each concentration and temperature, there are m sites which are bonded with the solvent, so-called clusters. The general picture is that the solubility of a polymer in water is due only to its hydration. This hydration decreases when temperature increases and there is a critical temperature above which the polymer recovers its own insolubility. Matsuyama and Tanaka[5] show that the value of the second virial coefficient can be positive even when the χ_{12} parameter is much higher than 0.5 through the following expression:

$$A_2 = \frac{1}{2} - [\chi_{12} - A'(T))] \quad (18)$$

where $A'(T)$ is a term which depends on the fraction m/f of clusters and decreases with T. There is a range of temperature where $A'(T)$ is higher than χ_{12} and the polymer becomes soluble. We can assume, as above, that the χ_{12} values for the three polymers are almost the same, and the differences in their solubility in water should be due to their differences in hydration only. Since we have observed that this hydration decreases when the fraction of EO units in the chain decreases, the depression of the LCST is consistent with Tanaka's theory. We may indeed consider that for PDXL, which is the less hydrated, the temperature at which the hydration number reaches the value at which $A_2 = 0$ is lower than for PEO and PTGF.

Nevertheless, even if the theories based on the site solvation are in our opinion the most attractive, we can also consider Goldstein's approach[45] and we cannot exclude the possibility of an influence of the chain conformation, as proposed by Karlström[6]. It seems quite evident that the *trans* and *gauche* populations must be different, according to the fraction of EO units.

CONCLUSION

We have compared a sample of PTGF in the pure state and in aqueous solutions, with other polyethers, mainly PEO and PDXL. PTGF is intermediate between the two others, if one considers the fraction of EO units in the chain, and the three polymers are not very different in terms of solubility parameters. However we have observed that PTGF often exhibits a very peculiar behaviour: the melting point, the expansion coefficient in the amorphous state and the flexibility in aqueous solutions are quite different from the other polymers. Some other properties, such as the LCST values, follow the expected variation. This work illustrates the great influence of the details in the chain conformation at the molecular level. Such behaviour should be studied through simulation techniques, in order to calculate the probability of each *trans–gauche* conformation and evaluate their influence on the polymer packing in the bulk and on the hydration effects.

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