Properties of ethylene oxide–propylene oxide statistical copolymers in aqueous solution

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This paper presents a thermodynamic study of aqueous solutions of ethylene oxide–propylene oxide statistical copolymers. In a first step, copolymer samples are carefully characterized by elemental analysis, ^1H and ^{13}C nuclear magnetic resonance, gel chromatography and light scattering. Secondly, the lower critical solution temperature is studied as a function of copolymer composition and concentration. This phase separation behaviour as well as the temperature dependences of intrinsic viscosity, second virial coefficient, Flory interaction parameter χ and partial specific volume are discussed in the background of different polymer theories.

(Keywords: poly(ethylene oxide); poly(propylene oxide); copolymers; phase diagram; lower critical solution temperature; intrinsic viscosity; molar partial volume)

INTRODUCTION

Ethylene oxide–propylene oxide (EO–PO) statistical copolymers have different industrial applications. If one excepts the early works of Bailey and Callard[1] and some reference data given in the review by Molyneux[2], there is a lack of available information about the thermodynamic properties of aqueous solutions of EO–PO copolymers.

In a first step, we have carefully characterized some copolymer samples, and the main purpose of this paper is to discuss their phase separation behaviour in aqueous solutions as well as the temperature dependence of various properties such as intrinsic viscosity, second virial coefficient and partial specific volume. The following paper will deal with the influence of different additives (mineral salts or organic compounds) on their solubility in water.

EXPERIMENTAL

Samples

The samples of ethylene oxide–propylene oxide copolymers have been furnished by Servimetal, France. The copolymer chains have star structure (three branches). Sample purity has been checked by gas chromatography (Hewlett–Packard 5880) from their aqueous solutions, and no low-molecular-weight impurities were found by this technique. We have used four samples: A, B, C and D (as in *Tables 1–3*).

Cloud-point measurements

The cloud points, T_t, were measured with a Mettler FP81 apparatus. The samples, contained in cylindrical cells (1 mm i.d. and 79 mm length), are heated at a given heating rate of 2°C min^{-1}. These cells are illuminated by a light source and the light scattered at 90° is measured as a function of temperature. The cloud point is considered as the temperature at which scattering abruptly increases.

Light scattering

Light scattering experiments were performed by using a home-built apparatus[3] equipped with a laser of wavelength 6320 Å. With the samples studied, the intensity of scattered light is independent of scattering angle, and weight-average molecular weight, M_w, and second virial coefficient, A_2, are simply deduced from measurements made at 90°.

The measurements of refractive index increments, dn/dc, were obtained with a Brice–Phoenix refractometer.

Viscosimetry

The viscosity measurements were made with an automatic capillary viscosimeter of high accuracy[4]. The capillary diameter was 0.7 mm and the water flow time was 33.700 ± 0.001 s at 25°C. The apparatus was thermostated at ±0.01°C.

Nuclear magnetic resonance

The ^{13}C n.m.r. spectra were obtained using a Brüker WT 200 SY spectrometer at 50.32 MHz. The samples were prepared in deuterated chloroform ($CDCl_3$) at 10% w/w.

The ^1H n.m.r. spectra were obtained using the same solutions and the same spectrometer at 200 MHz.

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Table 1 Characterization of the EO–PO copolymers by ^1H n.m.r. and elemental analysis. Symbols are explained in text (X_M is the value given by the manufacturer)

Sample	$r_{mol/mol}$	r_w	X_H	X_{el}	X_M
A	4.19	3.06	0.807	0.777	0.795
B	2.80	2.05	0.736	0.709	0.724
C	4.11	3.01	0.804	0.775	0.795
D	7.25	5.30	0.878	0.846	0.866

Gel permeation chromatography

The molecular-weight distributions of the samples have been obtained with two different g.p.c. apparatuses, working with water and tetrahydrofuran (THF) as eluents. The first one was equipped with large columns from Pharmacia (700 mm length and 30 mm diameter) filled with a mixture of Sepharose CL2B, CL4B and Sephacryl S300 gels. The eluent was water containing 0.1 N NaCl and 400 ppm NaN_3 as bacteriostat. The calibration was made with commercial poly(ethylene oxide) (PEO) standards. The second g.p.c. apparatus was equipped with five Styragel columns (porosity ranging between 500 and 10^6 Å) with a calibration obtained from polystyrene (PS) standards. The polydispersity index, *I*, obtained with the two types of apparatus are in good agreement, and this shows that there are no particular problems of adsorption or aggregation in aqueous g.p.c., at least with Sepharose gels.

Differential scanning calorimetry

A Mettler FP84 was employed. The samples were contained in a sapphire pan, quenched at −30°C and kept at this temperature for 30 min. Thermal analysis was performed at a heating rate equal to 2°C min^{-1}. The variation of the enthalpy of fusion of water, ΔH, with copolymer concentration is generally linear and the extrapolation to $\Delta H = 0$ gives a polymer concentration C'_p (grams of polymer per gram of solution) for which all the solvent is adsorbed. From the C'_p value, the ratio *R* of the number of solvent molecules adsorbed per monomer unit can easily be deduced from the following relation:

$$R = [(1 - C'_p)/m_s]/(C'_p/m_p) \qquad (1)$$

where m_s and m_p are respectively the molecular weights of solvent and monomer unit. This technique has already been widely applied to water-soluble systems[5,6] and polystyrene–organic solvent systems[7].

Density and partial specific volume measurements

For copolymer solutions, we used the method that relies on the difference of the frequencies of a vibrating tube filled by a solution and water as reference[8]. We used a densimeter of the DMA 02 type (Anton Paar) improved in our laboratory by the design of a cell which allows a precision of 5×10^{-6} g ml^{-1} on density measurements[9]. The apparatus is thermostated at ±0.005°C.

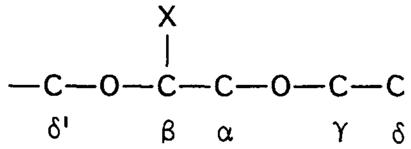
For pure copolymer, classical dilatometry was employed. Our dilatometer was made of a cylindrical cell (20 mm i.d. and 100 mm length) equipped with a graduated capillary (1 mm i.d. and 500 mm length) and calibrated with pure water at 25°C. The cell was filled with polymer samples, which are viscous liquids, and thermostated at 0.01°C. The determination of the thermal expansion coefficient was made by heating.

RESULTS

Characterization of the copolymer samples

^1H n.m.r. Starting from assignments of the different peaks in ^1H n.m.r. spectra of EO–PO copolymers given by Ramey[10], we have been able to determine the composition of each sample. In *Table 1*, we have reported the values of X, $r_{mol/mol}$ and r_w obtained from this analysis, where X is the molar fraction of the ethylene oxide in the copolymer, $r_{mol/mol}$ is the ratio of molar fractions of EO and PO and r_w is the ratio of the weight fractions of EO and PO. The samples have also been characterized by elemental analysis, and as seen in *Table 1*, the compositions obtained by both methods differ by 3% approximately (see X_H and X_{el}) and bracket the values given by the manufacturer and calculated from the monomer amounts used for the copolymerization.

^{13}C n.m.r. ^{13}C n.m.r. is a suitable method for the determination of the distribution of the EO and PO units along the chain. As previously shown by different authors[11–14], the determination of the dyad fractions of each sample can be made according to the Green–Whipple symbolism[13]. An example of such ^{13}C n.m.r. spectra is given in *Figure 1*. It can be decomposed into four groups of peaks, I, II, III and IV, corresponding to carbon atoms and to their substitutions by methyl groups:



$$\underset{\delta'}{-C}-O-\underset{\beta}{\overset{\overset{X}{|}}{C}}-\underset{\alpha}{C}-O-\underset{\gamma}{C}-\underset{\delta}{C}$$

I Substitution in α or β positions
II Substitutions in α and β or β and γ positions
III Unsubstituted segments
IV Substitution in γ position

There are six possible combinations of substitutions

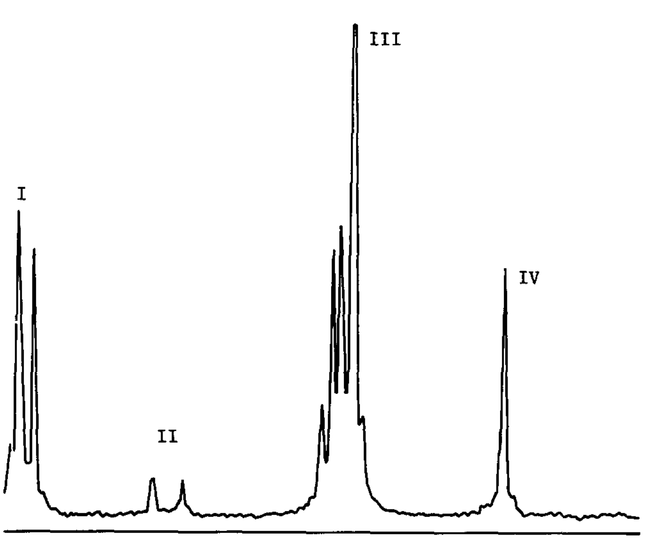


Figure 1 Example of ^{13}C n.m.r. obtained for our samples (sample B at 10% in $CDCl_3$)

Table 2 Dyad distribution (see text) as determined by ^{13}C n.m.r. and composition of the copolymers

Sample	f_{PE}	f_{PP}	f_{EP}	f_{EE}	X_C	X_C/X_H
A	0.1306	0.0249	0.1667	0.6788	0.8293	1.027
B	0.1566	0.0468	0.0247	0.5953	0.7759	1.053
C	0.1505	0.0228	0.1297	0.6970	0.8392	1.039
D	0.0969	0.000	0.0999	0.7988	0.9011	1.025

Table 3 Molecular parameters of copolymers as obtained by light scattering, gel chromatography and viscosimetry at 25°C

Sample	$10^{-4} M_w$	I	$10^{-3} A^2$ (cm^3 mol g^{-2})	$[\eta]$ (cm^3 g^{-1})	dn/dc (cm^3 g^{-1})
A	3.25	1.47	1.25	38.6	0.128
B	3.60	1.15	0.60	32.6	0.120
C	3.08	1.18	1.05	34.3	0.127
D	3.01	1.20	2.15	37.5	0.131

over a three-carbon segment. If we make the assumption that the numbers of head-to-head and tail-to-tail propylene oxide dyads are equal, we can write:

$$f_{PE} = 2A_{IV} \tag{2}$$

$$f_{PP} = 2A_{II} \tag{3}$$

$$f_{EP} = 2(A_I - A_{II} - A_{IV}) \tag{4}$$

$$f_{EE} = A_{III} + A_{II} + A_{IV} - A_I \tag{5}$$

where f is the fractional population of the subscripted dyad. E and P represent EO and PO monomers respectively. A_i is the normalized area of the subscripted band in the n.m.r. spectra. The relations (2) to (5) give the results summarized in *Table 2*. By comparison between X_H values (*Table 1*) and X_C values (*Table 2*) a discrepancy lower than 3% must be pointed out (see *Table 2*): ^{13}C n.m.r. leads to underestimates of the values of X. In the following, we will consider the X_H values, which are the closest to those given by the manufacturer.

By using the well known expressions of probability of finding the different dyads:

$$P_{EE} = \frac{r_E X/(1-X)}{(1+r_E X)/(1-X)} X \tag{6}$$

$$P_{PE} = \frac{1}{1+r_P(1-X)/X}(1-X) \tag{7}$$

where $r_E = k_{EE}/k_{EP}$ and $r_P = k_{PP}/k_{EP}$ (k_i is the reaction rate constant), we find, from *Table 2*: $r_E = 1.07$ and $r_P = 0.78$. Such values correspond to a quasi-Bernoullian statistics and these results are different from those obtained by Rastogi[15] ($r_E = 6.5$ and $r_P = 0.5$). With this last couple of r values, long sequences of ethylene oxide can be expected, which is apparently not the case with our copolymers. Nevertheless, we have not enough information about their preparation to draw a significant conclusion. Let us keep in mind that the samples studied can be considered, at least in a first approximation, as statistical copolymers of rather well defined composition.

Light scattering, viscosimetry, g.p.c. In *Table 3*, we have gathered the values of: (a) average molecular weight, M_w, and second virial coefficient, A_2, deduced from light scattering measurements in water at 25°C; (b) refractive index increment, measured under the same conditions; (c) polydispersity index, I, obtained in two different solvents, water and THF (see 'Experimental' part); and (d) intrinsic viscosity, measured in water at 25°C.

We only note here that M_w values are nearly the same for the four samples. The other results will be discussed later.

Thermodynamic study

Cloud point. As shown in *Figure 2a*, phase diagrams of EO–PO copolymer solutions are identical to that described for the PEO homopolymer[16]. The critical demixing temperature and critical concentration C_p^* decrease when the fraction of PO increases.

[We will call this critical demixing temperature *LCST'* since one can think that, as for PEO, it lies below the upper critical solution temperature (*UCST*). Such a behaviour is generally believed to be due to strong dipole–dipole interactions or hydrogen bonds[16–18] and is observed for polar systems[19–22]. It must be distinguished from that obtained in non-polar polymer solutions, e.g. polystyrene solutions[22–24] and poly-

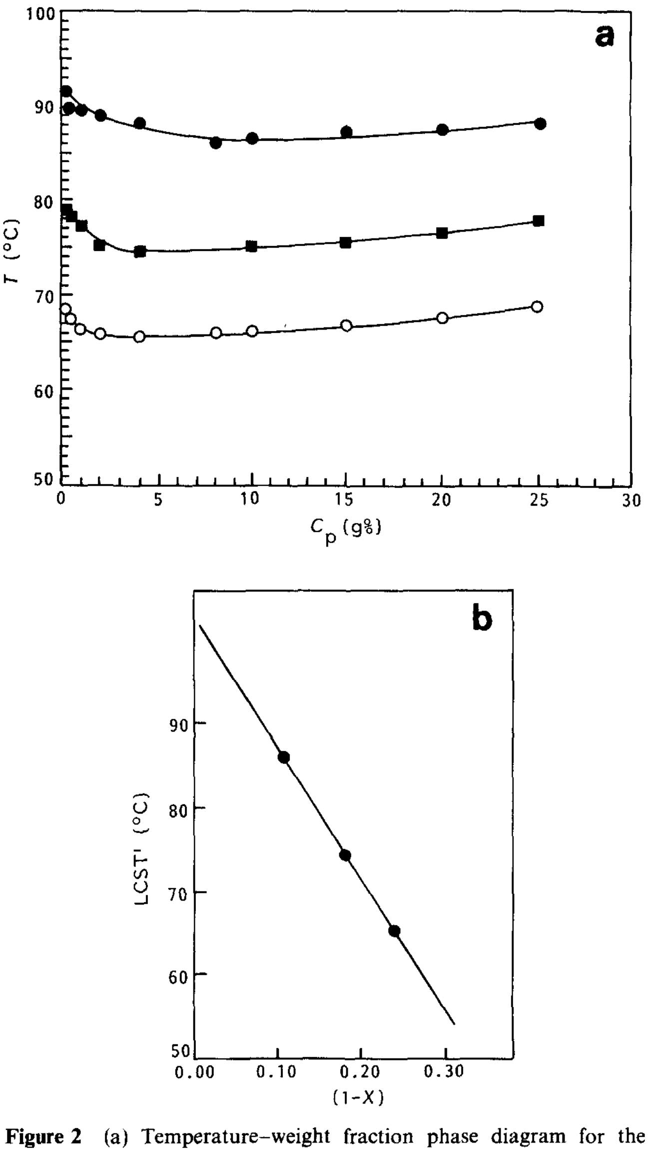


Figure 2 (a) Temperature–weight fraction phase diagram for the samples B (○), C (■) and D (●). (b) Variation of the lower critical solution temperature *versus* PO fraction in the copolymer

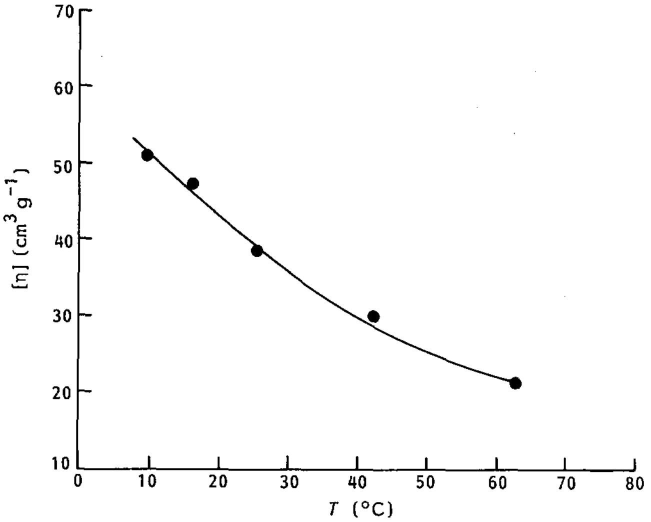


Figure 3 Temperature dependence of intrinsic viscosity for sample A

ethylene solutions[25]. In this second case, the lower critical temperature lies above *UCST* and it is generally called *LCST*.]

Figure 2b shows that *LCST'* is a linear function of the molar fraction of PO units. By extrapolating the points to $(1-X)=0$, the *LCST'* value (102°C) is in very good agreement with that found from results of Saeki *et al.*[16,26] for PEO. These authors have obtained $LCST' = 101.6$°C and 103.1°C for $M_w = 4.7 \times 10^4$ and $M_w = 2.1 \times 10^4$ respectively. For $M_w = 3.2 \times 10^4$ (averaged on the M_w values of samples B, C and D) one finds:

$$LCST' = 102.5 - 154.5(1-X) \qquad (8)$$

This relationship is also very near that deduced from Bailey and Callard's results[1] for higher M_w:

$$LCST' = 100.0 - 154.0(1-X) \qquad (9)$$

It is well known that an increase of molecular weight causes a lowering of *LCST'* and, as for *UCST*, the Flory θ temperature[27] is defined as *LCST'* obtained for a polymer of infinitely high molecular weight:

$$1/LCST' = 1/\theta - k'/n \qquad (10)$$

where n is degree of polymerization. By taking for our copolymers the value of $k' = 1.6 \times 10^{-3}$ found from ref. 17 for PEO, one can obtain approximate values of θ for each copolymer composition: $\theta = 76$, 65 and 56°C for $X = 0.88$, 0.80 and 0.74 respectively.

Intrinsic viscosity. *Table 3* shows that $[\eta]$ measured at 25°C is a decreasing function of PPO content $(1-X)$. These values are lower than that calculated for PEO of the same M_w from the Mark–Houwink law:

$$[\eta] = 5.4 \times 10^{-2} M^{0.66} \quad (\mathrm{cm^3\,g^{-1}}) \qquad (11)$$

determined by one of us under the same experimental conditions[29] (in pure water at 25°C) and using Toyo Soda standards: $[\eta]_{X=1} = 50\ \mathrm{cm^3\,g^{-1}}$.

For sample A, we have studied the temperature dependence of $[\eta]$ (see *Figure 3*). The results can be adjusted by an empirical law:

$$[\eta] = 59.25 - 0.91T + 0.004T^2 \qquad (12)$$

where T is expressed in degrees Celsius. For $T = \theta$, one finds $[\eta]_0 = 20.6\ \mathrm{cm^3\,g^{-1}}$. Two experimental laws are available in the literature for PEO in θ conditions[29]:

$$[\eta] = 0.1M^{0.5} \quad \text{and} \quad [\eta] = 0.13M^{0.5} \qquad (13)$$

For $M_w = 3.25 \times 10^4$ (sample A), one finds 18 and 23.4 cm^3 g^{-1} from these two relations respectively. Then, one can deduce that, at least for $X > 0.8$, unperturbed dimensions are not strongly modified by the presence of propylene oxide units.

[As pointed out in the 'Experimental' part, our copolymer samples have star-like structure (three branches) and the coil dimensions are expected to be slightly lower than those of a linear polymer.]

From this value of $[\eta]_0$, the viscosimetric expansion coefficient $\alpha_n = [\eta]/[\eta]_0$ is obtained as a function of T. We will discuss the results, which are reported in *Figure 5*, later.

Second virial coefficient A_2. At 25°C, the second virial coefficient, A_2, decreases on increasing X (see *Table 3*), and in *Figure 4*, we compare the $(1-X)$ dependences of θ temperature, A_2 and $[\eta]_{25°C}$. The X values (or $1-X$) at which $A_2 = 0$, $\theta = 25$°C and $[\eta]_{25} = [\eta]_0$ should theoretically be equal[28]. In fact, there is a rather good agreement between the three values, and the average value gives an approximate composition $(X = 0.5)$ at which EO–PO copolymers can be considered in θ conditions in pure water at 25°C.

In the same manner, A_2 measured for sample A tends to zero on increasing T (see *Figure 5*). The T value at which $A_2 = 0$ is compatible with the θ value previously given. From A_2 and α_n, the temperature dependence of

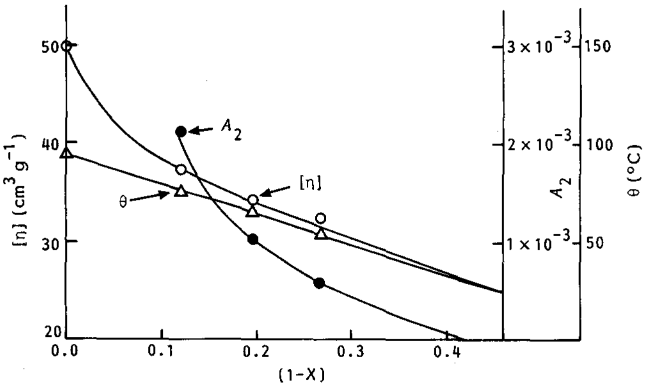


Figure 4 Second virial coefficient A_2 (●), intrinsic viscosity $[\eta]$ (○) at 25°C and calculated Flory temperature θ (△) *versus* fraction of PO units in the copolymer

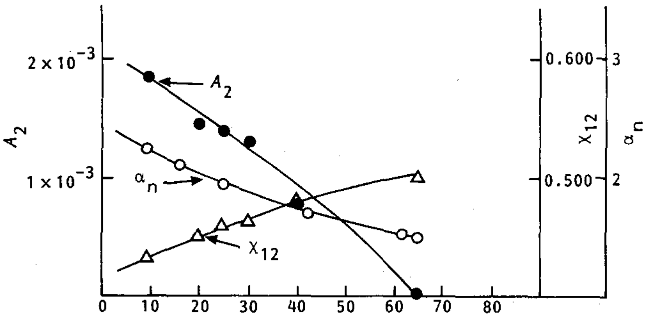


Figure 5 Interaction parameter χ_{12} calculated from relation (14) (△), second virial coefficient A_2 (●) and viscosimetric expansion coefficient α_n (○) *versus* temperature for sample A

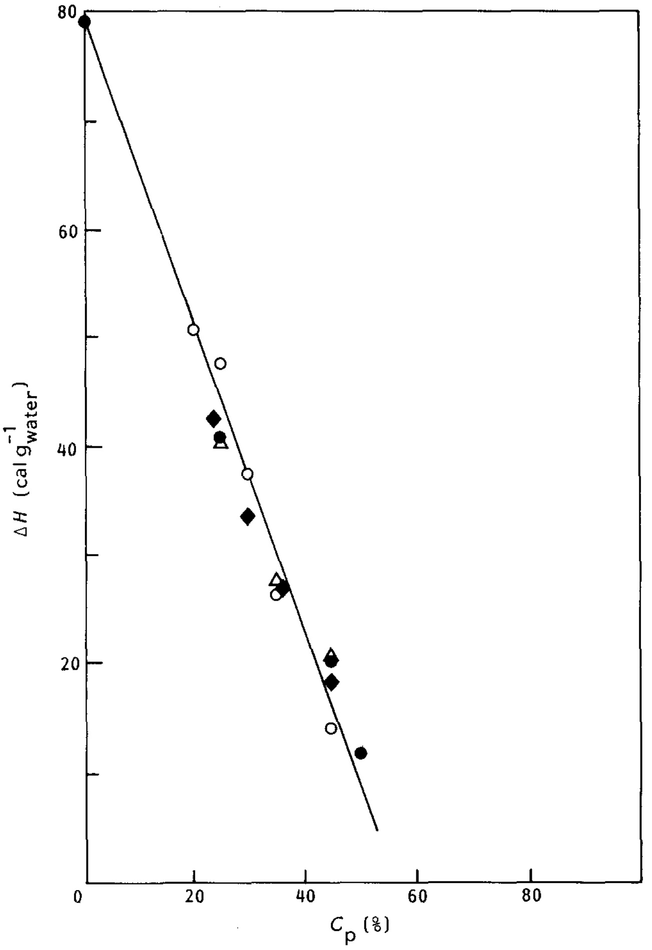


Figure 6 D.s.c. experiments: enthalpy of fusion of water as a function of polymer concentration. Sample A (●), sample B (○), sample C (△) and sample D (◆)

the interaction parameter χ_{12} can be calculated by using the Flory relation:

$$A_2 = (v_2^2/V_1)(1.2 - \chi_{12})\Psi(X) \quad (14)$$

where v_2 is the specific volume of the polymer (see below), V_1 is the molar volume of the solvent, $X = 2(\alpha^2 - 1)\alpha$ is the polymer expansion coefficient, with $\alpha = \alpha_n^{1/2.43}$ according to Yamakawa[31], and Ψ is a function defined in ref. 27.

One can see in *Figure 5* that χ_{12} for sample A varies between 0.43 and 0.50 in the investigated temperature range, which is usual for all polymers in the same temperature interval above *UCST*.

Unfreezing water. D.s.c. experiments were undertaken in order to establish the influence of propylene oxide units on the hydration state of the polymer. It has been suggested[29–33] that the solubility of PEO in water is due to the formation of some specific hydrogen bonds between the ether oxygens of PEO and water molecules, and it is generally expected that the water-structure effect plays an important role on the solution characteristics. We have measured by the d.s.c. method the enthalpy of fusion of water in concentrated solution of our copolymers and compared these results with those obtained with a PEO sample of approximately the same molecular weight. ΔH (cal g^{-1}) is plotted as a function of C_p in *Figure 6*. Despite experimental scatter, which is probably due to errors on the composition, it appears that PO units do not strongly perturb water structure around polymer. The results are quite consistent with a value of 2 for R, which represents the number of water molecules adsorbed per monomer unit (calculated from equation (1)).

In the case of the PEO sample, the same value has been found and it exactly corresponds to the hydrogen-bonding capacity of the ethylene oxide chain[34].

Nevertheless, the analysis of d.s.c. results is more difficult in this case because an endothermic melting peak of PEO crystallized domains is superimposed on that of water fusion. In *Figure 7*, we compare d.s.c. traces obtained for sample A and PEO at the same concentration (20%). In the PEO case, the low-temperature peak increases on increasing the polymer concentration while the water fusion peak progressively disappears. This first peak has never been observed with our copolymers even for sample C of high EO content. This means that a low fraction of PO completely hinders crystallization. This is important information because one can conclude that PO–EO copolymers are able to dissolve better in water than PEO, which is well known to form aggregates[35,36]. Then light scattering studies are made easier and the molecular-weight measurements are correct.

Specific volume. We have undertaken a study of the volume properties of our copolymers in the pure state and in aqueous solutions: values of partial specific volume are required for instance for the determination of χ_{12} from A_2 (relation (14)). On the other hand, the sign and the amplitude of the excess mixing volume constitutes interesting information about the thermodynamic properties of the system.

(*i*) *Partial specific volume* v_2 *at 25°C for* $C_p \to 0$. The apparent specific volume of polymers in solution is calculated from the classical law:

$$v_2 = v_1 + (v_{12} - v_1)/\omega_2 \quad (15)$$

v_1 and v_{12} being the specific volume of solvent and solution respectively and ω_2 the weight concentration of polymer. Values equal to 0.855 and 0.860 cm^3 g^{-1} were found for samples A and B respectively at 25°C.

It is known that the partial molar volumes V_{m2} of a large number of molecules, including non-ionic polymers,

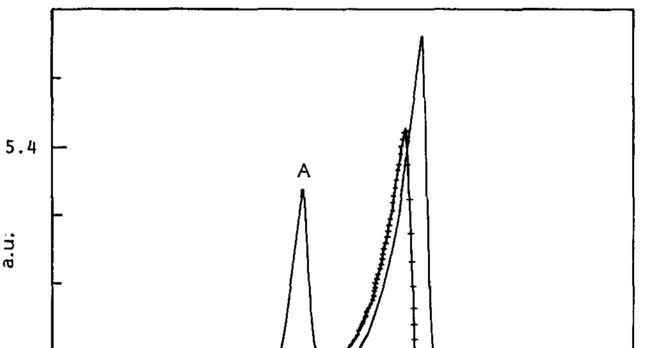


Figure 7 D.s.c. traces for PEO (A) and sample B (B) at the same polymer concentration (20%)

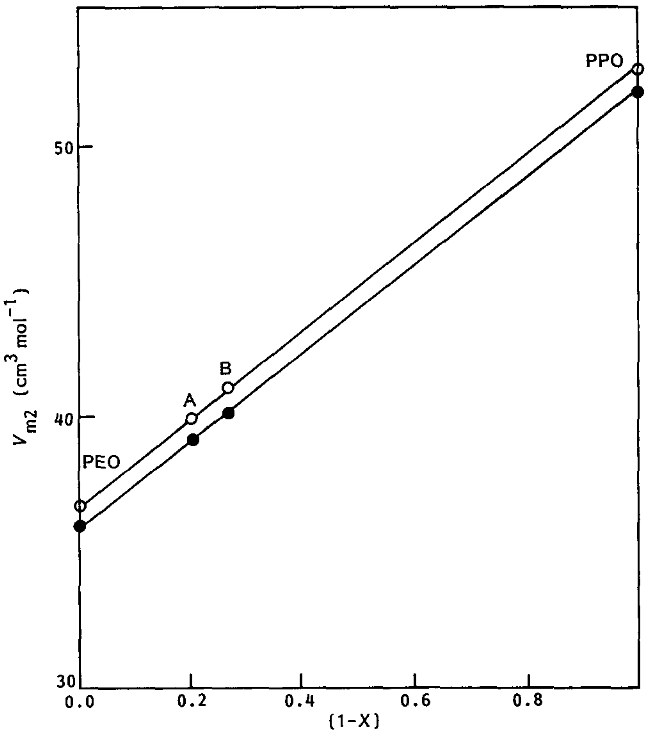


Figure 8 Calculated (○) and experimental (●) partial molar volume V_{m2} as a function of fraction of PO units

can be calculated from a simple law of additive partial molar volume group contributions[37–40]. For polymers, V_{m2} (with $V_{m2} = v_2 m_p$) represents the partial molar volume of the monomer unit. For our copolymers, we have considered an average value of m_p:

$$m_p = X m_{PEO} + (1 - X) m_{PPO} \tag{16}$$

The V_{m2} values are 39.92 and 41.01 cm^3 mol^{-1} for samples A and B respectively, to be compared with $V_{m2} = 36.74$ cm^3 mol^{-1} found for PEO of the same molecular weight[41]. By using the group contribution values given in ref. 41 ($v_{-CH_3} = 26.7$, $v_{-CH-} = 5.30$, $v_{-H} = 10.7$, $v_{-O-} = 4.10$ cm^3 mol^{-1}), one finds $V_{m2} = 36.10$, 39.19 and 40.31 cm^3 mol^{-1} for PEO, sample A and sample B, values which differ by -0.64, -0.72 and -0.70 from the experimental values.

In *Figure 8*, calculated and experimental values of V_{m2} are plotted as a function of X. Both straight lines have exactly the same slope. This indicates that the error could arise from the contribution of –O– to V_{m2} rather than from those of –CH$_3$, –CH– and –H. One could deduce from these results that the –O– contribution could be 4.8 instead of 4.1 cm^3 mol^{-1} at 25°C in water.

(*ii*) *Excess mixing volumes.* We have measured by densimetry the specific volumes of solutions for $0 < C_p < 0.4$ w/w. The volume of pure sample A has been measured by picnometry as a function of temperature and we have found $V_p = 0.9266$ cm^3 g^{-1} and thermal expansion coefficient $\alpha_p = 7.61 \times 10^{-4}$°C^{-1} $[\alpha_p = (1/V_p)(dV_p/dT)]$.

By combining these two series of measurements, we have determined the excess volume ΔV_E for different compositions and temperatures for sample A. *Figure 9* shows that ΔV_E is always negative and for a given composition seems to present a minimum at 20–30°C. We have reported in *Figure 10* the values obtained by Malcolm and Rowlinson[22] for PPO and PEO at 50 and 65°C respectively for the same concentrations (polymer weight concentration $\omega_2 = 0.2$ and 0.4). The agreement with these two sets of experiments is quite remarkable and means at first that the presence of methyl groups of PPO does not strongly change the water structure around the chain. This is consistent with our previous observations by d.s.c. But these results are more convincing since they include the case of PPO. Kjellander *et al.*[19] have developed the model previously proposed by Blandamer and Majigren[32,33], where a simple polymer chain could be incorporated in a hexagonal water lattice with hydrogen bonds between most of the ether oxygens and water. They themselves pointed out that in such a structural model (without interstitial water) the molar excess volume should be -18 cm^3 mol^{-1} or

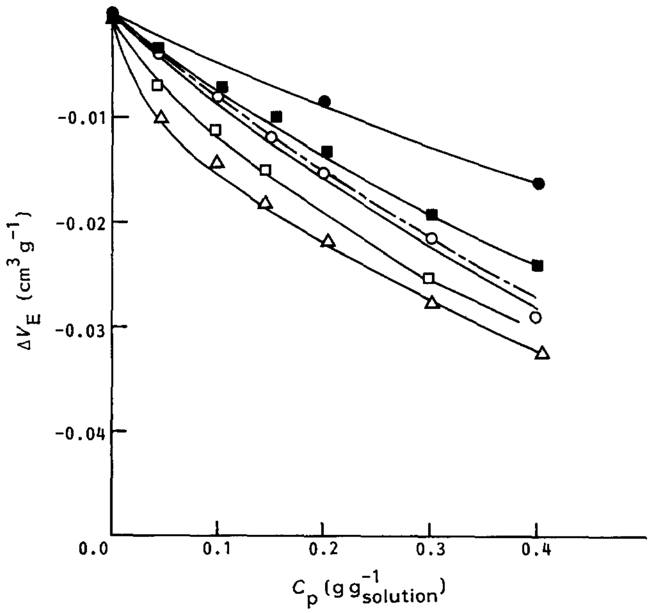


Figure 9 Excess volume ΔV_E as a function of polymer concentration at different temperatures: PEO at 65°C (●); PPO at 50°C (– – – –); sample A at 46.5°C (■), 30°C (○), 24.8°C (△) and 15°C (□)

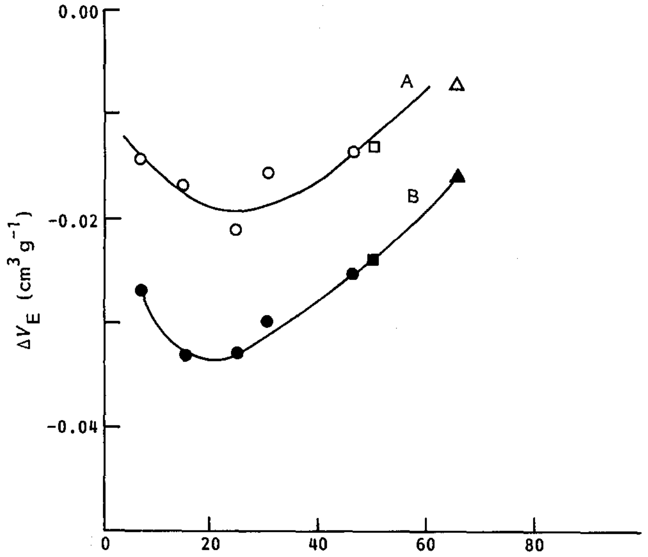


Figure 10 Excess volume ΔV_E as a function of temperature at two polymer concentrations, $c_p = 0.2$ g/g (curve A) and $c_p = 0.4$ g/g (curve B), for PEO (△), PPO (□) and sample A (○)

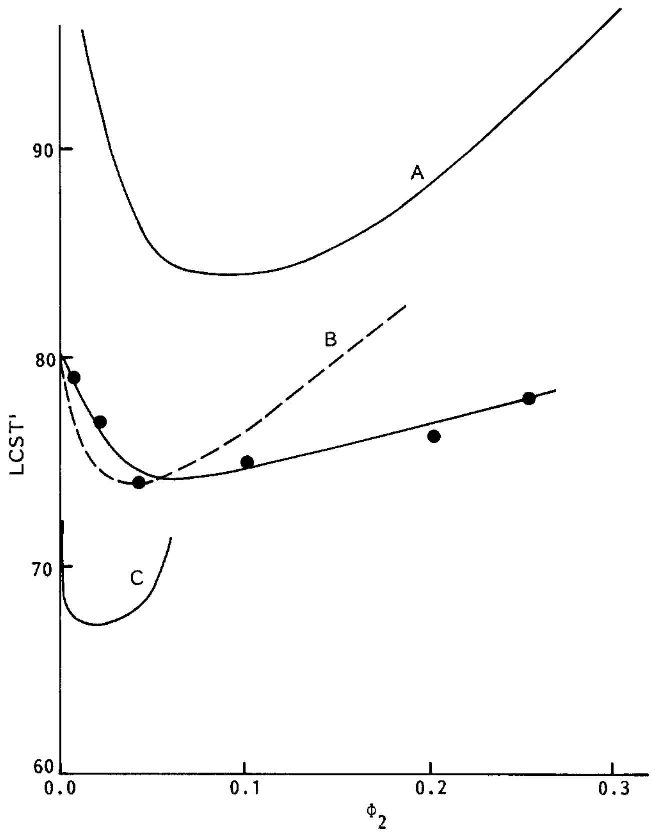


Figure 11 Experimental (●) and calculated binodal curves for $M = 5000$ (A), $M = 3.2 \times 10^4$ (sample A) (B) and $M = 5 \times 10^4$ (C)

$-10\ cm^3\ mol^{-1}$ if one takes into account that the methylene group of a PO unit occupies the interstitial volume in more than one cell. As a matter of fact, they concluded that their model cannot give a good account for the small absolute value of ΔV_M obtained from results of Malcolm and Rowlinson[22]. From values of *Figure 10*, ΔV_E is approximately -1.6 at 65°C and $-4.4\ cm^3\ mol^{-1}$ at the minimum of the curves. The partial thermal expansion coefficient α_p of sample A is $1.3 \times 10^{-3}\ °C^{-1}$. By comparing with α of water and sample A, a large excess of expansion is found, as already observed by Saeki *et al.*[42] for poly(ethylene oxide) in water.

DISCUSSION

Calculation of the binodal curve

The phase separation behaviour is generally analysed in the background of the Flory–Huggins theory.

The chemical potential for solvent and polymer in the solution are respectively given by:

$$\mu_1 - \mu_1^0 = RT[\ln(1-\Phi_2) + (1-r^{-1})\Phi_2 + \chi_{12}\Phi_2^2] \quad (17)$$

$$\mu_2 - \mu_2^0 = RT[\ln \Phi_2 - (r-1)(1-\Phi_2) + \chi_{12}r(1-\Phi_2)^2] \quad (18)$$

where Φ_2 is the volume fraction of the polymer, r the ratio of the molar volume of the polymer to that of the solvent (equal to n in a first approximation) and R the gas constant. The conditions of phase equilibrium for the two phases are given by:

$$\mu_1 = \mu_1' \qquad \mu_2 = \mu_2' \quad (19)$$

where the prime indicates the concentrated phase.

If the temperature dependence of χ_{12} is known, it is possible to calculate the binodal curve, using the procedure given by Flory[27]. The relationship $\chi_{12} = f(T)$ is based on the change in the observed critical temperature with molecular weight. For sample A, we have used the empirical expression:

$$1/LCST' = 1/(273+65) + 1.6 \times 10^{-3}(n)^{-1/2} \quad (20)$$

with

$$\chi_{12} = 1/2 - (n)^{-1/2} \quad (21)$$

It can be seen in *Figure 11* that (for sample A) the experimental binodal curve is broader than that calculated as shown by the broken curve and, although they are inversed, these plots look like those published by Shultz and Flory for polyisobutylene in diisobutyl ketone (*UCST* behaviour)[27].

Theoretical predictions of lower critical solution temperature

The main criteria for a lower critical solution temperature (*LCST*) can be briefly summarized as follows:

free energy excess	$\Delta G^E > 0$
enthalpy excess	$\Delta H^E \leqslant 0$
entropy excess	$\Delta S^E < 0$

and *LCST* results from large negative deviations from ideality. Since ΔG^E must be positive, it follows that:

$$T|\Delta S^E| > |\Delta H^E|$$

There are two main approaches for the predictions of phase separation behaviour of non-electrolyte polymer solutions such as PEO–water, which is characterized by a closed-loop type phase diagram.

Such characteristics have been explained by different authors who used models of highly directional bonds between molecules with more or less sophisticated approaches (Ising model[17], statistical-mechanical models[18] or simple structural models[19–21]). Recently, Saeki *et al.*[25] have shown that it is possible to predict these diagrams using the Flory–Huggins theory and a thermodynamic equation of state derived from the corresponding-states principle.

Among the theories of the first type, let us consider the simplest approach developed by Kjellander *et al.*[19]. This model is based upon the idea of a specific coupling between PEO and a connected water structure. Then the formulation for $\mu_1 - \mu_1^0$ is formally identical to the Flory–Huggins expression with a meaning of χ_{12} completely different. In the Flory–Huggins theory, it is assumed that all the solvent molecules have the same energy and, for the solvent molecules that are in the neighbourhood of the polymer, a correction due to the solvent–solute interaction is introduced. In the model applied to the PEO–water system, this correction also includes the change of state for the water molecules that constitute the hydration shells. From this point of view, the differences of solubility in water of the different polyethers is mainly due to the fact that only PEO satisfies geometric conditions to allow the formation of a continuous network around the chain.

In the particular case of PPO, Kjellander *et al.*[19] suggest that methyl groups constitute a steric hindrance to the formation of an 'optimal water structure'.

In fact, our measurements of density and enthalpy of fusion of water (d.s.c.) are not consistent with such a description since the same orders of magnitude of partial specific volume and fraction of 'bound water' have been found for PEO, PPO and copolymers. According to the Kjellander approach[20], one should observe a decrease of the absolute value of the excess mixing volume, ΔV, on increasing the content of PO in the copolymer, this effect being correlated to the lowering of $LCST'$. In fact, lowering of $LCST'$ can be observed without significant changes in the structure of the hydration shell.

This result qualitatively means that the excess enthalpy is much more sensitive to the hydrophobicity of the polymer than the entropy excess and the $LCST'$ lowering by decreasing X is essentially a consequence of large differences between energies of polymer–water interactions. This is consistent with the results of Malcolm and Rowlinson[22], which show that the differences between PEO–water or PPO–water are more pronounced for dilution enthalpy than for dilution entropy. In fact, what is said by Kjellander on the hindrance by methyl groups of water structuration is probably true, but one could suggest that this effect is compensated by the well known 'structuring effect' of hydrophobic compounds. Only slight changes in excess volumes or excess entropy result from the compensation of these two effects.

The second approach is that proposed by Saeki *et al.*[16,42], who apply the Patterson[43–48] theory to the case of polar systems. The well known Patterson expression for χ_{12} contains a term that reflects the dissimilarity of contact energies between solvent and polymer (decreasing function of temperature and in fact identical to χ_{12} of Flory) and a second term that reflects their dissimilarities of free volume:

$$\chi_{12} = \chi(\text{contact energy diss.}) + \chi(\text{free volume diss.}) \tag{22}$$

A more precise formulation has been derived, which only takes into account intermolecular energy of van der Waals type and cannot be applied to aqueous solutions. Saeki *et al.*[16,42] show that a more general expression can be obtained without neglecting polar interactions and which could be useful for all polar systems:

$$\chi_{12} = (\gamma_v V/R)\alpha^2 + (\gamma_v V T \alpha_p/R)\beta^2 + [VT(\partial\gamma_v/\partial T)_p/R]\sigma^2 \tag{23}$$

where γ_v and α_p are the thermal pressure and thermal expansion coefficients of the solvent respectively. In fact, the first two terms are identical to the terms of the Patterson relation and the parameters α^2 and β^2 must have the same meaning: 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 coefficients of the polymer and solvent.

On *Figure 12*, we reproduce the variations of the first three terms of the expression of χ_{12} with $\alpha^2 = \beta^2 = \sigma^2 = 1$. As pointed out by Saeki *et al.*, the temperature dependence of γ_v for water is very particular since it has a maximum around 150°C while γ_v for most organic liquids decreases monotonically with increasing temperature. By only considering the first term with $\alpha^2 = 0.2$, the closed-loop diagram characteristics of PEO behaviour has been obtained by these authors.

Let us also assume in a first approximation that $\alpha^2 \gg \beta^2$ and σ^2; the lowering of $LCST'$ on increasing PO content for EO–PO copolymers must be discussed from changes in the parameter α^2. On this basis, one finds $\alpha^2 = 0.14$ for PEO and $\alpha^2 = 0.167, 0.179$ and 0.193 for copolymers with $X = 0.88, 0.80$ and 0.74 respectively. Since α^2 reflects the dissimilarity of contact energies between water and polymer, one again finds that the variation of the enthalpic term seems to be the most important factor to

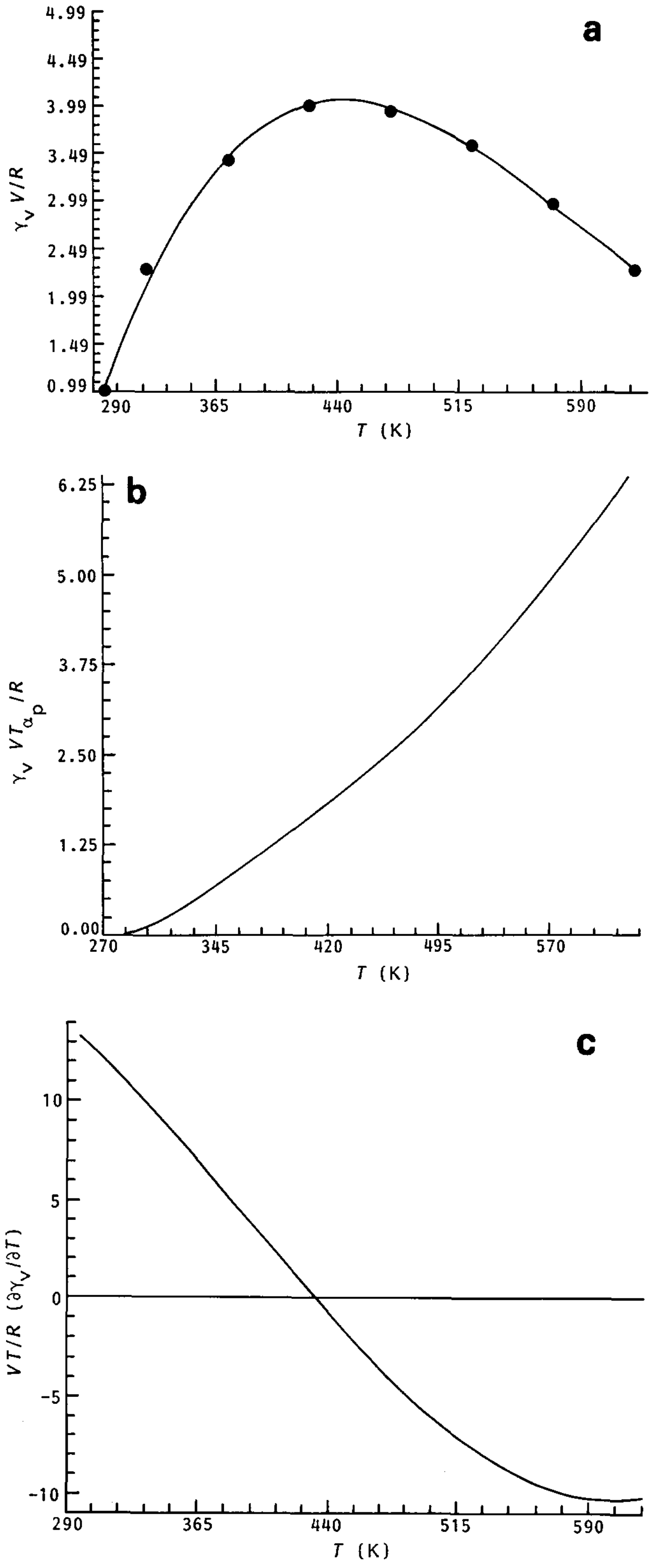


Figure 12 (a), (b) and (c) Temperature dependence of three terms of expression (23) of Saeki *et al.*[17,43]

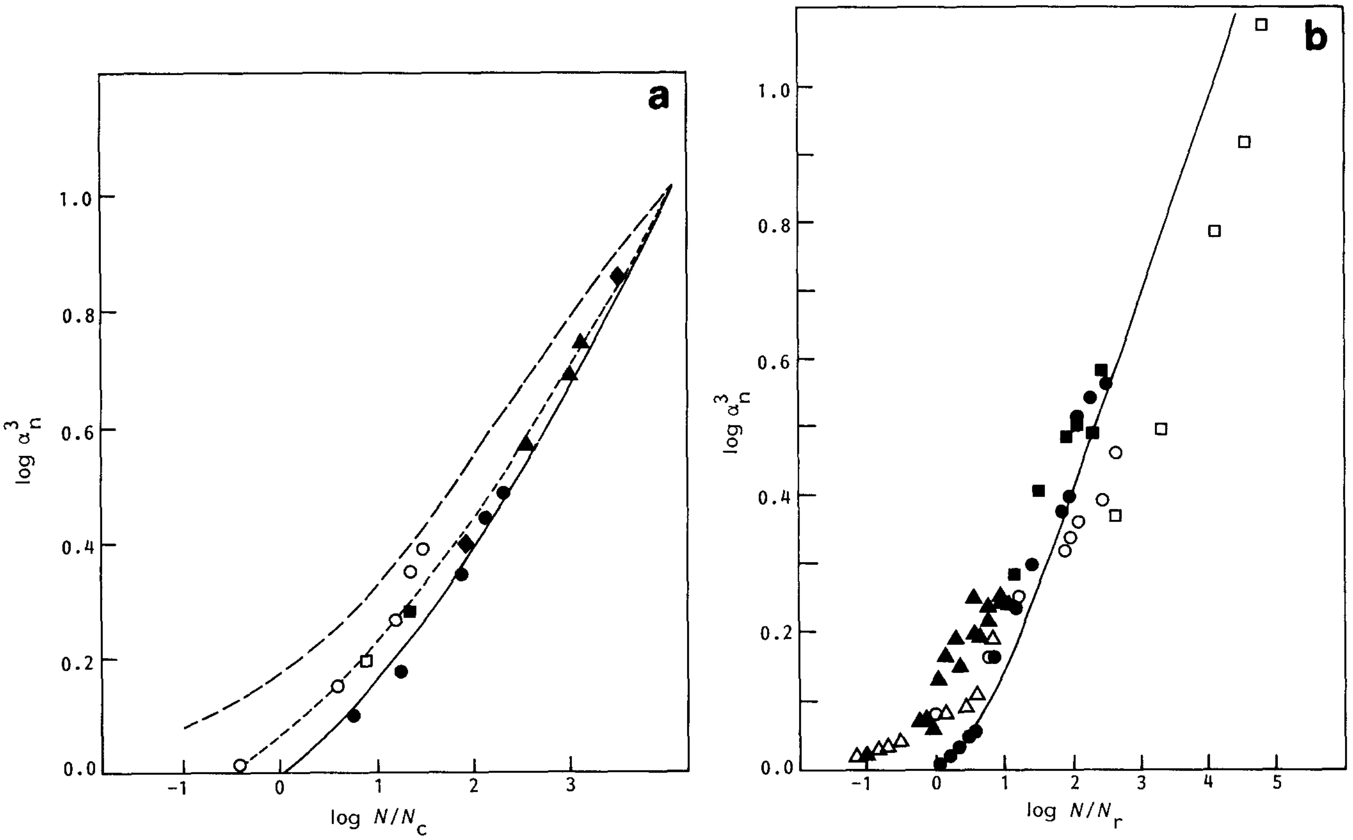


Figure 13 Comparison between Flory theory (– – –), blob theory (———) and experimental results. (a) $T < LCST'$: sample A at different temperatures (○); samples B and D at 25°C (□, ■); and PEO from results of ref. 52 (▲, ●). (b) $T > UCST$: experimental points corresponding to different data (see text)

explain the decrease of $LCST'$ on increasing the PO fraction in the copolymers.

Then the Saeki *et al.*[16,42] approach gives a good qualitative account of the $LCST'$ lowering if one considers that the main parameter is α^2 and the first term is dominant in the expression of χ_{12}.

Nevertheless, several questions are raised for the quantitative application of this theory:

(i) What is the meaning of σ^2 and, if the meanings of α^2 and β^2 are those defined by Patterson[44,45], how can one calculate them? Patterson and Delmas[46,47] have derived expressions for these parameters that depend on $3c_1$, the number of external degrees of freedom possessed by the solvent molecule. In the case of autoassociated solvent, the concept of degree of freedom is not clear.

(ii) In aqueous solutions of polyacrylamide, it has been shown that χ_{12} is a decreasing and not increasing function of T, for $0 < T < 100$°C; no combination of the three terms of *Figure 11* with different values of parameters α^2, β^2 and σ^2 allows one to predict such behaviour.

Some further theoretical developments should be necessary to understand the problem of phase separation in water–polymer systems.

Temperature dependence of polymer expansion

Many theoretical and experimental studies dealt with the problem of the temperature dependence of polymer expansion just above $UCST$ while there is a lack of information when phase separation is reached by heating.

For the first case, in the classical Flory theory[27] as well as in the more recent 'blob theory'[49–51], the linear expansion factor α_s is expressed as a function of the reduced temperature $\tau = 1 - \theta/T$.

Flory has obtained a relationship between α_s and the excluded-volume parameter z:

$$\alpha_s^5 - \alpha_s^3 = \gamma z \qquad (24)$$

where

$$z \propto (3/2\pi)^{3/2}(\tau/l^3)N^{1/2} \qquad (25)$$

and N is the number of beads in the equivalent statistical chain, and l is the statistical length.

In the blob theory, it is assumed that the pair correlation function jumps from Gaussian to excluded-volume statistics for a critical number of beads $N = N_c$, N_c being related to τ by:

$$N_c = \beta\tau^{-2} \qquad (26)$$

where β is an adjustable parameter. From such a hypothesis, Weill and des Cloiseaux[50] have calculated the N/N_c dependences of the static and hydrodynamic expansion factors, α_S and α_H, and have shown that the viscosimetric expansion holds:

$$\alpha_n = [\eta]/[\eta]_0 = \alpha_s^2\alpha_H \qquad (27)$$

By identifying the asymptotic limits of the two theories, Ackasu and Han[51] deduced a relation between N/N_c and z:

$$N/N_c = Cz^2 \qquad (28)$$

C being a proportionality constant. Such an identification allows one to compare the two types of theories and the experiments with a unique parameter (N/N_c), which can be obtained in terms of M_w and T:

$$N/N_c = \tau^2 M_w/\beta n' M_0 \qquad (29)$$

Here n', the number of monomers in the statistical element, can be calculated from the value of intrinsic viscosity $[\eta]_0$ measured in θ conditions:

$$n' = [\eta]_0^{2/3} M_0/\Phi^{2/3} M^{1/3} (l')^2 \qquad (30)$$

In these two last expressions, M_0 and l' are the molecular weight and the length of the monomer respectively.

By neglecting the difference in the origin of phase separation by cooling and heating, we have assumed that the main parameter is always the reduced temperature. In *Figure 13a*, we compare the N/N_c dependences of the viscosimetric expansion: $\alpha_n^3 = f(N/N_c)$

(i) as calculated from the blob theory with $\beta = 0.47$;

(ii) as calculated from Flory theory;

(iii) as obtained for sample A from viscosity measurements;

(iv) as obtained for samples B and D from $[\eta]$ values measured at 25°C with $\theta = 76$ and 56°C respectively; and

(v) as calculated from experimental viscosimetric data of Bakanova *et al.*[52] who have studied a series of PEO of various molecular weights at different temperatures.

In *Figure 13b*, we have reported experimental results obtained for $T > UCST$, for polystyrene–cyclohexane, polystyrene–benzene and polyacrylamide–water[53].

We will remark first that all the experimental points obtained with our copolymers and with PEO are approximately joined together on the same curve. Secondly, it is obvious that the discrepancies between theories and experiments are similar for $T < LCST$ and for $T > UCST$: for low values of N/N_c the blob theory underestimates the polymer expansion but the asymptotic limit is reached for N/N_c values much lower than that predicted by Flory's approach. This means that it is possible to find a universal variation of the polymer expansion as a function of a term depending on molecular weight and reduced temperature for $T < LCST$. The question is: are the agreements obtained with the two sets of values ($T < LCST$ and $T > UCST$) only fortuitous and can one use the same developments for both cases?

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