A study of the behaviour of poly(N-vinylcarbazole) in binary mixtures of tetrahydrofuran and poly(ethylene glycol) oligomers*

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In this paper we report studies on poly(N-vinylcarbazole) (PNVK) in binary mixtures of THF (1) and poly(ethylene glycol) (2) obtained by viscometry and laser light scattering measurements. From these data, total and preferential solvation parameters were calculated over the whole binary mixture composition range studied. We have not found any inversion in the solvation. Inter- and intra-molecular interactions, K_θ and B, were calculated using the Stockmayer–Fixman equation. Finally, we found that the compatibility between PNVK and PEG increases linearly as PEG molar mass increases.

(Keywords: PNVK; PEG oligomers; total and preferential solvation; miscibility)

INTRODUCTION

During the last few years a great number of papers on polymer solution studies have been published concerning polymer binary mixtures in solution[1-13]. Polymer mixtures have great practical industrial importance and these works are a part of it. The main goal is to calculate the Flory polymer–polymer interaction parameter. This is a key parameter in the analysis of the mechanism and thermodynamic miscibility of these mixtures. In general, it is very difficult to evaluate this interaction parameter in the solid state.

Unfortunately, except for very unique experimental conditions, the Flory parameter in solution is generally obtained with a large experimental error. The main reason is that the interactions of polymers with liquids are greater than the polymer–polymer ones. However, in this kind of study it is possible to use polymers of low molecular weight (oligomers), because they can be considered as a second liquid[14-17]. Hence one can apply the same equations as used in polymer–liquid–liquid systems. In this way we can also study how the interaction in the system changes as a function of oligomer molecular weight.

In this paper we report studies on poly(N-vinylcarbazole) (PNVK) in binary mixtures of tetrahydrofuran (THF) (1) and poly(ethylene glycol) (PEG) oligomers (2) obtained by viscometry and laser light scattering measurements. We have previously studied the PNVK–PEG mixture in the solid state[18]. The results obtained show that this system is incompatible.

EXPERIMENTAL

Tetrahydrofuran (THF) was purified by standard procedures and freshly distilled before use. Vinylcarbazole was obtained from Fluka (purum) and was purified by successive crystallizations[19]. A polymer sample was prepared via radical polymerization in benzene using 1,2-azobisisobutyronitrile (AIBN) (Fluka, puriss) as initiator at 340 K. The concentrations of initiator and monomer were 2.4×10^{-3} and 5 mol l^{-1}, respectively. The poly(N-vinylcarbazole) (PNVK) sample was resolved into 11 fractions by fractional precipitation from benzene solution with methanol. The fractions were purified and then freeze-dried from benzene[20].

Molecular weights of the fractions were characterized by gel permeation chromatography (g.p.c.). The chromatographic experimental system was formed by a Gilson pump, a Rheodyne injector, two Shodex columns (type A80M) and a Knauer differential refractometer. All the g.p.c. measurements were carried out in THF, with a flow of 1 ml min^{-1}, and the capacity of the loop was 0.5 ml. The two Shodex columns were calibrated with polystyrene standards and using universal calibration[21] for PNVK characterization, with the viscometric equation $[\eta](\text{g dl}^{-1}) = 1.44 \times 10^{-4} M^{-0.65}$ for PNVK–THF pair[22]. The polydispersity of the PNVK fractions was less than 1.4. Five of these fractions were used for the physical measurements.

The poly(ethylene glycol) (PEG) oligomers used were commercial samples from Aldrich. The molecular weights of the different PEG samples were determined by vapour-pressure osmometry in THF (Knauer osmometer). The obtained molecular weights (200, 300, 400 and 600 g mol^{-1}) are coincident with the Aldrich ones.

The solvent binary mixtures were prepared by dissolving weighed amounts of PEG in THF. We assign the subscript 1 to THF, 2 to PEG oligomers and 3 to the polymer.

Laser light scattering measurements were carried out, at 298 K, with a modified FICA 42000 light scattering photometer, where both light source and optical block of the incident beam were substituted by a He–Ne laser (Spectra Physics model 157), which emits at 633 nm with a power of 3 mW. The cell compartment was thermostated to maintain the cell at 298.0 ± 0.1 K. The light scattering cell was washed and rinsed with distilled water and acetone. Solutions were contained in cells fitted with glass stoppers to ensure that differential evaporation of THF was minimized during measurements. All liquids and polymer solutions were clarified by centrifugation for 2 h at 14 000 r.p.m. in a Heraus Labofuge 15 000.

The light scattering photometer was calibrated with benzene using vertically polarized light and taking the Rayleigh ratio as $R_B = 12.55 \times 10^{-6}$ cm^{-1} (ref. 23); the optical constant K' was found to be equal to 0.735 cm^{-3}.

All measurements of laser light scattering were carried out at 11 angles between 30 and 150° for each solution and using poly(N-vinylcarbazole) concentrations ranging between 0.2 and 0.8 g dl^{-1}.

Molecular weights M_w, second virial coefficients A_2 and radii of gyration R_G were calculated using the usual Zimm plot procedure. The experimental data are treated by a Commodore C128/64 computer employing a compiled BASIC program.

The necessary refractive-index increments for light scattering measurements, dn/dc, were obtained with a Brice–Phoenix differential refractometer (model BP-2000), using a He–Ne laser (Spectra Physics model 156) as a light source, which emits with a power of 1 mW, and employing a sealed-type differential cell with ground-glass stoppers to prevent loss of solvent. The calibration was made with aqueous solutions of highly purified KCl. The temperature was kept constant at 298 K. The error in determining the refractive-index increments was $\pm 10^{-5}$ units.

The refractive indices of the pure solvents and mixtures were measured on an Atago precision refractometer at 298 K at 633 nm, previously calibrated with several liquids in which the refractive index was known. The error in determining the refractive index was $\pm 2 \times 10^{-3}$ units.

An automatic Ubbelohde suspended-level dilution viscometer (Lauda Viscoboy 2) was used. The viscometer was reproducibly positioned by means of a three-point suspended system. The temperature of the bath was regulated to $298.00 \pm 0.01°$C. Kinetic energy corrections were applied, although often they were very small. The intrinsic viscosity was obtained by double extrapolation of η_{sp}/c and $\ln \eta_r/c$ to zero concentration. Intrinsic viscosity $[\eta]$ values were expressed in dl g^{-1}.

RESULTS AND DISCUSSION

Laser light scattering

From laser light scattering (LLS) measurements we can obtain information about the preferential solvation and the spinodal curves of the different PNVK(3)/THF(1)/PEG(2) systems studied.

Preferential solvation

From the equation proposed by Strazielle and Benoit[24]:

$$\bar{M}_w^* = \bar{M}_w \left(1 + \lambda_1 \frac{\mathrm{d}n/\mathrm{d}\phi_1}{\mathrm{d}n/\mathrm{d}c} \right)^2 \tag{1}$$

where $\bar{M}_w^*$ and $\bar{M}_w$ are, respectively, the apparent molecular weight of the polymer determined in the binary mixture and the true molecular weight of the polymer, which can be determined in a pure solvent; dn/dϕ_1 is the variation of the refractive index of the binary mixture with composition; dn/dc is the variation of the refractive index of the polymer in the binary solvent mixture with the polymer concentration at constant composition; and λ_1 is the preferential solvation coefficient, which gives a precise measure of the changes of composition in the liquid mixture due to the presence of the macromolecular component and could be written as[24,25]:

$$\lambda_1 = \frac{x_1 v_1}{\bar{M}_w} = -\lambda_2 \tag{2}$$

where x_1 and v_1 are the excess number of moles of solvent (1) and the partial molar volume of solvent molecules preferentially adsorbed per mole of polymer, respectively. Therefore, λ_1 represents the volume of THF selectively adsorbed per gram of polymer in excess (if $\bar{M}_w^* < \bar{M}_w$) or in deficit (if $\bar{M}_w^* > \bar{M}_w$) in the vicinity of PNVK. The extrapolation method proposed by Zimm has been used in all cases for molecular-weight determinations.

In order to use equation (1), it is necessary to know previously the values of dn/dϕ_1 and dn/dc of the different systems studied. We have found that for the four systems studied n is a linear function of ϕ_1 over the whole PEG composition range. The values of dn/dϕ_1 obtained were:

THF/PEG 200	dn/d$\phi_1 = -0.054$
THF/PEG 300	dn/d$\phi_1 = -0.070$
THF/PEG 400	dn/d$\phi_1 = -0.068$
THF/PEG 500	dn/d$\phi_1 = -0.069$

where ϕ_1 is the volume fraction of THF.

The dn/dc values for PNVK in THF(1)/PEG(2) are shown in *Tables 1–4*. In these tables we can see also the λ_1 values calculated from equation (1) in the composition range 0–25% PEG at different PEG molecular weights.

As can be seen, the preferential solvation, λ_1, is positive in all cases. This means that PNVK is preferentially solvated by THF. This result seems very logical because PEG molecules behave as a precipitant for the PNVK, while THF is a very good solvent for the polymer. On the other hand, the λ_1 values are very high and increase as PEG concentration in the binary mixture increases.

Table 1 Refractive indices n_0, refractive-index increments dn/dc, apparent molecular weight of PNVK $\bar{M}_w^*$ and preferential solvation coefficient λ_1 as functions of PEG composition (PEG 200)

PEG (%)	n_0	dn/dc (ml g^{-1})	$\bar{M}_w^* \times 10^{-3}$ (g mol^{-1})	λ_1 (ml g^{-1})
5	1.4062	0.245	660	0.07
10	1.4095	0.240	588	0.31
15	1.4122	0.240	566	0.39
20	1.4135	0.241	510	0.60
22.5	1.4157	0.238	442	0.86
25	1.4164	0.234	564	0.39

Table 2 Refractive indices n_0, refractive-index increments dn/dc, apparent molecular weight of PNVK $\overline{M}_w^*$ and preferential solvation coefficient λ_1 as functions of PEG composition (PEG 300)

PEG (%)	n_0	dn/dc (ml g^{-1})	$\overline{M}_w^* \times 10^{-3}$ (g mol^{-1})	λ_1 (ml g^{-1})
2	1.4049	0.249	624	0.15
5	1.4065	0.253	589	0.25
10	1.4102	0.250	581	0.27
15	1.4125	0.247	551	0.35
20	1.4158	0.243	523	0.43
25	1.4182	0.240	507	0.47

Table 3 Refractive indices n_0, refractive-index increments dn/dc, apparent molecular weight of PNVK $\overline{M}_w^*$ and preferential solvation coefficient λ_1 as functions of PEG composition (PEG 400)

PEG (%)	n_0	dn/dc (ml g^{-1})	$\overline{M}_w^* \times 10^{-3}$ (g mol^{-1})	λ_1 (ml g^{-1})
2	1.4050	0.245	643	0.10
5	1.4065	0.245	663	0.05
10	1.4100	0.242	622	0.16
15	1.4130	0.243	567	0.31
17.5	1.4152	0.240	542	0.38
20	1.4158	0.243	550	0.36
22.5	1.4172	0.237	527	0.42
25	1.4190	0.240	490	0.54

Table 4 Refractive indices n_0, refractive-index increments dn/dc, apparent molecular weight of PNVK $\overline{M}_w^*$ and preferential solvation coefficient λ_1 as functions of PEG composition (PEG 600)

PEG (%)	n_0	dn/dc (ml g^{-1})	$\overline{M}_w^* \times 10^{-3}$ (g mol^{-1})	λ_1 (ml g^{-1})
2	1.4056	0.24	650	0.08
5	1.4074	0.255	587	0.26
10	1.4103	0.256	487	0.57
15	1.4132	0.25	511	0.48
20	1.4152	0.25	455	0.66

This result suggests that the thermodynamic quality of the liquids is the main factor responsible for the λ_1 values obtained.

We have not found an inversion in the solvation at low PEG composition. However, Sasia[26] has reported an inversion in the preferential solvation using samples of poly(ethylene oxide) (PEO) of high molecular weight. On the other hand, if we plot the variation of λ_1 as a function of composition, as shown in *Figure 1*, we can see that in some cases there is a shoulder at compositions rich in PEG. We think that these deviations can be attributed to possible aggregation processes in PNVK. A simple analysis of equation (1) shows that, as apparent molecular weight increases, the value of λ_1 decreases.

Total solvation

Molecular weight is not the only parameter affected by preferential solvation; the second virial coefficient is also affected. In order to calculate values of real second virial coefficient A_2, we used the expression proposed by Yamakawa[27]:

$$A_2 = \frac{\overline{M}_w^*}{\overline{M}_w} A_2^*$$

(3)

where A_2^* is the apparent second virial coefficient. *Figure*

2 shows the variation of second virial coefficient for the binary mixture THF(1)/PEG 300 at several PEG compositions. For the other systems we have found a similar behaviour. As can be seen, as the content of PEG increases, the value of A_2 decreases. This behaviour means that the binary mixture becomes poorer as PEG composition increases, i.e. the PEG acts as a precipitant for PNVK. From the variation of A_2 against composition, it is possible to calculate the composition when the system is under theta conditions ($A_2 = 0$). We have found for the four systems studied the following values:

THF(1)/PEG 200	$\phi_0 = 0.229$
THF(1)/PEG 300	$\phi_0 = 0.231$
THF(1)/PEG 400	$\phi_0 = 0.215$
THF(1)/PEG 600	$\phi_0 = 0.195$

As can be seen, an increase of the molecular weight of PEG allows one to reach theta conditions at lower compositions. This means that the non-solvent character of PEG increases with its molecular weight. *Figure 3* shows this variation in the molecular-weight range studied. The equation obtained (on the basis of
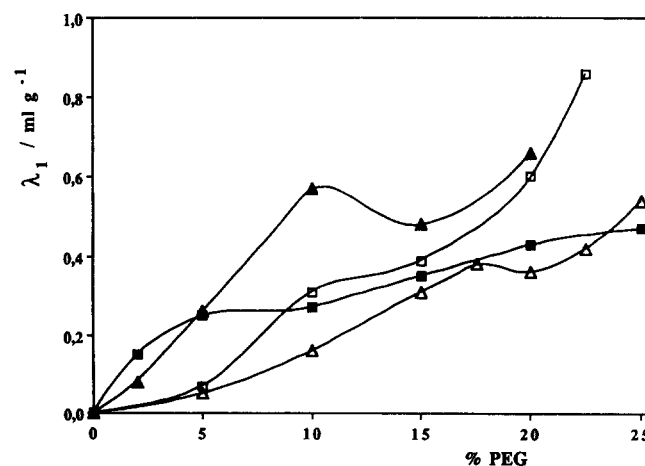

Figure 1 Preferential sorption coefficient for PNVK in TFH(1)/PEG(2) binary mixtures as a function of PEG volume percentage composition: (□) PEG 200; (△) PEG 300; (■) PEG 400; (▲) PEG 600
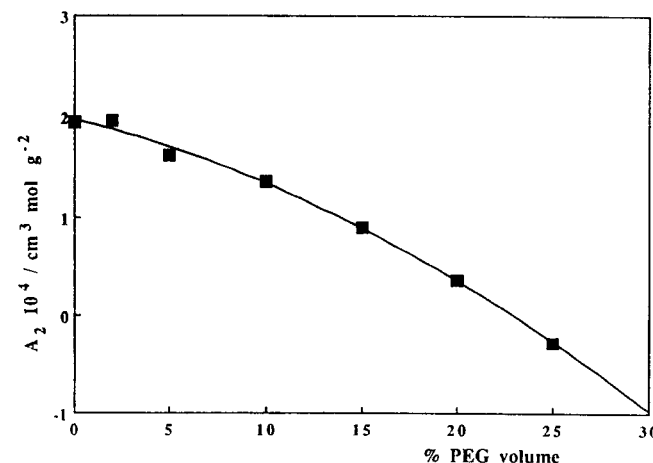

Figure 2 Second virial coefficient for PNVK in the binary mixture THF/PEG 300 as a function of PEG volume percentage composition
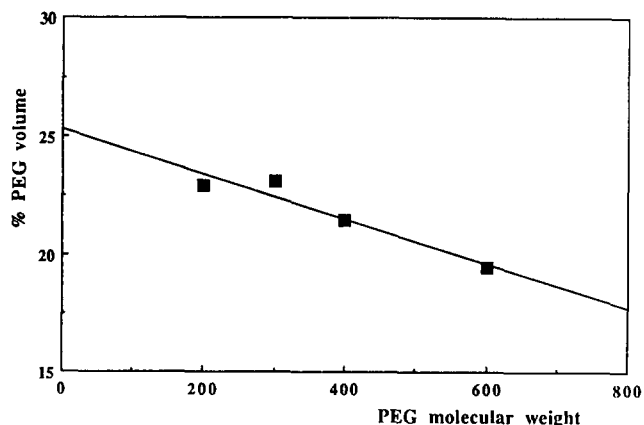
Figure 3 Plot of theta composition for PNVK in the binary mixture THF(1)/PEG(2) as a function of PEG molecular weight
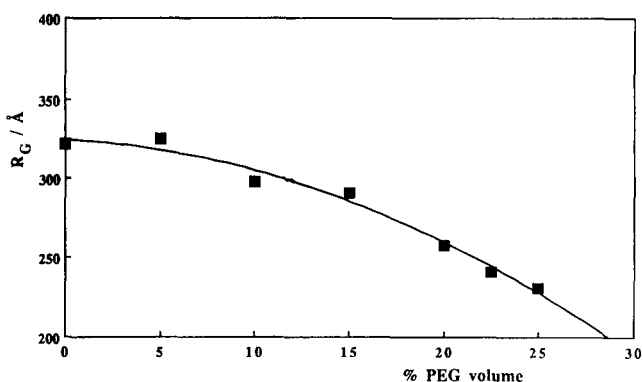

Figure 4 Variation of radius of gyration R_G for PNVK in the binary mixture THF/PEG 200 as a function of PEG volume percentage composition

percentage composition) was:

$$\phi_{2,\theta} = 25.2 - 9.31 \times 10^{-3} M \tag{4}$$

We can also analyse the influence of composition of the binary mixture on the molecular dimensions of PNVK. *Figure 4* shows the plot of $K'c/R(\theta)$ as a function of volume percentage for PEG 200. A similar behaviour using the other PEG samples was found. In this figure we can see that the molecular dimensions of PNVK decrease as the PEG content increases. This behaviour is explained by taking into account the fact that the solvent power of the binary mixture decreases.

Spinodal curves

Another parameter that we can obtain from laser light scattering measurements in ternary systems is the spinodal curve. Scholte[28,29], using the Flory–Huggins[30,31] free-energy function, shows that the Rayleigh ratio $R(\theta)$ can be written in the form:

$$R(\theta) = \frac{2\pi^2 kT}{\delta^2 \lambda^4} (1 + \cos^2 \theta) \left(\frac{\delta_2^2 g_{33} - 2\delta_2 \delta_3 g_{23} + \delta_3^2 g_{22}}{g_{22}g_{33} - g_{23}^2} \right) \tag{5}$$

where $\delta_i = dn/d\phi_i$, n is the refractive index of the solution, θ is the scattering angle, λ is the wavelength of the polarized light in the medium, and g_{ij} is $d^2g/d\phi_i d\phi_j$, where g is the Gibbs free energy.

Equation (5) is useful when the dissymmetry is equal to unity or when the scattering intensity is extrapolated to zero angle. The metastability condition is given by

$g_{22}g_{33} = g_{23}^2$. When the system reaches this condition, the Rayleigh ratio $R(\theta)$ given by equation (5) tends to infinity. In this case we can obtain from laser light scattering measurements the spinodal curve of a ternary system by extrapolating $1/R(\theta) \rightarrow 0^{5,32}$. *Figure 5* shows the variation of $K'c/R(\theta)$ as a function of PEG 300 volume percentage composition for four PNVK solutions with concentrations between 0.2 and 0.8 g dl^{-1}. As can be seen in this figure, in all cases $K'c/R(\theta)$ decreases as PEG percentage increases in the binary mixture. Again, our experimental results show that an increase of PEG in the binary mixture provokes a phase separation in the system. The experimental points plotted in *Figure 5* fit very well to a polynomial of second degree. This fact makes it easier to determine the spinodal compositions of the binary mixture. Experimental spinodal points for this system are shown in *Figure 6*, where the compositions are expressed in volume fractions.

Unfortunately, the extrapolation to $K'c/R(\theta) = 0$ for the other three systems studied is not as favourable as in the case of the system shown in *Figure 5*, because the experimental points do not fit very well to a second-order equation in the whole PEG volume percentage
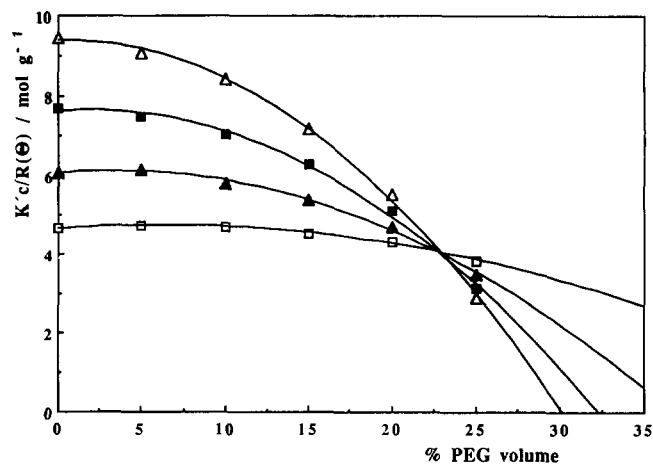

Figure 5 Plot of $K'c/R(\theta)$ as a function of PEG 300 composition for different PNVK concentrations: (△) 0.8 g dl^{-1}; (■) 0.6 g dl^{-1}; (▲) 0.4 g dl^{-1}; (□) 0.2 g dl^{-1}
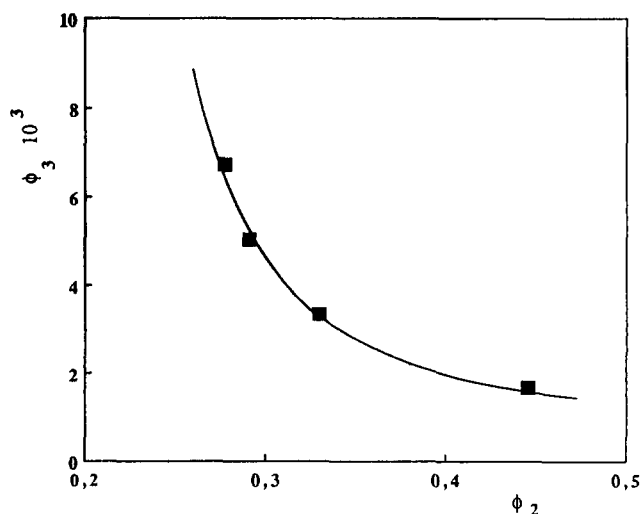

Figure 6 Spinodal curve for PNVK in the binary mixture THF/PEG 300: ϕ_2 and ϕ_3 are the volume fractions of PEG and PNVK, respectively

composition range. As the slope of the curves is high, the accuracy of the spinodal composition obtained from the extrapolation to $K'c/R(\theta)=0$ is bad. So, it is not possible to analyse correctly the influence of PEG molecular weight on the spinodal condition for this system. This is not usually a problem for other ternary systems previously reported in the literature[14,32], because a linear variation of $K'c/R(\theta)$ against composition is obtained.

Viscometry

The viscometric behaviour of the four PNVK fractions against composition for PEG 200 are plotted in *Figure 7*. For the other PEG we have found a similar viscometric behaviour. From these values we have calculated the exponent *a* of the Mark–Houwink–Sakurada (MHS) equation for all systems studied. In *Table 5* we can see these values as a function of PEG volume percentage and molecular weight of the different oligomers. In all systems, at lower PEG compositions, a linear variation of MHS parameter *a* has been found. Nevertheless, from the determined critical composition, ϕ_2^*, which depends on PEG molecular weight employed, a sharp decrease is observed. Taking into account that the MHS exponent *a* is an index of solvent power of the binary mixture, any decrease of this parameter indicates a decrease in the interaction between the PNVK and the binary mixture. This behaviour clearly indicates an incompatibility between PNVK and PEG.
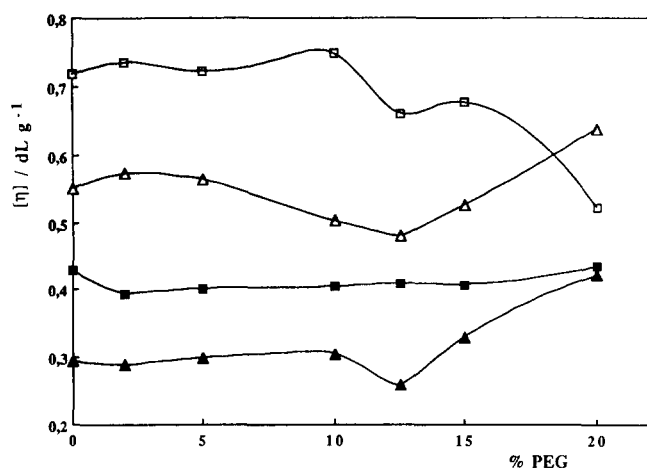
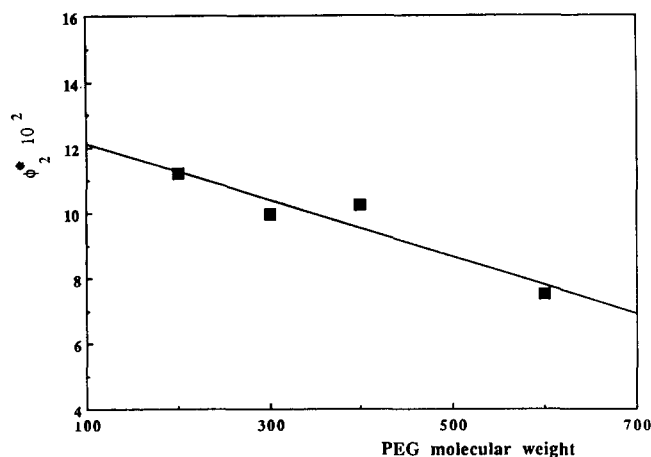If we plot the critical composition, obtained from the

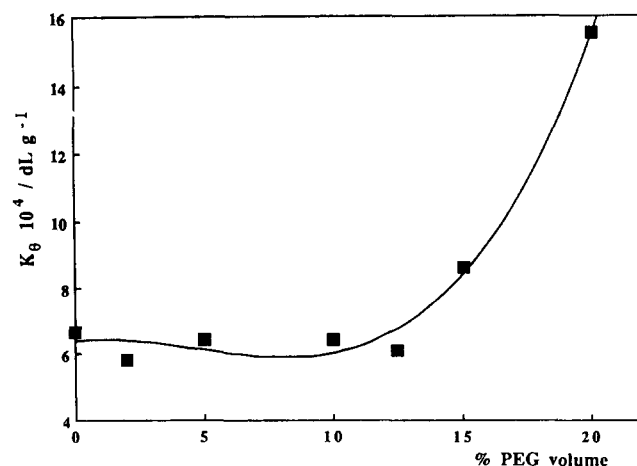Figure 8 Plot of the critical composition against PEG molecular weight

Figure 9 Variation of parameter K_θ against binary mixture composition for PEG 200

variation of *a* vs. ϕ_2, against PEG molecular weight, a linear dependence in the whole molecular-weight range studied is obtained, as can be seen in *Figure 8*. This means that the incompatibility between PNVK and PEG increases linearly as the molecular weight of PEG increases. This result agrees with that found from light scattering measurements (see *Figure 3*).

Another interesting point of our viscometric study is the determination of intra- and intermolecular interactions of the system, represented by the parameters K_θ and *B*, respectively. These two parameters can be determined simultaneously from the Stockmayer–Fixman equation:

$$[\eta]M^{-1/2}=K_\theta+0.51\Phi_\theta BM^{-1/2} \tag{6}$$

where Φ_θ represents the Flory–Fox viscosity constant for theta solvents, with theoretical value $2.87\times10^{-21}\,\text{mol}^{-1}$ for $[\eta]$ in dl g^{-1}. In *Figure 9* we can see the variation of K_θ against binary mixture composition for PEG 200. For the other binary mixtures, we have obtained similar results. In general, K_θ is still constant except for compositions higher than the critical composition, determined previously using the MHS exponent *a*. In all systems studied, above this critical composition we have observed a sharp variation of this parameter. This fact suggests the existence of aggregation processes in PNVK

Figure 7 Intrinsic viscosity $[\eta]$ against PEG 200 volume percentage for different PNVK fractions: (□) 4.94×10^5 g mol^{-1}; (△) 3.12×10^5 g mol^{-1}; (■) 2.07×10^5 g mol^{-1}; (▲) 1.26×10^5 g mol^{-1}

Table 5 Values of the MHS exponent *a* as a function of PEG volume percentage and molecular weight of the different oligomers studied

	a			
ϕ (%)	PEG 200	PEG 300	PEG 400	PEG 600
0	0.65	0.65	0.65	0.65
2	0.70	0.60	0.66	0.65
5	0.66	0.73	0.61	0.64
7.5	–	–	–	0.64
10	0.65	0.62	0.66	0.59
12.5	0.66	0.52	0.51	–
15	0.54	0.25	–	–
20	0.22	–	–	–

at higher PEG content. This behaviour could also explain the increase of MHS parameter a commented upon before and the shoulders in λ_1 values.

The K_θ values obtained under the critical composition agree with those reported in the literature by other authors[22] independently of the molecular weight of the PEG.

Studying the variation of the interaction parameter B, we have found a similar behaviour as in the case of the second virial coefficient. Therefore, we can reach the same conclusions as before.

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