

Polymer Communication

On the viscosity of moderately concentrated solutions of poly(ether imide) in a mixed solvent of marginal quality

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Abstract

Viscosities η were measured for moderately concentrated (15.5 wt%) solutions of poly(ether imide) (PEI) as a function of the composition of the cosolvent tetrahydrofuran (THF) plus γ -butyrolactone (γ -BL). The solutions are almost by a factor of four less viscous when THF predominates than when γ -BL is the major component of the solvent mixture. Furthermore, the viscosity passes a minimum as the composition of the mixed solvent is varied. Both observations can be well understood in terms of the viscosities of the mixed solvents and the hydrodynamic interaction between the polymer molecules. The pronounced dissymmetry of η as a function of the composition of the mixed solvent η results from the fact that the viscosity of γ -BL is three times larger than that of THF. The minimum in η reflects the dependence of the thermodynamic quality of the mixed solvent on its composition. With increasing predominance of one component the solvent deteriorates and additional polymer/polymer contacts—leading to an augmentation of η —are formed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ether imide); Cosolvency; Viscosity

1. Introduction

Poly(ether imide) has been successfully employed to make asymmetric porous membranes for gas separation [1,2]. Compared to other commercial polymers this material exhibits an unusually high He selectivity combined with a high He permeability. An interesting solvent mixture to prepare PEI membranes consists of tetrahydrofuran and γ -butyrolactone (THF, γ -BL). PEI exhibits phase separation with each of these pure solvents, but with some of their mixtures the polymer is completely miscible (cosolvency). This fact allows the preparation of homogeneous solutions of PEI which, when immersed in water, form high performance membranes.

For a better understanding of the physico-chemical background of the membrane forming processes, we have already determined the phase diagram of the ternary system THF/ γ -BL/PEI, calculated the binary interaction parameters [3] and investigated the kinetics of phase separation [4], as well as the morphology of the membrane formed at different

conditions. The present work was undertaken to obtain information on the viscosity of the phase separating solution. The viscosity of the casting solution is also an important aspect during the membrane preparation. It influences the solvent–non-solvent exchange after immersion in the coagulation bath and also affects the velocity of phase separation before gelation. Gelation and solidification fix the pore structure formed during the phase separation. We have measured for a polymer concentration of 15.5 wt% at 30°C, conditions which are usually chosen for membrane preparation, how η depends on the composition of the mixed solvent and on the proximity to phase separation.

2. Experimental

The poly(ether imide), poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylenediamine), is the commercial product ULTEM 1000 from General Electric Company. The number-average molar mass M_n is 18 kg mol⁻¹, as determined by osmometry. The solvent tetrahydrofuran (purity >99.5%) was purchased from Merck (Darmstadt, Germany), γ -butyrolactone (purity >99%) from Fluka (Buchs, Switzerland). All viscosities,

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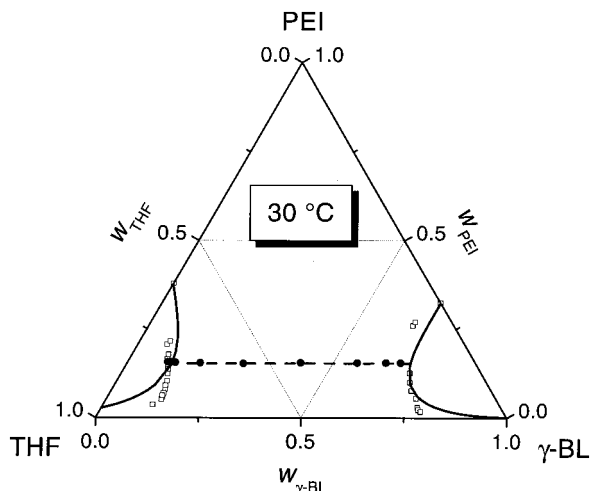


Fig. 1. Phase diagram of the system THF/ γ -butyrolactone/poly(ether imide) at 30°C [3] (open symbols: measured cloud points, full line: calculated binodal curves) indicating the compositions of the ternary mixtures (full circles on the broken line of constant polymer concentration) for which viscosity measurements were performed.

η , were measured at 30°C, preparing mixtures by weighing. An Ubbelohde Micro-Viscometer, capillary No. I (Schott, Hofheim am Ts., Germany) was used to determine the viscosity of the solvents and their mixtures. The instrument was calibrated by means of pure THF at 25°C (η from [5] and density ρ from [6]). The densities of the solvent mixtures and polymer solutions were determined by means of the commercial densitometer DMA 48 (Anton Paar GmbH, Graz, Austria).

The viscosities of the ternary system PEI/THF/ γ -BL were determined in the rotational rheometer Haake CV 100 (Karlsruhe, Germany) using the concentric cylinder geometry ZA 15. Flow curves were measured up to shear rates of $\dot{\gamma} = 300 \text{ s}^{-1}$. Special care was taken to avoid errors caused by THF evaporation: The measuring time for each sample was only 4 min, a solvent trough, filled with THF,

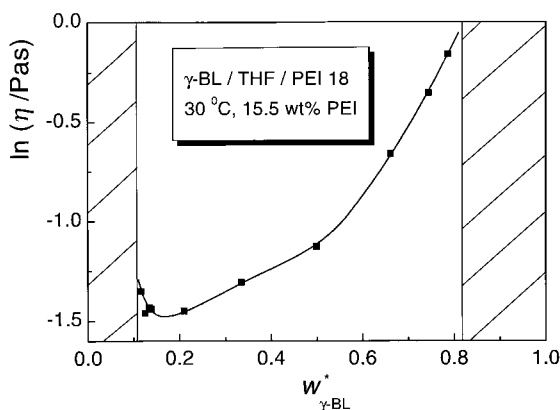


Fig. 2. Zero shear viscosity η for 15.5 wt% solutions of PEI in the mixed solvent γ -BL/THF as a function of the weight fraction $w_{\gamma\text{-BL}}^* = w_{\gamma\text{-BL}}/(w_{\gamma\text{-BL}} + w_{\text{THF}})$ it contains. The two-phase area is indicated by hatching.

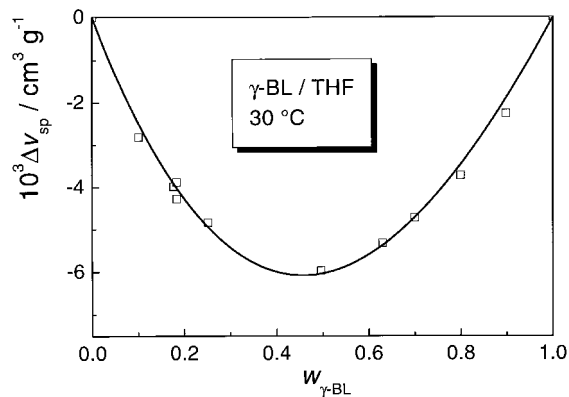


Fig. 3. Excess specific volumes Δv_{sp} for the mixed solvent γ -BL/THF; the specific volumes of the pure components are given in Table 1.

was placed tightly around the measuring device and a tight guard ring was fixed over the top of the inner cylinder.

3. Results and discussion

The positions of the different PEI solutions under investigation in the ternary phase diagram can be seen from Fig. 1. How the zero-shear viscosity varies at a constant polymer weight fraction of 15.5% with the γ -BL content of the mixed solvent is shown in Fig. 2.

The most obvious observations are the asymmetry of the η curve and a minimum close to the miscibility gap on the THF side of the phase diagram. The viscosity for γ -BL rich mixed solvents is approximately four times larger than in the opposite case. In order to check the supposition based on earlier results [7] that the latter effect is due to the variation of η_s , the viscosity of the mixed solvents, with composition, this parameter was measured by means of a capillary viscometer. For the conversion of the directly accessible kinematic viscosities to η , the densities of the solvents were also determined. These results are presented in Fig. 3 in terms of Δv_{sp} , the excess specific volumes

$$\Delta v_{\text{sp}} = v_{\text{sp}} - (w_{\text{THF}}v_{\text{sp,THF}} + w_{\gamma\text{-BL}}v_{\text{sp,\gamma-BL}}). \quad (1)$$

The results give evidence of negative volumes of mixing, despite an unfavorable Flory–Huggins interaction parameter $g_{\text{THF}/\gamma\text{-BL}}$ [3]. The densities of the mixed solvents at 30°C can be calculated from the following relation and the specific volumes of the pure compounds (Table 1):

$$\frac{10^3 \Delta v_{\text{sp}}}{\text{cm}^3 \text{g}^{-1}} = -28.4w_{\gamma\text{-BL}} + 36.9w_{\gamma\text{-BL}}^2 - 8.5w_{\gamma\text{-BL}}^3. \quad (2)$$

The viscosity of the mixed solvent (for all subsequent equations index 1 stands for THF and 2 for γ -BL) as a function of its composition is shown in Fig. 4 together with some calculated curves. The dashed line corresponds to the expression [8]

$$\ln \eta^{\text{Arrh}} = \varphi_1 \ln \eta_1 + \varphi_2 \ln \eta_2 \quad (3)$$

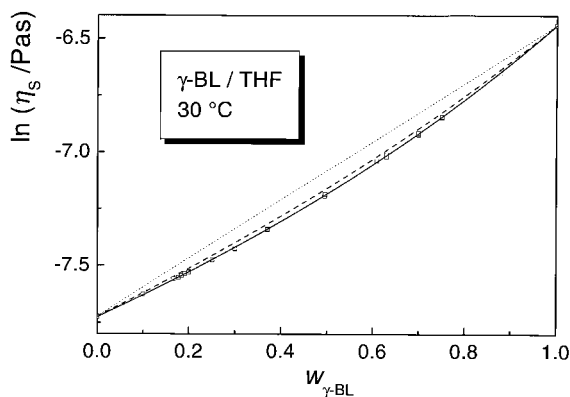


Fig. 4. Viscosity of the mixed solvent as a function of the weight fraction of γ -BL. Dotted line: Additivity in terms of weight fractions, broken line: in terms of volume fractions, full line: according to Eq. (4).

the full line is calculated by means of a new approach [9,10] which replaces volume or weight fractions by surface fractions in view of the fact that the dissipation of energy should take place between the molecules at their surfaces rather than in their bulk. On the basis of this consideration one obtains the following relation

$$\ln \eta^{\text{sf}} = \varphi_1 \ln \eta_1 + \varphi_2 \ln \eta_2 + \left\{ \frac{\gamma \delta}{1 + \gamma \varphi_2} + 2\alpha \frac{1 + \gamma}{(1 + \gamma \varphi_2)^2} \right\} \varphi_1 \varphi_2 \quad (4)$$

where γ is a geometric parameter, accounting for the differences in surface to volume ratios F/V of the components:

$$\gamma = \frac{F_2/V_2}{F_1/V_1} - 1 \quad (5)$$

and α measures the changes in flow behavior resulting from the specific interactions between the components of the mixture.

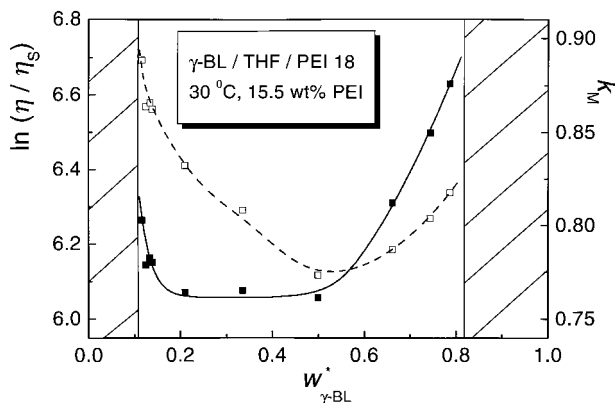


Fig. 5. Full line, left ordinate: Relative (zero shear) viscosities of 15.5 wt% solutions of PEI in the mixed solvent γ -BL/THF as a function of its composition; the viscosities η_s of the mixed solvent are taken from Fig. 4. The two-phase regime is indicated by hatching. Broken line, right ordinate: Martin coefficient k_M , calculated from the viscosities of the solutions according to Eq. (7).

The third term on the right hand side of Eq. (4) (vanishing for $\gamma = 0$) considers the differences between volume and surface fractions and contains the parameter δ , defined as

$$\delta = \ln \eta_2 - \ln \eta_1. \quad (6)$$

For mixtures consisting of two low molecular weight liquids of similar chemical nature and comparable intermolecular interaction in the pure state it suffices [9] to adjust either α or γ and to set the second parameter zero. In view of experimental uncertainties it is presently impossible to judge which alternative should be preferred for theoretical reasons. Setting $\alpha = 0$ and fitting γ leads to $\gamma = -0.07$ and to a very good description of $\ln \eta$ as a function of composition, as demonstrated by the solid line in Fig. 4.

Normalizing the viscosities η of the polymer solutions to η_s , the viscosities of the mixed solvents, yields a much more symmetrical dependence (Fig. 5) than the unreduced quantities (Fig. 2). For the further discussion we make use of the Martin equation [11]

$$\eta = \eta_s (1 + \tilde{c} e^{k_M \tilde{c}}) \quad (7)$$

which can describe the viscosity of polymer solutions as function of composition quite accurately up to relatively high polymer concentrations, particularly with thermodynamically poor solvents; $\tilde{c} = c[\eta]$ represents the degree of coil-overlap, calculated from the polymer concentrations (mass/volume) by means of intrinsic viscosities $[\eta]$, and k_M is the Martin coefficient which should not differ largely from the Huggins coefficient k_H , which describes the concentration dependence of η for dilute systems. According to this relation the higher unreduced viscosities of polymer solutions in γ -BL rich mixed solvents are mainly a natural consequence of the higher η_s value of this solvent component.

The pronounced increase in the reduced viscosities of the polymer solutions by a deterioration of solvent power, as one approaches the phase separation conditions, can be rationalized in terms of Eq. (7) if one introduces the degree of coil overlap \tilde{c} and calculates k_M . To that end the weight fractions of PEI were converted into concentrations (mass/volume) by means of the densities ρ measured for the solutions. The intrinsic viscosity of the PEI was estimated from previous measurements at 25°C [3] according to which $[\eta]$ amounts to 35 ml/g, almost irrespective of the composition of the mixed solvent. The difference in $[\eta]$ for 25 and 30°C, respectively, was neglected in view of the observation that the miscibility gaps change only little in their extension as T is raised from 30 to 50°C.

The Martin coefficients obtained in this manner vary with $w_{\gamma\text{-BL}}^*$ and exhibit the same characteristic features as the reduced viscosities shown in Fig. 5, i.e. they rise from ca. 0.78 in the middle range of composition to ca. 0.9 as one component becomes predominant. This result is in accord with the general experience that k_H and consequently k_M should rise as the solvent quality decreases [12]. This

Table 1
Characteristic data of the compounds of mixed solvent at 30°C

	v_{sp} (ml g ⁻¹)	η (mPa s)
THF	1.1410	0.432
γ -BL	0.8937	1.557

finding can be rationalized in terms of the so-called “pull-along” effect [13,14] As the interaction between solvent molecules and polymer segments becomes less favorable, the number of polymer/polymer contacts increases and the different strands move less independently. This situation leads to an extra (shear rate independent) contribution to the viscosity [15] and to a thermodynamically induced pull on polymer chains which can, under certain conditions, become so large that it may even lead to their rupture [16].

The difference in the shapes of k_M and of the reduced viscosities as a function of the composition of the mixed solvent shown in Fig. 5 is due to the fact that the density of the solution and therefore the concentration c_{PEI} and consequently the degree of coil overlap increase as the γ -BL content rises, even in the case of constant weight fraction of PEI. The already mentioned fact that the intrinsic viscosities are practically independent of the composition of the mixed solvent [3] indicates that the thermodynamic situation becomes more noticeable in k_M than in the volumes of the isolated coils ($[\eta]M$) for the relatively low molecular weight and rather stiff PEI.

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