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INVESTIGATIONS ON PHASE DIAGRAMS OF A COIL-POLYMER (PC) AND A SEMIFLEXIBLE THERMOTROPIC MAINCHAIN POLYMER (PET-CO-PHB) IN SOLUTION

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Abstract Cloud point curves of PET-co-PHB/PC/$CHCl_3$ mixtures show differences from Flory's calculations on coil-rod systems. An interpretation is attempted by calculating spinodals from Flory-Huggins interaction parameters obtained by vapour pressure osmometry.

INTRODUCTION

Starting point for this work are Flory's calculations on the statistical thermodynamics of ternary systems consisting of rodlike and coil-shaped molecules in a common solvent[1].

Based on Flory's theoretical work, it was intended to investigate the phase behaviour of mixtures containing a semiflexible thermotropic mainchain copolymer poly(ethyleneterephthalate-co-p-hydroxibenzoic acid), (PET-co-PHB) and the coil-shaped component poly(bisphenol-A-carbonate) (PC) in $CHCl_3$. The stiffness of the rodlike polymer was varied by using almost statistically distributed copolymers with different PHB content.

The copolyesters were prepared according to Jackson and Kuhfuss[2]. The PHB content and the segment distribution were analyzed as described by Lenz[3].

Copolyesters with 10-40 mole-% PHB are soluble in $CHCl_3$, and those with more than 30 mole-% PHB are thermotropic.

RESULTS AND DISCUSSION

Two cloud point curves were measured at 295 K for the ternary systems

a) $CHCl_3$ (1), PET/27% PHB (2), PC (3)
b) $CHCl_3$ (1), PET/35% PHB (2), PC (3)

$\langle M_n \rangle$ obtained by vapour pressure osmometry was 6,000 g/mol for most of the copolyesters and 19,300 g/mol ($\langle M_w \rangle / \langle M_n \rangle = 1.7$) for PC.

Starting with isotropic ternary solutions with a total polymer concentration of 2-4%, the polymer concentration was increased slowly in steps of 0.1 to 0.3 % by evaporating the solvent. The absorbance E at 800 nm measured by an UV-VIS-spectrometer was plotted against the polymer concentration and allowed to define the cloud point. Analoguous to [9] a solution was defined to be turbid when E reached an arbitrarily chosen low value. Plotting the cloud points of the systems a) and b) in a triangular diagram using segment fractions x_1^* as the concentration scale, results in fig. 1.

System a) shows better miscibility than b) which is quite reasonable by considering that the solubility limit in $CHCl_3$ at 40 mole-% PHB is almost reached by the copolymer in b).

Now the experimental results can be compared with Flory's theoretical calculations mentioned earlier. For ternary systems comprising a solvent (index 1), a rigid rod polmyer (2) of well defined geometrical shape and a randomly coiled polymer (3) different phase diagrams are obtained depending on the axis ratio of the rod and on the contour length of the coil[1]. Using x_i^* (base molecular fraction of component i) instead of volume fractions, figure 1 results for an axis ratio and contour length of 300[4].

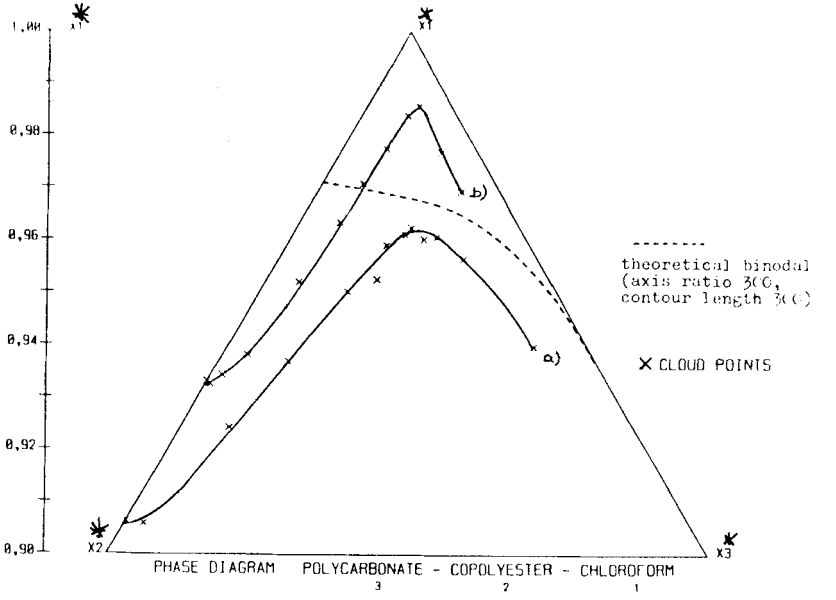

FIGURE 1. Cloud point curves for the mixtures a) and b) compared with Flory's calculation.

Obviously, there are great differences between the experimental cloud point curves and the calculated binodal. Several reasons may be responsible for this dissimilarity. First of all, it has to be emphasized that a cloud point curve can be similar but never be fully identical with the binodal. Furthermore, Flory's assumptions are only insufficiently fulfilled because all polymers used were polydisperse so that only average values of the axis ratio and the contour length can be defined. Thirdly, the copolyesters are semiflexible and do not behave like completely stiff rods as assumed by Flory. Even the PHB content and thus the flexibility varies from chain to chain.

Thus, the systems examined here seem to be too complex to be described by Flory's theory so that further investigations are necessary for a better understanding of the cloud point curves.

In the following it is attempted to interpretate figure 1 with the help of spinodals.

Using the degree of polymerization r instead of $m_i = \bar{V}_i/\bar{V}_1$ and x_i^* instead of volume fractions as approximation, the method of Zeman and Patterson[5] is applied to calculate the spinodals given by :

$$\sum_{i=1}^{3} r_i x_i^* - 2\sum_{\substack{i,j=1 \\ i\neq j}}^{i,j=3} r_i r_j (\chi_i+\chi_j) x_i^* x_j^* + 4 r_1 r_2 r_3 (\chi_1\chi_2+\chi_1\chi_3+\chi_2\chi_3) x_1^* x_2^* x_3^* = 0 \quad (1)$$

with the abbreviations

$$\chi_1 = 0.5(\chi_{12}+\chi_{13}-\chi_{23}) \quad (2)$$

$$\chi_2 = 0.5(\chi_{23}+\chi_{12}-\chi_{13}) \quad (3)$$

$$\chi_3 = 0.5(\chi_{13}+\chi_{23}-\chi_{12}) \quad (4)$$

The Flory-Huggins interaction parameters χ_{12} and χ_{13} were measured by vapour pressure osmometry at temperatures of 306, 312 and 318 K using a Knauer vapour pressure osmometer and squalane (M =422.83 g/mol) as calibration substance. The osmotic measurements were carried out in $CHCl_3$ for the following polymers:

PET/27% PHB, 1.35 g/cm^3 [6], $\langle M_n \rangle$= 6,000 g/mol
PET/32% PHB, 1.36 g/cm^3 [6], $\langle M_n \rangle$= 6,000 g/mol
PET/35% PHB, 1,37 g/cm^3 [6], $\langle M_n \rangle$= 6,000 g/mol
PET/39% PHB, 1,39 g/cm^3 [7], $\langle M_n \rangle$= 7,000 g/mol
PC, 1,20 g/cm^3 [7], $\langle M_n \rangle$,19,300 g/mol

Within the concentration range examined (c_2<75 g/l solvent) a linear correlation was observed between the reduced osmotic pressure π/c_2 and c_2.

$$\frac{\pi}{c_2} = \frac{RT}{\langle M_n \rangle} + B \cdot c_2 \qquad (5)$$

The second virial coefficient B gives access to the χ-parameters. (ρ_2 = density of the pure polymer, $\bar{V}_1$ = molar volume of chloroform)[10,11].

$$\chi_{12} = \frac{1}{2} - \frac{B}{RT} \cdot \bar{V}_1 \cdot \rho_2^2 \qquad (6)$$

The temperature dependence of χ_{12} is given by[8]

$$\chi_{12} = \alpha + \beta/T \qquad (7)$$

TABLE I. χ_{12}-parameters (±0.01) of PET/PHB copolyesters and PC at different temperatures.

T/K	copolyesters with 27%	32%	35%	39%	PHB	PC
306	0.35	0.38	0.44	0.46		0.24
312	0.34	0.37	0.42	x)		0.22
318	0.31	0.36	0.41	0.42		0.19

x) not measured

TABLE II. Parameters α and β according to eq.7 for PET/PHB copolyesters and PC.

	copolyesters with 27%	32%	35%	39%	PHB	PC
α	-0.704	-0.150	-0.359	-0.600		-1.082
β/K^{-1}	323.6	162.3	244.0	324.7		405.3

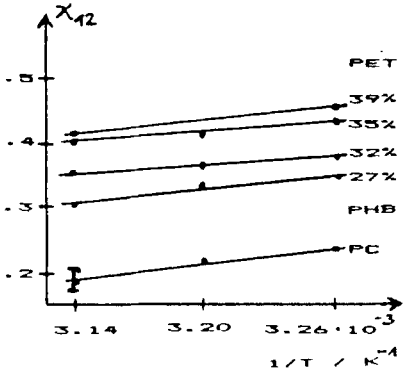

FIGURE 2.
χ_{12} as a function of 1/T for PET/PHB co-polyesters and PC.

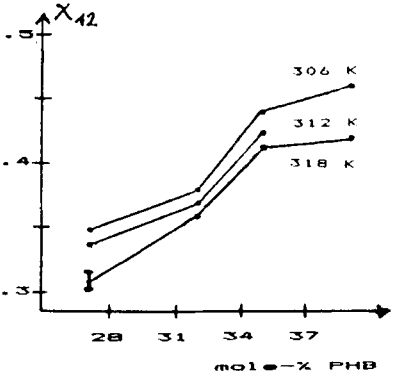

FIGURE 3.
χ_{12} as a function of the PHB content for PET/PHB copolyesters.

Extrapolating the χ_{12} and χ_{13} values to 295 K and using the unknown polymer/polymer interaction parameter χ_{23} as a parameter, a series of spinodals was obtained from eq. 1 for the mixtures a) and b) as shown in fig. 4 and fig. 5. When discussing these phase diagrams it has to be kept in mind that the three types of curves (cloud point curve, spinodal, binodal) are not identical.

Provided that the critical point is close to the maximum of the cloud point curve, χ_{23} can be estimated. Both the maximum and the right branch of the cloud point curve in a) and b) is described quite well by the spinodals calculated for χ_{23} = 1.1 or 2.5, respectively. The left part of the cloud point curves, however, varies evidently from the spinodals.

It seems that the cloud point curve measured for the system coil/semiflexible rod/solvent reflects an intermediate behaviour between the calculated spinodal and the theoretical binodal for a coil/rod/solvent mixture.

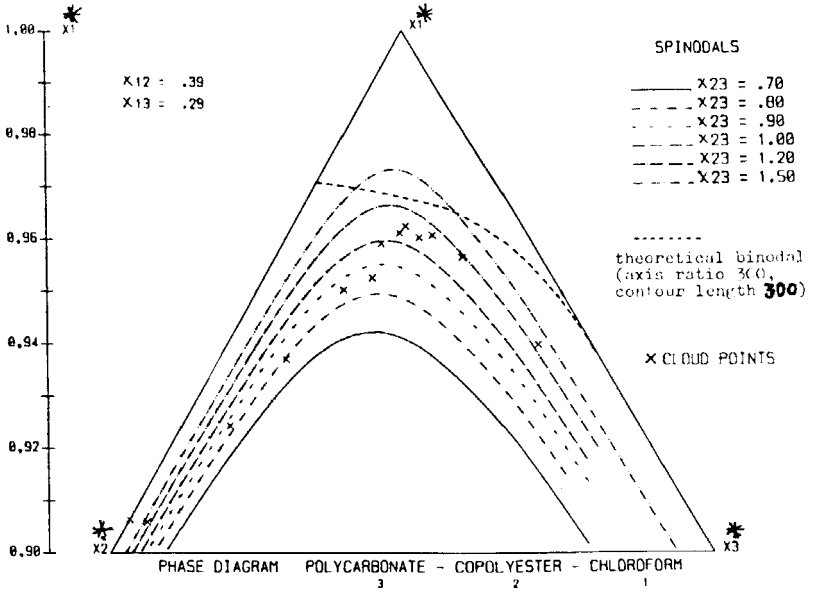

FIGURE 4 Phase diagram PET-27% PHB/PC/$CHCl_3$. Spinodals (calculated), cloud point curve (measured), binodal for a coil-rod system (axis ratio and contour length 300).

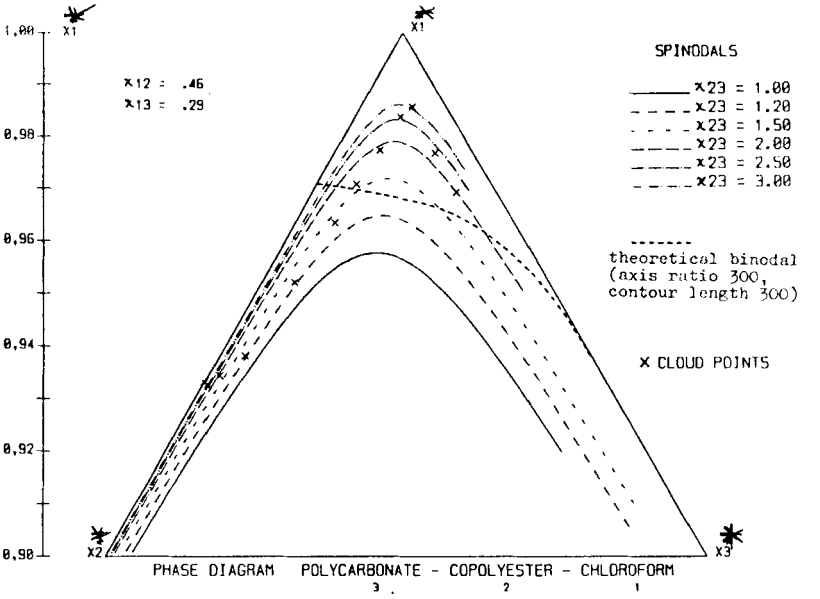

FIGURE 5 Phase diagram PET-35% PHB/PC/$CHCl_3$. Spinodals (calculated), cloud point curve (measured), binodal for a coil-rod system (axis ratio and contour length 300).

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