

# INTERACTION OF POLYMERS AND POLYMER BLENDS WITH SMALL MOLECULES AS A TOOL TO JUDGE POLYMER COMPATIBILITY

by

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## INTRODUCTION

Energetic aspects of polymer – polymer miscibility may be approached by thermodynamic analysis of one of the polymers and a low molecular weight molecule (LMM) corresponding to the other polymer. These findings may be transduced to understand polymer – polymer compatibility. However, this approach is a first approximation. LMM cannot take into account the characteristic conformational situation of a macromolecular chain.

Studies on polymer – LMM systems are described in the following over the whole polymer concentration range, by light scattering (1), equilibrium swelling measurements (2), and inverse gas-chromatography (3).

Furthermore investigations on three component systems, solvent -1-, polymer -2- and polymer -3-, by light scattering (4) under "optical  $\theta$  conditions" (5) as well as by gas-chromatography (6) are reported.

## RESULTS AND DISCUSSIONS

### Binary systems

Interaction parameters according to the Flory-Rehner theory (7) were estimated by equilibrium swelling measurements on poly (styrene) networks (2). Figure 1 presents the results in ketones as LMM's, with different length of the alkyl chain. The contributions of the specifically interacting keto-groups and of the dispersively interacting alkyl chain determine the Flory-Huggins parameter. After passing through the maximum at hexanone-2 the increasing influence of the methylene groups reduces the interaction quality.

Activity coefficients and thermodynamic mixing functions in the limiting case of infinite dilution of the LMM were established by gas-chromatography. Figure 2 gives the

data for poly (styrene) – alkylbenzene systems (3). For the short side chain alkylbenzenes the slightly negative  $\Delta H^\infty$  – values are a general proof for complete polymer – LMM miscibility. Propylbenzene shows athermic behaviour, whereas the larger alkylbenzenes are characterized by endothermic heats of mixing.

In the entire concentration range, growing, alkyl chain length of the LMM lowers the entropy of mixing and exceeds the influence of the specifically interacting groups and causes phase separation.

The phase behaviour of the binary system poly (styrene) – cyclohexane has been studied by swelling and gas-chro-

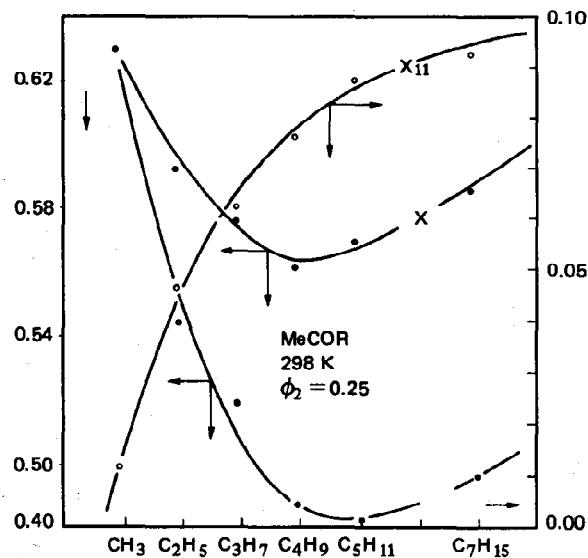


Fig. 1 Flory-Huggins parameters of ketones in poly(styrene), swelling data.

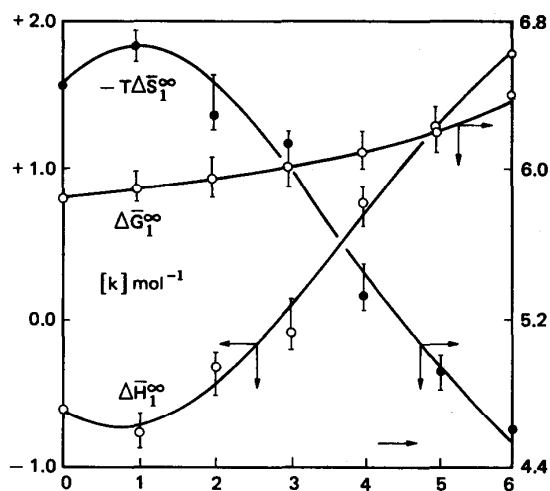


Fig. 2. Thermodynamic mixing functions of alkyl benzenes in poly(styrene), inverse gas-chromatography.

matography measurements. By combining both methods an upper critical solution temperature as well as a lower one were established (2).

### Ternary systems

In terms of Scott's ternary solution treatment (8) of the Flory-Huggins theory a negative polymer - polymer interaction parameter indicates miscibility, whereas a positive one means phase separation

$$X'_{23} = X_{12} \phi_3^{-1} + X_{13} \phi_2^{-1} - X_{1(23)} \phi_2^{-1} \phi_3^{-1}$$

Light scattering measurements of dilute ternary solutions, toluene-1-, poly(styrene)-2- and poly(vinylmethylether)-3- (4), have been carried out under "optical  $\theta$  condition" (5).

On the contrary gas-chromatography is a consistent method to determine polymer - polymer interaction in the limiting case of infinite dilution of the solvent probe. Best results will be obtained if the solvent probe has the same kind of interaction to both polymers (symmetrical case).

Both methods reveal a small negative interaction parameter for this miscible polymer pair.

The phase behaviour of mixtures of poly(styrene) and poly(vinylmethylether) has been investigated within a wide temperature and composition range (6). As demonstrated in figure 3 the polymer - polymer interaction is somewhat - polymer interaction is somewhat depending on the chemical nature of the solvent probe. Those differences are not decisive for the phase diagram. Consequently, gas-chromatography offers an approach for the quantitative thermodynamic description of the compatibility in the system poly(styrene)-poly(vinylmethylether). Figure 4 presents the interrelation of the polymer-polymer interaction parameter with temperature and composition.

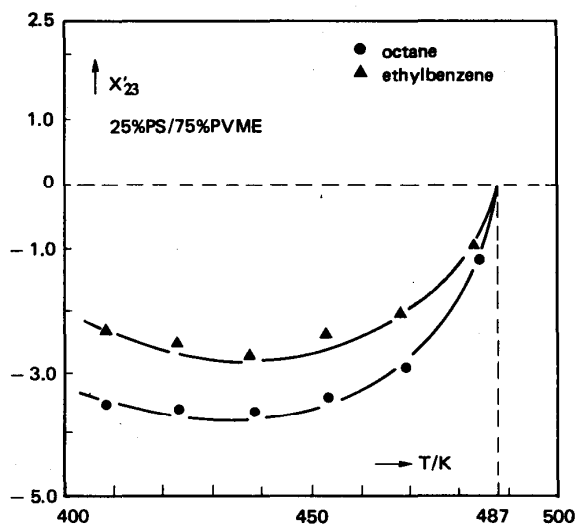


Fig. 3. Probe dependence of the polymer-polymer interaction parameter.

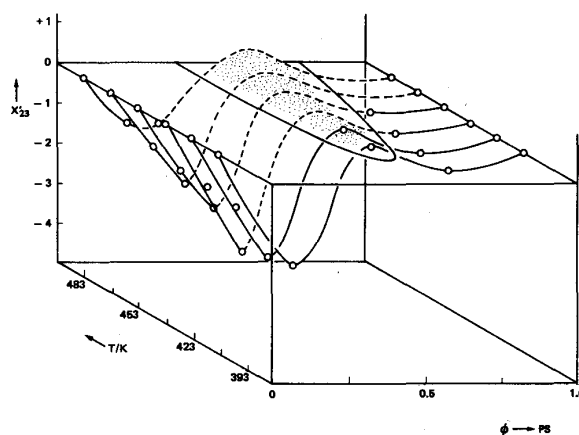


Fig. 4. Polymer-polymer interaction surface for poly(styrene)-poly(vinylmethylether), temperature and blend composition dependence by inverse gas-chromatography.

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