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Interaction in Polymer Blends Via Dilute Solution Light-Scattering under Optical θ-Conditions

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Summary

It is demonstrated that dilute solution light-scattering experiments under 'optical θ-conditions' offer rapid and reliable judgement of the interaction parameters in polymer blends. This has been verified with miscible blends of polystyrene with poly(vinylmethylether) and with the immiscible pair polystyrene – poly(vinylisobutylether).

The capabilities of the optical θ- approach in order to derive the influence of polymer-polymer interaction on chain dimensions are discussed shortly.

Introduction

Because of the experimental difficulties and sacrifice of time in determining the compatibility of polymer blends in the solid state fast methods are asked for to derive relevant data from measurements in solution. Accurate determinations of polymer-polymer interaction in solution are crucial, however, because the polymer-solvent interactions are much higher typically. Additionally, the choice of the 'right' solvent is problematical. Fukuda et al. 1) recently proposed a procedure which allows exact measurements of Flory-Huggins polymer-polymer interaction parameters, χ_{23}, 2) in dilute solution by light scattering. They demonstrated, for the incompatible mixture polystyrene – poly(methylmethacrylate), that measuring under 'optical θ-conditions' cancels the solvent-polymer interaction parameters, χ_{12} and χ_{13}, thus yielding exact values of χ_{23}.

In the following we expand this method to the investigation of miscible polymer blends, with polystyrene – poly(vinylmethylether) as the example. Further interest has been pointed at the molecular weight and blend composition dependence of χ_{23} in solution.

Equations

According to the theory of multicomponent systems 3) we obtain the forward scattering excess over the solvent, ΔR_0, for a ternary solution, solvent 1 – polymer 2 – polymer 3,

$$\Delta R_0 / K^* = c\,[\psi_2^2 M_2 x_2 + \psi_3^2 M_3 x^3] - \qquad (1)$$
$$2c^2\,[(\psi_2 M_2 x_2 + \psi_3 M_3 x_3)\cdot(\psi_2 M_2 x_2 B_{22} + \psi_3 M_3 x_{33} B_{33}) + 2\psi_2\psi_3 M_2 M_3 x_2 x_3 \Delta B_{23}]$$

with

$$K^* = 4\pi^2 n^2 / (N_A \lambda_0^4)$$
$$\psi_i = dn / dc_i \qquad i = 2,3$$
$$x_2 = 1 - x_3 = c_2 / (c_2 + c_3)$$
$$\Delta B_{23} = B_{23} - (B_{22} + B_{33}) / 2$$

The 'optical θ-condition' is fulfilled with

$$\psi_2 M_2 x_2 + \psi_3 M_3 x_3 = 0 \qquad (2)$$

With this condition equ. (1) reduces to

$$\Delta R_0 / K^* = c\,[\psi_2^2 M_2 x_2 + \psi_3^2 M_3 x_3] - 4\psi_2\psi_3 x_2 x_3 \Delta B_{23} c^2 \quad . \qquad (3)$$

With the assumption that the specific volumes of the polymer components, v_2 and v_3, are identical – which is valid for the investigated polymers – we combine equ. (3) with the classical Flory-Huggins expression and obtain

$$K^* c / \Delta R_0 = A + 2\psi_2\psi_3 M_2 M_3 x_2 x_3 \frac{v_2^2}{V_1} A^2 \chi_{23}\, c \qquad (4)$$

with

$$A = (\psi_2^2 M_2 x_2 + \psi_3^2 M_3 x_3)^{-1}$$

It is evident that the slope of the plot $K^*c/\Delta R_0$ versus polymer concentration yields direct information concerning the polymer-polymer interaction parameter, without interference of polymer-solvent interaction, if the 'optical Θ-conditions' are satisfied. The slope is positive for a miscible and negative for a immiscible polymer blend.

Experiments

Samples and Characterization : The low polydispersity atactic polystyrenes (PS) were Pressure Chemical products (M_w/M_n 1.06). Poly(vinylmethylether) (PVME) and poly(vinylisobutylether) (PViBE) were purchased from EGA, with $M_w/M_n = 1.85$ and 1.95, resp. Molecular weights were determined by light scattering, membrane osmometry and gel permeation chromatography. Data are given in Table 1.

Refractive Index Increments were measured with a differential refractometer in chlorobenzene at 20° C: $\psi_{PS} = 0.0820$, $\psi_{PVME} = -0.0552$ and $\psi_{PViME} = -0.0792$.

Light Scattering Experiments were carried out at 20° C on a Sofica light scattering photometer, in the same solvent. Scattered intensities were recorded from 30 – 150° in increments of 10°, with vertically polarized light of 436 nm wavelength. Solutions were clarified by filtration through 0.2 and 0.45 µm membrane filters, respectively.

Table 1 : M_{wi} of components and x_{PS}, A and χ_{23} for PS-PVME and PS-PViBE mixtures

$M_{wPS}\cdot10^{-4}$	$M_{wPVME}\cdot10^{-4}$	$M_{wPViBE}\cdot10^{-4}$	x_{PS}	$A_{exp}\cdot10^3$	$A_{calc}\cdot10^3$	χ_{23}
1.75	5.50	–	0.6791	7.74	7.48	– 0.018
3.75	5.50	–	0.5001	5.07	4.80	– 0.011
5.00	5.50	–	0.4254	4.51	4.18	– 0.009
6.85	5.50	–	0.3508	3.90	3.72	– 0.008
11.0	5.50	–	0.2518	3.28	3.21	– 0.006
126	–	116	0.4706	0.17	0.13	+ 0.013

Results and Discussion

Several mixtures of PS and PVME and a mixture of PS and PViBE have been investigated. Zimm-plots are shown in Figures 1 and 2. From the slopes of the reciprocal scattering intensities at zero angle versus concentration the χ_{23} have been obtained. Figure 3 presents the other results. Data are given in Table 1.

For all mixtures of PS and PVME negative values of χ_{23} have been found, indicating miscibility at 20° C for both polymers, over the entire region of molecular weights and mixing ratios investigated. According to expectations the polymer-polymer interactions are very small. They are in good agreement with measurements by other methods 4) – 6). Thus, for chlorobenzene, the appropriate choice of the common solvent is certified also. Being a thermodynamically good solvent for both components, it approaches the 'symmetrical case'. As expected χ_{23} varies with M_w and mixing ratio.

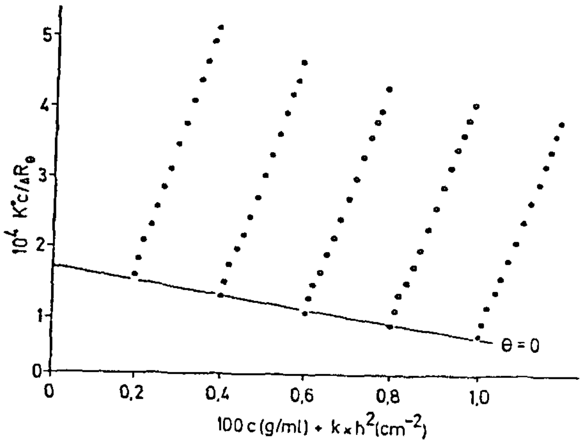
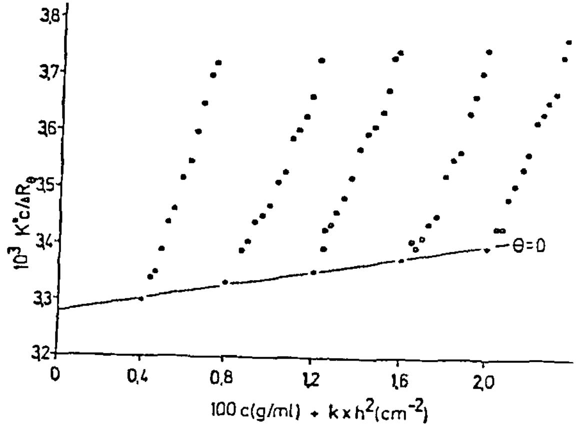


Figure 1: Optical θ- Zimm plot, PS_{1260k} - $PViBE_{1160k}$ chlorobenzene, 20° C



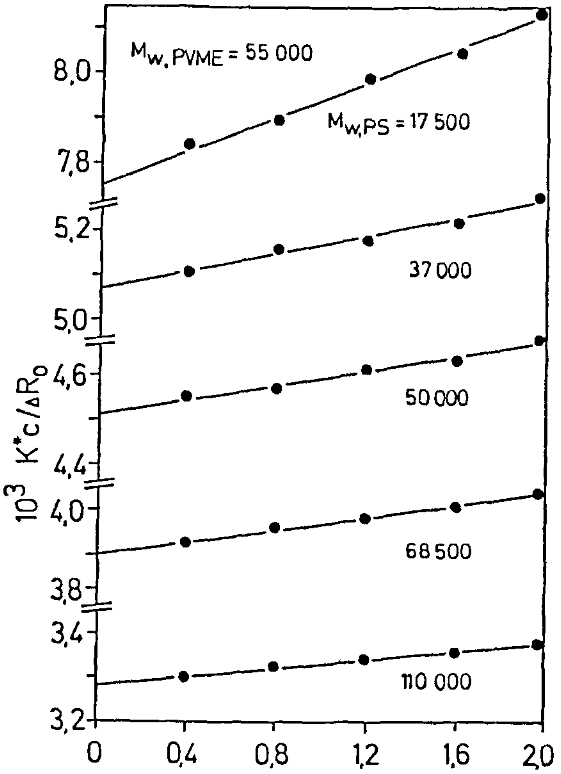


Figure 3: K^*c / R_0 versus c plot, optical θ- conditions $PVME_{55k}$ - M_{wPS} as indicated, chlorobenzene

Figure 2: Optical θ - Zimm plot, PS_{110k} - $PVME_{55k}$ chlorobenzene, 20° C

Additionally, the interaction between PS and PViBE has been studied in the same solvent. The positive value of χ_{23} reveals incompatibility of both polymers, in agreement with the solid state behaviour.

The exactness of the light scattering measurements may be proofed by comparing the calculated values of the constant A with the experimental ones, as derived from the intercepts in Figures 1 - 3. As shown in Table 1 the experimental error ranges within some percents only. Thus, the experimental uncertainity of χ_{23} is also small.

Influence of Polymer - Polymer Interaction on Coil Dimensions

The conformational balance of a macromolecular coil is altered by specific interaction with a low molecular weight solvent 7) as well as with another macromolecular component 5). Under optical Θ-conditions the angular dependence of the light scattered by the blend components is influenced by this effect in a complex way, due to the contributions of both the macromolecular components. The situation is less complicated, however, if one of the polymers exhibits molecular dimensions below those detectable by light scattering. This is the case approximately for the PVME engaged in the measurements discussed ($M_w = 5.5 \cdot 10^4$), even if one takes into consideration a possible chain stiffening due to interaction with the PS component. Consequently, under those conditions, the angular dependence of the scattered ligth is determined solely by the PS. Thus, for high molecular weight PS the influence of polymer-polymer interactions on the end-to-end distance should be analyzable.

Matching the refractive index of one polymer component with that of the solvent seems to offer an attractive alternative to the procedure discussed. One has to choose another solvent in this case, with the consequence that the absolute data for the interaction parameter and, possibly, the molecular dimensions may be altered. Fluorotoluene is an approximately isorefractive solvent for PVME. Thus, PS dimensions could be studied with and without specific interaction with PVME segments.

A chance may be offered also by deviating from optical Θ-conditions when applying the 'optical Θ-solvent', chlorobenzene, in the discussed case. By altering the components ratio for the mixture $PS_{11 \cdot 10^4}$ / $PVME_{5.5 \cdot 10^4}$, i. e., from x_{PS} = 0.2518 to x_{PVME} = 0.2518, the angular dependence of scattered light would be dominated by PS. When choosing an even lower molecular weight PVME, the effect of scattered light dissymmetry of this component could be suppressed to an amount nearby to the experimental error. Thus, a chance is offered to clarify the influence of specific interaction on molecular dimensions even with 'optical Θ-solvents'.

Studies are under progress to evaluate specific polymer interactions from light scattering experiments, with 'optical Θ-' and with refractive index matching solvents.

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