

Thermodynamics of Macromolecular Systems

1. Swelling of Polystyrene Networks in Cyclohexane

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SUMMARY

Swelling of polystyrene networks has been studied within the range from 288 to 323 K. Results are discussed following FLORY-HUGGINS and FLORY-REHNER approaches. Thermodynamic analyses with respect to the enthalpy and to the entropy part of the chemical potential of the solvent have been carried out. The volume fraction dependence of the thermodynamic properties derived could be cancelled applying the two-parameter KONINGSVELD-KLEINTJENS equation for polymer solutions to swollen gels. Thus, an unequivocal interpretation of swelling thermodynamics could be reached, irrespective crosslink density of the networks.

INTRODUCTION

Understanding problems of polymer miscibility is one of the challenges nowadays, from the scientific as well as from the applicational standpoint. The miscibility of polymers depends on competing contributions of dispersive and specific interactions as well as on the chain length of the components. Dispersive forces favour phase separation, specific favour miscibility. In order to realize miscible polymer blends it is favourable to design copolymers with a programmed amount of specifically interacting groups. Substantial experimental difficulties impede the direct investigation of the miscibility of polymers in the solid state. In order to approach the energetic part of the miscibility problem one may substitute macromolecular chains by representative low molecular weight models (LMWM). Such LMWM's could be for example members of a homologous series of components with one or more polar groups. It can also be a binary solvent mixture, in order to vary the ratio of "dispersive" and "specific" components.

In a series of papers we will try to approach the problem of polymer miscibility with the philosophy to substitute macromolecular components as far as possible by LMWM's. Besides studies in solution those in swollen state may be promising in this context, because by crosslinking of a polymer consequences of thermodynamic interactions are transduced into a macroscopic scale.

Polystyrene will be treated as a macromolecular component in the first paper, with cyclohexane as the first LMWM for a second macromolecular component. It will turn out that even if the system polystyrene - cyclohexane is the classical system in polymer solution thermodynamics (KONINGSVELD, R. and STAVERMAN, A. J., 1968; JENCKEL, E. et al., 1956; REHAGE, G. et al., 1965; REHAGE, G. and KONINGSVELD, R., 1965; CANTOW, H.-J., 1956), there are still deficiencies in our knowledge.

EXPERIMENTAL

Polystyrene networks were prepared by crosslinking copolymerization in bulk of dried, freshly distilled and degassed styrene with varying amounts of m-divinylbenzene (m-DVB) with 2×10^{-3} mole % AIBN at 55°C under nitrogen, in sealed

glass tubes. Linear polystyrene with $M_w = 5.1 \times 10^4$ and $M_w/M_n = 1.02$ was used for light scattering measurements.

Cyclohexane was dried over molecular sieves (MERCK, 4 Å) and distilled over a column.

Swelling measurements were carried out on cylindrical network samples with 5 mm diameter and 10 mm length typically, which were sealed with the swelling agent in glass tubes, excluding humidity. The degree of swelling, q , was measured during the swelling process by the length of the sample, with the aid of a horizontally travelling microscope, within a relative error of $\pm 3\%$. A number of experiments carried out by the conventional weighing method shows up good agreement, the error of the weighing procedure being somewhat higher ($\pm 6\%$). With quasielastic light scattering it has been proved that there is no detectable anisotropy in the swollen samples. The diffusion constant derived is independent on the scattering angle.

For swelling experiments in mixed solvents measurements in sealed tubes are even more favourable, because influences of differing boiling points are eliminated. The reproducibility of the temperature dependence of swelling was checked by up- and downwards change of temperature. An additional error of $\pm 2\%$ has been found.

Right angle light scattering measurements were performed within the temperature range from 288 to 323 K with solutions of polystyrene ($M_w = 5.1 \times 10^4$), with concentrations 2, 4, 6, 8 and $10 \times 10^{-3} \text{ g cm}^{-3}$.

The density of cyclohexane was measured with a KRATKY apparatus.

RESULTS AND DISCUSSION

The experimental results of the equilibrium swelling measurements of polystyrene networks in cyclohexane over a temperature range from 288 to 323 K are presented in Fig. 1, with the molecular weight of the chains between two crosslinks, M_c , as parameter.

The dependence of q on M_c at constant temperature is evident. In cyclohexane the temperature dependence of the equilibrium swelling is remarkable.

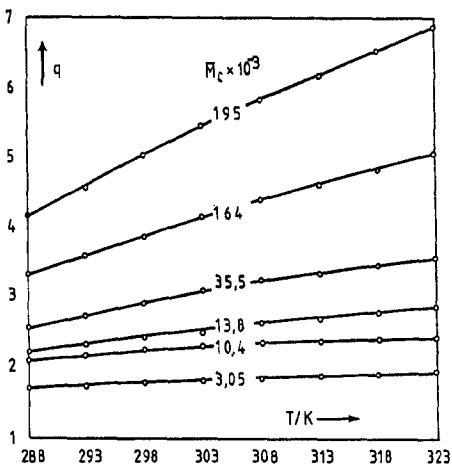


Figure 1: Degree of swelling of polystyrene networks as function of temperature, with M_c as parameter

In the thermodynamic treatment of swollen networks it is assumed, that the equilibrium is determined by the balance of the free energy of mixing with the solvent (ΔG^M) and the elastic or conformational free energy (ΔG^{el})

$$(\partial \Delta G^M / \partial n_1)_{P,T} = (\partial \Delta G^{el} / \partial n_1)_{P,T} \quad (1)$$

To derive thermodynamic information from the data FLORY's equation (1942) has been applied first. This equation implies a contribution of the lattice model entropy of mixing with a single VAN LAAR term representing the free energy contribution arising from the pair interactions. Assuming that no sol macromolecules are present in the liquid and applying the usual expression for

the free energy of elasticity (FLORY, P. and REHNER JR., J., 1943) condition (1) yields explicitly the interaction parameter χ

$$\chi = \left[\ln(1 - \Phi_2) + \Phi_2 + \frac{\nu_e \bar{v}_1}{v_0} (m^{-2/3} \Phi_2^{1/3} - \frac{2\Phi_2}{f}) \right] \Phi_2^{-2} \quad (2)$$

- Φ_2 the volume fraction of the network polymer in the system
- ν_e/v_0 the molar concentration of the network chains [mole cm^{-3}]
- \bar{v}_1 the partial molar volume of the solvent [$\text{cm}^3 \text{mole}^{-1}$]
- m the memory term
- f the functionality of the crosslinks.

In deriving Equ. (2) it is anticipated that χ is a concentration independent parameter and that the crosslinks have negligible influence on the free energy of mixing.

In the present work, because of crosslinking copolymerization with *m*-DVB in bulk, $f = 4$ and $m = 1$ may be inserted.

From the experimental results (Fig. 1) the χ -parameters for crosslinked polystyrene-cyclohexane have been calculated following Equ. (2). The three-dimensional graph of the Φ_2 - and T -dependence of χ is presented in Figure 2. It turns out that at all temperatures the χ -values exhibit a pronounced concentration dependence. The χ -values at $\Phi_2 = 0$ were taken from light scattering data using the transformation

$$\chi = 0.5 - A_2 \rho_2^2 \bar{v}_1^2 \quad (3)$$

The values for the density of polystyrene (ρ_2), partial molar volume of cyclohexane and the second virial coefficient of the osmotic pressure are summarized in Table I.

Table I: Temperature dependence of ρ_2 , \bar{v}_1 and A_2 from light scattering and density measurements on polystyrene ($M_w = 5.1 \times 10^4$) - cyclohexane solutions

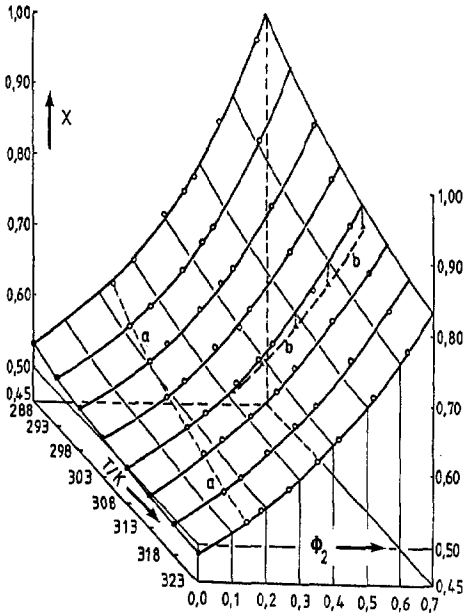


Figure 2: Φ_2 - and T -dependence of the χ -parameter. Line a for constant M_c

The basic trend of the χ -parameters vs. Φ_2 does not change if for the free conformational energy either the equation proposed by J. J. HERMANS (1947)

$$(\partial \Delta G^{el} / \partial n_1)_{p,T} = \frac{\nu_e \bar{v}_1}{v_0} (m^{-2/3} \Phi_2^{1/3} - \Phi_2) \quad (4)$$

or that derived by JAMES and GUTH (1956)

$$(\partial \Delta G^{el} / \partial n_1)_{p,T} = \frac{\nu_e \bar{v}_1}{v_0} (m^{-2/3} \Phi_2^{1/3}) \quad (5)$$

T	ρ_2	\bar{v}_1	$A_2 \times 10^{-4}$
[K]	[gcm^{-3}]	[$\text{cm}^3 \text{mole}^{-3}$]	[$\text{mole cm}^{-3} \text{g}^{-2}$]
288	1.060	107.20	- 2.66
293	1.058	107.91	- 1.75
298	1.056	108.55	- .99
303	1.054	109.21	- .33
308	1.052	109.87	+ .08
313	1.050	110.71	+ .33
318	1.048	111.21	+ .66
323	1.046	111.73	+ .98

is applied instead of the FLORY-REHNER equation (see Fig. 3).

The concentration dependence of the χ -parameters has been predicted theoretically by HUGGINS (1955) for polymer solutions, and it is evident that this Φ_2 -dependence is caused by

- flexibility blocking effects
- imperfect randomness of mixing (orientation effects)
- change of tightness of coiling with concentration.

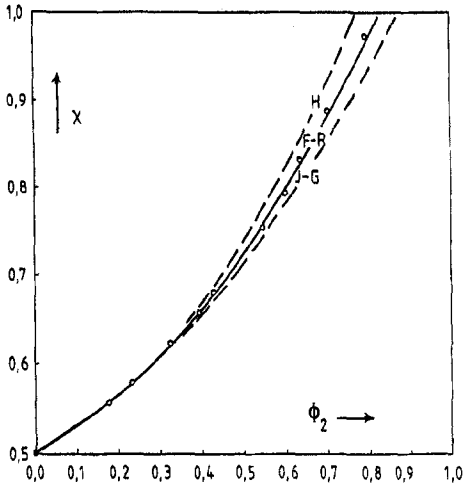


Figure 3: Comparison of the Φ_2 dependence of χ calculated using the equations of HERMANS (H), FLORY - REHNER (F-R) and JAMES - GUTH (J-G)

By osmotic pressure (KRIGBAUM, W. R. and GEYMER, D. O., 1959, REHAGE, G. and MEYS H., 1958, REHAGE, G., 1964), vapour pressure measurements (KRIGBAUM, W. R. and GEYMER, D. O., 1959) and pulse induced critical light scattering studies (SCHOLTE, T. G., 1971) on polystyrene - cyclohexane solutions it has been demonstrated that such a Φ_2 -dependence is effective, irrespective the molecular weight of the polymer. χ is shifted, however, slightly towards higher values with increasing molecular weight.

The dotted line **b** in Fig.2 at 307.5 K represents the trend of the χ -parameter derived from these measurements in solutions. There is a good agreement - within experimental error - in the concentration range up to $\Phi_2 \approx .45$. At higher Φ_2 the concentration dependence of χ becomes more significant. Formally the χ -values calculated from swelling data with the aid of Equ. (5) show up the best agreement with those derived from solution.

It has to be noted that no corrections for entanglement effects have been made.

Assuming thus that the influence of crosslinks is not negligible at all, we may offer a plausible qualitative explanation by supposing restricted conformations of the chains in the near vicinity of the crosslinks. A smaller mixing entropy contribution would be one of the possible consequences. Therefore the free energy parameter increases - more than in solution - in a Φ_2 region, where the effective volume fraction of crosslinks is no more negligible compared with the volume fraction of chains.

However, the Φ_2 -dependence of the χ -parameter makes it problematical to compare χ -values without indicating the M_c of the network as well as the temperature.

Focusing now to the temperature dependence of χ it is useful to treat the single parameter χ not as the exchange enthalpy parameter, but rather as an excess free energy so that:

$$\chi = (\Delta\mu_1^e / RT\Phi_2^2) = (\Delta h_1 / RT\Phi_2^2) - (\Delta s_1^e / R\Phi_2^2) \tag{6}$$

Consequently, χ can be split up into an enthalpy and an entropy term $\chi = \chi_H + \chi_S$ (7)

were $\chi_H = (\Delta h_1 / RT\Phi_2^2) = - T (\partial\chi / \partial T)_{p, \Phi_2}$ (8)

$$\chi_S = (\Delta s_1^e / R\Phi_2^2) = (\partial(T\chi) / \partial T)_{p, \Phi_2} \tag{9}$$

For the calculation of the enthalpy and entropy contributions of χ the experimental points presented in Fig. 2 were replaced by smoothed curves, which were considered to fit the data best. In order to characterize these curves, the coefficients of the polynomial are given in Table II.

The derived χ_H and χ_S parameters are not unequivocally determined for the system. They also are functions of Φ_2 and of the temperature. Above 308 K, at constant Φ_2 , the variation of χ_H with the temperature is not so pronounced as that of χ_S . Thus χ_S shows up to be the major contributor to the thermodynamic behaviour of the studied system. Under 308 K the temperature dependence of both, χ_H and χ_S , is somewhat enhanced as a consequence of beginning phase separation. Further, the Φ_2 -dependence of χ_H

and χ_S is of interest too. Below the Θ -temperature the relative increase of χ_H and χ_S with the volume fraction of the polymer in the swollen network is higher than above Θ , as shown in Fig. 4.

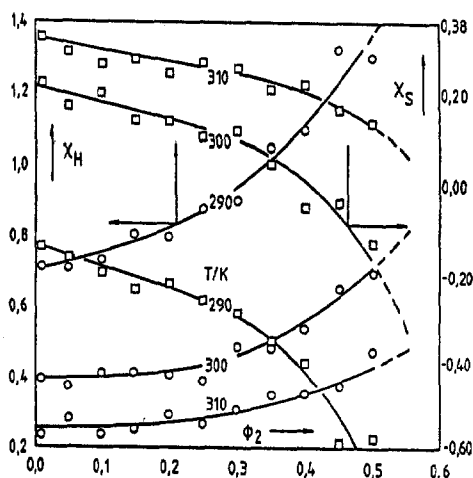


Figure 4: Φ_2 -dependence of χ_H and χ_S at temperatures indicated

swelling of polystyrene networks in cyclohexane indicating only M_c , Φ_2 and the corresponding temperature. Because of the Φ_2 dependence of χ it seems that the applicability of semiempirical free energy expressions involving only one adjustable parameter is somewhat limited.

To overcome these difficulties it seems to be promising to use an expression for the left side of condition (1), which takes account for the concentration dependence of the interaction enthalpy term. Such an equation for the chemical

Table II: Coefficients of the polynomial Φ_2 -dependence of χ . ($\chi = a + b\Phi_2 + c\Phi_2^2$)

T	a	b	c
288	.533	.2143	.6172
293	.522	.2107	.5543
298	.513	.2232	.4899
303	.507	.2308	.4433
308	.500	.2621	.3771
313	.497	.2625	.3668
318	.494	.2389	.3930
323	.489	.2349	.4093

The quantity χ_H appears to undergo little change with Φ_2 up to $\Phi_2 \approx .4$, but seems to increase significantly beyond this point. A comparison of χ_H and χ_S values at the limit $\Phi_2 \rightarrow 0$ with those obtained by light-scattering (CANTOW, H.-J., 1956) and by osmotic pressure measurements (KRIGBAUM, W. R. and GEYMER, D. O., 1959) shows good agreement, as shown in Table III, lit. a and b, resp.

Recalling that the combinatorial entropy of dilution, $-\Delta s_{1 \text{ comb}}/R\Phi_2^2$, contributes to the total chemical potential with $-.5$ at the limit $\Phi_2 \rightarrow 0$, it can be seen from Table III that the excess partial molar entropy χ_S is dominated by the combinatorial term over the entire temperature range.

The thermodynamic behaviour can be described for the equilibrium

Table III: χ_H and χ_S values at $\Phi_2 \rightarrow 0$ derived from data of this work and from literature

T	χ_H		χ_S	
	this work	literat.	this work	literat.
293	.60	.82 a	-.078	-.285 a
298	.45	.61 a	+.063	-.096 a
		.30 b		+.020 b
303	.36	.47 a	+.146	+.036 a
308	.30	.38 a	+.20	+.12 a
		.20 b		+.30 b
313	.25	.34 a	+.25	+.15 a
318	.22	.31 a	+.27	+.18 a

The success of this equation had been proved in the case of polystyrene - cyclohexane solutions, when it was shown that the concentration dependence of the excess chemical potential can be well described. The γ -value had been determined from the binodal and spinodal conditions by pulse induced critical light scattering. For polystyrene - cyclohexane solutions $\gamma = .238$ has been found.

Introducing Equ. (10) - after preliminary transformation for network forming - into the left side of condition (1) instead of the FLORY expression, a two-parameter equation for equilibrium swelling is obtained:

$$\ln(1 - \Phi_2) + \Phi_2 + \alpha_0 \Phi_2^2 + \frac{\beta_0(1 - \gamma)}{(1 - \gamma \Phi_2)^2} \Phi_2^2 + \frac{\nu e \bar{v}_1}{v_0} \left(\Phi_2^{1/3} - \frac{2\Phi_2}{f} \right) = 0 \quad (11)$$

Solving Equ. (11) for the Φ_2 's determined from equilibrium swelling at constant temperature the enthalpy parameter β_0 and the excess entropy parameter α_0 are available.

The identity of the coefficients of Equ. (11) and (2) permits to write:

$$\chi = \alpha_0 + \beta_0 (1 - \gamma) / (1 - \gamma \Phi_2)^2 \quad (12)$$

A representation of χ -values versus $(1 - \gamma) / (1 - \gamma \Phi_2)^2$ allows to receive the enthalpy term from the slope and the excess entropy term from the intercept. The experimental data yield the expected straight lines (Table IV).

Table IV: Enthalpy parameter β_0 and entropy parameter α_0 derived from the experimental data following Equ. (12)

T	$+\beta_0$	$-\alpha_0$	regress. coeff.
288	1.1692	.3577	.995
293	1.1111	.3249	.995
298	1.0782	.3084	.996
303	1.0451	.2896	.997
308	1.0311	.2854	.997
313	1.0106	.2733	.997
318	.9986	.2671	.998
323	.9851	.2616	.998

The temperature dependence of α_0 and β_0 shows a pronounced curvature below 308

potential of the solvent has been proposed by KONINGSVELD and KLEINTJENS (1971)

$$\left(\frac{\partial \Delta G^M}{\partial n_1} \right)_{p,T} = RT \left[\ln(1 - \Phi_2) + \left(1 - \frac{1}{\chi} \right) \Phi_2 + \left(\alpha_0 + \frac{\beta_0(1 - \gamma)}{(1 - \gamma \Phi_2)^2} \right) \Phi_2^2 \right] \quad (10)$$

with

- α_0 excess entropy parameter
- β_0 interaction entropy parameter
- $\gamma = 2/z$; - z coordination number of the lattice.

The two dimensionless parameters derived in this way are representative for the solvent - solute interaction at a given temperature. They have no concentration dependence. They may serve as a good base for comparative studies of different solvent - solute systems. Decreasing β_0 have to be interpreted as a trend towards exothermic solute - solvent interactions, whereas a smaller value of the module of α_0 indicates a trend towards the maximal entropic function, the combinatorial one.

K. This may be caused by beginning phase separation. Above this temperature β_0 can be described by a linear function of $1/T$:

$$\beta_0 = .0558 + 298.85/T \quad (13)$$

The comparison of our α_0 and β_0 values with those published by KONINGSVELD and KLEINTJENS (1971) for the polystyrene - cyclohexane solutions shows that the parameters measured from the network swelling are somewhat higher than those from solutions of linear polymers.

The pseudoideal conditions in the system, when entropy and enthalpy term cancel, corresponding to the GIBBS - HELMHOLTZ equation, are satisfied if

$$.5 - \alpha_0 = \beta_0(1 - \gamma) \quad (14)$$

This equality is satisfied at 307.5 K with a relative error of $\pm 1\%$.

The application of the two-parameter equation (10) proposed by KONINGSVELD and KLEINTJENS to swelling thermodynamics offer an unequivocal description of the system.

Thus it seems to be a fairly good base for the study of swelling as well as of solution properties of polystyrene in binary solvents containing cyclohexane. Hopefully it will be able to describe other three-component systems too, offering a chance in this manner to make progress in interpreting miscibility problems in macromolecular systems.

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