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Determination of Polymer-Solvent Interaction Parameter from Swelling of Networks: The System Poly(2-hydroxyethyl methacrylate)-Diethylene Glycol

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ABSTRACT: Poly(2-hydroxyethyl methacrylate) gels are prepared by cross-linking with various amounts of ethylene glycol dimethacrylate in diethylene glycol solvent. The degree of swelling of the networks in diethylene glycol is measured in the range $0 < v_2 < 0.35$ as a function of cross-link density and solvent content during cross-linking. Results of swelling measurements are used to determine the polymer-solvent interaction parameter χ of the system. An expression of the form $\chi = 0.49 - 0.25v_2$, where v_2 is the polymer volume fraction, is estimated for the investigated system at 25 °C, which is in agreement with Janáček and Ferry's results. The analysis of experimental data provides information about the effective network chain length, which is found to differ appreciably from the one expected from stoichiometry.

Introduction

The importance of the polymer-solvent interaction parameter χ in the thermodynamic behavior of polymer solutions has been established by various studies, as reviewed by Orwoll.¹ Recently, a detailed study of the thermodynamics of swollen networks was presented emphasizing the predominant role of the χ parameter.² A convenient experimental technique for the determination of the χ parameter is the measurement of equilibrium swelling of networks.¹

In this study, the degree of swelling of poly(2-hydroxyethyl methacrylate) (PHEMA) networks in diethylene glycol is measured by the same experimental technique as was recently employed for the swelling of polystyrene networks.³ The choice of the present system is motivated by both the wide range of biomedical application of PHEMA gels⁴ and the possibility to proceed as a next step to ionized gels such as PHEMA-methacrylic acid copolymers in polar solvents, which are important for membrane applications. Since diethylene glycol is a good solvent for PHEMA, the influence of parameters, such as the polymer concentration during cross-linking and the cross-link density, on the equilibrium degree of swelling was clearly discernible.

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Table I
Composition of the Samples

set	sample	v_2°	$w_x \times 100$	x_c^a
A	A ₁	0.50	7.41	5.0
	A ₂	0.50	5.19	7.3
	A ₃	0.50	2.94	13.1
B	B ₁	0.50	2.44	15.9
	B ₂	0.50	2.02	19.3
	B ₃	0.50	1.55	25.3
C	C ₁	0.50	0.86	45.8
	C ₂	0.50	0.32	123.9
	C ₃	0.50	0.25	158.6
D	D ₁	0.20	0.86	45.8
	D ₂	0.20	0.36	110.0
	D ₃	0.20	0.16	248.1

^a Calculated from eq 1.

The viscoelastic properties of the same system were investigated by Janáček and Ferry.⁵ In their study, the results from creep experiments were employed to determine the effective cross-link density, which, in turn, was used to evaluate the χ parameter according to a simplified expression⁶ for the solvent chemical potential. In the present treatment, the molecular theory of elasticity, introduced by Flory,^{2,7} is adopted to represent the elastic contribution to the chemical potential of the solvent. Only data from swelling experiments are used in calculations without recourse to mechanical property measurements. The calculated interaction parameters and their concentration dependence are compared with the results from viscoelastic measurements carried out by Janáček and Ferry⁵ in order to check the applicability of the swelling experiments as a practical means for determining the χ parameter.

The approach developed in the present study allows for the simultaneous determination of the effective cross-link density, which differs from the one expected from stoichiometry. The discrepancy between the stoichiometric cross-link density and the one calculated from experimental results is discussed.

Experimental Section

Preparation of Networks. 2-Hydroxyethyl methacrylate (HEMA) monomer was a Fluka material. It was extracted with *n*-hexane three times in order to diminish the amount of the diester ethylene glycol dimethacrylate (EGDM) present and was freshly distilled under reduced pressure (65 °C/3 mmHg) prior to use. Further EGDM additions required for some compositions were done from a Merck material (used as received). All HEMA and EGDM monomer mixtures were analyzed by gas chromatography before polymerization in order to determine the exact composition. A United Technologies Packard Model 439 GC was used with a 10% OV-17 column (oven temperature 120–200 °C programmed, detector temperature 250 °C, injection temperature 200 °C). The initiator, 2,2'-azobis(isobutyronitrile) (AIBN) was a Merck material and was recrystallized from methanol and dried prior to use. The diethylene glycol was a Riedel-de-Haen material and was used as received.

Proper mixtures of HEMA, EGDM, and diethylene glycol were placed in glass tubes, and N₂ gas was allowed to pass for 3 min. Two glass plates were covered with Melinex sheets (a heat-resistant polyester sheet; product of Boyden Data Papers Ltd., England), and a polyethylene gasket was placed between them to form a mold of dimensions 5 × 5 × 0.1 cm³, which was held by metal clips. The monomer mixture was injected into the mold with a syringe. The molds were kept in an oven for 2 days at 60 ± 0.5 °C and for 1 day at 90 ± 0.5 °C to complete the network formation.

Composition of the Samples. The networks were prepared as four sets, each consisting of three samples differing in the amount of cross-linking agent. The compositions of the networks

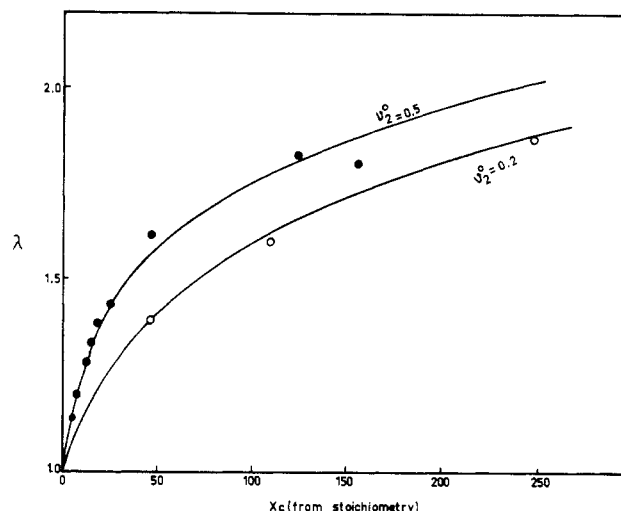


Figure 1. Results of swelling experiments for PHEMA networks in diethylene glycol. The linear swelling ratios λ are plotted against the stoichiometric chain length x_c . The filled circles represent results from sets A, B, and C with $v_2^\circ = 0.50$. Results from set D with $v_2^\circ = 0.20$ are shown by the empty circles. The curves are the best fit to experimental data.

are listed in Table I in terms of the weight fraction of EGDM in the monomeric mixture (w_x) and volume fraction (v_2°) of the polymer during cross-linking. The mean number of segments between successive junctions is denoted by x_c . A segment is defined as a portion of the chain whose volume along the backbone equals the molar volume of the solvent. Examination of the structures of the monomeric unit and the solvent reveals the fact that nearly half of a monomeric unit occupies a volume equal to that of a solvent molecule along the backbone, while the other half forms a branch, thus making no contribution to the length of the chains in the network. Relying on the above hypothesis and furthermore assuming a perfect tetrafunctional network, we calculated the x_c values in Table I according to the equation

$$x_c = (1 - w_x)M_x\bar{v}/(4V_1w_x) \quad (1)$$

where M_x is the molecular weight of the cross-linking agent, w_x is its weight fraction in the monomeric mixture, \bar{v} is the specific volume of the polymer ($\bar{v} = 1/1.313 \text{ cm}^3 \text{ g}^{-1}$), and V_1 is the solvent molar volume. The chain lengths x_c calculated from eq 1 represent the stoichiometric values expected from the conditions of preparation. The calculations from swelling measurements will show, however, that the effective chain lengths $x_{c,\text{eff}}$ deviate from those listed in Table I due to inefficient cross-linking.

Swelling Measurements. Samples with dimensions of ca. $1.5 \times 0.4 \times 0.1 \text{ cm}^3$ were immersed in diethylene glycol at 25 °C for several weeks until equilibrium was reached, where the measured lengths were constant. A period of about 30 days was required for the samples with relatively low degree of cross-linking to reach equilibrium. The length changes were measured as described in ref 3 with a traveling microscope (Gaertner 7109-C-46) with an accuracy of ±0.001 cm.

Results of Measurements

The results from swelling experiments are plotted in Figure 1. The ordinate λ in this figure denotes the ratio of the final length of the sample swollen to equilibrium to that before swelling. The filled circles represent the results of measurements for samples with $v_2^\circ = 0.5$ (sets A, B, and C) and the empty circles for samples with $v_2^\circ = 0.2$ (set D). The equilibrium dimensions are found to be strongly dependent on the polymer volume fraction during cross-linking. The composition of the swollen samples may be calculated from $v_2 = v_2^\circ\lambda^{-3}$, where v_2 denotes the volume fraction of the polymer in the final swollen samples. The results are presented in Table II. The effect of the initial solvent content on the degree of swelling of the network is apparent from the comparison of the results of sets C

Table II
Results of Equilibrium Swelling Measurements of
PHEMA-EGDM Gels in Diethylene Glycol and
Calculations of v_2

sample	λ	v_2
A ₁	1.140	0.337
A ₂	1.200	0.289
A ₃	1.285	0.236
B ₁	1.346	0.205
B ₂	1.384	0.188
B ₃	1.433	0.170
C ₁	1.606	0.121
C ₂	1.825	0.082
C ₃	1.800	0.086
D ₁	1.384	0.075
D ₂	1.596	0.049
D ₃	1.864	0.031

and D. Samples in these two sets differ in their initial solvent volume fractions v_2° , while their cross-link densities lie in about the same range. The equilibrium v_2 values corresponding to samples with lower v_2° (i.e., set D) are much smaller compared to those from set C. This result shows that the cross-linking efficiency decreases with increasing initial solvent content.

Comparison of Experimental Results with Theory

Theoretical Background. The chemical potential of the solvent in the network, $\Delta\mu_1$, may be written⁶ as the sum of two terms, one accounting for the effect of mixing and the other representing the elastic contribution:

$$\Delta\mu_1 = \Delta\mu_{\text{mix}} + \Delta\mu_{\text{el}} \quad (2)$$

The mixing term is satisfactorily represented by a Flory-Huggins type expression of the form

$$\Delta\mu_{\text{mix}} = \ln(1 - v_2) + v_2 + \chi v_2^2 \quad (3)$$

provided that the polymer-solvent interaction parameter χ is expressed as a series expansion in powers of the polymer volume fraction v_2 ; i.e.

$$\chi = \chi_1 + \chi_2 v_2 + \dots \quad (4)$$

where the coefficients χ_1 and χ_2 are functions of temperature and the molecular characteristics of the specific system.

As to the elastic contribution, experimental works⁹ indicate that the expression

$$\Delta\mu_{\text{el}} = \frac{v_2^\circ}{2x_{c,\text{eff}}} \lambda^{-1} [1 + K(\lambda)] \quad (5)$$

obtained from the recent theory introduced by Flory,⁷ accurately predicts the molecular behavior. Subscript "eff" is appended to indicate the effective chain length, which will be seen to differ from the one calculated on a stoichiometric basis (x_c). $K(\lambda)$ follows from the theory as

$$K(\lambda) = B\dot{B}/(1+B) + D\dot{D}/(1+D) \quad (6)$$

where

$$B = \kappa^2(\lambda^2 - 1)/(\lambda^2 + \kappa)^2$$

$$D = \lambda^2 B / \kappa$$

$$\dot{B} = \partial B / \partial \lambda^2 = B[(\lambda^2 - 1)^{-1} - 2(\lambda^2 + \kappa)^{-1}] \quad (7)$$

$$\dot{D} = \partial D / \partial \lambda^2 = \kappa^{-1}[\lambda^2 \dot{B} + B]$$

Here, κ is a parameter denoting the degree of the effect of constraints on the fluctuations of the junctions. The

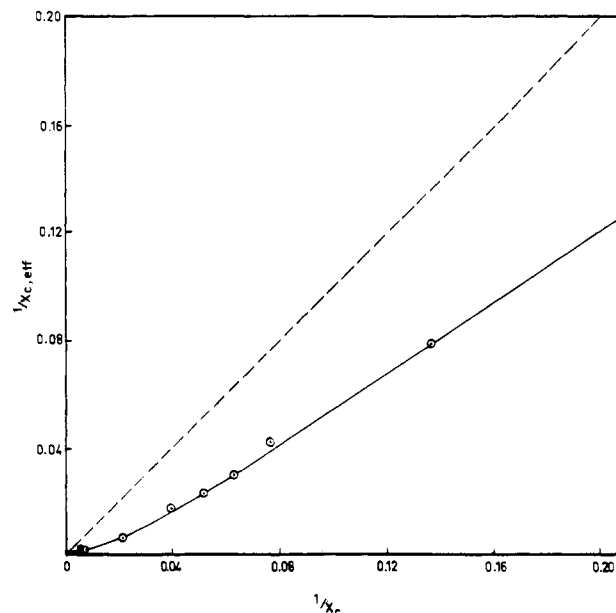


Figure 2. Variation of $1/x_{c,\text{eff}}$ with the stoichiometric $1/x_c$. The dashed line corresponds to 100% efficiency. The calculated points lie below the 45° line due to inefficient cross-linking, which is particularly strong at low cross-link density. The curve through the points is the best fitting one.

two extreme cases of $\kappa = 0$ and $\kappa = \infty$ correspond to the phantom and affine network theories, respectively.⁷ A convenient expression for calculating κ is²

$$\kappa = 1/4 P v_2^\circ x_{c,\text{eff}}^{1/2} \quad (8)$$

where P is a dimensionless parameter depending on the characteristics of the generic type of polymer and on the molar volume of the diluent according to²

$$P = (C_\infty l^2 / \bar{v} M_l)^{3/2} V_1^{1/2} N_A \quad (9)$$

where C_∞ is the characteristic ratio, M_l is the molecular weight per bond along the network chain, l is the average bond length, and N_A is Avogadro's number.

Calculations. When the network is swollen to equilibrium with pure solvent, the activity of the solvent in the network equals that of the surrounding pure solvent, i.e., unity. Consequently, the chemical potential of the solvent in the network equates to zero. From eq 2-5, the thermodynamic equilibrium condition may be written as

$$\ln(1 - v_2) + v_2 + \chi_1 v_2^2 + \chi_2 v_2^3 + \frac{v_2^\circ}{2x_{c,\text{eff}}} \lambda^{-1} [1 + K(\lambda)] = 0 \quad (10)$$

Equation 10 contains three unknowns, χ_1 , χ_2 , and $x_{c,\text{eff}}$, which are going to be determined from the numerical analysis of experimental data. The interpenetration parameter κ , which is implicitly present in eq 10 through the term $K(\lambda)$, will be calculated by using eq 8. The value $P = 2.5$ was used for the estimation of the parameter κ and based on the value¹⁰ of ca. 12 for the characteristic ratio.

The effective chain length may be assumed, as a first approximation to be related to the stoichiometric chain length by an expression of the form

$$x_{c,\text{eff}} = x_c / m \quad (11)$$

where the constant m is a measure of cross-link efficiency. m is expected to vary in the range $0 < m \leq 1$. Values of m exceeding unity may be attributed to effects such as entanglements. Subsequent calculation will show, however, that the above linear relationship is not valid over a wide

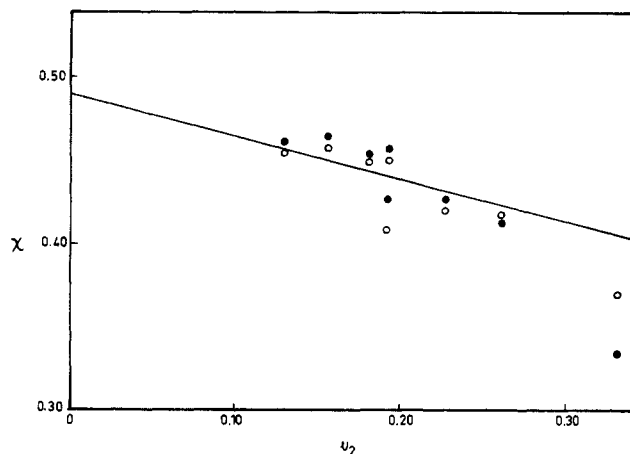


Figure 3. Variation of the polymer-solvent interaction parameter χ with polymer volume fraction. The line is calculated from the theory of the present study. Experimental points from the work of Janáček and Ferry are shown for comparison (empty circles). These are calculated by using the affine network model while filled circles follow from the calculations of the present study with $P = 2.5$.

range of cross-link density but may be applied with confidence to the treatment of experimental outcomes within a given set. On this basis, eq 10 may be applied, in conjunction with eq 11, to each set (A, B, C, and D) of data, leading each to three distinct equations to be solved simultaneously for the three unknowns χ_1 , χ_2 , and m .

Inasmuch as the interaction parameter χ is characteristic of the specific polymer-solvent system and does not depend on experimental conditions such as cross-link density or initial solvent content, the calculated χ_1 and χ_2 values are expected to be the same in each set. In fact, the simultaneous solution of the three equations in each set leads to constant values for χ_1 and χ_2 , such as $\chi_1 = 0.490 \pm 0.005$ and $\chi_2 = -0.25 \pm 0.02$. However, the parameter m , which reflects the cross-linking efficiency, assumes the values 0.60, 0.47, 0.33, and 0.17 in sets A, B, C, and D, respectively, thus decreasing with lower cross-link density and higher solvent content during cross-linking. Results are found to be rather sensitive to χ_1 values while slight variation in χ_2 ensures the postulate of constant m within a set. If, alternately, calculations are repeated by adhering to the values $\chi_1 = 0.49$ and $\chi_2 = -0.25$ and solving for m , the efficiency of cross-linking at various stages is obtained. Figure 2 illustrates the variation of $1/\chi_{c,eff}$ with $1/\chi_c$ for sets A, B, and C with $v_2^0 = 0.50$. The dashed line corre-

sponding to 100% efficiency ($\chi_c = \chi_{c,eff}$) is shown for comparison. The curve is the best fit to experimental data.

The analysis of swelling experiments with the PHEMA-diethylene glycol system leads to the following expression for the polymer-solvent interaction at 25 °C:

$$\chi = 0.49 - 0.25v_2$$

The corresponding line is drawn in Figure 3. The experimental points resulting from the work of Janáček and Ferry⁵ are shown in this figure for comparison by the empty circles. Their calculations were based on the affine network model. The results of the calculations based on the present study with $P = 2.5$ are shown by the filled circles. In general, satisfactory agreement between the line obtained in the present work and the results from previous experiments is observable.

Conclusion

PHEMA gels with various cross-link densities were prepared in diethylene glycol and swollen to equilibrium in the same solvent to estimate the polymer-solvent interaction prevailing in the system. Explicit expressions for the coefficients χ_1 and χ_2 are given by the equation of state theory.⁸ However, with the exception of a few systems whose thermodynamic behavior has been extensively studied, the lack of information about the enthalpy parameter X_{12} and entropy parameter Q_{12} in the theory renders practically impossible the theoretical calculation of χ_1 and χ_2 . Instead, the present treatment offers a practical means for estimating these coefficients and hence the χ parameter as a function of polymer concentration. In addition, the analysis of the data set leads to the determination of the effective cross-link density, which in fact differs appreciably from the one expected from stoichiometry.

Registry No. (HEMA)(EGDM) (copolymer), 25053-81-0.

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