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Swelling behavior of polystyrene networks in some aliphatic esters and linear polystyrene solutions

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Summary

Polystyrene networks were synthesized by free radical polymerization of styrene in the presence of dibenzoyl peroxide as an initiator, divinylbenzene as a crosslinker at 50°C in toluene under nitrogen atmosphere. The swelling behavior of the synthesized polystyrene networks were studied at different temperatures in methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, *tert*-butyl acetate, and isopentyl acetate. Equations were given for the variation of the polymer-solvent interaction parameter, χ_{12}, as a function of reciprocal absolute temperature in the temperature range from 25 to 75°C. Polystyrene networks were swollen in linear polystyrene solutions in toluene of different concentrations. Linear polystyrene samples were almost monodisperse and of high molecular weight. The equilibrium swelling degrees were evaluated using the Flory-Rehner theory. The relation of volume swelling ratio, q_v, to the volume fraction of the linear polymer in solution, ϕ, was evaluated and characterized by interaction parameter of crosslinked polystyrene with linear polystyrene, χ_{23}. The parameter χ_{23} was found around zero as expected from mixtures of similar chemical structures by extrapolating the values of χ_{23} at tested concentrations to zero solvent concentration.

Introduction

The basic derivation of the equilibrium swelling for ternary systems was established 60 years ago [1]. Also, swelling and deswelling of polymer networks with organic solvents has been the subject of research since many years ago. Many theories and modifications of them were proposed to explain swelling behavior [2-7]. The theory of swelling of polymer gels assumes that the network immersed in a liquid attains the thermodynamic equilibrium with the surrounding solution after a finite time such as a few weeks. Since the chemical potentials of all diffusible components inside and outside the network are equal, the theories predict the equilibrium volume of the

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network phase as a function of the solvent composition. Although a great number of investigations of the swelling behavior of a network in solvents have been reported, few studies were published related to the networks in their linear polymer solutions [8-16]. Among the theories, the Flory-Rehner theory is still successfully used to characterize the networks both in small-molecule solvents and in polymer solutions since it is simple, instructive, accurate and predictive.

In this study, we examined the swelling behavior of networks of polystyrene (NPS) in some low-molecular-weight solvents at various temperatures, as well as swelling behavior of NPS in linear polystyrene (LPS) solutions in toluene at room temperature.

Theoretical background

The experimental data were analyzed using the Flory-Rehner theory of swelling equilibrium. Swelling of a non-polar polymer in a non-polar medium is governed by the Gibbs energy composed of the two contributions: the Gibbs energy of mixing, ΔG_m, and the Gibbs energy of elastic deformation, ΔG_{el}.

If the Gibbs energy of a swollen network, ΔG_{swell}, in a solvent is differentiated with respect to the number of moles of the solvent, n_1, the chemical potential change of the solvent in the solution, $\Delta\mu_1$ is obtained for a binary system:

$$\frac{\partial \Delta G_{swell}}{\partial n_1} = \Delta\mu_1 = \mu_1 - \mu_1^o \tag{1}$$

$$\frac{\Delta\mu_1}{RT} = \ln(1 - v_2) + v_2 + \chi_{12} + \frac{1}{N}\left(\left(v_2^0\right)^{2/3} v_2^{1/3} - v_2 / 2\right)$$

where R is universal gas constant, T is absolute temperature, χ_{12} is interaction parameter between solvent and network, v_2^0 and v_2 are the volume fractions of polymer network after preparation and in the equilibrium-swollen gel, respectively. N is crosslink density defined as $1/N = \nu_e \times V_1$ where ν_e is the concentration of elastically active network chains and V_1 is molar volume of the solvent. The dimensionless v_2^0 can be obtained experimentally and calculated from the relationship

$$v_2^0 = \frac{V_{dry}}{V_0} = \frac{c_0}{\rho_P} \tag{2}$$

where V_0 is the network volume in the network formation and V_{dry} is the volume of dry extracted network, c_0 is initial monomer concentration in g.dm^{-3}, ρ_P is density of polymer. If the Gibbs energy of a swollen network, ΔG_{swell} in linear polymer solution is differentiated with respect to the number of moles of solvent, n_1, and linear polymer, n_3, the following four equations for the chemical potentials of the solvent and linear polymer in both the gel ($\Delta\mu_i^{gel}$) and solution phases ($\Delta\mu_i^{sol}$) are obtained:

$$\begin{aligned}\frac{\Delta\mu_1^{gel}}{\mathrm{R}T} &= \ln v_1 + (1 - v_1) - v_3 / y + (\chi_{12} v_2 + \chi_{13} v_3)(1 - v_1) \\ &\quad - \chi_{23} v_2 v_3 + N^{-1}\left(v_2^{1/3} (v_2^0)^{2/3} - v_2 / 2\right)\end{aligned} \tag{3}$$

$$\frac{\Delta\mu_1^{sol}}{\mathrm{R}T} = \ln(1 - \phi) + \phi(1 - 1/y) + \chi_{13}\phi^2 \tag{4}$$

$$\frac{\Delta\mu_3^{\text{gel}}}{y\text{R}T} = (1/y)\ln v_3 + (1/y)(1-v_3) - v_1 + (\chi_{13}v_1 + \chi_{23}v_2) \\ (1-v_3) - \chi_{12}v_1v_2 + N^{-1}(v_2^{1/3}v_2^{0^{2/3}} - v_2/2) \quad \textbf{(5)}$$

$$\frac{\Delta\mu_3^{\text{sol}}}{y\text{R}T} = (1/y)\ln\phi - (1-\phi) + (1/y)(1-\phi) + \chi_{13}(1-\phi)^2 \quad \textbf{(6)}$$

where y is the number of segments in the linear polymer and ϕ is its volume fraction in the solution phase. Equilibrium swelling is reached when the solvent and the polymer inside the network are in thermodynamic equilibrium with those outside. In the equilibrium state, the chemical potential, μ, of these components in both phases is equal:

$$\Delta\mu_1^{\text{gel}} = \Delta\mu_1^{\text{sol}} \quad \textbf{(7)}$$

$$\Delta\mu_3^{gel} = \Delta\mu_3^{sol} \quad \textbf{(8)}$$

Combining Eqs. (1)-(6) under the thermodynamic swelling equilibrium condition given in Eqs. (7) and (8), the following two equations were obtained for a network immersed in a polymer solution:

$$\ln\left(\frac{1-v_2-v_3}{1-\phi}\right) + (v_2+v_3-\phi) - (v_3-\phi)/y + \chi_{12}v_2^2 \\ +\chi_{13}(v_3^2-\phi^2) + (\chi_{12}+\chi_{13}-\chi_{23})v_2v_3 + N^{-1}\left(v_2^{1/3}(v_2^0)^{2/3} - v_2/2\right) = 0 \quad \textbf{(9)}$$

$$-\ln\left(\frac{1-v_2-v_3}{1-\phi}\right) + (1/y)\ln(v_3/\phi) \\ + 2\chi_{13}(v_3-\phi) + (\chi_{23}-\chi_{12}-\chi_{13})v_2 = 0 \quad \textbf{(10)}$$

Equations (9) and (10) predict the equilibrium swelling ratio, q_v of the networks in polymer solution defined:

$$q_v = \frac{1}{v_2} = \frac{V}{V_{\text{dry}}} = \frac{\left(V/V_0\right)}{v_2^0} = \frac{(D/D_{\text{o}})^3}{v_2^{\text{o}}} \quad \textbf{(11)}$$

Experimental

Materials

Styrene was of chemical reagent grade from Merck A.G. It was washed with NaOH and distilled water to remove inhibitor and distilled under vacuum. Molecular weights of the linear monodisperse polystyrene (LPS) purchased from Aldrich were 8.91×10^5 and 1.8×10^6. The concentrations of LPS in toluene were 0.5, 1.0, 1.5 and 2.0 wt.-%. Methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, *tert*-butyl acetate, isopentyl acetate were purchased from Merck and used as received. Dibenzoyl peroxide purchased from Aldrich was dissolved in chloroform, crystallized from cold methanol and dried in vacuum. Divinylbenzene produced by Merck was used as received.

Synthesis of NPS

PS networks were prepared by polymerization of 0.21 mol of styrene in 25.5 ml of toluene in the presence of 2.11 mmol of dibenzoyl peroxide as free-radical initiator and 2.45 mmol of divinylbenzene, the crosslinker, under nitrogen atmosphere. The reaction proceeded in vacuum oven at 50°C for 48 h. Curing of the networks continued for 48 h. The crosslink density of the resulting material was characterized by N in Eq. (1) being equal to 130 from its equilibrium swelling in toluene using Eq. (1).

Swelling of NPS in low-molecular-weight solvents

The network samples cut as cylinders of 0.5 cm height were immersed in a large amount of toluene in order to extract uncrosslinked polymer, then the samples were dried in a vacuum oven until constant weight was reached. The samples were immersed into 100 ml vials filled with the solvent for at least one week in order to reach equilibrium degree of swelling. The experiments were carried out with the precision ± 0.5°C at varying constant temperatures in an oven. The diameter of the networks, D, was measured with calibrated Mitutoyo 500-191 model digital compass. The equilibrium volume swelling ratio, q_v was obtained from Eq. 11. Each swelling ratio reported in this study is an average of at least two separate measurements.

Swelling of NPS in LPS solutions in toluene

The NPS samples cut as cylinders of 0.5 cm height and 1 cm diameter were left standing in a large amount of toluene to extract in uncrosslinked polystyrene. Then they were kept immersed in 100 ml vials filled with LPS solutions in toluene with linear polystyrene of two different molecular weights at various concentrations for at least ten days in order to reach the equilibrium degree of swelling. The concentration of the polystyrene solution was corrected by considering the amount of toluene in swollen sample. The experiments were carried out at 25 ± 0.1°C. The diameter of the networks, D, was measured with a calibrated digital compass and the equilibrium volume swelling ratio, q_v was obtained from Eq. 11.

Determination of volume fraction of the linear polymer, v_3, in the networks

After the network polystyrene samples in the linear polystyrene solution reached equilibrium, they were washed with pure toluene. Then, they were left in a large amount of pure toluene to extract linear polymer from the network. The amount of LPS diffused out of the network was determined from the absorption peak of the extract using an Agilent 8453 Model UV-spectrophotometer. The intensity of absorption peaks were averaged values of three measurements. By using a calibration, the amount of extracted LPS was determined. The ratio of the volume of LPS to total volume of the swollen NPS was used as v_3.

Results and discussion

Using the volume fractions of NPS, v_2, in the equilibrium-swollen sample in pure toluene obtained from Eq. 11 and volume fraction of NPS after preparation, v_2^0, obtained from Eq. 2, the average number of segments in the network chains, N, was found by substituting the difference of chemical potentials of the solvent, $\Delta\mu_1$ to zero (Eq. 1). Then, the polymer solvent interaction parameter, χ_{12}, of the NPS was found from the equilibrium swelling ratio of the network in the low-molecular-weight solvents. By assuming that χ is independent of concentration, the variation of χ_{12} with the reciprocal value of absolute temperature was determined and it seems that the plots were almost linear obeying the equation $\chi_{12} = a+b/T$. The constants a and b and the regression coefficient, R^2 are given for temperatures between 25 and 75 °C in Table 1.

Table 1. The intercept, *a*, the slope, *b*, of the equation $\chi_{12} = a+b/T$ and regression coefficients, R^2 of the linear plots of polymer-solvent interaction parameter, χ_{12}, against reciprocal absolute temperature ($1/T$) for NPS with some aliphatic esters in the temperature range from 25 to 75°C

solvent		*a* (intercept)	*b* (slope)	R^2 (regression coefficient
methyl acetate	MA	0.5955	6.4770	0.9677
ethyl acetate	EA	0.5646	4.8318	0.9590
propyl acetate	NPA	0.5572	3.8917	0.7501
isopropyl acetate	IPA	0.5666	8.6461	0.8329
butyl acetate	NBA	0.5540	4.6687	0.6892
isobutyl acetate	IBA	0.5191	20.040	0.9582
tert-butyl acetate	TBA	0.5485	18.568	0.8851
isopentyl acetate	IAA	0.5529	7.0225	0.9003

The plots of the above linear equations are given in Fig. 1. Therefore, NPA and NBA are good solvents; however, MA, IPA and TBA are moderately poor solvents for NPS. The results suggest that the solvent quality decreases with decreasing molecular weight of the solvent and branching of the solvent molecule. In the case of MA and EA, the experiment could not be performed at temperatures higher than 55 °C because of their high vapor pressure. For all the studied solvents, the parameter χ_{12} decreases with temperature, indicating that the polymer-solvent systems exhibit upper critical solution temperature (UCST).

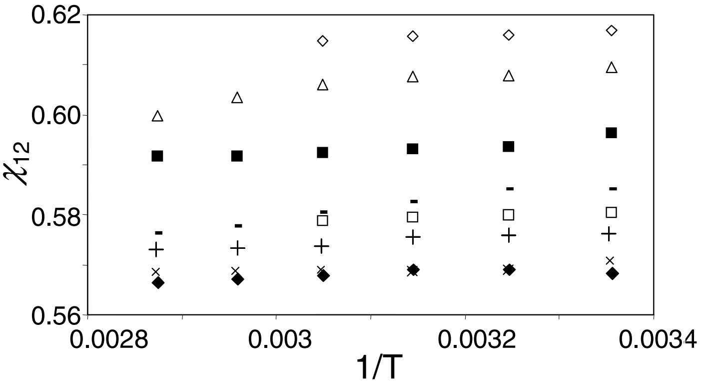

Figure 1. Temperature dependence of the polymer-solvent interaction parameter, χ_{12}, of NPS with the solvents: MA (◇), EA (□), NPA (×), IPA (■), NBA (◆), IBA (–), TBA (△), IAA (+).

Table 2. Comparison of polymer-solvent interaction parameters, χ_{12}, with literature.

		φ							
Solvent	t [°C]	0	0.2	0.4	0.6	0.8	1.0	Method	Ref.
EA	27	0.49						op	20
	50	0.49						op	20
	25			0.58				sw	ts
	75			0.58				sw	ts
NPA	25			0.66	0.66	0.66		vs	20
	70			0.61	0.60	0.59		vs	20
	25			0.68	0.68	0.68	0.68	vs	19
	25			0.57				sw	ts
	75			0.57				sw	ts
NBA	20	0.50	0.56	0.67	0.76	0.85	0.93	vs	19
	30	0.47						op	20
	25			0.57				sw	ts
	75			0.57				sw	ts
TBA	30	0.50	0.53	0.63				ls, cm	21
	50	0.49	0.53	0.63				ls, cm	21
	25			0.61				sw	ts
	75			0.60				sw	ts

op: osmotic pressure; sw: swelling; ls: light scattering; vs: vapor sorption; cm: critical miscibility, ts: this study.

Data related to the values of χ_{12} of polystyrene-ester systems vary in the literature. It was reported that polystyrene-ester systems have both lower critical solution temperatures and upper critical solution temperatures [17, 18]. The dependence of χ_{12} on volume fraction of the polymer in the mixture is ambigious [19]. Data in the literature were compared with our results in Table 2. In the case of TBA, the agreement is good but the χ_{12} values for other esters are somewhat different.

From the equilibrium swelling measurements of NPS in LPS solutions in toluene at different concentrations, the equilibrium swelling ratio, q_v, was determined and plotted in **Fig. 2**. The swelling ratios of NPS do not change dramatically with the molecular weight and volume fraction of LPS, ϕ, in the solution.

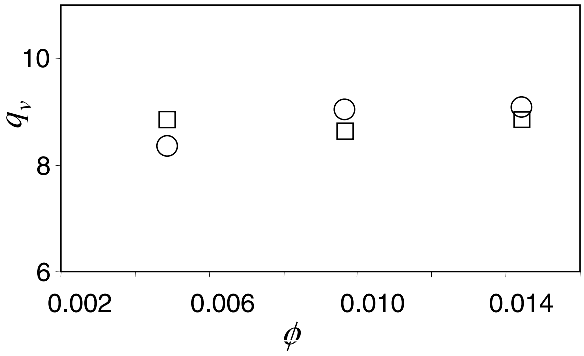

Figure 2. Dependence of equilibrium swelling ratio, q_v, of NPS on volume fraction of LPS at different molecular weights: 8.91×10^5 g mol^{-1} (○), 1.8×10^6 g mol^{-1} (□).

The volume fraction of linear polymer, v_3, in the swollen network was determined experimentally as described in the Experimental section. The network-linear polymer interaction parameter, χ_{23}, was found from the equation derived by summing the right-hand and left-hand sides of Eqs. (9) and (10)

$$\chi_{23}(v_2 v_3 - v_2) = (v_2 + v_3 - \phi) - (v_3 - \phi)/y + \chi_{12} v_2^2 + \chi_{13}(v_3^2 - \phi^2) + 2\chi_{13}(v_3 - \phi) + \frac{1}{y}\ln\left(\frac{v_3}{\phi}\right) + \frac{1}{N}\left(v_2^{1/3}(v_2^2)^{2/3} - v_2/2\right) + 2v_2\chi_{12}(v_3 - 1) \qquad \mathbf{(12)}$$

The values of the parameter χ_{23} are given in Table 3 for NPS together with experimental data.

Table 3. Calculated χ_{23} values

$M_w \times 10^{-5}$ [g/mol]	M_w/M_n	N	y	c [g/ml]	ϕ	D/D_0	q_v	$v_3 \times 10^4$	χ_{23}
18.80	1.02	130	16311	0.005	0.0048	1.55	8.78	9.73	-0.24
				0.010	0.0096	1.54	8.682	0.40	-0.15
				0.015	0.0144	1.56	8.93	5.93	-0.08
8.91	1.03	130	8074	0.005	0.0048	1.53	8.50	9.68	-0.24
				0.010	0.0096	1.56	8.95	1.10	-0.14
				0.015	0.0144	1.57	9.087	0.78	-0.06

Molecular weight, M_w; number of segments of LPS, y; initial concentration of LPS in the toluene solution, C; volume fraction of LPS in the solution, ϕ; volume fraction of LPS inside the swollen NPS, v_3; average number of segments in NPS, N; ratio of diameters of swollen and unswollen NPS, D/D_o; equilibrium swelling ratio of NPS in LPS solution,q_v; network-linear polymer interaction parameter, χ_{23}.

The values of parameter χ_{23} were plotted against the reciprocal of the LPS concentration, c, in order to find the value of χ_{23} at zero solvent concentration, i.e. in the bulk NPS/LPS mixture. The parameter χ_{23} has negative values for the studied LPS concentrations. This is surprising, but there is no information about the relation between χ_{23} and $1/c$ in the literature; it seems that the dependence is linear and independent of the molecular weight of LPS for the molecular weights in this study. The extrapolated value of χ_{23} is -5×10^{-3}, from the mean of the intercepts of the linear plots in Figure 3. This can be accepted as zero within experimental error, which is the expected value of χ_{23} for the networks in their linear polymer since there is no attractive or repulsive force between their segments. Actually, the found value of χ_{23} was very close to those in Table 3 when v_3 was put equal to zero.

It seems that swelling of a network in a linear polymer solution can be used for the determination of the polymer-polymer interaction parameter of a polymer-polymer mixture.

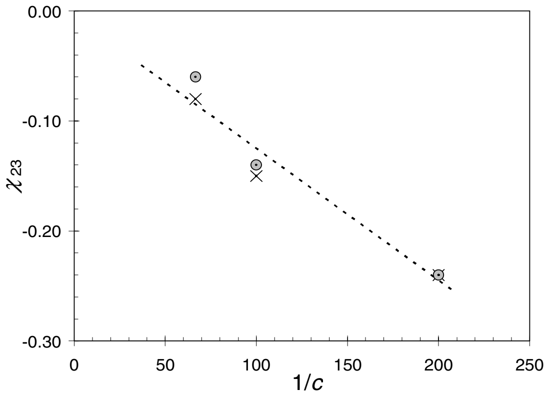

Figure 3. Extrapolation of network-linear polymer interaction parameter, χ_{23} to the zero solvent concentration for NPS with two different molecular weights: M_w=8.91×10^5 g mol^{-1} (○), and M_w =1.8×10^6 g mol^{-1} (×).

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