

A Study on Swelling Behavior of Poly(*p*-chloro styrene) Networks in Some Aromatic Hydrocarbons and Linear Poly(*p*-chloro styrene) Solutions

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ABSTRACT: Crosslinked networks (NPPCS) and linear polymers (LPPCS) of poly (*p*-chloro styrene) were synthesized by free-radical polymerization of *p*-chloro styrene. NPPCS networks were swollen in four different molecular weights of LPPCS solutions in toluene at three different concentrations. The equilibrium swelling results were evaluated by means of Flory-Rehner theory to obtain network-linear polymer interaction parameter, χ'_{23} between NPPCS and LPPCS. It was concluded that the parameter χ'_{23} decreased with molecular weight but increased with concentration of LPPCS in outer solution. The solvent independent interaction parameter between NPPCS and PPCS

was estimated as 0.7 by extrapolation of the values of χ'_{23} to zero value of the fraction ratio of solvent to linear polymer, v_1/v_3 inside the network. As well as, the binary interaction parameters, χ_{12} of NPPCS with benzene, ethyl benzene, *n*-propyl benzene and isopropyl benzene were obtained by means of Flory-Rehner theory at temperatures between 25 and 55°C. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1328–1334, 2009

Key words: poly(*p*-chloro styrene); network; swelling behavior; polymer-solvent interaction parameter; polymer-polymer interaction parameter

INTRODUCTION

Theoretical analysis of the experimental swelling data of polymer networks assumes that the network immersed in a liquid attains its thermodynamic equilibrium state with the surrounding solution after a finite time like a few weeks.^{1–6} The equilibrium volume of the network phase as a function of the solvent composition can be theoretically predicted as the chemical potentials of diffusible components in and outside the network are equal. Investigations on the swelling behavior of a network in the solvents have been reported for the last 60 years.^{1–7} Recently, Horta and Pastoriza⁸ have reviewed the polymer-solvent interaction parameters reported for crosslinked, star, and linear polymers. It was appeared that the polymer-solvent interaction parameters of the crosslinked networks are higher than those of their uncrosslinked linear polymers. This was because the network acts as a copolymer of the repeating units in the chain and the network junctions,

as well as it has an extra entropic contribution related to the constraints imposed by the junctions.

A polymer network placed in a linear polymer melt barely swells as the entropy of mixing of the polymer is very small, then, it is very difficult to obtain a measurable swelling degree. Polymer networks swollen in a good solvent deswell when transferred to a solution of a linear polymer in the same solvent because of the osmotic pressure of the polymer solution. Long time ago, it was suggested to use this property to measure linear polymer molecular weight⁹ or the interaction parameters of the pairs between solvent, linear polymer, and network.¹⁰

Among the theories, Flory-Rehner is still used successfully to explain the experimental swelling/deswelling observations of the networks both in small molecule solvents, in polymer melts and in polymer solutions. In the literature, limited number studies were published concerning the networks in their linear polymer solutions.^{9–18} In these studies, it was concluded that the Flory-Rehner theory explain successfully the experimental swelling/deswelling measurements on gels. Therefore, the Flory-Rehner theory is quite adequate to determine the parameter χ'_{23} between a network and a linear polymer. Sakurada et al.¹⁰ assumed that the interaction parameter χ'_{23} between a network and a linear polymer is independent on molecular weight and concentration of

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the linear polymer. However, it was appeared that the interaction parameter between a network and a linear polymer decrease with molecular weight of the linear polymer.^{16–18} It is well known also that the interaction parameter of a mixture is a function of the composition. Thus, we have attempted to study the variation of interaction parameter between a network and linear polymer of PPCS with molecular weight and concentration of the linear polymer. Then, we have tried to obtain the interaction parameter being independent on molecular weight and concentration of the linear PPCS. We have used several PPCS samples in which three of them have low molecular weight and one has high molecular weight in narrow dispersity index, i.e., better than 1.9, to exhibit dependence on molecular weight and very dilute solutions to attain equilibrium conditions, quickly.

THEORETICAL BACKGROUND

In the Flory-Rehner theory, equilibrium swelling of a nonpolar polymer in a nonpolar medium is governed by at least two free energy terms: the changes in the free energy of mixing, ΔG_m and the changes in the free energy of elastic deformation, ΔG_{el} . By combining these terms, the free energy of mixing can be derived as given in the related literature.^{16–19} If the free energy of a swollen network, ΔG_{sw} 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 relative to its chemical potential in the pure state, $\mu_1 - \mu_1^0$ is obtained for a binary system:

$$\frac{\partial \Delta G_{sw}}{\partial n_1} = \mu_1 - \mu_1^0 = RT \left[\ln(1 - v_2) + v_2 + \chi_{12} v_2^2 + \frac{1}{N} \left(v_2^{0^{2/3}} v_2^{1/3} - \frac{v_2}{2} \right) \right] \quad (1)$$

where R is universal gas constant, T is absolute temperature, χ_{12} is interaction parameter between solvent and network, N is average number of monomers between crosslinks in the network chains, v_2^0 and v_2 are volume fractions of the polymer network after preparation and in the equilibrium swollen gel, respectively.²⁰ The fraction v_2 can be determined experimentally from the linear swelling ratio, α of the gel sample

$$v_2 = v_2^0 / \alpha^3 = v_2^0 / (D/D_0)^3 \quad (2)$$

where D and D_0 are diameters of swollen and unswollen gels, respectively. The fraction v_2^0 can be determined experimentally as described in Swelling of NPPCS in low molecular weight solvents section or calculated from initial monomer concentration in

g/cm^3 , c_0 and polymer density in g/cm^3 , ρ_p are as follows:

$$v_2^0 = \frac{c_0}{\rho_p} \quad (3)$$

The monomer number on the segments between crosslink junctions, N can be determined experimentally from elastic modulus of the swollen gel, G with the equation in the affine theory of networks in the following¹⁹:

$$G = \frac{RT}{NV_1} (v_2^0)^{2/3} (v_2)^{1/3} \quad (4)$$

where V_1 is molar volume of solvent. In a ternary system consisting of a solvent (1), a network (2), and a linear polymer (3), the following four equations for the chemical potential μ_i of the component i in the solution relative to its chemical potential in the pure state in both phases, i.e., gel ($\mu_i^{\text{gel}} - \mu_i^0$) and solution ($\mu_i^{\text{sol}} - \mu_i^0$)¹⁹

$$\begin{aligned} \frac{(\mu_1^{\text{gel}} - \mu_1^0)}{RT} = & \ln v_1 + (1 - v_1) - v_2 \frac{x_1}{x_2} - v_3 \frac{x_1}{x_3} \\ & + (\chi_{12} v_2 + \chi_{13} v_3)(v_2 + v_3) \\ & - \chi_{23} \left(\frac{x_1}{x_2} \right) v_2 v_3 + N^{-1} \left(v_2^{1/3} v_2^{0^{2/3}} - v_2/2 \right) \end{aligned} \quad (5)$$

$$\frac{(\mu_1^{\text{sol}} - \mu_1^0)}{RT} = \ln(1 - \phi) + \phi \left(1 - \frac{1}{x_3} \right) + \chi_{13} \phi^2 \quad (6)$$

$$\begin{aligned} \frac{(\mu_3^{\text{gel}} - \mu_3^0)}{x_3 RT} = & \frac{1}{x_3} \left[\ln v_3 + (1 - v_3) - v_1 \left(\frac{x_3}{x_1} \right) \right. \\ & \left. - v_2 \left(\frac{x_3}{x_2} \right) + (\chi_{31} v_1 + \chi_{32} v_2)(v_1 + v_2) - \chi_{12} \left(\frac{x_3}{x_1} \right) v_1 v_2 \right] \\ & + N^{-1} (v_2^{1/3} v_2^{0^{2/3}} - v_2/2) \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{(\mu_3^{\text{sol}} - \mu_3^0)}{x_3 RT} = & \left[(1/x_3) \ln \phi - (1 - \phi) + (1/x_3)(1 - \phi) \right. \\ & \left. + \chi_{13}(1 - \phi)^2 \right] \end{aligned} \quad (8)$$

where ϕ is volume fraction of the linear polymer in the outer solution phase, x is number of segments of the indicated components. When the solvent and polymer inside the network are in thermodynamic equilibrium with those of the outside, the equilibrium swelling is established. The chemical potentials, μ_i of these components in both phases are equal in the equilibrium state:

$$\mu_i^{\text{gel}} = \mu_i^{\text{sol}} \quad (9)$$

By substituting $x_1 = 1$, $x_2 = \infty$, and $x_3 = y$ for the segments of solvent, network, and linear polymer,

respectively; also $\chi'_{23} = \chi_{23}/x_2 = \chi_{32}/x_3$ and $\chi_{31} = \chi_{13}(x_3/x_1)$ for binary interaction parameters and combining eqs. (5–8) under the thermodynamic swelling equilibrium conditions given in the eq. (9), the following two equations were obtained for a network immersed in a polymer solution^{16–19}:

$$\ln \frac{v_1}{1-\phi} + 1 - v_1 - \phi - \frac{v_3}{y} + \frac{\phi}{y} + (\chi_{12}v_2 + \chi_{13}v_3)(1 - v_1) - \chi_{13}\phi^2 - \chi'_{23}v_2v_3 + N^{-1}(v_2^{1/3}v_2^{0^{2/3}} - v_2/2) = 0 \quad (10)$$

$$\frac{1}{y} \ln \left(\frac{v_3}{\phi} \right) + 1 - v_1 - \phi - \frac{v_3}{y} + \frac{\phi}{y} + (\chi_{13}v_1 + \chi'_{23}v_2)(1 - v_3) - \chi_{13}(1 - \phi)^2 - \chi_{12}v_1v_2 + N^{-1}(v_2^{1/3}v_2^{0^{2/3}} - v_2/2) = 0 \quad (11)$$

In this study, the following equation was derived for the network–linear polymer interaction parameter, χ'_{23} equating the eqs. (10) and (11).

$$\frac{1}{yv_2} \ln \left(\frac{v_3}{\phi} \right) - \frac{1}{v_2} \ln \left(\frac{v_1}{1-\phi} \right) = \chi_{12} + \chi_{13} - \chi'_{23} - \frac{2\chi_{13}}{v_2}(\phi - v_3) \quad (12)$$

Note that the last equation contains no variable related to the elastic energy term. It should also be noted that the eq. (12) has a few differences compared to the similar equation, eq. (6) in Ref. 10 derived by Sakurada et al. (i.e., the second term of r.h.s, χ_{13} has negative sign and there is $-v_2$ term inside the parenthesis of the last term of r.h.s.)

EXPERIMENTAL

Materials

p-Chloro styrene (PCS) was purchased as a chemical reagent grade from Merck A.G. It was washed with NaOH and distilled water for releasing inhibitor and distilled under vacuum. PCS was polymerized by using dibenzoyl peroxide as free-radical generator, and obtained LPPCS was fractionated by dissolving in a large amount of toluene and precipitating by methanol. Four samples were used among fractionated LPPCS with the molecular weights in g/mol: 1920, 4550, 6020, and 1,130,000. The concentrations of LPPCS in toluene were 0.1, 0.5, and 1.0 g/dL. Benzene (B), toluene (T), ethyl benzene (EB), *n*-propyl benzene (nPB), isopropyl benzene (IPB), and divinyl benzene (DVB) were purchased from Merck and used as received. Dibenzoyl peroxide purchased from Aldrich was solved in chloroform, crystallized from cold methanol and dried under vacuum.

Synthesis of NPPCS

NPPCS was prepared by free-radical crosslinking of PCS with DVB. The procedure recommended to synthesize almost ideal styrene(S)-DVB network, which was followed by taking into account the indicated problems.^{21,22} S-DVB system exhibits some deviations from an ideal network such as cyclization reactions with intramolecular linkage, microgel-like particles at high DVB contents, free-chain ends, closed loops, permanent entanglements and unequal length of the chains in the network. If the amount of diluent present in the gel exceeds the maximum swelling capacity of the gel, heterogenous structures form. Therefore, the recommended precautions were taken to avoid network defects in synthesis of NPPCS as much as possible. 0.55% mole DVB used to minimize the cyclization reactions. NPPCS was synthesized under nitrogen atmosphere by polymerization of 9.25 g PCS in the presence of 0.00094 mol dibenzoyl peroxide as the free-radical initiator and 0.104 cm³ DVB as crosslinker. The total volume of ingredients was completed to the 15 cm³ by toluene. The reaction time was 48 h in a vacuum oven at 50°C. The curing of the networks continued to 48 h at 50°C.

Mechanical measurements

Uniaxial compression measurements were performed on equilibrium swollen gels in toluene by using a Hounsfield H5KS mechanical test apparatus (Force transducer: HTE1-5N). The stress–strain elastic modulus, G was determined from the slope of the linear dependence.

$$\sigma = G(\lambda - \lambda^{-2}) \quad (13)$$

where σ is stress applied vertically to the unit cross-sectional area of the undeformed gel, λ is the uniaxial deformation ratio (deformed length/initial length) of the specimen under stress. The specimens were cut from synthesized NPPCS as cylinders with diameter of 1.03 cm and height of 1.5 cm. The cut specimens were swollen in toluene for 1 week until swelling equilibrium before mechanical measurements. Data on the Figure 1 were given as an example. The elastic modulus, G was determined as 52 kPa on average of three different specimens. The monomer number, N of the network chains was determined as 170 from the elastic modulus of the swollen specimen ($v_2 = 0.198$) by eq. (4).

Swelling of NPPCS in low molecular weight solvents

The gel samples cut as cylinders in diameter of 1.03 cm and height of 0.5 cm were immersed repeatedly in a large amount of toluene to exclude

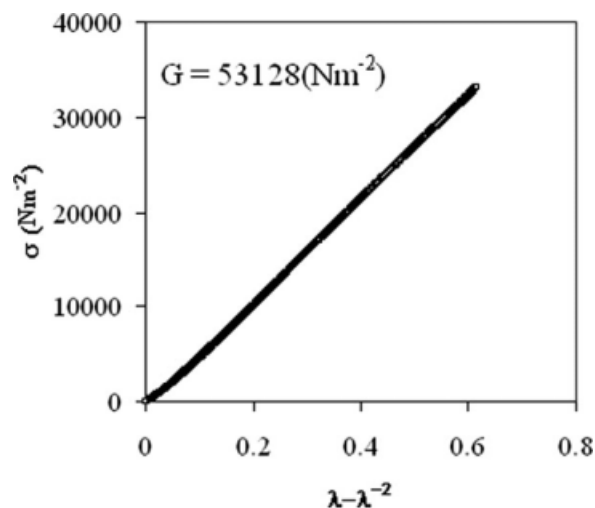


Figure 1 Stress–strain curve of NPPCS after preparation.

uncrosslinked polymer during synthesis of the network, and then, the samples were collapsed by immersing in solvent/nonsolvent (toluene/methanol) mixtures by increasing gradually the amount of nonsolvent. After immersing in the pure methanol, they were dried in a vacuum oven until constant weight. The average value of volume fraction of network chains after synthesis, v_2^0 was experimentally determined as 0.493 by dividing the volume of dried sample to its initial total volume. The same value can be obtained from eq. (3) by calculation. Then, the samples were immersed at vials (100 mL) filled with the solvent at least 1 week to reach the equilibrium degree of swelling. The experiments were carried out in the precision of $\pm 0.5^\circ\text{C}$ at varying constant temperatures in a water bath. Diameter of the gel samples was measured by a calibrated digital compass and consequently, the fraction v_2 was obtained from eq. (2). Each swelling ratio reported in this study is an average of at least three separate measurements. The standard deviations of the measured swelling ratios were less than 10% of the mean value.

Swelling of NPPCS in their own linear polymer solutions in toluene

The uncrosslinked polymers in the network samples cut as cylinders in diameter of 1.03 cm and in height

of 0.5 cm were excluded by immersing in a large amount of toluene. Then, they were left at vials (100 mL) filled with their own linear polymer solutions in toluene with four different molecular weights of LPPCS at various concentrations at least 10 days to reach the apparent degree of swelling. No further change was observed in the dimension of specimens by much time. The concentration of polymer solution was arranged by adding the amount of absorbed toluene by NPPCS during immersing in the blank solvent, previously. The experiments were carried out at $25 \pm 0.1^\circ\text{C}$ in a constant temperature bath. Diameter of the gel sample was measured by a calibrated digital compass and volume fraction v_2 was obtained from eq. (2).

Determination of linear polymer volume fraction, v_3 inside the network

After the network samples in the polymer solution reached to the equilibrium, they were washed with pure toluene and then left in a large amount of blank toluene to take off the linear polymer inside the network. The solvent was replaced twice and collected in a flask during experiments. The absorption peak of the collected solution was measured using Agilent 8453 Model UV-spectrophotometer. The amount of linear polymer diffused outside the network was determined from a calibration curve prepared with absorption peaks of the solutions at certain concentrations of the same linear polymer. Then, the volume fraction of linear polymer inside the network, v_3 was obtained by dividing its volume to the total volume of the swollen gel.

RESULTS AND DISCUSSION

The volume fraction, v_2 of the network was determined from eq. (2) as described in the Swelling of NPPCS in low molecular weight solvents section. Then, the polymer–solvent interaction parameters, χ_{12} of the NPPCS were found from the equilibrium swelling ratios of the networks in the low molecular weight solvents from eq. (1) and given in Table I at temperatures between 25 and 55°C . The swelling ratio of the gel samples is higher in good solvents; therefore, the volume fraction of NPPCS is lower in

TABLE I
Polymer–Solvent Interaction Parameter, χ_{12} of Crosslinked PPCS with
Some Aromatic Solvents at Various Temperatures and Volume Fractions, v_2
(Given in the Parenthesis)

Temperature ($^\circ\text{C}$)	25	35	45	55
Benzene	0.47 (0.21)	0.47 (0.21)	0.45 (0.20)	0.43 (0.19)
Ethylbenzene	0.47 (0.21)	0.47 (0.21)	0.47 (0.21)	0.45 (0.20)
<i>n</i> -Propylbenzene	0.52 (0.25)	0.52 (0.25)	0.51 (0.24)	0.50 (0.23)
Isopropylbenzene	0.51 (0.24)	0.50 (0.23)	0.50 (0.23)	0.49 (0.22)

TABLE II
Comparison of Polymer–Solvent Interaction Parameter, χ_{12} with Literature

Solvent	χ_{12} (30°C)			
	This study	Ref. [20]	Ref. [21]	Ref.[22]
Benzene	0.47 ($v_2 = 0.21$)	0.5 ($v_2 = 0.2$)	–	–
Ethylbenzene	0.47 ($v_2 = 0.21$)	0.5 ($v_2 \rightarrow 0$)	0.47	–
<i>n</i> -Propylbenzene	0.52 ($v_2 = 0.25$)	–	–	0.50 ($v_2 \rightarrow 0$)
Isopropylbenzene	0.51 ($v_2 = 0.24$)	0.3 ($v_2 \rightarrow 0$)	0.48	0.50 ($v_2 \rightarrow 0$)

benzene, which is a better solvent than others. As aliphatic hydrocarbons are poor for PPCS, the degree of swelling decreases and consequently the interaction parameter, χ_{12} , increases slightly by increasing aliphatic character of the aromatic solvent. For all the studied solvents, parameter χ_{12} decreases with temperature at the studied temperature ranges, indicating that the solubility of PPCS in the studied solvents is endothermic. In Table II, the values of the parameter χ_{12} of NPPCS were compared with scarce data for LPPCS in literature^{23–25} as there is no any data related to the interaction parameters of NPPCS in any solvent in literature. The values of the parameters χ_{12} found in this study are in agreement with those given for linear PPCS in the literature although the polymer–solvent interaction parameters of the crosslinked networks are expected higher than their corresponding linear polymers. The parameters χ_{12} of PS with aromatic solvents in literature are close to those of PPCS–aromatic solvent systems. The reported values of the parameter χ_{12} varies from 0.38 to 0.56 for benzene and toluene at $v_2 \cong 0.2$ and their mean values are 0.45.²⁶ The mean value of the interaction parameter of PS–ethyl benzene is 0.46. It seems that the chlorine atom in PPCS does not create any noticeable difference than PS in its solubility in aromatic solvents.

From the equilibrium swelling measurements of NPPCS in LPPCS solutions at different concentrations and molecular weights, the volume fraction of

the network chains, v_2 in swollen gel was obtained as described in Swelling of NPPCS in their own linear polymer solutions in toluene section, and their values were reported in Table III together with other results. The fraction v_3 was determined as described in Determination of linear polymer volume fraction, v_3 inside the network section and was reported in Table III also. The distribution of the linear polymer inside and outside the network, v_3/ϕ was plotted in Figure 2. The ratio v_3/ϕ decreases exponentially by volume fraction of LPPCS, ϕ in outer solution phase. The smaller is the linear PPCS in the outer solution, the higher is the v_3/ϕ ratio. If the molecular weight of PPCS is sufficiently high, it does not penetrate inside the NPPCS. This indicates that the small coils of the linear polymer in dilute solutions can enter largely into the network rather than its large coils in more concentrated solutions. The variation of the ratio v_3/ϕ with ϕ is similar to the results reported for nonionic organic and hydrogels in linear polymer solutions in literature.^{16,17}

The network–linear polymer interaction parameter χ'_{23} was found from the eq. (12), and its numerical values were also given in Table III. In Figure 3, the values of parameter χ'_{23} were plotted against to the reciprocal of LPPCS segment number, y at three different concentrations to exhibit the dependence of χ'_{23} on the molecular weight and volume fraction of the linear polymer in the outside solution phase.

TABLE III
Molecular Weight, M_w , Number of Segments, y , Volume Fraction, ϕ of LPPCS in the Solution, Volume Fraction, v_3 of LPPCS Inside the Swollen NPPCS, Diameter Ratio of Swollen and Unswollen NPPCS, D/D_0 , Equilibrium Swelling Ratio of NPPCS in LPPCS Solution, q_w , Network–Linear Polymer Interaction Parameter, χ'_{23}

$M_w(\times 10^{-3})$ (g/mol)	y	v_3/ϕ ($\times 10^3$)	ϕ	D/D_0	$v_3(\times 10^5)$	v_2	χ'_{23}
1130	8519	0.0750	0.8	1.310	6.0	0.219	–0.04
		0.0195	4.0	1.280	7.8	0.235	–0.05
		0.0054	8.0	1.260	4.3	0.246	–0.06
6.02	43.5	0.1262	0.8	1.369	10.1	0.192	0.23
		0.0408	4.0	1.355	16.3	0.198	0.34
		0.0331	8.0	1.344	26.5	0.203	0.35
4.55	32.9	0.1175	0.8	1.400	9.4	0.180	0.35
		0.0442	4.0	1.385	17.7	0.186	0.49
		0.0286	8.0	1.375	22.9	0.190	0.54
1.92	13.7	0.4975	0.8	1.410	39.8	0.176	0.27
		0.2002	4.0	1.392	80.1	0.183	0.62
		0.1041	8.0	1.386	83.3	0.186	0.87

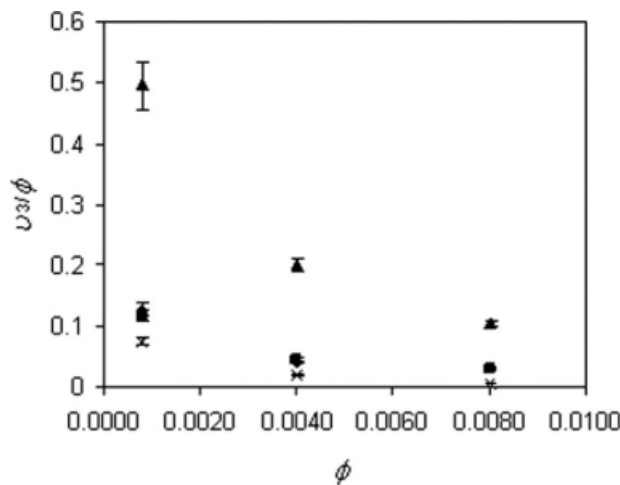


Figure 2 Dependence of the LPPCS distribution inside and outside the NPPCS at different molecular weight in g/mol: 1920 (filled triangle), 4550 (filled circle), 6020 (filled square), and 1.13×10^6 (x mark).

The data represent that the parameter χ'_{23} decreases with molecular weight and increases with concentration of the linear polymer in the outside solution phase and tend to attain to a horizontal plateau.

However, in linear polymer mixtures, it is expected that the miscibility of polymers decreases and subsequently the polymer–polymer interaction parameter increases with their molecular weights. In the same time, the magnitude of the interaction parameter should be close to zero for a mixture of polymers having similar chemical structure, whereas it should have negative signed values if attractive forces are present between the constitutive polymers or vice versa. On the contrary to the earlier statements, in this study, the parameter χ'_{23} was found to be close to zero (small negative) in high molecular weight linear polymer solutions, whereas they increased with the decreasing molecular weight of linear polymer. Similar results are reported in literature.^{16–18} In these studies, experimental swelling results could be fitted to the theoretical expectations of Flory-Rehner theory if higher values for the parameter χ'_{23} are used for lower molecular weight linear polymer. The interaction between a network and a high molecular weight linear polymer should be

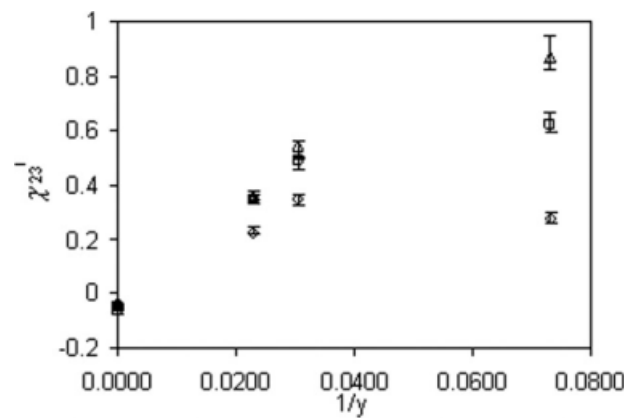


Figure 3 Variation of parameter χ'_{23} with the number of segments, y of LPPCS at three different volume fractions of LPPCS in outer solution: 0.8×10^{-3} (hollow diamond), 4.0×10^{-3} (hollow square), and 8.0×10^{-3} (hollow triangle).

limited since networks behave as molecular sieves to the large polymeric coils. Therefore, lower values of χ'_{23} cannot indicate favorable interactions between NPPCS and LPPCS with higher molecular weight.

To consider the expectations of eq. (12), the parameter χ'_{23} at limit values of independent parameters (y and ϕ) were given in Table IV. It can be seen from the table that at highly dilute outer solution ($\phi \rightarrow 0$), the parameter χ'_{23} closes to zero with small negative sign for infinitely high molecular weight linear polymer ($y \rightarrow \infty$); however, it increases with decreasing molecular weight ($y \rightarrow 1$) if χ_{12} and χ_{13} are close to 0.5. At highly concentrated outer solution ($\phi \rightarrow 1$), the parameter χ'_{23} should have small positive value which increases with decreasing molecular weight of the linear polymer. If concentrations of the linear coils inside and outside the swollen network equal ($\phi \rightarrow v_3$), the parameter χ'_{23} becomes independent on molecular weight of the linear polymer. It should have a small negative value if $v_3 \rightarrow 0$, but it should have a small positive value if $v_3 \rightarrow 1$. It is apparent that the experimental χ'_{23} found in this study in agreement with the expectations of the Flory-Rehner theory. However, this analysis may indicate that the Flory-Rehner theory needs some modification, as the miscibility should decrease subsequently the parameter χ'_{23} increase with molecular weight.

TABLE IV
The Value of χ'_{23} at Limit Values of Independent Variables, ϕ and y

No.	ϕ	y	χ'_{23}	Expected value	Notes
1	0	∞	$\chi_{12} + \chi_{13} + (1/v_2) \ln v_1$	Small negative	$\chi_{12} \cong \chi_{13} \cong 0.5; v_3 \rightarrow 0; v_2 < 0.5$
2	0	1	$\chi_{12} + \chi_{13} + (1/v_2) \ln v_1 - (1/v_2) \ln (v_3/\phi)$	Higher than No:1	$v_3 < \phi$
3	1	∞	$\chi_{12} - \chi_{13} + (1/v_2) \ln [v_1/(1-\phi)]$	Negative	$v_1 \leq (1-\phi) \rightarrow 0$
4	1	1	$\chi_{12} - \chi_{13} + (1/v_2) [\ln (v_1/(1-\phi)) - \ln v_3]$	Higher than No:3	$v_1 \leq (1-\phi) \rightarrow 0; v_3 < 1$
5	v_3	∞	$\chi_{12} + \chi_{13} + (1/v_2) [\ln (v_1/(1-v_3))]$	Higher than No:1	$v_3 < 1$
6	v_3	1	$\chi_{12} + \chi_{13} + (1/v_2) [\ln (v_1/(1-v_3))]$	Higher than No:1	$v_3 < 1$

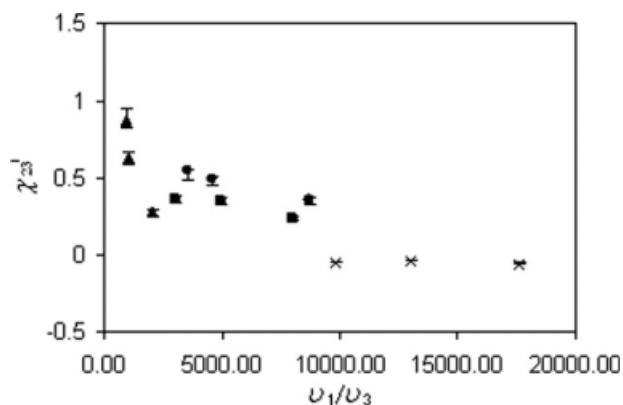


Figure 4 Variation of the parameter χ'_{23} with the volume fraction ratio of solvent to linear polymer, v_1/v_3 inside the swollen network. Symbols are as described in Figure 2.

The parameter χ'_{23} was plotted against to the ratio v_1/v_3 in Figure 4 to exhibit its variation with the linear polymer concentration inside the swollen network. It seems that all experimental data overlap in a master curve. The infinitely small value of v_1/v_3 can be assumed as a mixture of the network and the linear polymer without solvent. The value of χ'_{23} at $(v_1/v_3) \rightarrow 0$ can be assumed as the network–linear polymer interaction parameter being independent on solvent, as the solvent fraction is infinitely low, and the linear polymer fraction is infinitely high inside the network. In this case, solvent independent network–linear polymer interaction parameter of NPPCS and LPPCS system can be estimated as around 0.7 from Figure 4. In the same time, the variation of the data suggest that an increase of solvent concentration inside the swollen network decreases the value of the parameter χ'_{23} . It can be stated that the solvent inside the swollen network inhibits the interaction between the segments of network and linear polymer thermodynamically. The parameter χ'_{23} between linear polymers with almost same chemical structure was expected to be zero, theoretically if there are no strong attractive or repulsive forces between segments of the polymers in the mixture.

CONCLUSIONS

The swelling of NPPCS in aromatic hydrocarbons was studied at temperatures close to ambient conditions. The parameter χ_{12} decreases with temperature and decreases the aliphatic character of the solvent.

As expected, the ratio v_3/ϕ (i.e., the amount of interpenetrating polymeric chain coils into the network) decreases with molecular weight and increases with volume fraction of LPPCS in outer solution, ϕ . An equation for network–linear polymer interaction parameter χ'_{23} was derived from the relations in Flory–Rehner theory. This equation suggests that the parameter χ'_{23} decreases with molecular

weight and increases with concentration of linear polymer in outer solution, as well as the parameter χ'_{23} is independent on the molecular weight of linear polymer if $v_3 = \phi$. The experimental data obtained in this study support these suggestions. The value of χ'_{23} at $(v_1/v_3) \rightarrow 0$ was estimated around 0.7 as the network–linear polymer interaction parameter being independent on solvent. This study suggests that the equation derived from the Flory–Rehner theory can be used to obtain network–linear polymer interaction parameter χ'_{23} which depends on molecular weight and concentration of the linear polymer. Solvent independent network–linear polymer interaction parameter can be obtained by extrapolating of the values of χ'_{23} to zero value of v_1/v_3 . However, the subject needs some further studies with network–linear polymer systems having noninteractive or attractive forces between their segments.

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References

1. Flory, P. J.; Rehner, J. *J Chem Phys* 1944, 12, 412.
2. Wall, F. T.; Flory, P. J. *J Chem Phys* 1951, 19, 1435.
3. Dusek, K.; Prins, W. *Adv Polym Sci* 1969, 6, 1.
4. Erman, B.; Flory, P. J. *J Chem Phys* 1978, 68, 5363.
5. Erman, B.; Flory, P. J. *Macromolecules* 1982, 15, 806.
6. Erman, B.; Flory, P. J. *Macromolecules* 1982, 15, 800.
7. Goiti, E.; Huglin, M. B.; Rego, J. M. *European Polym J* 2004, 40, 219.
8. Horta, A.; Pastoriza, M. A. *Eur Polym J* 2005, 41, 2793.
9. Boyer, R. F. *J Chem Phys* 1945, 13, 363.
10. Sakurada, I.; Nakajima, A.; Aoki, H. *J Polym Sci* 1959, 35, 507.
11. Hild, G.; Froelich, D.; Rempp, P.; Benoit, H. *Makromol Chem* 1972, 151, 59.
12. Good, W. R.; Cantow, H. J. *Makromol Chem* 1979, 180, 2605.
13. Bastide, J.; Candau, S.; Leibler, L. *Macromolecules* 1981, 14, 719.
14. Horkay, F.; Zrinyi, M. *J Macromol Sci B* 1986, 25, 307.
15. Hect, A. M.; Stanley, H. B.; Geissler, E.; Horkay, F.; Zrinyi, M. *Polymer* 1993, 34, 2894.
16. Kayaman, N.; Okay, O.; Baysal, B. M. *J Polym Sci: Polym Phys* 1998, 36, 1313.
17. Kayaman, N.; Okay, O.; Baysal, B. M. *Polym Gels Networks* 1997, 5, 167.
18. Adachi, K.; Nakamoto, T.; Kotaka, T. *Macromolecules* 1989, 22, 3106.
19. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
20. Erman, B.; Flory, P. J. *Macromolecules* 1986, 19, 2342.
21. Okay, O. *Die Angewandte Makromolekulare Chemie* 1987, 153, 125.
22. Okay, O. *Makromol Chem* 1988, 189, 2201.
23. Kok, C. M.; Rudin, A. *J Appl Polym Sci* 1982, 27, 353.
24. Izumi, Y.; Miyake, Y. *Polym J* 1972, 3, 647.
25. Yilmaz, F.; Baysal, B. M. *Polym Int* 1993, 31, 107.
26. Barton, A. F. M. *CRC Handbook of Polymer Liquid Interaction Parameters and Solubility Parameters*; CRC Press: Boca Raton, FL, 1990.