Validity of the swelling method for the determination of the interaction parameter

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By selecting solvents with a very weakly concentration-dependent interaction parameter χ with poly(dimethylsiloxane) (PDMS) and using experimental values of the elastic modulus of dry, end-linked PDMS networks, the Flory–Rehner theory and the phantom network assumption we obtained good agreement between the values of χ from equilibrium swelling and those obtained from intrinsic viscosity measurements on solutions of linear chains. The solvents used were 2,3-dimethylpentane and 2,2,4-trimethylpentane at 25°C.

(Keywords: swelling method; poly(dimethylsiloxane); interaction parameter)

INTRODUCTION

With the assumption of the additivity of the free energy of mixing and the elastic free energy of the Flory–Rehner model in question[1], and the suggestion that the interaction parameter χ may have a dependence on crosslink density in addition to its dependence on polymer concentration[2], we performed swelling experiments to test the validity of the common practice of using swelling measurements to determine χ. We used well-defined, end-linked poly(dimethylsiloxane) (PDMS) networks previously prepared. Dynamic mechanical experiments were performed on these networks to test rubber elasticity models[3]. For the range of molecular weights of the precursor chains studied, $2500 < M_n < 58\,000$, the equilibrium shear moduli G_e of the networks were clearly larger than those predicted by the affine model. For the model networks prepared with precursor chains with $M_n > 20\,000$, the modulus was essentially constant and equal to the rubbery plateau modulus of high-molecular-weight PDMS melts[3]. This indicates that the contribution from the increasing number of trapped entanglements dominates over that from the chemical crosslinks. These model networks, as well as 'imperfect' PDMS networks containing large amounts of pendant chains, were swollen to equilibrium in both toluene and benzene[3]. The experimental values of the modulus were employed in conjunction with the Flory–Rehner expression[4] and the phantom network model to predict the swelling data of both model and imperfect PDMS networks. With the assumption of a phantom network, the Flory–Rehner model can be expressed quantitatively by[3]

$$-\left[\frac{\ln(1-v_2)+v_2+\chi v_2^2}{v_1 v_2^{1/3}}\right]=\frac{G_e}{RT} \tag{1}$$

where v_2 is the network volume fraction at equilibrium swelling, χ is the polymer–solvent interaction parameter, v_1 is the solvent monomer unit molar volume, R is the gas constant, T is the absolute temperature and G_e is the equilibrium shear modulus of the unswollen network. G_e/RT has replaced the $(\nu-\mu)$ term in the original Flory–Rehner equation, where ν is the number of moles of elastic chains per unit volume of the network and μ is the number of moles of junctions per unit volume of the network. Any effect of trapped entanglements on swelling is incorporated in equation (1) when the experimental value of the modulus is used. Equation (1) can be rearranged to solve for χ and its dependence on v_2, as given by

$$\chi=-\left[\frac{\frac{G_e}{RT}v_1 v_2^{1/3}+\ln(1-v_2)+v_2}{v_2^2}\right] \tag{2}$$

Values of the χ parameters and their concentration dependence from PDMS networks swollen in toluene and benzene using equation (2) compared reasonably well to literature values obtained on linear PDMS solutions[3]. However, the concentration dependence of χ for these two solvents creates a complication that is best left out of the issue.

Two solvents, 2,3-dimethylpentane (DMP) and 2,2,4-trimethylpentane (TMP), were chosen to obtain swelling equilibria with PDMS networks previously synthesized. The selection of these two solvents was guided by the following considerations. Firstly, the interaction parameters of these solvents with PDMS are known to be fairly concentration independent[5], allowing us to sidestep the issue and avoid possible complications that arise from a v_2-dependent χ. Also, a comparison can be made between interaction parameters obtained from networks using equation (2) and interaction parameters obtained from linear PDMS solutions at infinite dilution by intrinsic viscosity. Secondly, these are appreciably better solvents than benzene or toluene previously studied, and lead to greater swelling of the networks. This increased swelling may cause deviations from

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the Flory–Rehner theory in equation (1) owing to possible excluded volume effects unaccounted for by the Flory–Huggins theory for high swelling ratios.

EXPERIMENTAL

Materials

The preparation of the networks was described in detail in an earlier paper[3]. In brief, the model networks were prepared by end-linking pure difunctional PDMS (B2) chains, whereas the imperfect networks were prepared by end-linking mixtures of B2 and monofunctional PDMS (B1) chains. The polydispersities of the precursor chains ranged from 1.15 to 1.27. Both types of networks were synthesized using a hydrosilation reaction[6–8], where the vinyl groups at the ends of the polymer molecules react with the silane hydrogens of the crosslinker molecule tetrakis(dimethylsiloxy)silane in the presence of the platinum catalyst *cis*-dichlorobis(diethylsulfide)platinum (II). *Tables 1* and *2* list the properties of the model and imperfect networks, respectively, including the amount of soluble fraction w_{sol}, the equilibrium shear moduli reported as G_e/RT and $G_e/RT(1-w_{sol})^{1/3}$, and the equilibrium polymer volume fractions υ_2^{DMP} and υ_2^{TMP} in DMP and TMP, respectively. The term x in *Table 2* is the molar fraction of B1 in the initial mixture before crosslinking. The moduli which were reported earlier[3] were obtained after the samples had cured *in situ* between the parallel plates of a Rheometrics System Four mechanical spectrometer. The soluble material fraction of the networks acts as a diluent during the measurement of the elastic modulus. Since the soluble material was not removed prior to the mechanical experiments, the volume fraction u_2 of polymer in the network is

$$u_2 = 1 - u_{sol} = 1 - w_{sol} \tag{3}$$

where the density of the soluble material is equal to the density of the network chains. A correction to the measured modulus can be made by taking $G_e/(1-w_{sol})^{1/3}$ as the modulus of the network after extraction of the soluble material[3,9]. However, from *Tables 1* and *2* it can be seen that this correction is usually very small and affects the results only slightly, as will be indicated later. The values of the equilibrium polymer volume fraction υ_2 were determined using standard gravimetric procedures assuming additivity of volumes[10].

The linear PDMS samples used in the viscosity experiments are listed in *Table 3*. The molecular weights

Table 1 Model network characteristics

Sample	M_n [a] (g mol^{-1})	$10^2 w_{sol}$	G_e/RT (mol m^{-3})	$G_e/RT(1-w_{sol})^{1/3}$ (mol m^{-3})	υ_2^{DMP}	υ_2^{TMP}
A-1	2460	0.374	303	303	0.373	0.385
A-2	6160	0.281	184	184	0.292	0.301
A-3a	8350	0.450	149	149	0.253	0.262
A-3b	8350	0.436	154	154	0.263	0.270
A-4	10 300	0.353	156	156	0.256	0.275
A-5	10 900	0.556	149	149	0.237	0.271
A-6	16 800	2.78	74.2	74.9	0.186	0.192
A-7a	18 500	0.259	130	130	0.228	0.235
A-7b	18 500	1.21	102	102	0.200	0.208
A-8a	19 800	0.254	107	107	0.221	0.226
A-8b	19 800	0.573	109	109	0.218	0.228
A-9	20 100	1.14	82.2	82.5	0.204	0.211
A-10	28 200	0.550	82.2	82.3	0.205	0.202
A-11	53 500	0.236	79.4	79.4	0.195	0.198
A-12	58 000	2.63	74.2	74.9	0.162	0.175

[a] Molecular weight of precursor chains

Table 2 Imperfect network characteristics

Sample	x	$10^2 w_{sol}$	G_e/RT (mol m^{-3})	$G_e/RT(1-w_{sol})^{1/3}$ (mol m^{-3})	υ_2^{DMP}	υ_2^{TMP}
			$M_{n,B2}=20\,100$, $M_{n,B1}=19\,800$			
B-2	0.051	2.52	66.2	66.7	0.187	0.205
B-3	0.146	4.36	57.3	58.2	0.178	0.150
B-4	0.296	7.74	36.0	36.9	0.154	0.165
B-5	0.445	11.8	29.0	30.2	0.132	0.136
B-6	0.596	18.9	17.0	18.2	0.105	0.113
			$M_{n,B2}=58\,000$, $M_{n,B1}=71\,200$			
B′-1	0.152	6.98	35.6	36.5	0.135	0.139
B′-2	0.306	14.5	21.8	23.0	0.105	0.108
B′-3	0.448	27.8	11.8	13.2	0.069	0.072
B′-4	0.589	39.6	4.45	5.26	0.047	0.048

Table 3 Uncrosslinked PDMS sample characteristics

Sample	M_w (g mol^{-1})	d^a	$10^2[\eta]^{DMP}$ (dl g^{-1})	$10^2[\eta]^{TMP}$ (dl g^{-1})
V1	7180	1.17	6.3	5.6
V2	16000	1.26	10.5	9.9
V3	20200	1.20	13.0	11.7
V4	24300	1.21	14.2	13.3
V5	39300	1.12	21.2	18.8
V6	46800	1.25	23.5	21.4
V7	58300	1.16	28.0	24.8
V8	67900	1.27	32.0	29.5

[a] Polydispersity determined by g.p.c.

used in the calculations were the weight average M_w values and these were determined by gel permeation chromatography (g.p.c.). The solvents DMP (Aldrich, 99+%) and TMP (Aldrich, 99+%) were filtered through 0.20 μm filter paper prior to using for viscosity measurements. Their densities at 25°C were 0.6909 g cm^{-3} for DMP and 0.687 g cm^{-3} for TMP, corresponding to molar volumes of 145.0 cm^3 mol^{-1} and 166.3 cm^3 mol^{-1}, respectively.

RESULTS AND DISCUSSION

Interaction parameter

The value of χ in infinitely dilute systems with TMP and DMP can be obtained from intrinsic viscosity measurements. The method is based on the relationship originally developed by Stockmayer and Fixman[11] which allows the determination of χ for flexible chain polymers in any solvent from intrinsic viscosity and molecular weight values. The relation is based on an expansion in terms of the square root of the molecular weight, i.e. $M^{1/2}$, and is thus limited to low and moderate molecular weights[12]. The relationship may be written as

$$\frac{[\eta]}{M^{1/2}} = K_\theta + 0.51\Phi_0 B M^{1/2} \tag{4}$$

where K_θ is related to the unperturbed radius of gyration R_g^0 of the polymer chain by

$$K_\theta = 6^{3/2}\Phi_0(R_g^0)^3 M^{-3/2} \tag{5}$$

and should be a constant independent of M and the solvent if draining effects are negligible[9].

The parameter B is related to the interaction parameter by

$$B = \frac{v_{sp}^2(1-2\chi_0)}{v_1 N_A} \tag{6}$$

where v_{sp} is the specific volume of the polymer, v_1 is the solvent molar volume, N_A is Avogadro's number and χ_0 is the polymer–solvent interaction parameter at infinite polymer dilution. The quantity Φ_0 is the 'universal' viscosity constant whose value will be discussed below. For low dispersity polymer chains, M_w may be used for M in equation (4). A plot of $[\eta]/M_w^{1/2}$ against $M_w^{1/2}$ should give a linear function whose intercept equals K_θ and whose slope is directly proportional to $(1-2\chi_0)$.

Viscosity measurements were carried out for all eight linear PDMS samples of *Table 3* with an Ubbelohde-type viscometer in a water bath at 25 ± 0.1°C. Flow times were measured to a precision of 0.1 s. The intrinsic viscosities $[\eta]$ were determined by extrapolating plots of η_{sp}/c and $(\ln \eta_r)/c$ *versus* c to zero concentration, where η_r is the relative viscosity and η_{sp} is the specific viscosity. The values of $[\eta]$ from the two methods did not differ by more than 2%. *Table 3* lists the values of $[\eta]$ determined for the polymer samples and the Stockmayer–Fixman relationship is graphically shown in *Figures 1a* and *1b* for each solvent. As can be seen, a least-squares line fits the data quite well. The parameter B in equation (4) is related to the slope m of these lines by

$$B = m/0.51\Phi_0 \tag{7}$$

The interaction parameter χ_0 can then be obtained from equations (5) and (7) as

$$\chi_0 = \frac{1}{2} - \frac{m v_1 N_A}{2.04 v_{sp}^2 \Phi_0} \tag{8}$$

The value of χ_0 will depend on the value of Φ_0 chosen. Although called a 'universal' viscosity constant, Φ_0 has been shown to be dependent on the polymer–solvent system chosen[13–15] and for a polymer–solvent pair[16], Φ_0 may also depend on M_w. Konishi *et al.*[16] used static and dynamic light scattering with viscosity measurements to determine Φ_0 for PDMS in bromocyclohexane at its theta temperature. For their range of molecular weights ($386000 < M_w < 1140000$) they observed that Φ_0 increased with M_w from 2.38×10^{23} mol^{-1} to 2.67×10^{23} mol^{-1}. They explain this observation as draining effects due to the hydrodynamically thin PDMS chains. An extrapolation of the data of Konishi *et al.* using a log–log relationship would give a value of $\Phi_0 = 2.0 \times 10^{23}$ mol^{-1} for the molecular weights studied here, assuming their dependence of Φ_0 on M_w holds for samples of lower molecular weight. This value of Φ_0 gives good agreement between χ_0 calculated from intrinsic viscosity data of uncrosslinked

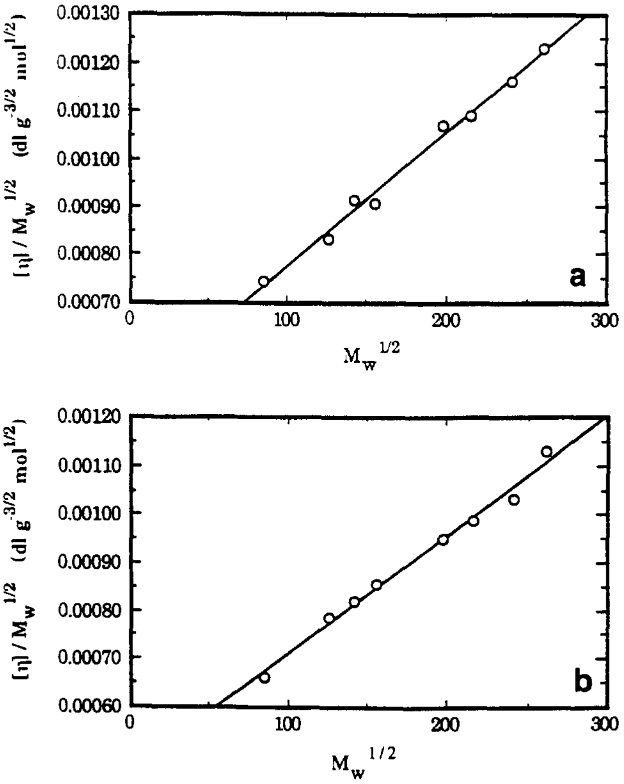

Figure 1 Stockmayer–Fixman relationship plotted as $[\eta]/M_w^{1/2}$ *versus* $M_w^{1/2}$ for the (a) PDMS–DMP and (b) PDMS–TMP systems. The slopes of the best-fit lines are (a) 2.77×10^{-6} dl g^{-2} mol$^{1/2}$ and (b) 2.50×10^{-6} dl g^{-2} mol$^{1/2}$

PDMS chains in toluene, covering a similar range of molecular weights[17], and χ_0 obtained from both osmometry and swelling measurements. The molecular weights of the PDMS chains from ref. 17 were calculated from the viscosity data of the PDMS–toluene system using the Mark–Houwink parameters obtained by Lapp *et al.*[18]. Using the Stockmayer–Fixman relation (equation (4)) and a value of $2.0\times10^{23}\,\mathrm{mol}^{-1}$ for Φ_0, the corresponding value of χ_0 for the PDMS–toluene system would be 0.440. This χ_0 value is within 1% of the value reported in the literature using osmometry[19] ($\chi_0=0.445$) and within 3% of the value obtained from equilibrium swelling[3] ($\chi_0=0.452$).

For the molecular weight range of PDMS studied here, a value of $\Phi_0=2.0\times10^{23}\,\mathrm{mol}^{-1}$ is therefore a good approximation. Taking this value of Φ_0, the values of χ_0 for PDMS–DMP and PDMS–TMP can be extracted from the slopes of *Figures 1a* and *1b* employing equation (8). We obtain $\chi_0=0.388$ for PDMS–DMP and $\chi_0=0.385$ for PDMS–TMP. The values of K_θ for PDMS in all of the solvents (toluene, DMP and TMP) are consistent with each other and lie in the range 0.045 to $0.050\,\mathrm{mol\,g^{-3/2}\,ml}$. These values are appreciably smaller than the value of $0.075\,\mathrm{mol\,g^{-3/2}\,ml}$ reported by Lapp *et al.*[18] for PDMS chains in solution with toluene using equation (4). Two effects may have contributed to the higher value of K_θ previously reported. First is the applicability of the Stockmayer–Fixman relationship (equation (4)) in the high-molecular-weight range used in that study (up to $M_w\approx625\,000$), and second is the dependence[16] of Φ_0 on M_w, which by equation (5) leads to a higher average value of K_θ for higher ranges of molecular weights. Both of these effects may have contributed to the curvature that is apparent in the data of Lapp *et al.* when plotted as $[\eta]/M^{1/2}$ *versus* $M^{1/2}$.

Table 4 Comparison of χ_0 values of PDMS in various solvents

Solvent	χ_0(swell)[a]	χ_0(visc)[b]
Toluene	0.452[c]	0.440[d]
DMP	0.392	0.388
TMP	0.380	0.385

[a] Determined by least-squares fit to χ *versus* v_2 data
[b] Determined using $\Phi_0=2.0\times10^{23}\,\mathrm{mol}^{-1}$
[c] Data obtained from Patel *et al.*[3]
[d] From unpublished data of Patel[17]

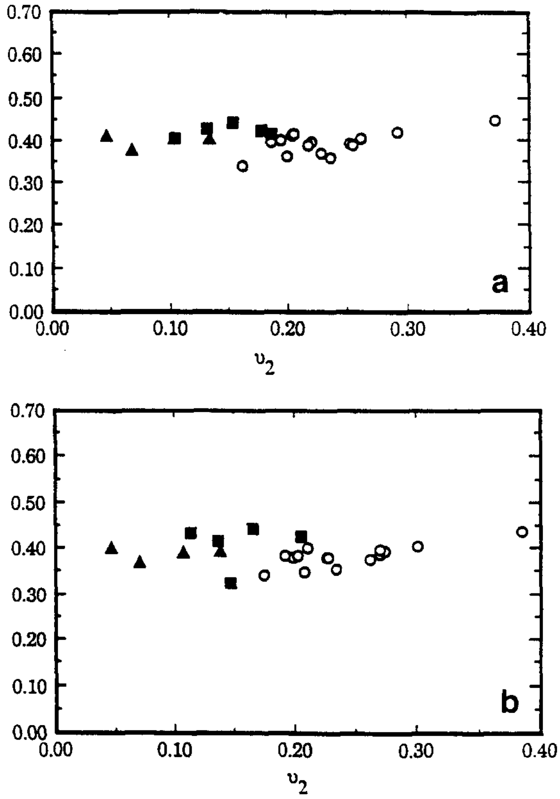

Figure 2 Plots of χ as a function of v_2 for the networks swollen in (a) DMP and (b) TMP where χ is calculated from equation (2). The open circles are for the model networks and the filled symbols are for the (■) B and (▲) B′ imperfect network series from *Table 2*

We now consider the values of χ obtained by performing equilibrium swelling of the PDMS networks separately in DMP and TMP, as was done earlier for toluene and benzene[3]. The values of χ obtained using equation (2) with the experimental values of G_e and v_2 and plotted as a function of v_2 for the PDMS networks swollen in DMP and in TMP at 25°C are shown in *Figures 2a* and *2b*, respectively. There is some scatter in the data, but the data show qualitatively that χ for PDMS in DMP and TMP has very little v_2 dependence as compared to benzene or toluene previously studied[3]. We suspect that the scatter in the data is primarily due to the accuracy in the modulus measurement as opposed to the measurement of v_2, which was very reproducible. The weak v_2 dependence of χ for PDMS in DMP had previously been reported by Zhao and Eichinger[5], who used differential swelling experiments to determine χ for this system. They reported $\chi=(0.3485\pm0.0327)v_2$. The equilibrium swelling data were fitted by a least-squares method to give $\chi=(0.392\pm0.025)+0.038v_2$ for PDMS–DMP and $\chi=(0.380\pm0.030)+0.045v_2$ for PDMS–TMP. The values of χ_0 are within 1% and 2% of the values obtained from the intrinsic viscosity experiments of PDMS chains in DMP and TMP, respectively. A comparison of the χ_0 values for toluene, DMP and TMP is shown in *Table 4*. When the value $G_e/RT(1-w_{sol})^{1/3}$ is used in equation (2), only the χ values of the imperfect networks are affected (lowered by less than 10%), therefore slightly lowering the intercept of the least-squares fit to give $\chi_0=0.385$ for PDMS–DMP and $\chi_0=0.365$ for PDMS–TMP. The dependence of χ on v_2 increases but the slope remains less than 0.1. This low v_2 dependence is in contrast with that found for the same networks swollen in toluene and benzene, where the χ dependence on v_2 was much greater (slope ≈0.3). Our results indicate that TMP as a solvent is comparable to or slightly better than DMP at infinite dilution. However for the range of v_2 values studied here (0.047 to 0.385), DMP consistently swelled the networks to a slightly higher extent, as shown in *Tables 1* and *2*, with the difference diminishing as we go to lower values of v_2. This is consistent with a slightly greater dependence of χ on v_2 in TMP than in DMP.

Because of the very weak dependence of χ on v_2, the value of χ can, to a good approximation, be taken as a constant and equation (1) can now be tested using the values of χ_0 obtained from the viscosity experiments. *Figures 3a* and *3b* represent how well the Flory–Rehner model coupled with the phantom network assumption describes the swelling data of PDMS in DMP and TMP, respectively, using constant interaction parameters.

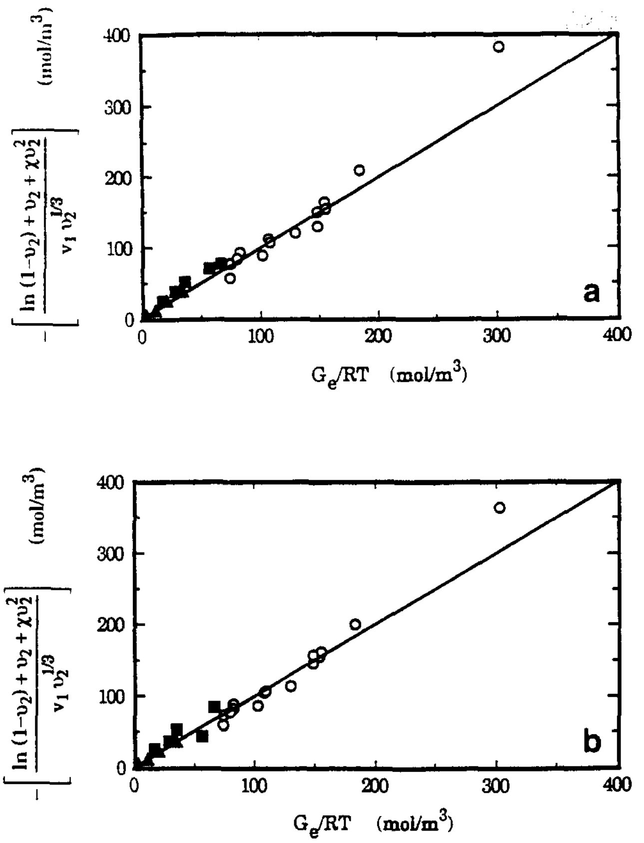

Figure 3 Comparison of swelling results from equation (1) of all networks swollen in (a) DMP ($\chi_0 = 0.388$) and (b) TMP ($\chi_0 = 0.385$). The symbols have the same significance as in *Figure 2*

CONCLUSIONS

Intrinsic viscosity measurements were used to find values for the interaction parameter at infinite dilution χ_0 from uncrosslinked PDMS chains in solution with 2,3-dimethylpentane (DMP) and 2,2,4-trimethylpentane (TMP) through the use of the Stockmayer–Fixman relationship. The values of χ_0 agree quite well with those determined from the equilibrium swelling experiments assuming a value of $2.0 \times 10^{23}\,\mathrm{mol}^{-1}$ for the universal viscosity constant in the molecular weight range $7100 < M_w < 68\,000$. Overall, for both solvents the Flory–Rehner model coupled with the phantom network assumption adequately predicts the experimental swelling results when the experimental modulus and the interaction parameter from intrinsic viscosity are used.

With the solvents used in this work, the validity of the swelling method for the determination of the interaction parameter from both model and imperfect PDMS networks was demonstrated for solvents that are better than those previously used and that have an interaction parameter that is essentially concentration independent. Despite the better quality of DMP and TMP relative to benzene and toluene, the equilibrium volume fractions of the PDMS networks have remained quite high, with the exception of four samples (see *Table 2*) that lead to $\upsilon_2 \leq 0.105$. Although one would expect excluded volume effects to start appearing in the semi-dilute regime[20], i.e. $\upsilon_2 < 0.1$, these effects must not be pronounced enough at the swelling values obtained here to show deviations from the Flory–Rehner model. Much higher swellings in gels have typically led to behaviour consistent with the presence of excluded volume effects and the scaling laws of semi-dilute solutions[21–23]. That the interaction parameter of the solvents used here is practically concentration independent and that the swelling can be described well with a constant χ indicate that no crosslink dependence on χ is necessary to describe the data presented here except at very high crosslink densities (see *Figure 3*), where further investigations might be in order.

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