Effect of crosslinks on the thermodynamics of poly(vinyl alcohol) hydrogels

Gregory B. McKenna* **and Ferenc Horkay†**
National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
(Received 12 April 1994)

The Flory–Huggins interaction parameter χ_{gel} was determined for chemically crosslinked poly(vinyl alcohol) (PVA) hydrogels from swelling pressure and elastic modulus measurements. The PVA gels were prepared in aqueous solutions of different molecular weight ($22\,000 < M_w < 346\,000$). Crosslinks were introduced at different polymer concentrations (3% w/w $\leqslant c_0 \leqslant 12\%$ w/w). It is found that in all systems the values of χ_{gel} for the crosslinked polymer are greater than the values of χ_{sol} for the uncrosslinked material at identical concentrations. The χ_{gel} data reported here seem to be a function only of the polymer concentration and are independent of the details of the network structure. The results are discussed in relation to other work on the crosslink dependence and volume fraction dependence of χ_{gel}.

(Keywords: crosslinks; PVA hydrogels; thermodynamics)

INTRODUCTION

There has been considerable interest recently in the elastic and swelling behaviours of polymer networks[1–11]. In particular, there is still much debate over the validity of the Frenkel–Flory–Rehner (FFR) hypothesis and the various aspects of it[12–14]. Firstly, the basic premise of the FFR hypothesis is that the free energy of a swollen network is separable into elastic and mixing components. Implicit in this is that 'a stretch is a stretch' and the elastic contribution to the free energy is determined simply by the degree of stretch of the chains and therefore described by the same strain energy density function as that obtained in the dry state, but evaluated at the appropriate degree of swelling[3,4,11]. Another aspect of the FFR hypothesis is that the mixing contribution to the free energy should be unaffected by the chain stretching upon swelling. In addition to these main features of the hypothesis, it is common practice to make assumptions about the Flory–Huggins expression that is often used to describe the mixing contribution to the free energy. In particular, the polymer–solvent interaction parameter χ can be assumed to be independent of volume fraction and crosslink density. While the former is generally recognized to be false, the crosslink dependence of χ is a subject of much current discussion[1–6,9,10,15,16]. It has been observed that the mixing free energy for the network polymer is significantly smaller than for the corresponding polymer solution[4,6,9,10]. Freed and Pesci's calculations[15,16], which include bond correlations in a systematic cluster expansion of the mixing free energy, predict a substantial dependence of the effective polymer–solvent interaction parameter on crosslink density, in addition to the normally observed dependence on, for example, the volume fraction of polymer. However, Freed and Pesci's theory is restricted to concentrated systems. Swelling and mechanical measurements performed on crosslinked natural rubber swollen in different solvents[4] indicate reasonable agreement with this prediction. It was found that the apparent value of the Flory–Huggins interaction parameter χ_{gel} in the crosslinked polymer, determined for fully swollen gels in equilibrium with the pure diluent, is a linear function of crosslink density

$$(\chi_{gel} - \chi_{0,sol})/\chi_{0,sol} = \alpha\nu \tag{1a}$$

where $\chi_{0,sol}$ is the value of χ in the uncrosslinked polymer at the dilute solution limit for good solvents and at the limit of miscibility for poor solvents, respectively, α is a constant and ν is the crosslink density. McKenna *et al.*[2,4] reported that α was nearly independent of the solvent type. Furthermore, it was suggested[2,4] that a 'universal' relationship might describe the crosslink dependence of the interaction parameter

$$(\chi_{gel} - \chi_{0,sol})/\chi_{0,sol} = \alpha'\nu/\nu^* \tag{1b}$$

where now α' is a dimensionless ('universal') parameter and ν^* is a normalization parameter which may be related to the crosslink density at the gel point. It should be appreciated, however, that the extent of crosslinking has an effect on the equilibrium concentration of the fully swollen gel. We present below results that imply a more complicated picture of the behaviour of χ_{gel} that requires an understanding of the crosslink and volume fraction dependences.

In this paper we examine the general validity of the FFR hypothesis by carrying out measurements of swelling pressure and shear modulus as a function of polymer concentration on poly(vinyl alcohol) (PVA) hydrogels prepared by crosslinking in solutions of different polymer molecular weight and concentration.

---

*To whom correspondence should be addressed

† On leave of absence from the Department of Colloid Science, Loránd Eötvös University, Budapest, Hungary

0032-3861/94/26/5737–06
© 1994 Butterworth-Heinemann Ltd

Furthermore, we investigate the validity of the above equations. An attempt is made to discriminate between the effects of crosslinks and polymer concentration on χ_{gel}.

THEORY

According to the Frenkel–Flory–Rehner hypothesis[12–14], the free energy of a swollen network is the sum of elastic and mixing free energy contributions. For a crosslinked polymer in equilibrium with a diluent of activity a_1 the chemical potentials are given by the relation[14]

$$RT\ln a_1 = \Delta\mu_1^{el} + \Delta\mu_1^{mix} \qquad (2)$$

where $\Delta\mu_1^{el}$ and $\Delta\mu_1^{mix}$ are the elastic and mixing components of the solvent chemical potential in the swollen network, R is the gas constant and T is the absolute temperature.

In terms of directly measurable quantities (shear modulus G and swelling pressure ω), equation (2) can be expressed as[17]

$$\omega = \pi_{mix} - G = -(RT/V_1)\ln a_1 \qquad (3)$$

where π_{mix} is the mixing contribution of the swollen network, a_1 is the activity of the diluent and V_1 is the partial molar volume of the swelling agent. (We note that the use of G in equation (3) is strictly valid only when the network exhibits neo-Hookean behaviour. This is a reasonable assumption for systems crosslinked in solution, as were the gels prepared for this study.)

The osmotic pressure of a polymer solution is given by the Flory–Huggins equation

$$\pi_{(FH)} = -(RT/V_1)[\ln(1-\varphi) + (1-1/P)\varphi + \chi_{sol}\varphi^2] \qquad (4a)$$

where φ is the volume fraction of the polymer, χ_{sol} is the Flory–Huggins interaction parameter and P is the degree of polymerization of the chains (for a crosslinked polymer $P = \infty$). In general, χ_{sol} depends on the polymer concentration[18,19], i.e.

$$\chi_{sol} = \chi_0 + \chi_1\varphi + \cdots \qquad (4b)$$

where χ_0 and χ_1 are constants.

From equations (3) and (4a) the swelling pressure is given by

$$\omega = -(RT/V_1)[\ln(1-\varphi) + \varphi + \chi_{gel}\varphi^2] - G \qquad (5)$$

Thus, using equation (5) the value of the polymer–solvent interaction parameter can be calculated from the measured swelling pressure and shear modulus data.

EXPERIMENTAL

Sample preparation

Experiments were performed using hydrolysed and fractionated PVA samples. A detailed description of the materials and the gel preparation procedure has been reported elsewhere[5,20]. Some characteristics of the PVA samples are listed in *Table 1*. PVA gels were obtained by crosslinking in aqueous solutions with glutaraldehyde at pH 1.5. Crosslinks were introduced at four different polymer concentrations: $c_0 = 3.0$, 6.0, 9.0 and 12.0% (w/w). At each concentration four sets of gel samples were prepared having different crosslink densities (the molar ratios of crosslinker to monomer units of polymer were 1:50, 1:100, 1:200 and 1:400).

Table 1 Intrinsic viscosities and molecular weights of PVA fractions

Fraction	$[\eta]_{303K}$ (dl g^{-1})	M_w[a]
I	0.26	22 300
II	0.45	52 600
III	0.70	102 700
IV	0.84	139 600
V	1.50	345 500

[a] M_w was calculated using the equation[21] $[\eta]_{303K} = 4.28 \times 10^{-4} M_w^{0.64}$

Swelling pressure and elastic modulus measurements

The diluent activity in the gels was measured using the modified deswelling method described elsewhere[5,20,22]. Swollen PVA networks were equilibrated with aqueous poly(vinyl pyrrolidone) solutions with known osmotic pressure *versus* concentration dependence[23]. Gels were separated from the solution by a semipermeable membrane to prevent the penetration of polymer molecules into the network. The activity of the water was varied in the range $0.995 < a_1 < 1.00$. The swelling pressure was obtained from equation (3). In several experiments the swelling measurements were performed at successively decreasing solvent activities followed by sequences of measurements carried out with increasing solvent activities. The two sets of experimental data showed no appreciable differences.

The elastic (shear) moduli of the gels were calculated from uniaxial compression measurements performed on gel cylinders of equal height and diameter (approximately 1 cm) prepared in a special mould. The stress–strain data were determined for the deformation ratio range $0.7 < \lambda < 1.0$. The absence of volume change and barrel distortion during the experiments was carefully checked.

The mechanical and swelling properties of the gels were investigated at 25°C.

RESULTS

Shear modulus and swelling pressure observations

In *Figure 1* the shear moduli of PVA gels prepared at three different concentrations are plotted as a function of the average molecular weight of the primary chain. The molar ratio of crosslinker to monomer units of the polymer was 1:100 for each gel. The value of the shear modulus significantly increases with increasing molecular weight and seems to approach a plateau at sufficiently high molecular weight. It can also be seen that G is higher in the gels prepared from the more concentrated polymer solutions.

For a perfect (ideal) network it is assumed that above the gel point each crosslinker molecule leads to the formation of elastic chains. In real networks, owing to imperfections such as pendent chains, unreacted functionalities, etc., the number of elastic chains is always reduced[17,24]. The pendent chains relax during the shear modulus measurements, and therefore they do not contribute to the equilibrium value of the modulus. The number of pendent chains is expected to increase when the molecular weight of the primary polymer is decreased, in qualitative agreement with the data shown in *Figure 1*.

The observed increase in the shear modulus as a function of the initial polymer concentration indicates the involvement of other topological interactions. Several experimental studies show that in aqueous PVA solutions the polymer chains are clustered because of hydrogen bonding[25–29]. Formation of physical contacts between the polymer segments may result in an increase of the shear modulus.

From equation (5) the Flory–Huggins interaction parameter χ_{gel} in the crosslinked polymer can be calculated

$$\chi_{gel}=[-V_1(\omega+G)/RT-\ln(1-\varphi)-\varphi]/\varphi^2 \qquad (6)$$

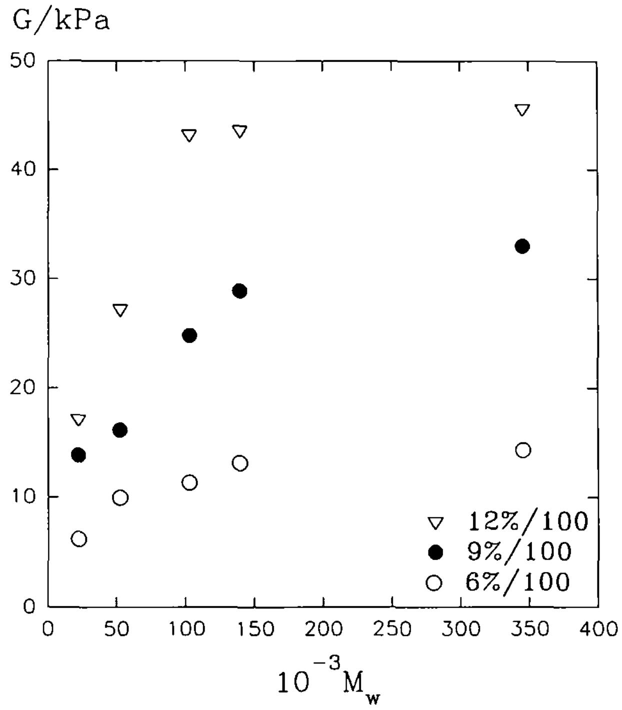

Figure 1 Shear modulus G *versus* M_w for PVA hydrogels. M_w is the average molecular weight of the polymer used to prepare the networks. The moduli were measured at a polymer concentration of 9.0% (w/w). The crosslink density was 1:100

In *Figure 2a* the values of $(\chi_{gel}-\chi_{0,sol})/\chi_{0,sol}$ are presented according to equation (1) for four series of PVA gel systems swollen into equilibrium ($\omega=0$). In the calculation of χ_{gel} the shear modulus data measured at swelling equilibrium in the pure diluent were used. The linear increase of χ_{gel} with crosslink density is in qualitative agreement with results reported elsewhere[2,4]. Unlike the data reported for natural rubber in different solvents by McKenna *et al.*[2,4], this reduction scheme does not collapse the data to a single line. In that work it was felt that the collapse of the data by equation (1a) was perhaps the result of a 'universal' behaviour and it was suggested that the normalization parameter ν^* (related to the amount of crosslinking agent used up below the gel point) might provide the necessary insight into the observations. The data presented in *Figure 2a* are sufficient to test this hypothesis. It is reasonable to assume that ν^* depends upon both the molecular weight of the uncrosslinked polymer M_p (ν^* increases as M_p decreases) and the concentration φ_0 at crosslinking (ν^* decreases as φ_0 increases). Then from equations (1a) and (1b) we would expect that the slopes α of the straight lines in *Figure 2a* would increase with both φ_0 and M_p. The ratio of the slopes is approximately the same as that of the initial polymer concentrations (2:1), in agreement with the expectation. However, no systematic dependence of α on the molecular weight of the uncrosslinked polymer is observed.

An alternative representation of the data is shown in *Figure 2b*, where the same χ_{gel} values are plotted as a function of φ. In this representation all data points for the various crosslink densities collapse onto a single line, i.e. $\chi_{gel}=\chi_{0,gel}+\chi_{1,gel}\varphi+\ldots$. This result suggests that the variation of χ_{gel} with crosslink density may be partially caused by the fact that the maximum swelling degree

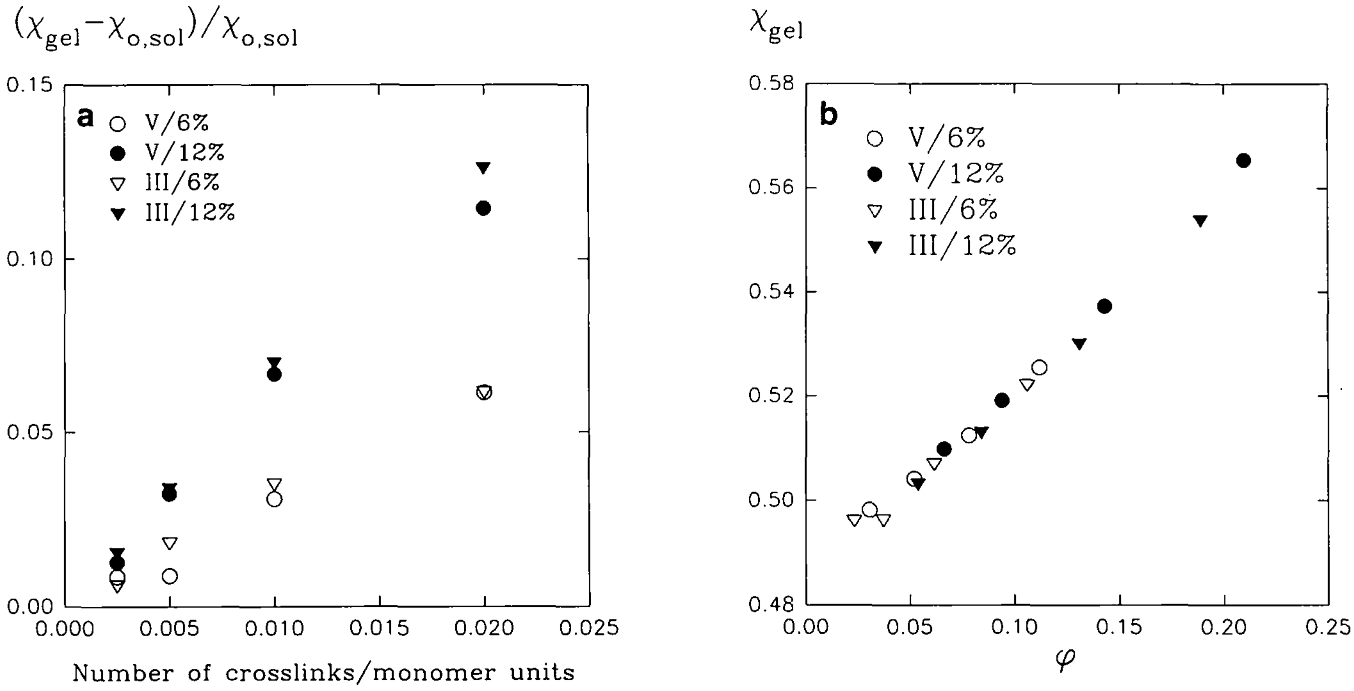

Figure 2 (a) Variation of $(\chi_{gel}-\chi_{0,sol})/\chi_{0,sol}$ with crosslink density for typical sets of PVA hydrogels. (b) Variation of the Flory–Huggins interaction parameter χ_{gel} with polymer volume fraction φ for the same PVA hydrogels as shown in (a)

decreases as the crosslink density increases[14,17]. From such results it appears that the dependences of the interaction parameter on crosslink density and volume fraction are in need of further investigation. In the following sections an attempt is made to discriminate between these dependences.

In *Figure 3* χ_{gel} is plotted as a function of polymer volume fraction for PVA gels having different crosslink densities (1:50, 1:100, 1:200 and 1:400). The gels were prepared from fraction III at $c_0 = 9\%$ (w/w). In *Table 2* are listed the values of $\chi_{0,gel}$ and $\chi_{1,gel}$ obtained by least-squares fitting of the χ_{gel} data displayed in *Figure 3* to equation (4b). The numerical values obtained for the interaction parameters are in excellent agreement with previously reported data[27] ($\chi_{0,gel} = 0.477$ and $\chi_{1,gel} = 0.414$). It is clear from the figure that χ_{gel} does not exhibit a systematic dependence on the crosslink density. Yet, as seen in *Figure 4*, where the volume fraction dependences of χ_{gel} and χ_{sol} are plotted, not only is χ_{gel} always greater than χ_{sol} at identical polymer concentrations, but the difference depends upon the concentration. In *Table 3* the $\chi_{0,gel}$ and $\chi_{1,gel}$ values for gels prepared from different PVA fractions are listed. It can be seen that neither $\chi_{0,gel}$ nor $\chi_{1,gel}$ depends on the initial molecular weight of the polymer.

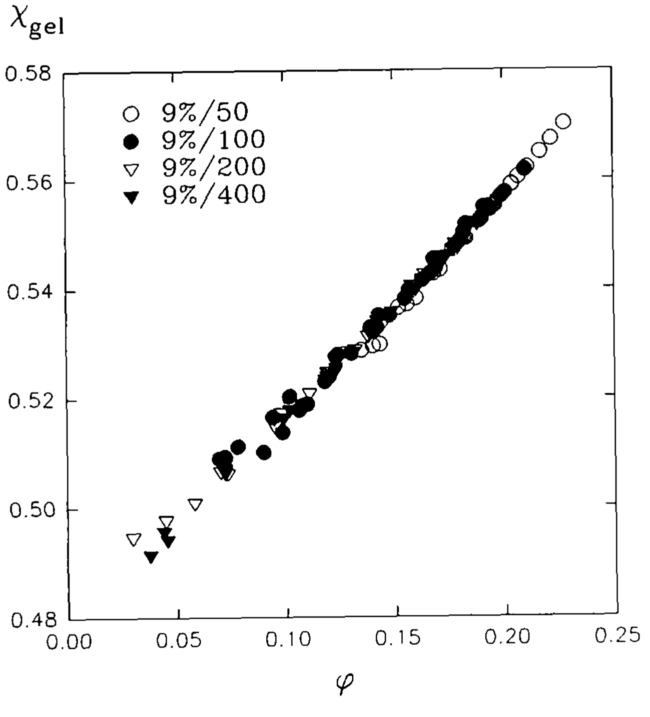

Figure 3 Flory–Huggins interaction parameter χ_{gel} *versus* polymer volume fraction φ for PVA hydrogels having different crosslink densities. Crosslinks were introduced at a polymer concentration of 9.0% (w/w)

Table 2 Values of $\chi_{0,gel}$ and $\chi_{1,gel}$ for PVA/water gels (concentration at crosslinking 9.0% w/w)

Crosslink density	$\chi_{0,gel}$	$\chi_{1,gel}$
1:50	0.464 ± 0.003	0.456 ± 0.010
1:100	0.475 ± 0.003	0.411 ± 0.009
1:200	0.477 ± 0.003	0.403 ± 0.008
1:400	0.477 ± 0.003	0.404 ± 0.008

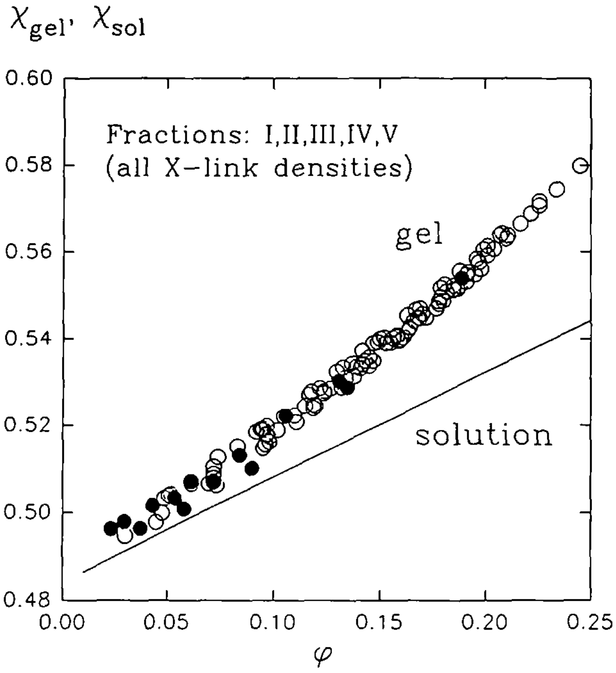

Figure 4 Flory–Huggins interaction parameters χ_{gel} and χ_{sol} *versus* polymer volume fraction φ for PVA hydrogels (circles) and a PVA/water solution (continuous line). The PVA gels were prepared from fractions I–V at different polymer concentrations: (●) fully swollen gels ($a_1 = 1$); (○) partially deswollen gels ($a_1 < 1$)

Table 3 Values of $\chi_{0,gel}$ and $\chi_{1,gel}$ for gels prepared from different PVA fractions

Fraction	$\chi_{0,gel}$	$\chi_{1,gel}$
I	0.480 ± 0.003	0.393 ± 0.008
II	0.481 ± 0.003	0.387 ± 0.008
III	0.474 ± 0.004	0.411 ± 0.010
IV	0.478 ± 0.004	0.417 ± 0.012
V	0.478 ± 0.004	0.416 ± 0.014

DISCUSSION

In the above, we have shown that the data for PVA hydrogels and solutions show two important features. Firstly, the Flory–Huggins interaction parameter for the gels is greater than that for the solution, i.e. $\chi_{gel} > \chi_{sol}$. This is an observation that has been made previously for natural rubber in a range of solvents[2,4] and also for several other polymer/solvent systems[6,9,10]. Secondly, the observations here show that, while the crosslinked networks exhibit a different interaction parameter from the solutions, there is no trend of χ_{gel} with crosslink density. This differs substantially from the interpretations made for the natural rubber (NR) systems studied elsewhere[2,4] as well as for more recent work by McKenna and Crissman[30] where the data are taken at the limit of $\varphi \rightarrow 1$. Here we try to examine some of the discrepancies.

In *Figure 5* the values of χ_{gel} and χ_{sol} are displayed as a function of φ for different polymer/solvent systems (PVA/water, NR/various solvents). While the qualitative features of the gel data are similar, i.e. each set follows a single curve and at identical polymer concentrations $\chi_{gel} > \chi_{sol}$, there appear to be two classes of behaviour. The PVA/water system and the rubber/dichloroethane

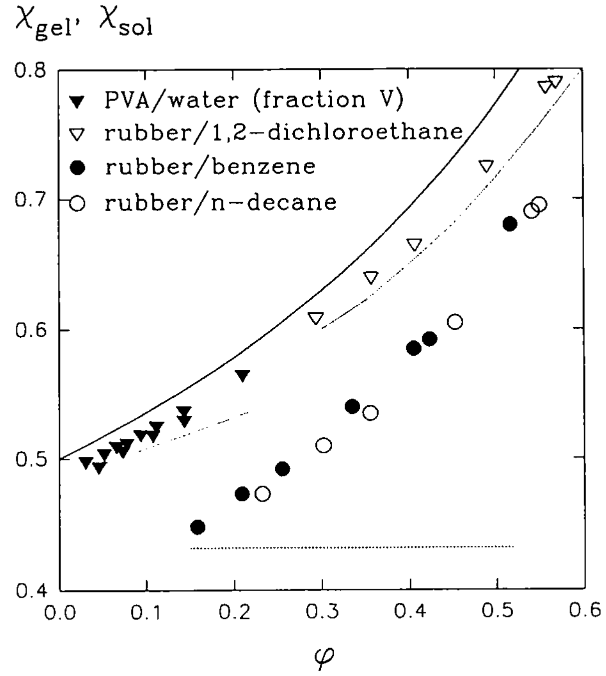

Figure 5 Dependence of the Flory–Huggins interaction parameter χ_{gel} on the polymer volume fraction φ for PVA hydrogels and crosslinked natural rubber samples swollen in different diluents. The data points refer to fully swollen gels ($a_1 = 1$) having different crosslink densities. The continuous curve, calculated from equation (6) with $G = 0$, corresponds to the limit of miscibility. The discontinuous curves were calculated using χ_{sol} values reported in the literature (PVA/water[27], rubber/benzene[31] and rubber/dichloroethane[32])

system appear to fall on one curve and the rubber/benzene and rubber/n-decane systems fall on another curve. Evidently, the concentration dependence and the crosslink dependence are not simply separated. It is interesting to remark that the PVA/water and rubber/dichloroethane systems are 'marginal' to 'poor' solvent systems, while the rubber/benzene and rubber/n-decane systems are 'good' solvent systems.

Note that the data shown in *Figure 5* refer to gel systems having entirely different structues: PVA hydrogels were prepared by crosslinking in aqueous solutions at relatively low polymer concentrations (3% w/w $\leqslant c_0 \leqslant$ 12% w/w), while natural rubber samples were cured with dicumyl peroxide in the dry state. The fact that the gel curves are apparently unaffected by the network topology (crosslink density, network imperfections, etc.) suggests that the deviation between the gel and solution mixing terms is a general phenomenon.

A possible source of the observed differences in χ_{sol} and χ_{gel} is the decrease in the translational part of the mixing free energy caused by crosslinking. In a polymer solution the macromolecules are free to diffuse throughout the sample. Introduction of crosslinks significantly decreases the degree of freedom of the system. In the network the polymer chains are restricted to limited regions because of the presence of permanent elastic constraints, and the segments exhibit limited thermal fluctuations around fixed average positions. The effects of the crosslinking constraints on the thermodynamic properties of swollen polymer networks are not considered in the existing theories.

Turning now to the additivity of the elastic and mixing free energy contributions, we recall *Figure 4* where the concentration dependence of χ_{gel} is shown for PVA hydrogels. It is clear from this figure that χ_{gel} exhibits identical behaviour for fully swollen ($a_1 = 1$) and partially deswollen ($a_1 < 1$) gels. In other words, the quantity $\omega + G(= \Pi_{mix})$ is a function only of the polymer concentration and does not depend on the detailed structure of the network. Π_{mix}, however, significantly differs from the osmotic pressure of the corresponding polymer solution, i.e. the mixing term is severely perturbed by the presence of crosslinks. Using this 'perturbed' mixing contribution, the results of the swelling measurements are consistent with the assumption that the elastic and mixing free energies are separable. This latter finding is in agreement with the results of similar mechanical and swelling measurements performed on other polymer/solvent systems[3,4,6,9,10].

CONCLUSIONS

Measurements on chemically crosslinked poly(vinyl alcohol) hydrogels indicate a systematic increase of the shear modulus with the average molecular weight of the polymer and the concentration of the solution at which crosslinks are introduced. The effective value of the Flory–Huggins interaction parameter for the swollen network deduced from swelling pressure and shear modulus data is found to be larger than that for the corresponding (uncrosslinked) polymer solution, i.e. $\chi_{gel} > \chi_{sol}$.

While for the PVA system $\chi_{gel} > \chi_{sol}$, χ_{gel} itself is a function only of the polymer concentration and is independent of the details of the network structure. Reanalysis of previous results obtained for crosslinked natural rubber swollen in different solvents supports the main conclusion of the present work, i.e. in a given polymer/solvent system χ_{gel} seems to be well represented as a function of the polymer concentration alone. Further work is required to explain why the gel and solution volume fraction dependences are different and the differences in behaviour among specific polymer/solvent systems.

ACKNOWLEDGEMENTS

F. H. acknowledges the tenure of a Visiting Scientist position at the National Institute of Standards and Technology, Gaithersburg, MD, USA. Part of this work was supported by the Hungarian Academy of Sciences under research contract OTKA 2158.

REFERENCES

1 Neuburger, N. A. and Eichinger, B. E. *Macromolecules* 1988, **21**, 3060
2 McKenna, G. B., Flynn, K. M. and Chen, Y. *Polym. Commun.* 1988, **29**, 272
3 McKenna, G. B., Flynn, K. M. and Chen, Y. *Macromolecules* 1989, **22**, 4507
4 McKenna, G. B., Flynn, K. M. and Chen, Y. *Polymer* 1990, **31**, 1937
5 Horkay, F. and Zrinyi, M. *Macromolecules* 1982, **15**, 1306
6 Horkay, F., Hecht, A.-M. and Geissler, E. *J. Chem. Phys.* 1989, **91**, 2706
7 Soni, V. K. and Stein, R. S. *Macromolecules* 1990, **23**, 5257
8 Patel, K. S., Malone, S., Cohen, C., Gillmor, J. R. and Colby, R. H. *Macromolecules* 1992, **25**, 5241

9 Horkay, F., Geissler, E., Hecht, A.-M., Zrinyi, M. and Pruvost, P. *Polymer* 1991, **32**, 835

10 Hecht, A.-M., Horkay, F., Mallam, S. and Geissler, E. *Macromolecules* 1992, **25**, 6915

11 Douglas, J. F. and McKenna, G. B. *Macromolecules* 1993, **26**, 3282

12 Frenkel, J. *Rubber Chem. Technol.* 1940, **13**, 264

13 Flory, P. J. and Rehner Jr, J. J. *J. Chem. Phys.* 1943, **11**, 521

14 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953

15 Freed, K. F. and Pesci, A. I. *J. Chem. Phys.* 1987, **87**, 7342

16 Freed, K. F. and Pesci, A. I. *Macromolecules* 1989, **22**, 4048

17 Treloar, L. R. G. 'The Physics of Rubber Elasticity', 3rd Edn, Clarendon Press, Oxford, 1975

18 Flory, P. J. *Faraday Discuss. Chem. Soc.* 1970, **49**, 7

19 Freed, K. F. and Dudowicz, J. *Theor. Chim. Acta* 1992, **82**, 357

20 Horkay, F. and Nagy, M. *Polym. Bull.* 1980, **3**, 457

21 Matsumoto, M. and Ohyanagi, Y. *Kobunshi Kagaku* 1960, **17**, 17

22 Nagy, M. and Horkay, F. *Acta Chim. Acad. Sci. Hung.* 1980, **104**, 49

23 Vink, H. *Eur. Polym. J.* 1971, **7**, 1411

24 Dusek, K. and Prins, W. *Adv. Polym. Sci.* 1969, **6**, 1

25 Komatsu, M., Inoue, T. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 303

26 Wu, W., Shibayama, M., Roy, S., Kurokawa, H., Coyne, L. D., Nomura, S. and Stein, R. S. *Macromolecules* 1990, **23**, 2245

27 Geissler, E., Horkay, F. and Hecht, A.-M. *Macromolecules* 1991, **24**, 6006

28 Horkay, F., Burchard, W., Geissler, E. and Hecht, A.-M. *Macromolecules* 1993, **26**, 1296

29 Horkay, F., Hecht, A.-M. and Geissler, E. *Macromolecules* 1994, **27**, 1795

30 McKenna, G. B. and Crissman, J. M. *Polym. Mater. Sci. Eng.* 1993, **68**, 280

31 Gee, G., Herbert, J. B. M. and Roberts, C. *Polymer* 1965, **6**, 541

32 Huggins, M. L. *Ann. N. Y. Acad. Sci.* 1943, **44**, 431