Crosslinking studies of poly(dimethylsiloxane) networks: a comparison of inverse gas chromatography, swelling experiments and mechanical analysis

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Finite concentration inverse gas chromatography (i.g.c.) was used to determine the crosslink density of three poly(dimethylsiloxane) (PDMS) samples, which were crosslinked with different doses of γ-rays. Crosslink density data of the same materials were also obtained in swelling measurements and, in one case, in stress–strain mechanical analysis. Results yielded by the different techniques agreed very well considering the different nature of the approximations made in the various experiments. Information obtained by i.g.c. also included the Flory–Huggins interaction parameters of the linear and crosslinked PDMS samples.

(Keywords: inverse gas chromatography; poly(dimethylsiloxane); crosslink density)

INTRODUCTION

The research and development of novel, high-value, engineered polymeric materials require new and improved analytical methods to study the macromolecular architecture. For example, characterization of the macromolecular architecture of non-soluble polymers, e.g. rubbers, has been a notoriously difficult task. There is great need for novel techniques that are suitable for studying the microstructure of molecular networks. Inverse gas chromatography (i.g.c.), pioneered for studies of polymers, for the most part by Guillet and coworkers[1,2], has the potential to become one of the major methods for the characterization of crosslinked macromolecular structures.

A large variety of applications of i.g.c. have been developed for polymer analysis and characterization[1,3]. For example, the average size of the chains in the amorphous domains separating crystalline regions of semicrystalline polyethylene and polypropylene was studied by Brockmeier *et al.*[4] by using the elution-on-a-plateau technique of finite concentration i.g.c. Later, Price *et al.*[5] used this technique to determine the crosslink density of ethylene–propylene rubbers (EPR). The crosslink density, γ_e, can be described by the number of moles of subchain units (chains between crosslinkages) per gram of sample[6]. The value of γ_e was calculated from the Flory–Huggins interaction parameter by using the Flory–Rehner equation, and by measuring the concentration of n-hexane in the EPR. The column support was coated by the uncrosslinked polymer, and the network was formed by subsequent irradiation. Owing to the preparation procedure of the column, comparison of the γ_e values with data from experiments utilizing different techniques was not possible. For practical characterization studies of rubbers that are already crosslinked, however, a new procedure for the preparation of the columns is required.

In this paper we report on the results of a quantitative study of the crosslink density of poly(dimethylsiloxane) (PDMS) networks by using (a) the i.g.c. technique, (b) results of swelling experiments, and (c) data obtained in mechanical analysis of bulk samples. The crosslinking was performed in bulk samples of the polymer prior to the characterization experiments. Thus, a comparison of crosslink density determined by i.g.c. and the other two techniques was possible for the first time, using the same samples. Packing of the i.g.c. column was carried out using ground specimens of crosslinked PDMS. Thus, the technological importance of the i.g.c. technique for the determination of elastomers crosslinked in the bulk phase has been demonstrated.

A variety of different methods have been developed to determine the crosslink density of polymers, such as tensile tests[6], swelling rate data[7] and swelling equilibrium[6] techniques, vapour sorption techniques[8,9], vapour pressure osmometry[10], neutron scattering[11], dielectric relaxation measurements[12] and nuclear magnetic resonance[13]. It is beyond the scope of this publication to discuss the advantages and disadvantages of these techniques. However, it is worth mentioning that the advantage of the i.g.c. method is that it yields thermodynamic data such as the Flory–Huggins interaction parameter and its concentration dependence in addition to the crosslink density[5]. Also, the i.g.c. method is much faster than the vapour sorption technique.

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Crosslinked PDMS samples were chosen as the model material because of the easy sample preparation procedure. In addition, PDMS rubbers have been well studied theoretically, as well as widely used in practice, and therefore an abundance of information is available for comparison[14,15].

THEORETICAL BACKGROUND

Finite concentration i.g.c.[16–26]

In the elution-on-a-plateau (EP) method of finite concentration i.g.c., a saturator is set up between the source of an inert carrier gas and the column, which is used to saturate the carrier gas and provide a constant concentration of solvent in the stream. The basis of the EP method is to determine the amount of solvent vapour (carried by the inert gas) absorbed in the stationary phase (of the polymer being studied). The net retention volume, V_N, is determined by injecting a small amount of probe into the column. The time required for this perturbation of the plateau concentration to travel through the stationary phase is measured in order to obtain V_N. The dead volume is excluded by measuring the retention volume of an inert matter injected together with the probe. Since the polymer is equilibrated with the solvent vapour at known concentrations, V_N can be used to determine the concentration of the solvent in the stationary phase, and therefore the activity coefficient. The activity coefficient can be used for further calculations using various thermodynamic models of polymer solutions.

The simplified Conder–Purnell treatment[17] of the finite concentration chromatographic procedure describes the partition of the probe between its vapour and the solution phase. The concentration of the solvent probe in the dissolved phase can be expressed within this approach by the following equation:

$$q=\frac{1}{w_p}\int_0^c \frac{jV_N(c')}{1-\psi(c')}\,dc' \qquad (1)$$

where q (in mol g^{-1}) and c (in mol m^{-3}) are the concentrations of the solvent probe in the dissolved and vapour phases, respectively, j is a correcting factor which takes into account the compressibility effects and non-ideality of the gas phase caused by the pressure gradient along the column, w_p is the weight of the polymer in the i.g.c. column, and ψ is the corrected mole fraction of the solvent in the mobile phase.

The value of the weight fraction of the solvent probe, w_1, can be written in the following form:

$$w_1=\frac{qM_1}{(1+qM_1)} \qquad (2)$$

where M_1 is the molar mass of the solvent probe. The concentration of the probe in the mobile phase can be determined from a virial expansion series:

$$c=\frac{\psi P_A}{(jRT_c+\psi^2 B_{11}P_A)} \qquad (3)$$

where P_A is the total pressure of the carrier gas at the column exit, R is the gas constant and B_{11} is the second virial coefficient of the pure solvent at the column temperature T_c[5,16,20–26].

The thermodynamic activity, a_1, of the solvent in the stationary phase can be written:

$$a_1=\frac{f_1}{f_1^0} \qquad (4)$$

where f_1 is the fugacity of the solvent probe in the mobile phase at the column temperature, and f_1^0 is the fugacity of the saturated vapour of the pure solvent at the column temperature. The fugacity can be calculated from the following equation:

$$\ln f_1=\ln P_1-\frac{P_A J_3^{(4)}}{RT}[(B_{11}-2B_{13}+B_{33})(1-\psi)^2]+\frac{B_{11}P_A J_3^{(4)}}{RT} \qquad (5)$$

For $\psi=1$, the expression reduces to

$$\ln f_1=\ln f_1^0 \qquad (6)$$

In equation (5), P_1 is the average partial pressure of the solvent in the mobile phase in the column, $P_1^0\ (T_c)$ is the saturated vapour pressure of the solvent at the column temperature, $J_3^{(4)}$ is a correcting factor for the column pressure gradient using Conder and Purnell's notation (see equation 1.2. in ref. 22), B_{13} is the cross second virial coefficient, and B_{11} and B_{33} are the second virial coefficients of the pure solvent and the pure inert gas, respectively. In our calculations, the values of B_{13} and B_{33} have been neglected without introducing significant error. The partial pressure of the solvent can be expressed by using ψ and the average column pressure $P_A J_3^{(4)}$:

$$P_1=\psi P_A J_3^{(4)} \qquad (7)$$

The value of ψ can be calculated from the following formula:

$$\psi=\frac{a_{\mathrm{corr}}jP_1^0(T)}{P_t} \qquad (8)$$

where a_{corr} is a correcting factor for gas-phase non-ideality (for exact definitions of a_{corr} and j see equations 32a and 33a in ref. 20), and P_t is the total pressure in the saturator. The partial pressure of the solvent at the temperature of the saturator (T) from the saturator condenser, $P_1^0(T)$, and the saturated vapour pressure of the solvent at the column temperature T_c, $P_1^0(T_c)$, can be calculated by using empirical equations such as the Antoine equation (see, for example, ref. 16).

The activity and the concentration of the solvent in the stationary phase are the fundamental experimental information delivered by the i.g.c. experiment. It will be shown later that by using the Flory–Huggins theory for polymer solutions[6], the interaction parameter χ can be determined from the activity coefficient of the non-crosslinked polymer. The value of the crosslink density can be determined from the activity of the crosslinked and uncrosslinked samples by using the Flory–Rehner equation (chapter XIII-3a in ref. 6) for the swollen polymer networks. The response of the elastic network with respect to the directly measured experimental quantity must, of course, be known.

Theories of rubber elasticity[27–30]

Although the description of the rubbery state has been the focus of many theoretical and experimental studies, there is still a lack of a unified, satisfactory treatment of elastomers on the molecular level. In our study the affine and the phantom network models[24] were used to calculate γ_e. The simplest phantom network model was used to interpret data of swelling measurements, since in a swollen elastomer, fluctuations in the end-to-end distance of the network chains are important. The affine model is used in i.g.c. and in mechanical analysis. This assumes that end-to-end chain fluctuations are confined by interferences of the macromolecules in the bulk. In both models, the influence of the molar mass distribution of the linear polymers prior to crosslinking is not taken into account.

The total Gibbs free energy, ΔG, is the sum of the free energy of mixing, ΔG_{mix}, and the free energy of deformation (or elastic energy), ΔG_{el}, assuming that intermolecular interactions in a polymer–solvent system are independent of the configuration[6]:

$$\Delta G=\Delta G_{\mathrm{mix}}+\Delta G_{\mathrm{el}} \tag{9}$$

In swelling experiments, the pressure–volume product does not change significantly. Therefore, the Helmholtz free energy, ΔF_{el}, is approximately equal to the Gibbs free energy[27].

By assuming that the material is homogeneous and the distribution of the lengths of the network chains follows the Gaussian distribution, the general expression for the Gibbs free energy of deformation, ΔG_{el}, can be obtained by the following models.

In the mainframe of the phantom network model, the distances between the junctions fluctuate randomly, and ΔG_{el} can be written in the following form[27]:

$$\Delta G_{\mathrm{el}}=\frac{\xi RT}{2}(\lambda_x^2+\lambda_y^2+\lambda_z^2-3) \tag{10}$$

where ξ is the cycle rank of the network, which is the molar number of cuttings necessary to reduce an ideal network structure to a tree structure[27], and λ_i ($i=x$, y and z) represents the elongation or compression in three dimensions, caused either by osmotic pressure or by mechanical force.

The following expression can be obtained for a swollen network by using the affine model[27]:

$$\Delta G_{\mathrm{el}}=\frac{\gamma_e RT}{2}[\lambda_x^2+\lambda_y^2+\lambda_z^2-3]-\frac{2\gamma_e}{\Lambda}RT\ln\left(\frac{V}{V_0}\right) \tag{11}$$

where V is the total volume of the polymer–solvent system, V_0 is the volume of the pure polymer (reference state), and Λ is the average functionality of the network (in the case of PDMS crosslinked by γ-ray irradiation, this value is usually taken as 4). The following relations generally exist[27]:

$$\xi=\left(1-\frac{2}{\Lambda}\right)\gamma_e \tag{12}$$

$$\mu=\frac{2\gamma_e}{\Lambda} \tag{13}$$

where μ is the number of moles of the crosslinks. Using the Flory–Huggins theory for the non-elastic part of the free energy, ΔG_{mix}, and deriving the equation for ΔG with respect to the number of moles of the solvent n_1 in the system, one obtains the following expression for the thermodynamic activity for the phantom network model[27]:

$$\ln a_1=\ln(1-v_2)+\left(1-\frac{1}{r}\right)v_2+\chi v_2^2+Zv_2^{1/3} \tag{14}$$

where v_2 is the volume fraction of the polymers in the polymer–solvent system, and r is the ratio of the molar volume of the polymer and the solvent. For the affine network model, the corresponding expression can be written[27]:

$$\ln a_1=\ln(1-v_2)+\left(1-\frac{1}{r}\right)v_2+\chi v_2^2 +Z\left(1-\frac{2}{\Lambda}\right)^{-1}\left(v_2^{1/3}-\frac{\mu}{\gamma_e}v_2\right) \tag{15}$$

where, with the density of the polymer, ρ_p, and the molar volume of the solvent, V_1,

$$Z=\rho_p\xi V_1 \tag{16}$$

In the mechanical measurements there is no solvent present in the rubber, i.e. $V=V_0$. The Helmholtz free energy of the deformed network then has the following form:

$$\Delta F_{\mathrm{el}}=\tfrac{1}{2}\gamma_e RT(\lambda_x^2+\lambda_y^2+\lambda_z^2-3) \tag{17}$$

For uniaxial extension (or compression), the mechanical stress, σ (in Pa), can be written[24]:

$$\sigma=\frac{1}{A}\left(\frac{\partial\Delta F_{\mathrm{el}}}{\partial l}\right)_{T,V}=\rho_p\gamma_e RT(\alpha-\alpha^{-2}) =\rho_p\gamma_e RT\left[1+\varepsilon-\frac{1}{(1+\varepsilon)^2}\right] \tag{18}$$

where A is the area of the sample under the force action, $\alpha=l/l_0$ is the elongation (or compression), l and l_0 are the dimension of the sample under the force action and the dimension without the force action, respectively, and $\varepsilon=\alpha-1$.

EXPERIMENTAL

Materials and chemicals

The solvent probe used in the i.g.c. experiments was n-hexane in h.p.l.c. grade which was purchased from Caledon Laboratories Ltd, and was used without further purification. The benzene used in the swelling measurements was a BDH assured product. The PDMS sample was supplied by Polysciences, Inc. with a number average molar mass of $3.6\times10^4\,\mathrm{g\,mol^{-1}}$. The chromatographic support was Chromosorb G with 60/80 mesh size, treated by dimethyldichlorosilane and acid-washed, purchased from Chromatographic Specialties Inc. High purity helium was used as the inert carrier gas which reduced the systematic error in i.g.c. calculations to a minimum[25,31]. The crosslinked PDMS samples were obtained by ^{60}Co γ-ray irradiation of the liquid linear PDMS. Then the samples were annealed for 24 h by heating at 120°C. The approximate doses were estimated from the activity and the known decay rate of the γ-source supplied by the manufacturer (see *Table 1*). The crosslinked PDMS samples were subjected to successive extractions of ether, benzene and n-hexane for approximately 24–48 h. The densities of the samples (see *Table 1*) were measured by using a pycnometer.

Inverse gas chromatography

Apparatus. The instrument was set up exactly as described by Price and Guillet[16,24]. Fine needle valves were used to control the flow rate. The temperature at the

Table 1 Density data of PDMS samples and solvent

Sample	Density ($g\,cm^{-3}$) at 20°C	25°C	75°C	Dose (Mrad)
PDMS	0.980	0.970	0.925	–
SR1	0.977	0.972	0.925	24
SR2	0.976	0.972	0.927	69
SR3	0.989	0.985	0.949	290
n-Hexane[a]	0.660	0.655	0.607	–
Benzene[b]	–	0.874	–	–

[a] Data obtained from ref. 43
[b] Data obtained from ref. 16

condenser and at the columns was controlled by water thermostats with an accuracy of ±0.02°C. The pressure in the saturator was measured by a mercury manometer with an accuracy of ±0.2 torr (26.7 Pa). Another mercury manometer was set right at the inlet of the sample-containing column to measure the inlet pressure (P_{in}). All the temperatures were measured with AMTS mercury thermometers (±0.02°C). The detector was a twin-channel Gow Mac 40-001 thermoconductivity device. The atmospheric pressure (P_A) was measured using a barometer (±0.05 mmHg).

Experimental procedure. Coating of the linear PDMS onto the solid support Chromosorb G was carried out in the usual manner employing n-hexane as a solvent[15]. The samples were carefully prepared in order to calculate the polymer loading, and this was checked by exhaustive Soxhlet extraction with n-hexane.

In order to pack the crosslinked PDMS, the sample was ground to a size of 5–40 μm which was checked by observation under a microscope. An exact amount of the sample was swollen in n-hexane. An amount of Chromosorb G was mixed with the sample while stirring, according to approximately the same percentage loading as for the linear PDMS packing (4%). Stirring was then continued and the mixture was heated slightly until it appeared to be dry. It was then dried in vacuum at 120°C to eliminate the solvent remaining in the system. All packings were loaded into 6.35 mm copper columns in the usual manner[17]. Experiments with a blank column showed a negligible adsorption effect caused by the support at 75°C.

The columns were first conditioned with helium at 75°C until a straight and stable baseline of the gas chromatograph set-up was achieved. Air was used as the inert marker. The peaks obtained were symmetric at lower concentration, and became front-sharpened with increasing concentration. The flow rate was timed with a stop-watch to 0.1 s for 10 ml passing gas. The size of the injections ranged from 0.2 to 1.0 μl, and the concentration of the probe in the stream was varied. The finite concentration experiments were always run at a lower flow rate so that $\psi \Delta P/P_{in}$ did not exceed 1% (where ΔP denotes the difference of the inlet pressure, P_{in}, and outlet pressure, P_A, at the column); i.e. the pressure drop ΔP was nearly zero[20–26]. This procedure is important for the adequate use of the correction factors. The flow rate should also be slow enough to achieve instant local equilibrium at all points within the columns. An average of three to six values of the retention volumes (which agreed to within 4%) was taken. After running the finite concentration i.g.c. experiment, an infinite concentration i.g.c. experiment was performed in order to obtain a reference point for the term $jV_N(c)/[(1-\psi(c))w_p]$ from equation (1).

Swelling measurement

The experiments were carried out in the usual way in benzene at 25±0.05°C[32,33]. The temperature was controlled by using a water-bath thermostat. Homogeneous polymer pieces were used. For the calculation of γ_e, the values of χ for benzene and PDMS were taken from the literature[12,14,34,35]. It was assumed that the specific hard-core volume does not change upon crosslinking.

For calculation of γ_e, the following equation was used[27]:

$$\gamma_e = -2\frac{\ln(1-v_2)+(1-1/r)v_2+\chi v_2^2}{\rho_p V_1 v_2^{1/3}} \qquad (19)$$

This relationship was obtained under the assumption of the additivity of the volume of the system, and by setting $\ln a_1 = 0$ in equation (14). Various weight and volume fractions used for the polymer in the swelling equilibrium systems are listed in *Table 2*.

Mechanical analysis

For the mechanical analysis of the crosslinked PDMS samples, a Perkin Elmer DMA7 dynamic mechanical analysis (d.m.a.) instrument, operated by a DEC Station Personal Workstation, was used. In order to obtain stress–strain diagrams, the compression of the sample (caused by a linearly increasing uniaxial pressure) was measured. In all experiments a force rate $\Delta f/\Delta t = 50\,mN\,min^{-1}$ was used. Pressure was applied to the sample using a circular-shaped probe tip with diameter of 1 mm.

Applying a force rate of $5\,mN\,min^{-1}$ did not alter the results. We therefore concluded that a force rate of $50\,mN\,min^{-1}$ was small enough to maintain the mechanical equilibrium of the sample. However, the sample may show slow relaxations with relaxation times longer than the typical timescale of the performed experiments. All measurements were carried out at 20°C.

Equation (18) was used to evaluate the mechanical measurements, leaving γ_e and an offset to the strain as adjustable parameters. It is necessary to take this offset into account since the d.m.a. measured the initial dimension (thickness) of the sample l_0 by applying a small pressure. Typical strain values were low, in the order of a few per cent. Thus, in order to obtain reproducible d.m.a. results, it was very important to have homogeneous samples with well defined geometry (i.e. parallel and smooth surfaces). Only the sample with the lowest crosslink density satisfied these conditions. The other two specimens were brittle and it was not possible to adjust their shape and prepare samples which would meet the requirements mentioned above. The d.m.a. results

Table 2 Equilibrium data from swelling measurements: w_2, weight fraction of polymer; v_2, volume fraction of polymer

	w_2	v_2
SR1	0.228	0.210
SR2	0.349	0.326
SR3	0.462	0.436

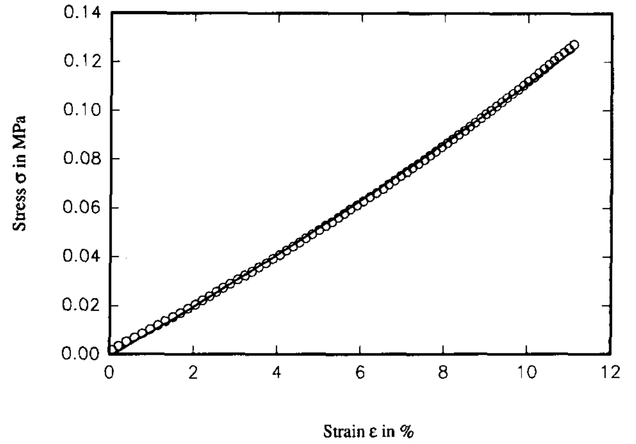

Figure 1 A typical strain–stress diagram obtained in mechanical analysis of the crosslinked poly(dimethylsiloxane) sample SR1

obtained on the samples with high crosslink density were not reproducible and are not included in this analysis. The experimental error of the results discussed was estimated to be less than 15%. A typical stress–strain diagram is shown in *Figure 1*.

RESULTS AND DISCUSSION

Prior to crosslinking studies, a sample of linear PDMS was examined by differential scanning calorimetry and d.m.a. to determine the glass transition temperature and the melting temperature of the material. Ordered phases, if present, can cause a diffusion-controlled retention process in i.g.c. experiments, and can contribute to crosslink densities as physical crosslinks. In addition, the performance temperature of the i.g.c. should be well above the glass transition temperature of the materials if the crosslink densities are to be determined. Transitions were found in the linear PDMS at −125°C (glass transition), and at −83°C (crystallization)[36].

In order to obtain the integral in equation (1), experiments have to be performed on several concentration plateaus to obtain the plot of $jV_N(c)/[(1-\psi(c))w_p]$ vs. concentration c. The retention time was used to calculate the retention volume, which was used to obtain the value of $jV_N(c)/[(1-\psi(c))w_p]$. The plot of $jV_N(c)/[(1-\psi(c))w_p]$ vs. concentration c is shown in *Figure 2* for the linear and the three crosslinked polymers. The lines in this plot were fitted by using a third order polynomial equation to perform the integration in equation (1) to obtain the value of q. In this calculation, the Antoine equation[37] was used to obtain $P_1^0(T)$ and $P_1^0(T_c)$. The value of the second virial coefficient B_{11} of n-hexane ($-1.23\,\mathrm{l\,mol^{-1}}$ at 75°C) was obtained by fitting data taken from the literature[38]. The value of q was used in equation (2) to obtain w_1.

The volume fraction of the polymer v_2 in the stationary phase was calculated under the assumption that the volume of the polymer–solvent system is additive[35]:

$$v_2 = \frac{(1-w_1)/\rho_p}{w_1/\rho_s + (1-w_1)/\rho_p} \tag{20}$$

where ρ_s is the density of the solvent. The volume fraction of solvent in the stationary phase can simply be expressed by $v_1 = 1 - v_2$.

If the contribution of the elastic energy to the chemical potential is taken into account in the expression of the interaction parameter, the following equations can be obtained from equation (15):

$$\Delta\ln a_1 = \ln[a_1^{(C)}/a_1^{(L)}] = \ln[f_1^{(C)}/f_1^{(L)}] = \rho_p V_1 \gamma_e \left[v_2^{1/3} - \frac{v_2}{2} \right] \tag{21}$$

where superscript C denotes data obtained for a crosslinked PDMS sample, and superscript L refers to data obtained for a linear PDMS sample. It follows from equation (15) that the difference for the logarithmic activities of the linear and crosslinked polymers can be written in the following form:

$$\Delta\ln a_1 = \Delta\chi v_2^2 \tag{22}$$

where the apparent Flory–Huggins interaction parameter of the network can be written in the following form:

$$\chi = \chi_{F\text{-}H} + \Delta\chi \tag{23}$$

where $\chi_{F\text{-}H}$ stands for the Flory–Huggins interaction parameter of the linear polymer, and $\Delta\chi$ denotes the contribution of the elastic energy associated with the network to the apparent interaction parameter χ.

The procedure for determining crosslink density values included i.g.c. experiments on linear and crosslinked networks at about five to ten different saturator temperatures for each sample (i.e. five to ten different probe concentrations, c, in the mobile phase). The temperature of the column was kept constant at 75°C, which is significantly higher than the highest temperature utilized in the saturator. In these experiments $V_N(c)$ values were obtained. The next step included calculations of $\ln a_1^{(L)}$ values from equation (4) by using the fugacities which were obtained from equation (5). For f_1^0 we assumed $\psi = 1$, thus $P_1 = P_1^0$ holds. From the measured $V_N(c)$ we obtained q from equation (1), then calculated w_1 with q using equation (2), v_2 from equation (20), and v_1 from the relation $v_1 + v_2 = 1$. Prior to the determination of the crosslink density the relation of $\Delta\ln a_1$ vs. $[v_2^{1/3} - v_2/2]$ must be known. This was achieved by plotting $\ln a_1^{(L)}$ vs. $[v_2^{1/3} - v_2/2]$ and of $\ln a_1^{(C)}$ vs. $[v_2^{1/3} - v_2/2]$ and subsequent fitting and subtraction. The value of γ_e was fitted from $\Delta\ln a_1$ at $v_2 = 1$, i.e. $[v_2^{1/3} - v_2/2] = 0.5$, from equation (21).

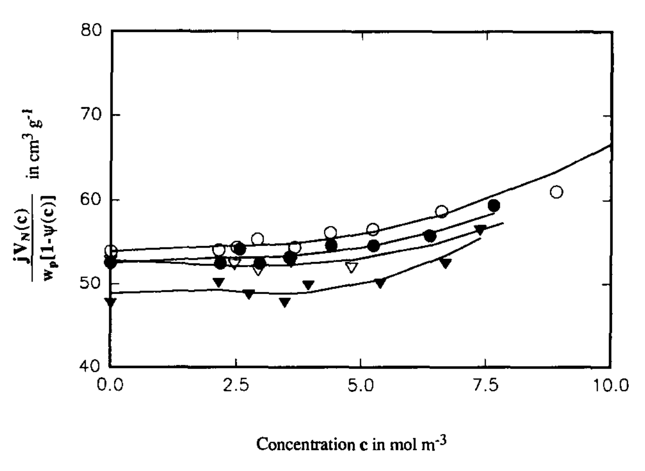

Figure 2 Plot of $jV_N(c)/[(1-\psi(c))w_p]$ vs. concentration c for crosslinked and linear PDMS samples in n-hexane at 75°C: ○, PDMS; ●, SR1; ▽, SR2; ▼, SR3. The values on the y-axis were obtained in infinite dilution i.g.c. experiments

The value of γ_e was then used to calculate the average molar mass, $\bar{M}_c$, of network chains using the following equation:

$$\bar{M}_c = \gamma_e^{-1}(1 + 2/(\gamma_e \bar{M}_n))^{-1} \qquad (24)$$

In this expression, the chain-end effect of the primary macromolecules forming the networks was taken into account with the term $2/(\gamma_e \bar{M}_n)$.

Figure 3 shows the plots of $\Delta \ln a_1$ vs. $[v_2^{1/3} - v_2/2]$ for the three networks with different crosslink densities. *Figure 4* gives the apparent Flory–Huggins χ parameters (see equation (23)) as a function of the volume fraction of the probe calculated by using equation (22). Infinite dilution i.g.c. data were obtained by following a standard protocol such as that described in ref. 1. The infinite dilution i.g.c. experiments were performed following the finite concentration measurements after the saturator was disconnected and the polymer equilibrated at the column temperature. The third order fits used included the infinite dilution data at $c=0$. On the $jV_N(c)/[(1-\psi(c))w_p]$ vs. c plots, a positive deviation from linearity was observed at low concentrations, which resulted in a slight curvature in the concentration dependence of the apparent χ parameter (see *Figure 4*).

The same samples were also studied in swelling experiments and static mechanical experiments in order to obtain the corresponding crosslink densities. The experimental values of γ_e are listed in *Table 3* together with i.g.c. results. The values of the crosslink density obtained by i.g.c. are slightly higher than the data delivered by the swelling measurements and mechanical analyses. One possible reason for the deviation between i.g.c. and swelling measurements could be related to the assumption that the Flory–Huggins interaction parameter does not change upon crosslinking, which results in the expression for the total free energy ΔG shown in equation (9). As obtained by vapour pressure measurements, this assumption is often not fulfilled[39–42]. In fact, the χ_{F-H} parameter obtained in vapour pressure measurements for crosslinked materials is usually higher than the corresponding value of the linear polymer. This makes the crosslink density value obtained in swelling measurements lower than data obtained from vapour pressure measurements. The situation in i.g.c. measurements resembles vapour pressure measurements. Therefore the γ_e values obtained in the i.g.c. method can exceed the values from swelling measurements. Another reason for the slight deviation between i.g.c. and swelling data might be that in the i.g.c. experiment, the samples were ground into very small particles. It is possible that surface effects caused by the grinding of the rubbery materials and adsorption on the gas–liquid interface were introduced. In this research the particle size ranges from 5 to 40 μm. Therefore, we can assume that these effects cause a negligible error[24]. The support used is of much larger size than the particles of rubber in the column. Therefore, the packing will not stretch the rubber. Also, as long as the work is done at low solvent concentration range, the swollen rubber will not be compressed[24].

Table 3 Crosslink density, γ_e (mol g^{-1}) and average molar mass, M_c (g mol^{-1}) of network chains

	I.g.c.		SM[a]		D.m.a.	
Sample	$\gamma_e \times 10^{-4}$	M_c	$\gamma_e \times 10^{-4}$	M_c	$\gamma_e \times 10^{-4}$	M_c
SR1	1.3(±0.2)	5400	1.0(±0.2)	6500	1.0(±0.1)	6500
SR2	3.7(±0.6)	2300	2.7(±0.5)	3100	–	–
SR3	11.6(±1.5)	830	7.1(±1.5)	1300	–	–

[a] SM, swelling measurements

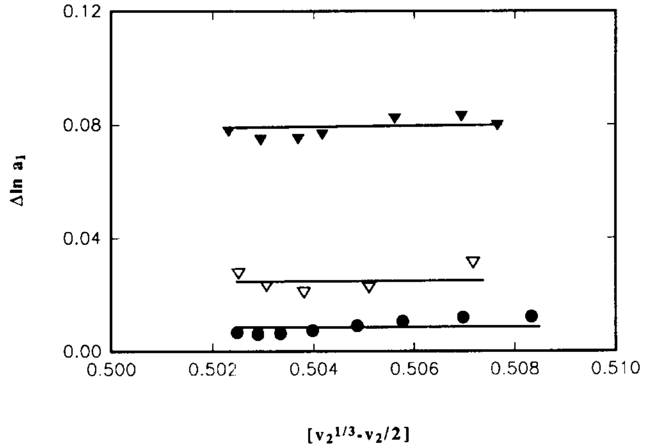

Figure 3 Plot of $\Delta \ln a_1$ vs. $[v_2^{1/3} - v_2/2]$ for the crosslinked PDMS samples in n-hexane at 75°C: ●, SR1; ▽, SR2; ▼, SR3

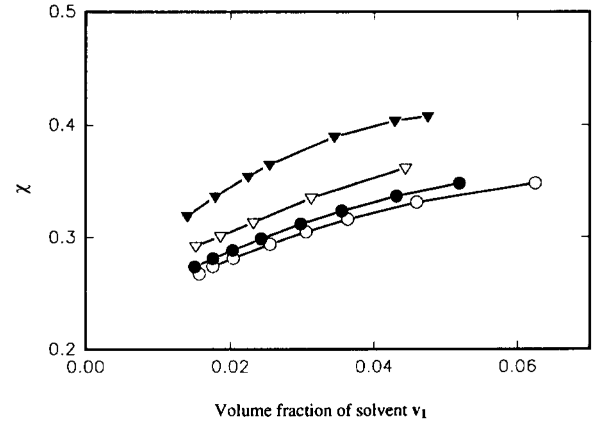

Figure 4 Plot of χ vs. volume fraction v_1 for the crosslinked and uncrosslinked PDMS samples at 75°C: ○, PDMS; ●, SR1; ▽, SR2; ▼, SR3

CONCLUSIONS

I.g.c. experiments performed on ground crosslinked polymers showed that the technique can be used to characterize networks obtained in bulk. Crosslink density values obtained by i.g.c., swelling measurements and mechanical analyses were compared. The agreement is satisfactory, although the i.g.c. method yields slightly higher values of crosslink densities than do swelling measurements. This can be explained by the change of the Flory–Huggins interaction parameter upon crosslinking in addition to the contribution related to the elastic free energy of the swollen network.

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