

Motional restrictions and chain conformation in various swollen crosslinked polystyrene gels from ^1H n.m.r. line-shape analysis

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^1H high resolution (HR), broad-line (BL) and magic-angle rotation n.m.r. spectra of polystyrene crosslinked with 2–10 mol% divinylbenzene or ethylene dimethacrylate, swollen to equilibrium in CCl_4 , CDCl_3 and benzene, were measured. The spectra were analysed as a folding of a narrow line-shape function approximated by the MAR n.m.r. spectrum, and an orientation-dependent dipolar broadening function. A molecular interpretation of the parameters obtained is presented. From MAR n.m.r. spectra, the rate of conformational transition depends on solvent, temperature and degree of crosslinking, but it remains very rapid even at 10% crosslinking. The second moment of the dipolar broadening function depends on the degree of crosslinking and is almost independent of temperature and solvent. The linear dependence of the dipolar broadening parameter on degree of crosslinking indicates that, in gels swollen to equilibrium, the statistical-average conformation of inter-crosslink chains is independent of their length, and is equal to that of linear polystyrene chains in dilute solution.

(Keywords: crosslinked polystyrene; swollen networks; chain conformation; ^1H nuclear magnetic resonance static line-shapes; ^1H magic-angle rotation nuclear magnetic resonance)

INTRODUCTION

In previous studies from this laboratory it has been shown¹ that the 'super-Lorentzian' line-shapes appearing in static ^1H n.m.r. spectra of swollen crosslinked polymer gels can be reduced to Lorentzian shape by magic-angle rotation (MAR). It has also been shown that the static line-shapes can be described as a folding of a narrow line-shape function R , near to the MAR line-shape and related to the correlation times of rapid segmental (conformational) motions, and an orientation-dependent distribution of dipolar broadening functions S , governed by residual near-static dipolar interactions. The parameter A_0 characterizing the width of the function S for a specific orientation of the inter-crosslink vector is thus a measure of the spatial restrictions of motion induced by the crosslink points.

In this paper the described approach was applied to the characterization of polystyrene networks crosslinked by ethylene dimethacrylate (EDM) and divinylbenzene (DVB) at several degrees of crosslinking, swollen to equilibrium in CCl_4 , CDCl_3 and C_6D_6 . Techniques for obtaining the dipolar broadening parameter A_0 by line-shape analysis of spectra with a single line were discussed in ref. 1. In the present analysis of polystyrene spectra, these techniques were refined to permit analysis of more complicated spectral patterns. The primary aim of this paper was the correlation of the obtained dipolar broadening parameters with the molecular parameters of the crosslinked chain.

EXPERIMENTAL

Materials

The samples of crosslinked polystyrene were prepared by suspension copolymerization of styrene with ethylene dimethacrylate (EDM) or divinylbenzene (DVB). For the latter, the content of crosslinking agent was calculated on the basis of gas chromatographic analysis of a technical DVB mixture. Polymerization initiated with azo-bis-isobutyronitrile took place at 70°C in aqueous suspension stabilized by poly(vinylpyrrolidone), with vigorous stirring; polymerization time was 12–15 h. Low-molecular weight impurities were extracted with benzene, acetone and methanol; the product was vacuum-dried. The completeness of extraction of low molecular-weight compounds was controlled by ^1H n.m.r. of the swollen gel. All crosslinking data refer to mole% of EDM or DVB in the copolymerization mixture ('nominal' degree of crosslinking).

The room temperature swelling ratio of the copolymers was determined gravimetrically after swelling of copolymer particles for 24 h and centrifugation of the excess solvent under equilibrium pressure of saturated solvent vapours. For copolymers crosslinked with 2% EDM, the swollen particles contained about 0.3 g copolymer per ml of solvent, for copolymers with 2% DVB about 0.4 g ml^{-1} with 5% EDM about 0.5 g/ml. The contents of polymer were in all cases slightly higher for CCl_4 than for the other two solvents. For the crosslink contents 8% DVB and 10% EDM, the equilibrium swelling ratios were difficult to

determine reliably because of the long equilibration times; they are roughly of the order of 1 g per ml of solvent.

For the measurement of static ^1H n.m.r. spectra, the crosslinked polymers were suspended in excess solvent directly in 5 mm n.m.r. cells and equilibrated for several days for the lightly crosslinked and up to several months for the most highly crosslinked copolymers. The cells were sealed, air bubbles were expelled and uniform sedimentation secured by several (up and down) centrifugations. Floating of the copolymer particles in the solvents of higher density was prevented by cotton plugs. In all measurements, the layer of equilibrium swollen cross-linked polymer particles was covered by a layer of solvent. The solvents used were CCl_4 (reagent grade, distilled), CDCl_3 (CEA, France, isotopic enrichment 99.8%), and C_6D_6 (IBJ, Poland, isotopic enrichment 99.2%).

Measurement of n.m.r. spectra

Static spectra of swollen networks with 2% and 5% crosslinking agent could be measured in the high-resolution (HR) regime using the PS-100 (JEOL) spectrometer operating at 100 MHz, with a 5.4 kHz sweep range. The intensities of the RF field, AF modulation and the rate of sweep were adjusted so as to reproduce correctly the line-shape both in the range of the very sharp peaks, and in the very broad wings. Great care was paid to phase adjustment. Measurements of parallel samples containing the same amount of linear and crosslinked polystyrene in the measured volume have shown that in spectra of copolymers with 2% EDM, 80–90%, and of copolymers with 2% DVB and 5% EDM about 70% of total matter are revealed in the 5.4 kHz range.

For copolymers with 8% DVB and 10% EDM, less than 50% of total matter could be detected in HR spectra. Therefore the static spectra of the copolymers with 5, 8 and 10% crosslinking agent were also recorded in the broad-line (BL) regime using a JNM-3-60 (JEOL) spectrometer operating at 60 MHz, with maximum sweep width of 10 G. By means of the spectra analyser TN-4000, for the sample with 5% EDM, the static line-shapes for mathematical analysis were constructed from the HR spectrum for the line centre and the BL spectrum for the line wings; for the samples with 8% DVB and 10% EDM from several BL spectra, measured with different values of RF field and AF modulation amplitudes, suited for optimum reproduction of line-shape in the ranges near and far from the line centre. Several runs were accumulated for each parameter setting.

MAR n.m.r. spectra were measured in a previously described apparatus² suited for variable temperature measurement. Samples were filled into the glass rotor-cells either dry with subsequent introduction of solvent, and left to stand overnight (samples with 2% EDM and DVB); the slowly-swelling samples were filled in the preswollen state, and only shortly equilibrated with excess solvent after filling. MAR n.m.r. spectra were measured with instrumental parameters (1) suited for optimum reproduction of the shape of the narrow line-shape component (function R); and (2) equal to those used to measure the peak range of the static spectrum. Spectra measured as for (1) yielded the 'true' MAR n.m.r. line width to be used in further physical considerations. Spectra measured as for (2) yielded the slightly larger MAR n.m.r. width to be used in static line-shape analysis, in search of the width parameter function S .

Analysis of line-shapes

Line-shapes in CW n.m.r. spectra, measured without sample rotation, of swollen crosslinked polymer gels are described by the relation^{1,3}

$$I(\omega - \omega_0) = \int_0^{\pi/2} \int_{-\infty}^{\infty} \left\{ R(\omega - \omega_1) S\left(\frac{\omega_1 - \omega_0}{|3\cos^2\theta - 1|}\right) \right. \\ \left. / |3\cos^2\theta - 1| \right\} d\omega_1 \sin\theta d\theta \quad (1)$$

where θ is the angle between the inter-crosslink vector and the magnetic field, the function R corresponds roughly to the MAR n.m.r. signal and the function S is the dipolar broadening function. Based on theoretical considerations^{1,4}, the shape of the function S should be Gaussian, or a distribution of Gaussians. In a previous communication¹, super-Lorentzian static line-shapes of swollen crosslinked polymer gels with only a single line were analysed both in terms of a Lorentzian and of a Gaussian dipolar broadening function S . The difference between the fit obtained by the two types of analysis was quite small. The Gaussian shape is better suited for interpretation in terms of molecular mechanics, Lorentzian shape of the function S gives slightly better fits and has the advantage of greater mathematical simplicity. When both functions R and S are of Lorentzian shape, the line-shape equation can be formulated as^{1,3}

$$I(\omega - \omega_0) = \int_0^1 \frac{A_{0L}|3\cos^2\theta - 1| + B_L}{\pi\{(\omega - \omega_0)^2 + [A_{0L}|3\cos^2\theta - 1| + B_L]^2\}} d\cos\theta \quad (2)$$

where $2B_L$ is the width at half-height of the Lorentzian function R , and $2A_{0L}$ is the width of the Lorentzian dipolar broadening functions S for $\theta = 90^\circ$.

Even in fitting the shape of a single band by means of equation (1), it is not easy to obtain unambiguous values of the parameters of the functions R and S by simple adjustment procedures, because these parameters mutually compensate to some extent. In static n.m.r. spectra of crosslinked polystyrene gels, bands of aromatic and aliphatic protons overlap, which makes an unambiguous determination of all the parameters by direct adjustment near to impossible. Therefore, some simplified procedure had to be devised. As shown in Figure 3, MAR n.m.r. spectra of polystyrene gels are well described by a system of Lorentzian lines, so that use of Lorentzian shape of the function R was indicated. Based on previous experience about the similarity of MAR n.m.r. line widths and $2B$ values obtained by line-shape adjustment⁵, the parameter $2B$ was set equal to the width at half-height of the respective line in the MAR n.m.r. spectrum ($\Delta\nu_{\text{MAR}}$). The Lorentzian shape of the function S was used for the sake of mathematical simplicity, so that equation (2) could be applied, with a single adjustable parameter, equivalent to A_{0L} , for each line. In our spectra with a system of overlapping lines, we have found it useful to determine the parameter A_{0L} characterizing the function S , by means of an auxiliary parameter $P = (\text{total band area}) : (\text{peak height})$. This parameter has the same dimension as band width, it is independent of the measurement amplitude and it can be suitably determined even for overlapping bands.

Both static (Figure 1) and MAR (Figure 3) n.m.r. spectra of polystyrene gels prepared with 2 and 5 mol% cross-linking agent exhibit a doublet band of aromatic protons at lower field and a doublet band of aliphatic protons at higher field, similarly as in n.m.r. spectra of linear polystyrene. In our analysis it was assumed that the relative intensities and the chemical shifts of these bands are the same as for linear polystyrene in the corresponding solvents. It was further assumed that the n.m.r. spectra of these polystyrene gels can be described by only two pairs of A_{OL} , B_L values, one for the aromatic protons ($A_{OL,Ar}$; $B_{L,Ar}$) and one for the aliphatic protons ($A_{OL,Al}$; $B_{L,Al}$). By means of equation (2), plots were generated relating $A_{OL,Ar}$ and P_{Ar} (total band area/aromatic peak height) and $A_{OL,Al}$ and P_{Al} (total band area/aliphatic peak height) for various values of $B_{L,Ar}$ and $B_{L,Al}$, respectively. The first trial values of A_{OL} were obtained from the experimental values of P and graphs calculated under the assumption that $A_{OL,Ar} = A_{OL,Al}$. The obtained values of $A_{OL,Ar} \neq A_{OL,Al}$ were further refined by means of correction graphs.

Swollen gels of polystyrene prepared with 8 and 10% crosslinking agent exhibit resolved bands of aromatic and aliphatic protons in MAR n.m.r. spectra, but in static spectra only one slightly asymmetric band appears (Figure 2). These spectra were analysed with the assumption that the A_{OL} , and also the B_L parameters are equal for all protons, with chemical shifts and band intensities still equal to those of uncrosslinked polystyrene.

It is estimated that from our experimental data, the values A_{OL} can be determined with an accuracy of ca. 10%.

RESULTS AND DISCUSSION

Representative static n.m.r. spectra of the studied swollen crosslinked polystyrene gels are shown in Figures 1 and 2. All static spectra exhibit typical super-Lorentzian shapes.

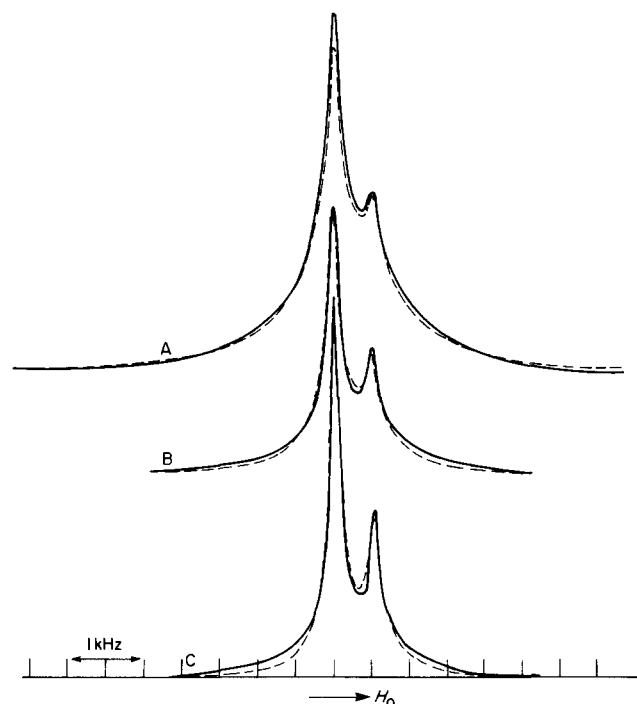


Figure 1 Static ^1H n.m.r. spectra of polystyrene gels swollen in CCl_4 measured in the high-resolution mode. Crosslinking: (A) 5 mole % EDM; (B) 2 mole % DVB; (C) 2 mole % EDM (—) experimental; (-----) calculated with the parameters given in Table 1

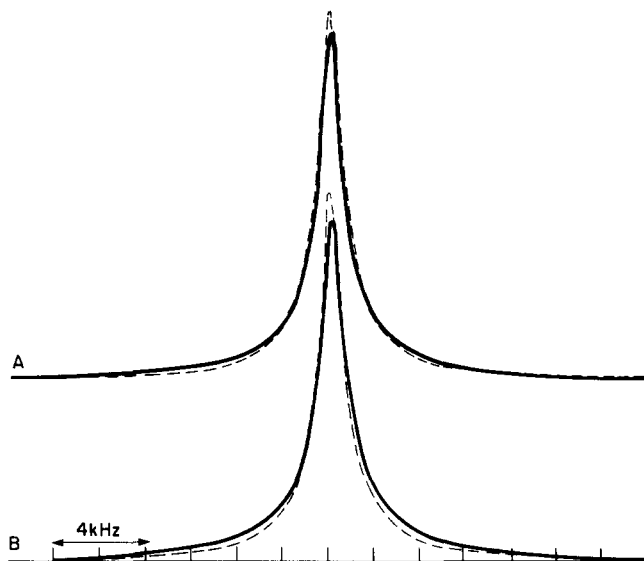


Figure 2 ^1H n.m.r. spectra of polystyrene gels swollen in CCl_4 measured in the broad-line mode. Crosslinking: (A) 8 mole % DVB; (B) 10 mole % EDM (—) experimental; (-----) calculated with the parameters given in Table 1

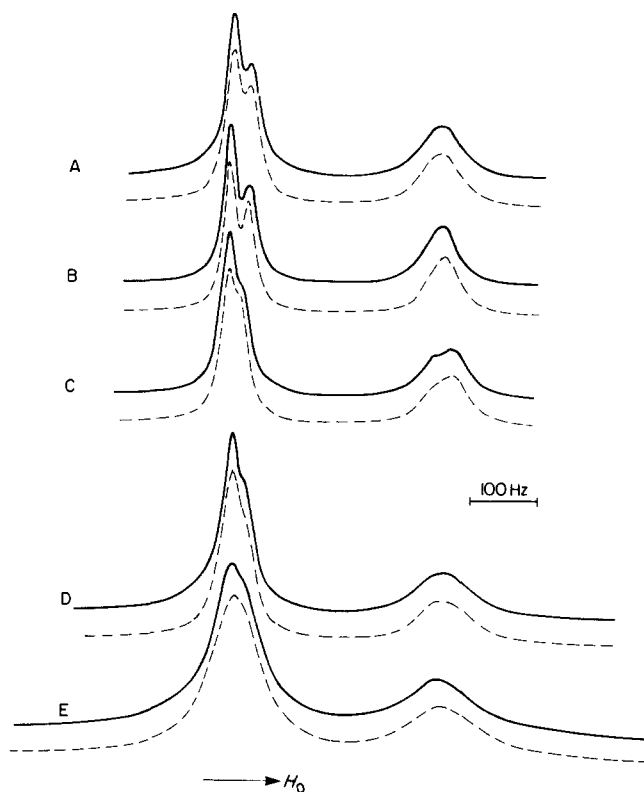


Figure 3 MAR n.m.r. spectra of polystyrene gels crosslinked with 2 mole % DVB (A,B,C); 5 mole % EDM (D); 10 mole % EDM (E). Swelling: CCl_4 (A); CDCl_3 (B,E); C_6D_6 (C,D). (—) experimental; (-----) calculated for decomposition into four Lorentzians with four (A,B,C) and two (D,E) adjusted line widths

At lower degrees of crosslinking, aromatic and aliphatic proton peaks are well resolved, irrespective of the fact that the wings extend over several kHz. In samples with the highest degree of crosslinking which have to be measured in the BL regime, this fine structure (corresponding to 0.07 G) is no longer perceptible.

In Figure 3, representative MAR n.m.r. spectra are compared with theoretical spectra calculated with parameters obtained by decomposition of experimental spec-

tra into four Lorentzians. It can be seen that the MAR n.m.r. spectra are well described in this approximation. The determined MAR n.m.r. line widths, $\Delta\nu_{\text{MAR}}$, are summarized in Table 1. In all studied samples line narrowing by MAR is very pronounced, corresponding to a factor between 20 and 100; aromatic and aliphatic protons are resolved in MAR n.m.r. spectra of all samples, with the exception of the sample with 10% EDM in CCl_4 .

The dipolar broadening parameters A_{OL}/π determined by static line-shape analysis as described in the previous section are also included in Table 1. Representative theoretical static line-shapes calculated with these parameters are included in Figures 1 and 2. Considering the complicated functional shape, line overlap and troubles with phase adjustment, the agreement is reasonable.

For polystyrene networks crosslinked with 2% EDM, swollen in CCl_4 , the temperature dependence of static and MAR n.m.r. spectra was also measured. The temperature dependence of MAR n.m.r. line width, $\Delta\nu_{\text{MAR}}$, and of the dipolar broadening parameter, A_{OL} , obtained from static line-shape analysis, is shown in Figure 4. Both for the aromatic and for the aliphatic protons, $\Delta\nu_{\text{MAR}}$ increases sharply with decreasing temperature, while A_{OL} remains practically constant. The plot of $\log \Delta\nu_{\text{MAR}}$ vs. $1/T$ is not linear, indicating that $\Delta\nu_{\text{MAR}}$ cannot be interpreted in terms of a simple activation energy. In view of the constancy of A_{OL} , the sharp increase of $\Delta\nu_{\text{MAR}}$ can also not be interpreted by contribution of permanent (lifetime \gtrsim ms) physical crosslinks. The plot of $T_2 = 1/(\Delta\nu_{\text{MAR}})$ vs. $1/T$ for polystyrene crosslinked with 2% EDM swollen in CCl_4 is practically identical with our earlier analogous plot for polystyrene crosslinked with 2% DVB and for a parallel solution of linear polystyrene of equal concentration in CCl_4 (ref. 3). From this it is evident that the motional mechanisms limiting $\Delta\nu_{\text{MAR}}$ in swollen crosslinked polystyrene (at least at the 2% crosslinking level) are the same as those limiting the n.m.r. line width in solution of the linear polymer of equal concentration, i.e. are of the character of rapid segmental (short-range conformational) motions, and that the frequencies of these motions are not much affected by crosslinking.

The values of A_{OL} for various degrees of crosslinking and various solvents are summarized in Table 1. For purposes of molecular interpretation it is suitable to transform A_{OL} to A_{OG} , the parameter characterizing the width of the dipolar broadening function S of Gaussian shape. The transformation was performed so that the peak height and area of the overall line shape $I(\omega)$ in

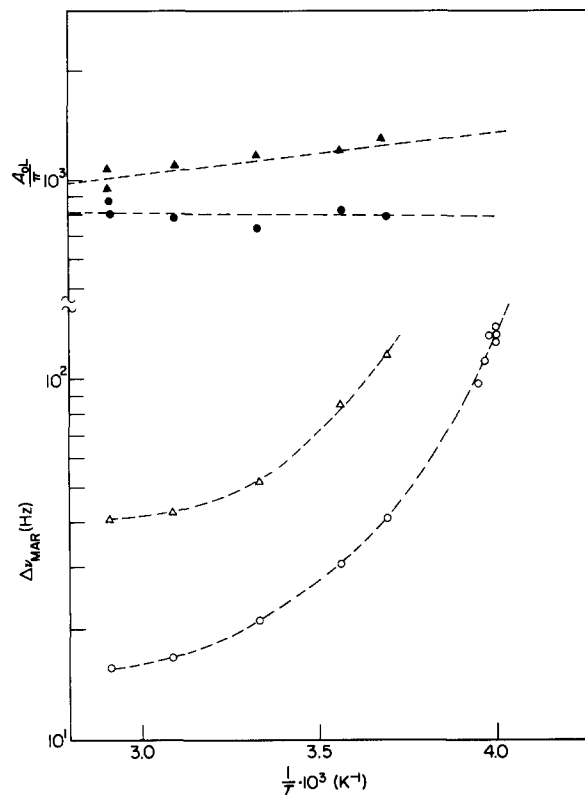


Figure 4 Temperature dependence of ^1H n.m.r. line-shape parameters for polystyrene crosslinked with 2 mole % EDM swollen in CCl_4 . Dipolar broadening parameter A_{OL}/π : (\blacktriangle); width at half-height in MAR n.m.r., $\Delta\nu_{\text{MAR}}$: (\triangle). Aromatic protons: (\bullet); aliphatic protons (\circ) (Broken lines only drawn as visual aid, do not represent calculation or theory)

Table 1 Characteristics of swollen crosslinked polystyrene gels

Crosslink (mol %)	$(1/n)^a$	Solvent	MAR $\Delta\nu_{1/2}^b$ (Hz)		arom. ^c	A_{OL}/π		$(A_{\text{OG}}/2\pi)^2/\nu_2^{2e}$ $\times 10^2$
			arom. ^c	aliph. ^c		aliph. ^c	mean ^d	
EDM 2	0.01	CCl_4	24	58	0.83	1.28	1.00	0.41
		CDCl_3	20	40	0.97	1.06	1.00	0.41
		C_6D_6	20	43	0.68	1.34	0.93	0.36
EDM 5	0.025	CCl_4	46	102	2.5	3.8	3.0	3.72
		CDCl_3	34	63	3.3	4.4	3.7	5.65
		C_6D_6	34	69	2.0	4.1	2.8	3.26
EDM 10	0.05	CCl_4	240 ^f	360 ^f	—	—	5.1 ^g	10.8
		CDCl_3	83	121	—	—	5.1 ^g	10.8
		C_6D_6	100	144	—	—	5.1 ^g	10.8
DVB 2	0.01	CCl_4	28	57	1.34	2.12	1.63	1.10
		CDCl_3	21	42	1.51	2.02	1.70	1.20
DVB 8	0.04	C_6D_6	25	45	0.98	2.32	1.48	0.91
		CCl_4	170	282	—	—	5.4 ^g	12.1
		CDCl_3	108	130	—	—	5.8 ^g	14.0
		C_6D_6	103	170	—	—	5.9 ^g	14.4

^a n = nominal number of C—C bonds between points of crosslinkage

^b ν_{whole} width at half-height

^cfrom HR measurements

^dweighted average of aromatic and aliphatic protons

^e% of experimental 2nd moment at 77 K, $\nu_2^2 = 217.5 \text{ kHz}^2$

^faromatic and aliphatic peaks unresolved; $\Delta\nu_{\text{mean}} = 284 \text{ Hz}$, estimated ratio $\Delta\nu_{\text{aliph}}/\Delta\nu_{\text{arom}} = 1.5$

^gfrom BL measurements

equation (1) was preserved. The transformation factor depends somewhat on the ratio A_{OL}/B_L . For all line-shapes analysed in this study, $A_{OG} = 1.90 \pm 0.06 A_{OL}$, and therefore the factor 1.9 was used throughout. In Figure 5 the values of A_{OG} are plotted vs. $1/n$, where n is the 'nominal' number of C-C bonds between points of crosslinkage, calculated from the mol% of crosslink agent. It appears that within the accuracy of the method, the dipolar broadening parameter does not depend on type of solvent, but differs considerably for different crosslinking agents at equal nominal degrees of crosslinking, indicating a difference in the character of the network. From the results obtained for the series of EDM crosslinked copolymers it is evident that the dependence A_{OG} on $1/n$ is linear up to relatively high degrees of crosslinking. For both EDM and DVB copolymers, the dependence of A_{OG} on $1/n$ passes through the origin of coordinates.

In our previous paper¹ it was shown that A_{OG} can be related to the residual second moment of the interacting spin system defined as

$$\omega_{2,res}^2 = \frac{1}{5} K^2 \sum_k \frac{(3\overline{\cos^2 \beta_{jk}} - 1)^2}{r_{jk}^6} = \frac{4}{5} A_{OG}^2 \quad (3)$$

where $\overline{\cos^2 \beta_{jk}}$ is the time-averaged value of the angle between the inter-nuclear vector \vec{r}_{jk} of the interacting spin system and the corresponding inter-crosslink (end-to-end) vector \vec{h}_i ; K represents a collection of basic constants¹. In deriving this relation, several simplifying assumptions were made: (a) the polymer chains between two crosslink points (inter-crosslink chains) are

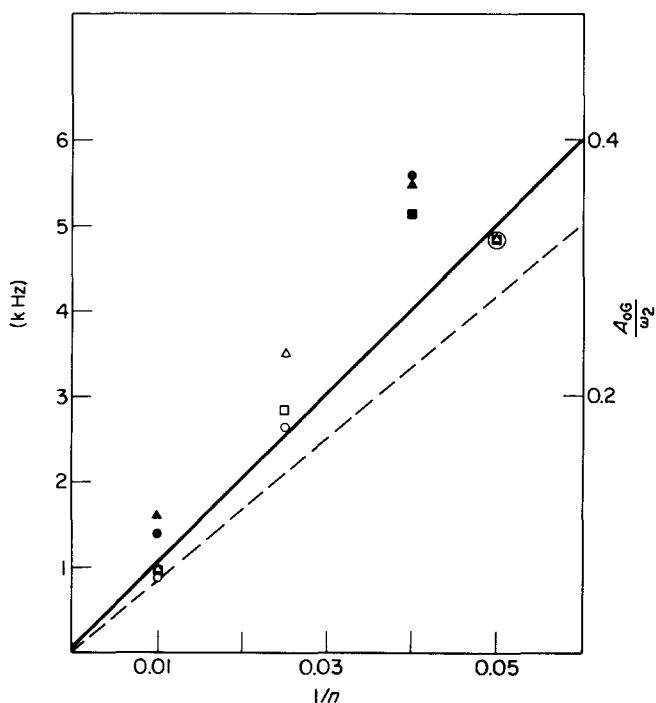


Figure 5 Plot of the dipolar broadening parameter $A_{OG} = 1.9 A_{OL}$ (left scale) and its relation to square root of rigid lattice second moment, $\omega_2 = 15$ KHz (right scale), for polystyrene networks swollen to equilibrium, vs. $1/n$, the reciprocal 'nominal' number of C-C bonds between points of crosslinkage. Solvent: CCl_4 (\square); $CDCl_3$ (\triangle); C_6D_6 (\circ). Crosslinked with EDM (\square , \triangle); DVB (\blacksquare , \blacktriangle). (—) linear fit for gels crosslinked with EDM; (---) plot of the theoretical value of $\frac{\omega_{2,res}^2}{\omega_2^2} \left(\frac{5}{4}\right)^{1/2}$ for $(3\overline{\cos^2 \beta} - 1) = 10/n_0$

so long that the contribution of monomer units near to the crosslink points can be neglected, and all monomer units (interacting spin systems) can be treated as equal; (b) the network is swollen to such an extent that inter-chain interactions can be neglected; (c) all intercrosslink chains exhibit similar behaviour.

The angular term in the sum of equation (3) is a measure of spatial restrictions of motion induced by the crosslink points. For motion isotropic in space, $(3\overline{\cos^2 \beta_{jk}} - 1) = 0$, and therefore $\omega_{2,res}^2$ and A_{OG}^2 should also be zero. When the interacting spin system is represented by a proton pair H_a , H_b , with a constant internuclear distance r_{ab} , the residual 2nd moment $\omega_{2,res}^2$ can be simply related to the rigid-lattice 2nd moment $\omega_2^2 = (4/5)K^2 r_{ab}^{-6}$:

$$\begin{aligned} \omega_{2,res}^2 &= (1/5)K^2 r_{ab}^{-6} (3\overline{\cos^2 \beta_{ab}} - 1)^2 \\ &= (1/4)\omega_2^2 (3\overline{\cos^2 \beta_{ab}} - 1)^2 \end{aligned} \quad (4)$$

For a more complicated interacting spin system, such a simple relation cannot be formulated explicitly because of the impossibility to separate the angular from the r terms in equation (3). Nevertheless, the expression of $\omega_{2,res}^2$ as % of the rigid-lattice 2nd moment gives some quantitative insight into the extent of spatial restrictions of motion, and the corresponding numbers are therefore included in Table 1. With the experimental⁶ value of $\omega_2^2 = 12$ G² for polystyrene at 77 K, $\omega_{2,res}^2$ values range from less than 1% for copolymers crosslinked with 2% EDM, up to ca. 10% for copolymers with 10% EDM, and 14% for copolymers with 8% DVB.

Results of MAR n.m.r. measurements have shown that the motional process which has led to the reduction of the rigid-lattice second moment to these very low values is of the character of rapid segmental motions, of correlation time $\tau_c \ll 1/(\omega_2^2)^{1/2}$. In this situation the time average of $\overline{\cos^2 \beta_{ab}}$ may be substituted by the statistical average over possible conformations of the intercrosslink chain, which can be obtained by well known methods^{7,8}. For swollen polymer networks with low degrees of crosslinking (less than 2 mol% crosslinking agent), such approach was used by Gotlib *et al.*⁹ in relating the T_2 relaxation time values measured in the so called plateau region to degree of crosslinking, with the application of the freely-jointed model of the polymer chain. For more highly crosslinked networks, studied by us, such model is clearly inapplicable, and an attempt was made to correlate our experimental data with a model respecting the bond rotational potentials. The corresponding expressions for sufficiently large n_0 have the general form⁷

$$\begin{aligned} (3\overline{\cos^2 \beta} - 1)_i &= \frac{1}{n_0} \left(a_i \cot^2 \alpha \frac{1+\eta}{1-\eta} + b_i \frac{\gamma}{1-\gamma} + c_i \frac{\eta}{1-\eta^2} \right. \\ &\quad \left. + d_i \frac{\cos \alpha}{\sin^2 \alpha} \frac{1+\eta}{1-\eta} \right) \end{aligned} \quad (5)$$

where n_0 is the real number of C-C bonds between points of crosslinkage, α is the valence bond angle, $\eta = \cos \phi$, $\gamma = \cos^2 \phi$ and ϕ is the bond rotational angle, and the factors $a_i \dots d_i$ depend on the orientation of the inter-nuclear vector with respect to a coordinate system x, y, z defined by the backbone $\text{C}-\text{C}-\text{C}$ bonds of the respective segment. For various orientations these factors differ by

± 2 at most. For a spin pair oriented perpendicularly to the plane of the neighbouring C–C bonds (e.g. methylene group protons which contribute about one half of the intragroup second moment of polystyrene).

$$a_y = b_y = -\frac{4}{5}, \quad c_y = -\frac{12}{5} \quad \text{and} \quad d_y = -\frac{6}{5}$$

The parameter η can be estimated from the characteristic ratio of atactic polystyrene⁸,

$$C_\infty = \frac{1+\eta}{1-\eta} \cdot \frac{1+\cos\alpha}{1-\cos\alpha} = 10$$

For tetrahedral angles, $(1+\cos\alpha)/(1-\cos\alpha)=2$, therefore $(1+\eta)/(1-\eta)=5$ and $\eta=2/3$. The value of γ was estimated assuming⁸ a fraction of s units 0.6, of conformation tt , and a fraction of i units 0.4, of conformation tg , yielding $\gamma=0.85$. With these numbers, $(3\cos^2\beta_{ab}-1)=-10.17/n_0$. This relation, which is to be regarded as a very rough estimate of the largest contribution to the second moment of polystyrene, is plotted in *Figure 5*, to be compared with experimental data in the sense of equation (4). The order-of-magnitude agreement of experimental and calculated data indicates that the conformation of inter-crosslink chains in the equilibrium-swollen state is similar to that of free polymer molecules of equal length. However, absolute values should not be taken too seriously, due to the approximations involved. Also, the difference in data for EDM and DVB crosslinked networks probably reflects a difference in network structure at equal nominal mol% crosslink agent. More important is the similarity of functional behaviour, i.e. linearity of plot of experimental data and their passing through the origin. The latter aspect indicates correctness of our analysis of experimental data. A linear plot of A_{OL} or A_{OG} vs. $1/n$ implies constancy of the expression in the brackets in equation (5). Constancy of valence angles being granted, a constant value of the bracket in equation (5) indicates constant values of the rotational angle functions η and γ . The only other possibility is accidental compensation of the changes of angular functions at changing n in the contributions for various spin pairs. This we regard as highly improbable. Consequently the linear plot of A_{OG} vs. $1/n$ is interpreted so that in networks swollen to equilibrium, in the whole studied range of crosslinking, the statistical average conformation of polystyrene chains is equal to

that of linear polystyrene in the same solvent. This finding parallels some recent observations by SANS concerning swollen polystyrene¹⁰ and poly(dimethylsiloxane)¹¹ networks.

By the above analysis we have shown that the parameters of the dipolar broadening function obtained by analysis of line shapes carry information on the equilibrium conformation of inter-crosslink chains. The Δv_{MAR} values, on the other hand, carry information on correlation times. Qualitatively, Δv_{MAR} values are supposed to be limited by the slowest of those motional modes which are more rapid than the spinning frequency.

Table 1 reveals that not only A_{OL} , but also Δv_{MAR} values increase with degree of crosslinking. Contrary to the A_{OL} , which are practically independent of type of solvent, Δv_{MAR} differ for different solvents used. The largest values appear in CCl_4 , and also their increase with crosslinking is the steepest in this solvent. An increase of Δv_{MAR} values probably indicates a broadening of the distribution of correlation times in the direction of slower modes. This effect would be expected to be more pronounced in a poor solvent such as CCl_4 . The observed increase of Δv_{MAR} with increased crosslinking does not contradict the proposed constancy of conformation. A change of height and distribution of potential barriers, affecting correlation times, does not automatically imply a change of height and distribution of energy minima, determining the equilibrium conformation.

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