Dynamic structure of swollen crosslinked poly(ethylene oxide) gels from n.m.r. line-shape analysis and magic angle rotation n.m.r.

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Chemically crosslinked poly(ethylene oxide) gels swollen to equilibrium in $CDCl_3$ (22.3 w/w% of polymer) and CCl_4 (77.5 w/w% of polymer) were characterized by combination of the results of ^1H n.m.r. spectra measured with magic angle rotation (*MAR*–n.m.r.) and numerical analysis of static ^1H n.m.r. line shapes. From *MAR*–n.m.r., activation energies of rapid segmental motions were found to be 1.7 ± 0.3 kcal mol^{-1} in $CDCl_3$ and 9.4 ± 0.6 kcal mol^{-1} in CCl_4. Static line-shape analysis yields a parameter which characterizes the deviation of segmental motions from isotropy in space. This parameter was found to be independent of temperature and equal in both systems.

INTRODUCTION

Swollen networks of chemically crosslinked polymers are of some interest in both technical and medical applications. The properties of these systems are governed both by the rapid segmental motions which are comparable to those of related linear polymers in semi-dilute solutions, and by the motional restrictions imposed by the existence of the crosslink points. In previous communications[1,2] it has been shown that both these aspects are manifested in the shapes of ^1H n.m.r. lines of such systems, and that they can be separated by measurement with magic angle rotation (*MAR*-n.m.r.). While the dynamics of rapid segmental motions can be characterized by analysis of the *MAR*-n.m.r. spectra, a line-shape function has been proposed[2,3] permitting characterization of the motional restrictions from line shapes measured without sample rotation. In the present paper the method of line shape analysis has been refined so as to yield parameters with well defined confidence limits from lines of very widely differing shapes. Crosslinked poly(ethylene oxide) (PEO), with essentially only a single n.m.r. signal, has been selected as the model network, in order to avoid complications arising from bands overlapping. A physical interpretation of the obtained line-shape parameters is sought, with the aim of characterizing the dynamics of the studied network in a good ($CDCl_3$) and poor (CCl_4) swelling agent.

EXPERIMENTAL

Crosslinked PEO was the product of polycondensation of PEO (*MW* 600) with toluene diisocyanate (TDI), crosslinked by reaction with trimethylolpropane (TMP), in the ratio 0.2 TPM OH groups per 1 OH of the original PEO. The resulting polymer gels, swollen to equilibrium in $CHCl_3$ contained 22.3, in CCl_4 77.5% (w/w) of polymer at room temperature. The temperature dependence of equilibrium swelling was determined by microscopic measurement of volume changes of a polymer block. In the studied temperature range, the volume changed less than 2% in CCl_4, and less than 10% in $CDCl_3$. For measurement of n.m.r. spectra, the polymer gel was disintegrated to small pieces and suspended in excess solvent to ensure equilibrium swelling in the sealed n.m.r. cell.

For the determination of standard band shapes, ^1H n.m.r. spectra were measured on the PS-100 (JEOL) spectrometer at 100 MHz, without sample spinning, with external lock in the field sweep mode. With a sweep width of 5400 Hz, the scanning speed was adjusted to the shape of the curve, not exceeding 5 Hz s^{-1} in the peak centre, but more rapid in the wings, in order to avoid excessive measuring times and possible errors resulting from phase fluctuations. For the determination of a correct base line, parallel spectra were also measured in the wide sweep mode, without lock, using 8 kHz modulation side bands for field scale calibration. The studied temperature range was limited to such values where the main band and side band were separated by a horizontal plateau in this measurement. This confined the studied line shapes to such for which (a) the base line could be determined correctly, (b) the technically accessible spinning frequency was sufficient for line narrowing in *MAR*-n.m.r. Temperatures were determined from chemical shifts in methanol or ethylene glycol spectra[4] measured immediately before and after the studied sample.

MAR-n.m.r. spectra were measured on the JNM-3-60 (JEOL) n.m.r. spectrometer at 60 MHz, using a variable-temperature *MAR*-n.m.r. probe head and glass rotor-cells described elsewhere[5]. Spinning frequencies were calibrated by means of spinning side bands, the chemical shift scale by interpolation between modulation side bands and averaging for several upfield and downfield

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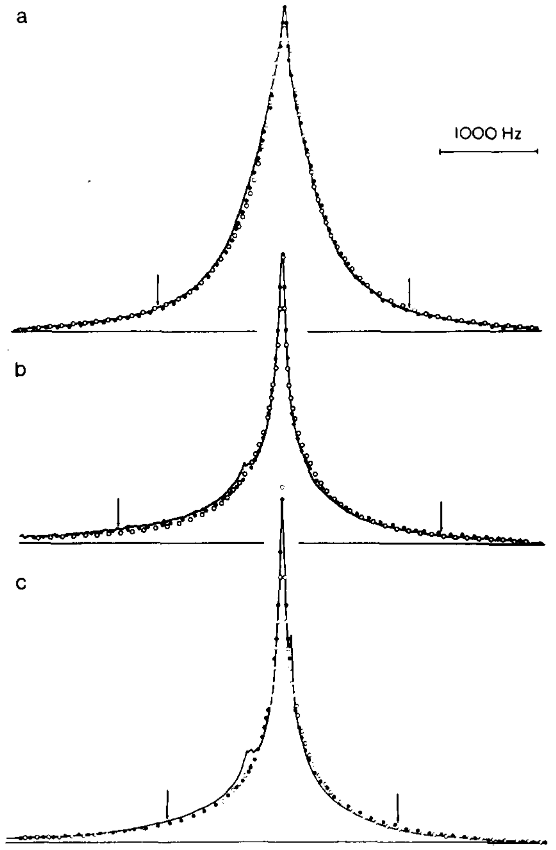

Figure 1 Static ^{1}H n.m.r. spectra of crosslinked poly(ethylene oxide) gels swollen to equilibrium. (a) in CCl_4, 23°C; (b) in $CDCl_3$, −13°C; (c) in $CDCl_3$, +50°C. ~~~ experimental; ● idealized experimental; ○ calculated; arrows indicate the limit of range used for parameter fitting (corresponds to 80% of total peak area)

runs, and temperatures by relating thermocouple readings to chemical shifts of ethanol measured under comparable spinning conditions.

^{13}C n.m.r. spectra were measured on the FX-60 (JEOL) n.m.r. spectrometer at 15 MHz, with proton noise decoupling. For removal of the ^{13}C–^1H dipolar coupling, decoupling power up to the available maximum ($\gamma H_2/2\pi$ ~5 kHz) was applied. Care was taken to prevent heating of the sample due to the high irradiation power used. T_1 values were measured at 25 and 60°C for samples in both solvents. For spectra measurements, $\pi/2$ pulses and pulse repetition rates exceeding 5 T_1 were applied.

RESULTS

^{1}H n.m.r. spectra

^{1}H n.m.r. spectra of crosslinked PEO gels swollen to equilibrium in $CDCl_3$ and CCl_4, measured without sample spinning, are shown in *Figure* 1. Particularly for the gels swollen in $CDCl_3$, the peculiar line shape is conspicuous, with very sharp peaks and very broad wings, similar to that observed in swollen gels of crosslinked polystyrene. The shape of the PEO line is distorted by the peak of the TDI methyl group at the high-field flank, and by the aromatic proton band of TDI at the low-field flank. According to the polymer composition, the TDI lines should constitute ~10% of the total proton peak area. The multiplets of the protons of TMP, contributing ~3.5% of total peak area, are not resolved in the spectra. The same is true of the PEO CH_2 groups neighbouring with the TDI units which are expected to be shifted downfield from the main CH_2 peak of PEO by ~0.3 ppm. As a result of all these effects, the experimental line shape is not quite regular, and not quite symmetrical. The lack of symmetry is caused by the difficulty in choosing a perfect phase correction in lines with such extremely broad wings as in the spectra discussed. An effect of the physical inhomogeneity of the samples might also be present. Because of all these reasons, in the numerical analysis idealized line shapes were used, symmetrized with respect to the main PEO CH_2 peak, and omitting the resolved TDI methyl and aromatic resonances, as indicated by the black dots in *Figure* 1 (only a part of the points actually used in the analysis are shown in the *Figure*).

In ^{1}H n.m.r. spectra measured without sample rotation, widths at half height, $\Delta\nu_{1/2}$, vary between 200 and 160 Hz (−13 to +50°C) for PEO gels swollen in $CDCl_3$ (*Figure 2a*) and between 700 and 380 Hz (+23 to +50°C) for PEO gels swollen in CCl_4 (*Figure 2b*) in the measured temperature range. For qualitative characterization of line shapes it was found useful to relate widths at 10, 25 and 75% of maximum height to width at half height, and compare with the corresponding numbers for Lorentzian and Gaussian shape. Such line-shape characteristics are summarized in *Table* 1. From this table it is seen that the line shape for gels swollen in CCl_4 does not differ much from Lorentzian shape, in spite of larger total line width, whereas for gels swollen in $CDCl_3$, the deviation from Lorentzian shape is striking. For both solvents the line shapes are practically independent of temperature, in spite of considerable temperature variation of line width.

^{1}H MAR-n.m.r. spectra

By magic angle spinning, lines of the PEO gels in both solvents undergo substantial narrowing (*Figures 2a, b*),

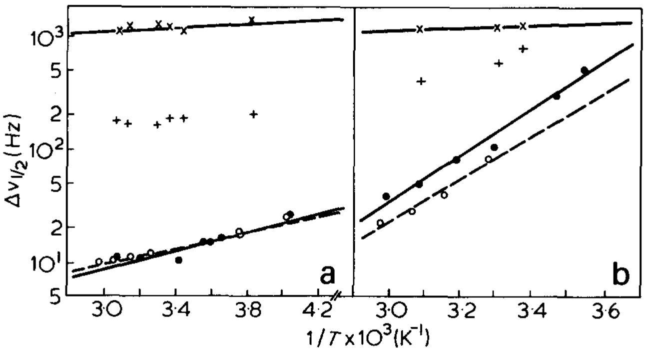

Figure 2 Temperature dependence of line width at half-height in n.m.r. spectra of poly(ethylene oxide) gels swollen to equilibrium (a) in $CDCl_3$; (b) in CCl_4. + ^{1}H static; ● ^{1}H, *MAR*; × parameter 2*A* from ^{1}H static line-shape analysis; ○ ^{13}C, static, with strong proton decoupling

Table 1 ^{1}H n.m.r. static line shapes of swollen PEO gels

	$\Delta\nu_I/\Delta\nu_{1/2}$*			
I/I_{max}	$CDCl_3$†	CCl_4†	Lorentzian	Gaussian
0.75	0.39 ± 0.07	0.34 ± 0.03	0.58	0.64
0.50	1	1	1	1
0.25	3.16 ± 0.10	2.05 ± 0.05	1.73	1.40
0.10	9.04 ± 0.46	3.77 ± 0.16	3.00	1.82

* The ratio of width at the indicated intensity to width at half-height
† Standard deviation for shapes measured in the temperature range −13°C to +50°C in $CDCl_3$ and +23°C to +50°C in CCl_4

indicating the presence of near-static dipolar interactions. The residual line width amounts to 5–10% of static line width in $CDCl_3$, where deviation of the static line shape from Lorentzian is large, and to 10–50% in CCl_4, where the deviation of static line shape from Lorentzian is not conspicuous. The dependence of *MAR*–n.m.r. parameters on spinning speed was followed for spinning frequencies between 650–4500 Hz. The measured width at half height of *MAR*–n.m.r. lines, $\Delta\nu_{1/2,MAR}$, was constant in this frequency range, the total integrated intensity of the lines increased up to 2 kHz and was constant at higher spinning speeds, indicating that at spinning frequencies above 2 kHz the line-narrowing process is complete. All *MAR*–n.m.r. spectra further discussed were obtained with spinning speeds of 2.5–3 kHz. Line shapes in *MAR*–n.m.r. spectra thus obtained are close to Lorentzian and independent of temperature.

The temperature dependence of $\Delta\nu_{1/2,MAR}$ of PEO gels swollen in $CDCl_3$ and CCl_4 is shown in *Figures 2a, b*. In both cases, this dependence is reasonably linear in a semilogarithmic plot, with a slope steeper than that of the static line width.

^{13}C *n.m.r. spectra*

In ^{13}C n.m.r. spectra, near-static dipolar interactions are removed by proton decoupling[6], within the limits given by the decoupling field strength. If the decoupling field strength is high enough with respect to the near-static dipolar field, and the residual anisotropy of chemical shifts is sufficiently low, the parameters of ^{13}C n.m.r. spectra should be characteristic of the rapid segmental motions of the polymer gel, similarly as *MAR*–n.m.r. parameters. With the studied swollen PEO gels, ^{13}C n.m.r. shapes were recorded for several values of irradiating field strength and band width. It was found that line width remains constant, with line shape nearly Lorentzian, for irradiation power above 70 db/15 W at 1 kHz bandwidth $\left(\frac{\gamma H_2}{2\pi} > 5 \text{ kHz}\right)$. The ^{13}C n.m.r. data discussed below were obtained under these measuring conditions.

The temperature dependence of the widths of ^{13}C n.m.r. lines, $\Delta\nu_{1/2,C}$, of PEO gels swollen in $CDCl_3$ and CCl_4 is shown in *Figures 2a, b*. Similarly as in *MAR*–n.m.r., in a semi-logarithmic plot this dependence is linear in both solvents, with slopes practically identical with those of the *MAR*–n.m.r. data.

Static line-shape analysis

By the *MAR*–n.m.r. measurement described above, the presence of near-static dipolar interactions in the studied systems was established. Therefore the static line shapes should be described by a convolution of the Lorentzian line revealed by *MAR*, with some broadening function. Convolution with orientation-independent broadening functions of Lorentzian or Gaussian shape would lead to overall Lorentzian or Voigt shapes, respectively. For the studied gels, these are readily excluded by inspection of *Table* 1. The width of the wings and sharpness of peaks suggested the application of an orientation-dependent dipolar broadening function *G* introduced originally by Wennerström[3] and used by us previously in the line-shape equation[2]

$$L(\nu-\nu_0)=$$
$$\int_0^1\int_{-\infty}^{+\infty}\left\{S(\nu-\nu_1)G\left[\frac{\nu_1-\nu_0}{|3\cos^2\theta-1|}\right]\Big/(3\cos^2\theta-1)\right\}d\nu_1 d\cos\theta \tag{1}$$

where the function *S* should be of Lorentzian shape, of width corresponding to that of the *MAR*–n.m.r. experiment, θ is the angle between a specified direction and the static magnetic field, and the specified directions should be distributed at random. A plot of $L(\nu_i-\nu_o)$vs. $1/(\nu_i-\nu_o)^2$ favours application of Lorentzian shape also for the function *G*, permitting use of the explicit equation[2]:

$$L(\nu-\nu_o)=\int_0^1\frac{A|3\cos^2\theta-1|+B}{\pi\{(\nu-\nu_o)^2+[A|3\cos^2\theta-1|+B]^2\}}d\cos\theta, \tag{2}$$

where $2B$ is $\Delta\nu_{1/2,MAR}$ and $2A$ is the width at half-height of the dipolar broadening function $G[(\nu-\nu_o)/|3\cos^2\theta-1|]$ for $\theta=90°$.

For ideal line shape, both parameters *A* and *B* should be obtainable by fitting the function (2) to experimental line shape. However, the parameter *B* is governed mainly by the shape of the peak centre, which in the static spectrum is very sensitive to various irregularities of structure, like the presence of small amounts of uncrosslinked polymer, free chain ends of the network, freely-rotating methyls of the crosslink groups, etc. Therefore we found it much more reliable to derive the parameter *B* from *MAR*–n.m.r. spectra where all of the measured matter is reflected in a narrow peak to which the irregularities contribute only a few percent. Using equation (2) and the values of *B* from *MAR*–n.m.r., the parameters *A* of the broadening function were adjusted by a least squares fit of experimental and calculated spectra, minimizing the value of

$$[(y_o^{exp}-y_o^{calc})/w_o]^2/2+\sum_{i=1}[(y_i^{exp}-y_i^{calc})/w_i]^2,$$

where the y_o, y_i are intensities and the w_o, w_i are weight functions of points of the experimental spectrum. Adjustment to absolute accuracy of measured intensities ($w_i=1$) favours the peak centre, with a poorer fit in the wings; adjustment to relative accuracy ($w_i=y_i^{exp}$) favours the wings, with poorer fit in the peak centre. As the peak centre suffers from the structural imperfections discussed above, and in the wings intensity measurements are inaccurate because of low *S/N* and uncertainty of phase adjustment, weight functions were sought favouring the intermediate range, with optimum measuring accuracy, resulting in a good fit for the whole spectrum. The function $w_i=\frac{y_i^{exp}}{2}+y_i^{exp}$ was found to meet these requirements and was applied for adjustment of the broadening parameters *A* with all spectra in this study. The statistical weight of the wings was further suppressed by fitting the experimental points with a step of 20 Hz up to the $(\nu_i-\nu_o)$ value for which the integrated intensity of the spectrum reached 60% of total peak area, and with a step of 40 Hz in the range between 60 and 80% of total peak area. Points

Table 2 Static dipolar broadening parameters $2A$ (Hz) from line-shape analysis with $2B$ values from *MAR* n.m.r.

	$CDCl_3$		CCl_4	
t (°C)	$2B$*	$2A$	$2B$*	$2A$
−13	18.3	1237	–	–
17	13.0	1084	–	–
23	12.2	1133	180	1096
29	11.5	1124	130	1103
42	10.2	1140	–	–
50	9.5	1057	48	1008

*Values obtained by linear regression of experimental data ($\ln \Delta\nu_{1/2,MAR}$ vs. $1/T$)

beyond this range were not used in the least-squares adjustment of parameter A. This truncation limit was selected so as to include all the studied systems in the 5400 Hz measuring range. The integrated peak areas were calculated by the trapezoidal method, and the total peak area was corrected for the wings beyond the measured range (5400 Hz) by assuming that in this part of the spectrum intensity is inversely proportional to $(\nu_i - \nu_o)^2$. The goodness of fit obtained by this procedure for spectra of very differing shape is demonstrated in *Figure* 1 (only a part of the calculated points are shown). The resulting parameters are summarized in *Table* 2 and plotted in *Figures* 2*a* and *b*. These data are remarkable for the negligible variation of the parameter A both with temperature and with solvent.

In order to establish the confidence limits of the obtained values of A, their dependence on the accuracy of the B values from *MAR* and on the truncation limits of the analyzed spectrum was checked. An increase of the truncation limit from 80 to 90% of total peak area leads in the case of $CDCl_3$ solvent to an increase of A by 2.6%, in the case of the CCl_4 solvent to a decrease of A by 5%. The dependence of the uncertainty in A, due to error in B, is shown in *Figure* 3. The standard deviation of *MAR*-n.m.r. linewidths in $CDCl_3$ solvent, where lines are very narrow, was of the order of ±20%, for the somewhat broader lines in CCl_4 solvent of the order of ±10%. Data of *Figure* 3 therefore indicate an uncertainty of the A values equal to or better than 5% in all analyzed cases. The values $2A$ in *Table* 2, of the order of 1000 Hz, may be regarded as accurate within ±50 Hz.

DISCUSSION

As follows from theoretical considerations, at sufficient spinning speeds the line width in *MAR*-n.m.r. spectra should be proportional to the correlation frequency of the rapid motions which have led to the partial line narrowing in the static spectrum[7,8]. From the temperature dependence of $\Delta\nu_{1/2,MAR}$ the activation energy of these motions can be obtained using the relation $\Delta E_{MAR} = (R\Delta\ln\tau_c)/(\Delta(1/T)) = (R\Delta\ln\Delta\nu_{1/2MAR})/(\Delta(1/T))$. From the data plotted in *Figures* 2 and 3, ΔE_{MAR} of the PEO network in $CDCl_3$ and CCl_4 solvent is 1.7±0.3 and 9.4 ±0.6 kcal mol^{-1}, respectively.

As the absolute values of ^{13}C line widths $\Delta\nu_{1/2} = \frac{1}{\pi T_2}$ fall in the range of the non-linear portion of the $(\pi T_2)^{-1}$ vs. τ_c plot, $\Delta E_{13C} = (R\Delta\ln\tau_c)/(\Delta(1/T)) \neq (R\Delta\ln\Delta\nu_{1/2,C})/(\Delta(1/T))$ and the ΔE_{13C} values are higher than the ΔE_{MAR} values (2.3 ±0.2 kcal mol^{-1} in $CDCl_3$ and 15.8±1.0 kcal mol^{-1} in CCl_4). As the ^{13}C line widths (which are of the order of 10 Hz) may be affected by sample inhomogeneity, and possibly also by small residual anisotropy of chemical shifts, we regard the ΔE_{13C} values as less reliable than ΔE_{MAR}, where the effects of sample inhomogeneity and chemical shift anisotropy are removed. The identical slopes of the *MAR* and ^{13}C $\ln\Delta\nu_{1/2}$ vs. $1/T$ plots for both solvents suggest that the motional mechanisms determining the temperature dependence of the line widths in *MAR* and ^{13}C-n.m.r. spectra are very similar.

Because of the presence of TDI units, a direct comparison between the n.m.r. parameters of our PEO network and those of linear PEO[9,10] is not possible. Nevertheless, similarly as for linear PEO, also in the case of our PEO network differences of local conformation and viscosity, and also of concentration are assumed to be responsible for the large difference between the ΔE_{MAR} values in $CDCl_3$ and CCl_4.

In benzene solution, ^1H T_1 relaxation of linear PEO was shown[11] to be well described in terms of the isotropic motional model, to be predominantly of intragroup origin, and dominated by the geminal proton interaction. Therefore we assume that also in the interpretation of the results of our static line shape analysis, to a first approximation the interacting proton pair model may be applied. For an interacting proton pair, the motional model corresponding to the situation described by equations (1), and (2), is shown in *Figure* 4. Here the axis z is identical with the direction of H_o, the axis z' represents a preferred direction, the existence of which in a swollen crosslinked gel is a consequence of the fixation of chain ends at the crosslink points, and β is the angle between the interproton vector $\vec{r}$ and the direction z'. In the derivation of equation (1) it has been assumed[3], that the components of r in the plane perpendicular to z' average to zero as a consequence of motions that are rapid on the n.m.r. scale. In such a case substituting the angles β and θ for the angle α, the residual dipolar field can be described by the equation

$$H_{loc} = \pm\Delta H[(1/2)(3\cos^2\theta - 1)(3\overline{\cos^2\beta} - 1)]$$

where $\Delta H = 3\gamma h/4r^3$ and $\overline{\cos^2\beta}$ designates the value time-averaged on the n.m.r. scale. For motion isotropic in space, the value of $(3\overline{\cos^2\beta} - 1)$ is equal to 0, and $\overline{\cos^2\beta}$

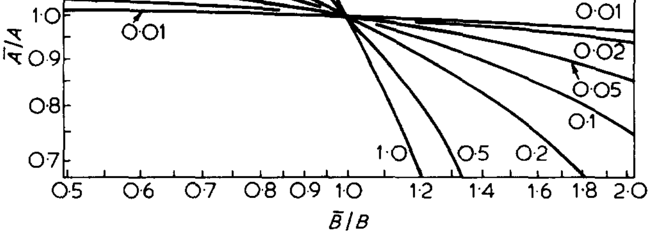

Figure 3 Dependence of relative accuracy of A upon relative accuracy of B, for various values of the ratio B/A. $\overline{B}$—inaccurate value of parameter B; $\overline{A}$—value of parameter A giving best fit, for fixed $\overline{B}$, with the line shape $f(B, A)$ of equation (2). $\overline{B}/B$ and $\overline{A}/A$ are plotted on logarithmic scale

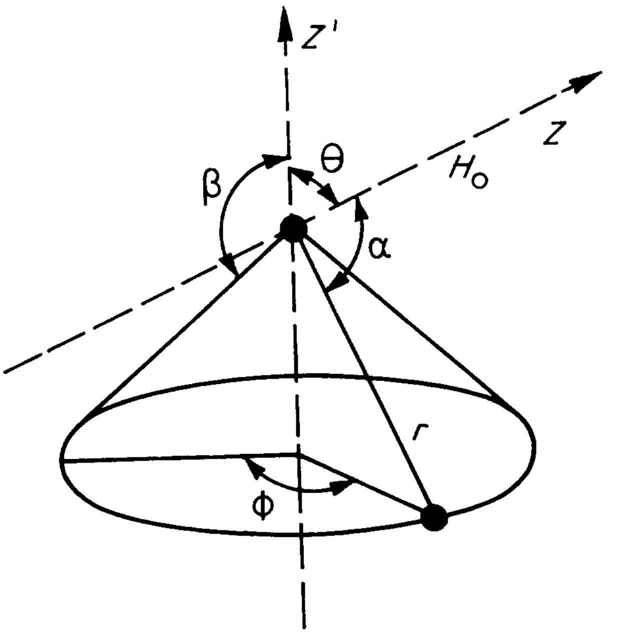

Figure 4 Motional model of equations (1), (2) for an interacting nuclear pair

$=1/3$ (the 'magic angle' value). In terms of this description, the parameter A corresponds to

$$(1/2)\Delta H(3\,\overline{\cos^2\beta}-1).$$

As a consequence, the degree of spatial anisotropy of motion may be visualized as deviation of $\overline{\cos^2\beta}$ from 1/3. In the swollen PEO network, the situation certainly is not so simple. Firstly, the basic spin groups to be dealt with comprise at least four-spin systems, with a dominant geminal CH_2 proton interaction[11]. Secondly, the spatial anisotropy of motion is not as sharply defined as in the depicted model. Owing to crosslinking there is a specific direction z' for each proton pair such that, in the plane perpendicular to it, the components of dipolar interactions are averaged out more completely than in any other plane. Nevertheless, the success of the line-shape fitting procedure based on equation (2) indicates that the above described approximation represents a practical model for analysing and characterizing systems of the studied type.

From our analysis, the parameter $2A$ was found to be near to 1kHz. This corresponds to 3% of the spacing of a Pake doublet of a system of rigid isolated CH_2 groups, with $\overline{\cos^2\beta}=0.3433$; the deviation from spatial isotropy of motion is seen to be extremely small. A appears to be almost independent of temperature, and also equal for the two studied solvents of greatly differing swelling ability. This indicates that it primarily depends on the density of crosslink points, and on the time-averaged conformation of the polymer chain. For the studied gels, the similarity of A in $CDCl_3$ and CCl_4 rules out the possibility of the existence of stable (i.e. near-static on n.m.r. scale) physical crosslinks for the PEO network swollen in CCl_4. The differences in the behaviour of the studied PEO network in $CDCl_3$ and CCl_4 are predominantly due to differences in the character of the rapid segmental motions, as characterized by the parameter B and ΔE_{MAR}.

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