NMR STUDIES OF SWOLLEN CROSSLINKED POLYMER GELS

D. Doskočilová and B. Schneider

Institute of Macromolecular Chemistry, Czechoslovak
Academy of Sciences, 162 06 Prague 6, Czechoslovakia

Abstract – ^{1}H-HR-NMR spectra of swollen crosslinked polymer
gels (poly(methyl methacrylate), polystyrene, poly(ethylene
oxide), poly(dimethylsiloxane)) measured without sample
rotation and with magic-angle rotation (MAR) are described.
The static line shapes are analyzed as a convolution of
a narrow line-shape function R revealed by MAR-NMR and
governed by rapid segmental motions, and an orientation-
dependent dipolar broadening function S. The parameter A_{OG}
characterizing the width of the function S is interpreted as
a measure of spatial restrictions of motion induced by the
crosslink points, and related to the rigid-lattice second
moment of the interacting spin system.

INTRODUCTION

NMR methods have been widely applied in studies of polymer structure and
dynamics both in the solid state and in solution. Swollen crosslinked polymer
gels, which are of interest in technical and medical applications, have been
very little studied by NMR so far. This is due to a number of circumstances:
It is difficult to prepare physically homogeneous samples of such gels; the
line widths are much larger than in NMR spectra of analogous linear soluble
polymers at equal temperature and concentration – they often lie in a range
intermediate between the conventional broad-line and high-resolution regimes;
consequently, meaningful NMR parameters are not easily obtained from the
spectra of such systems.

In Fig.1, some of these circumstances are demonstrated in the ^{1}H-NMR spectra
of linear and crosslinked poly(methyl methacrylate) (PMMA) swollen in $CDCl_3$
to the concentration of 15% w/w (Ref. 1). From the figure we see that the
spectrum of the sample with the lower crosslink density (Fig.1a) exhibits
a number of very narrow lines, superimposed upon a very broad background.
These narrow lines represent only about 13% of the total mass of the sample,
as determined from the integrated intensities of the bands. They may
correspond partly to signals of normal (linear) PMMA, or "loose ends" of the
polymer network, partly to residual monomer. By increase of temperature
a further narrowing of the narrow lines takes place, but the ratio of the
integrated intensities of the narrow lines and of the broad background does
not change appreciably. Possible information on the structure of the polymer
based on the "high resolution spectrum" thus pertain only to a small fraction
of the studied material. At higher crosslink densities, the narrow lines
disappear completely (Fig.1b) and lines corresponding to various proton groups
of the polymer remain unresolved.

The increased line width in conventionally measured spectra of swollen cross-
linked polymers is due mainly to insufficient averaging of dipolar
interactions in consequence of slow or anisotropic internal motions, but may
be also partly due to the anisotropy of magnetic susceptibility caused by
simple physical heterogeneity of the sample. Both these effects can be
suppressed by measurement of NMR spectra with rapid spinning of the sample
about an axis inclined at the magic angle (MAR-NMR) (Ref. 2).

The effect of MAR upon the spectrum of swollen crosslinked PMMA is
demonstrated in Fig.1c. We see that with MAR, the spectrum exhibits resolved
signals of OCH_3, CH_2 and α-CH_3 protons, and can be decomposed graphically
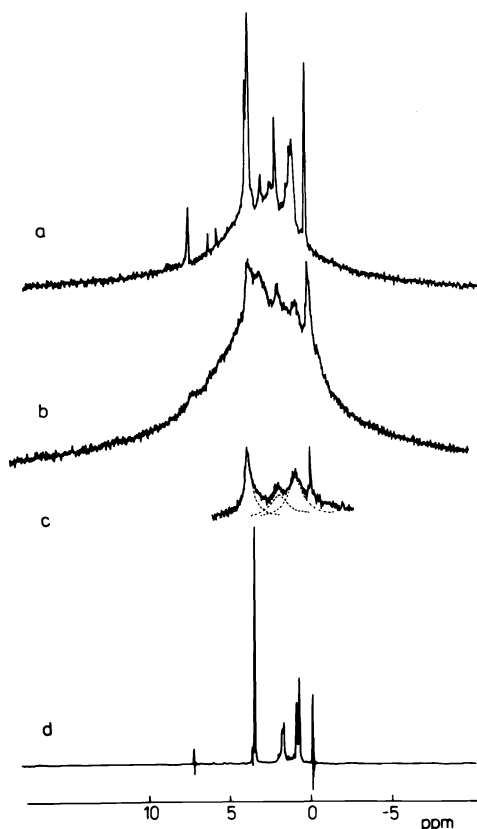into lines of Lorentzian shape representing the total mass of the sample.

Fig. 1. ^{1}H-NMR spectra of crosslinked and linear poly(methyl
methacrylate), 15% w/w in $CDCl_3$, 60°C. Concentration of ethylene
dimethacrylate (mol.%): a 0.5; b,c 1; d 0; a,b,d conventional
HR at 100 MHz; c MAR-NMR at 60 MHz.

The sharp lines observed in the static spectrum are no longer conspicuous,
because of their low relative integrated intensity.

Standard 100 MHz ^{1}H-NMR spectra of crosslinked polystyrene swollen
to equilibrium in CCl_4, and of linear polystyrene at equal concentration and
temperature are compared in Fig.2. The spectra of the crosslinked polymers
exhibit not only much larger line width than those of the linear polymer, but
also a peculiar line shape, with sharp peaks and very broad wings (Ref. 3).
Lines of this shape have previously been observed in the spectra of various
liquid-crystalline systems, and have been termed "super-Lorentzian" (SL) by
some authors (Ref. 4,5). These SL line shapes disappear at magic angle
spinning, yielding spectra practically identical with those of the linear
polymer (Ref. 3). The SL line shapes appearing in conventionally measured
spectra of swollen crosslinked polystyrene could be interpreted in a number
of ways, most simply by a distribution of phases with different mobility.
Such explanations are customary in interpreting line shapes in NMR spectra of
amorphous or semi-crystalline solid polymers.

The disappearance of the SL shapes by magic angle spinning at spinning
frequencies of less than 2 kHz indicates that such an explanation would not
be correct, and that they are caused by near-static dipolar interactions,
with correlation times $\tau_c > 10^{-4}$ s. Therefore the dynamics of conformational
or segmental motions in crosslinked systems can only be studied after these
near-static dipolar effects have been removed, e.g. by magic angle spinning.
In the case of crosslinked polystyrene swollen in CCl_4, the MAR-NMR residual
line width and its temperature dependence in spectra measured with magic
angle spinning are equal to those of the linear polymer in solution (Ref. 3).
This result is in accord with the observed near-identity of the [13]C T_1 and
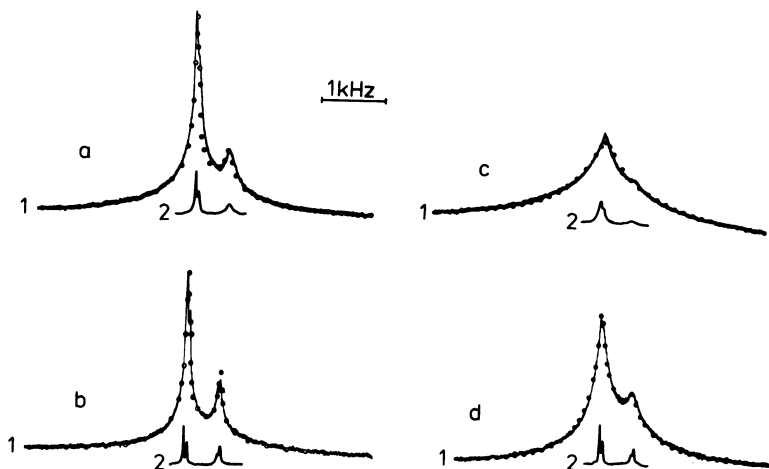
Fig. 2. Static ^{1}H-NMR (100 MHz) spectra of linear (2) and
crosslinked (1) polystyrene swollen to equilibrium in CCl$_4$.
Concentration of ethylene dimethacrylate (mol.%): a,b 2;
c,d 5. Concentration of polymer in solvent (w/w %): a,b 14;
c,d 25. Temperature of measurement: a,c -15°C; b,d +60°C.
(Intensity scale reduced for spectra of linear polymer.)
(o) part of calculated points (Eq. (10)), with adjustment of
A_{oL}.

NOE vs. temperature curves in dissolved linear and swollen crosslinked poly-
styrene (Ref. 3). All these parameters are related to the dynamics of rapid
internal motions which are evidently very similar in the crosslinked and
linear polymers in the case studied. The ^{13}C T_1 and T_2 data, as well as the
temperature course of the proton T_2 values derived from MAR-NMR line widths
indicate a distribution of correlation times, typical of polymer systems.
Even the character of this distribution is evidently very similar in the
swollen crosslinked and dissolved linear polymer, and the width of the
distribution is not very broad.

From the above it is clear that the peculiarities of crosslinked polymer
systems, differentiating them from analogous linear systems, are most
pronounced in the conventionally measured, static line shapes of proton NMR
spectra. Therefore we tried to find an interpretation of these line shapes,
permitting us to obtain some information on the properties of swollen
crosslinked polymer gels by their analysis.

THEORETICAL

Our subsequent treatment will be concerned with swollen polymer gels of low
or moderate crosslink densities, where the swelling ratio is such that inter-
chain interactions are of minor importance and the near-static dipolar
interactions revealed by MAR-NMR are predominantly intragroup in origin. It
can be shown that even in highly swollen networks with low crosslink
densities, the mobility of the crosslink points is substantially less than
that of the chain segments, so that inter-crosslink vectors $\vec{h}_i$ can be defined
by their equilibrium average positions (Fig. 3). Also in networks of this
type, the inter-crosslink chains are so long that the segments in the
immediate vicinity of the crosslink points can be neglected and the mobility
of all segments in one inter-crosslink chain can be treated as equal. We
further make the simplifying assumption that the motional behaviour of all
inter-crosslink chains is equal.

Under these conditions, the motion of a spin-system in a single inter-cross-
link chain (chain (i)) can most simply be described by the correlation
function (Ref. 6)
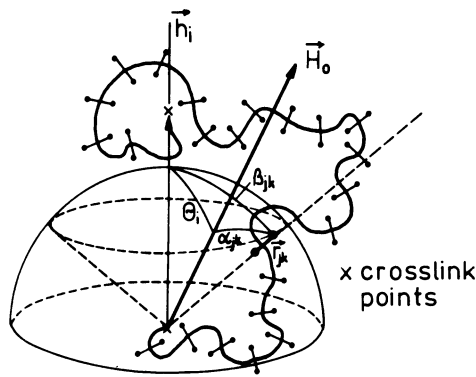
$$G_i(\tau) = G_{1i}(\tau) \, G_{2i}(\tau) \tag{1}$$

Fig. 3. Schematic diagram of coordinate system related to one inter-crosslink chain.

where $G_{1i}(\tau) = \omega^2_{2ai} \exp(-|\tau|/\tau_a) + \omega^2_{2bi}$ corresponds to the spatially restricted rapid segmental motions, with $\omega^2_{2ai} + \omega^2_{2bi} = \omega^2_{2i}$. The residual part ω^2_{2bi} of the rigid-lattice second moment ω^2_{2i} originates from the fact that in a three-dimensional network, reorientation of each internuclear vector $\vec{r}_{jk}$ cannot proceed through the whole space angle, leaving a non-zero average residual projection into the direction of the inter-crosslink vector $\vec{h}_i$. The second correlation function, $G_{2i}(\tau) = \exp(-|\tau|/\tau_b)$ corresponds to all other (much slower) processes leading to final loss of coherence. The total correlation function then has the form

$$G_i(\tau) = \omega^2_{2ai} \exp\left\{-|\tau|\left(\frac{1}{\tau_a} + \frac{1}{\tau_b}\right)\right\} + \omega^2_{2bi} \exp(-|\tau|/\tau_b). \qquad (2)$$

For $\tau_b \gg \tau_a$, this can be simplified to

$$G_i(\tau) \doteq \omega^2_{2ai} \exp(-|\tau|/\tau_a) + \omega^2_{2bi} \exp(-|\tau|/\tau_b) \qquad (3)$$

The line-shape equation for the single chain (i) can be obtained as the Fourier transform of the relaxation function

$$\Phi_i(t) = \exp\left\{-\int_o^t (t-\tau) G_i(\tau) d\tau\right\} \qquad (4)$$

For each chain (i), the value of the residual second moment (Ref. 7) ω^2_{2bi} is a time-averaged function of the angle α_{jk} between the internuclear vectors $\vec{r}_{jk}$ of the interacting spin system and the direction of the applied field, $\vec{H}_o$ (Fig. 3):

$$\omega^2_{2bi} = \frac{3}{4} \gamma^4 \hbar^2 I(I+1) \sum_k \overline{(3\cos^2\alpha_{jk} -1)}^2 r_{jk}^{-6} \qquad (5)$$

Substituting α_{jk} by the angles β_{jk} (between $\vec{r}_{jk}$ and $\vec{h}_i$) and θ_i (between $\vec{h}_i$ and $\vec{H}_o$) (Fig. 3), we obtain

$$\omega^2_{2bi} = \frac{3}{16} \gamma^4 \hbar^2 I(I+1)(3\cos^2\theta_i -1)^2 \sum_k \overline{(3\cos^2\beta_{jk} -1)}^2 r_{jk}^{-6} \qquad (6)$$

The value of ω^2_{2bi} is seen to depend on the orientation of the inter-crosslink

vector $\vec{h}_i$ with respect to the applied field, and on the time-averaged value of the sum over k. According to our simplifying assumption, this sum should be equal for all chains (i), so that we can write

$$\omega_{2bi} = \omega_{2bo}|3\cos^2\theta_i - 1| \tag{6a}$$

where $\omega_{2bo} = \frac{3}{8}\gamma^2\hbar[\sum_k \overline{(3\cos^2\beta_{jk}-1)^2\, r_{jk}^{-6}}]^{1/2}$ for systems with $I = \frac{1}{2}$.

This value of ω_{2bo} is the actual measure of the motional restrictions induced by the network junctions: for motion isotropic in space $(3\cos^2\beta_{jk}-1) = 0$ and ω_{2bo} is equal to zero. For swollen polymer networks measured by us, preliminary estimates indicated that the values of ω_{2bi} averaged over all random orientations of the inter-crosslink vectors $\vec{h}_i$, amount to a few % of the intragroup rigid-lattice second moment of the respective spin system. Therefore in these systems, $\omega_{2ai}^2 \gg \omega_{2bi}^2$. For sufficiently long inter-cross-link chains this also implies that the number of orientations over which the time-average is taken for the spin system in chain (i) is so large that ω_{2ai}^2 is almost equal for all chains and therefore may be approximated by ω_2^2, the rigid-lattice second moment of the interacting spin system averaged over all random orientations in space.

Under these conditions the relaxation function for chain (i) can be formulated as follows:

$$\Phi_i(t) = \exp\{-\omega_2^2\int_o^t(t-\tau)\exp(-|\tau|/\tau_a)d\tau\}\times\exp\{-\omega_{2bi}^2\int_o^t(t-\tau)\exp(-|\tau|/\tau_b)d\tau\}, \tag{7}$$

i.e. as a product of two exponentials. The line shape resulting from the Fourier transform of this r laxation function, $I_i(\omega)$, has the form of a convolution of two functions, the "narrow" line-shape function R, governed by rapid segmental motions, and the dipolar broadening function S:

$$I_i(\omega) = \int_{-\infty}^{\infty} R(\omega-\omega_1)S(\omega_1-\omega_o,\omega_{2bi})d\omega_1\ ,$$

where $R(\omega) = Q(\omega,\omega_2,\tau_a)$, $S(\omega,\omega_{2bi}) = Q(\omega,\omega_{2bi},\tau_b)$ and Q is the general Fourier transform of the relaxation function:

$$Q(\omega,\omega_{2x},\tau_x) = \int_{-\infty}^{\infty}\exp(-i\omega t)\exp(-\omega_{2x}^2\int_o^t(t-\tau)\exp(-|\tau|/\tau_x)d\tau)dt\ . \tag{8}$$

The shape of the functions R and S depends on the respective second moments ω_2^2, ω_{2bi}^2 and the respective correlation times, τ_a, τ_b. For $\omega_{2x}^2\tau_x^2 \ll 1$, the line shape limits to Lorentzian, of width $\omega_{2x}^2\tau_x$; for $\omega_{2x}^2\tau_x^2 \gg 1$, the line shape limits to Gaussian, defined as $Q(\omega,\omega_{2x}) = [(2\pi)^{1/2}\omega_{2x}]^{-1}\exp(-\omega^2/2\omega_{2x}^2)$; for intermediate values it is given by the general expression (8) (Ref. 8). Both ^{1}H-MAR-NMR and ^{13}C experimental data cited above have indicated that the rapid segmental motions in swollen polymer networks differ very little from spatially isotropic motion in comparable solutions of linear polymers (Ref. 3, 9,10) with $\omega_2^2\tau_a^2 \ll 1$, so that the first exponential in Eq. (7) (describing rapid segmental motions) will correspond to Lorentzian shape of $R(\omega)$. In the second exponential of Eq. (7), from ^{1}H-MAR-NMR line-narrowing experiments, τ_b is known to be 10^{-4} s or longer, and following our simplifying assumption, should be equal for all chains (i). The value of ω_{2bi}^2 depends on the angle θ_i of the respective internuclear vector $\vec{h}_i$ with the direction of $\vec{H}_o$, and always decreases to zero for the magic-angle value of θ_i. Consequently the shape of $S(\omega,\omega_{2bi})$ for various chains (i) will follow the general expression (8) and range from Lorentzian shape for values of θ_i very near to the magic-angle value, to Gaussian shape for θ_i values yielding $\omega_{2bi}^2\tau_b \gg 1$. We expect the greatest part of the experimentally measured shape to correspond to the latter condition.

For a random distribution of inter-crosslink vectors $\vec{h}_i$, the overall static
line shape is given by integration over all chains (i):

$$I(\omega) = \int_{o}^{\pi/2} \int_{-\infty}^{\infty} R(\omega-\omega_1) S(\omega_1-\omega_o, \omega_{2bo} |3 \cos^2\theta - 1|) d\omega_1 \sin\theta \, d\theta \qquad (9)$$

In the approximation where only the width, but not the shape of $S(\omega, \omega_{2bi})$
depends on ω_{2bi} for the whole range of ω_{2bi}, the angular dependence of S
may be separated from the shape and characteristic width of S:

$$S(\omega-\omega_o, \omega_{2bo} |3 \cos^2\theta - 1|) = S\{(\omega-\omega_o)/|3 \cos^2\theta - 1|, \omega_{2bo}\}/|3 \cos^2\theta - 1|$$

In this form, Eq. (9) is analogous to that suggested originally by
Wennerström (Ref. 5) for describing typical line shapes of some liquid
crystalline systems.

For a dipolar broadening function S which can be approximated by Gaussian
shape in the whole range of the spectrum, we define the characteristic width
of the dipolar broadening function S_G as $A_{oG} = \omega_{2bo}$ (ω_{2bi} for $\theta_i = 90°$). If we
approximate S by Lorentzian line shape in the whole range of the spectrum,
the characteristic width cannot be related directly to the residual second
moment. For this case we define $S_L = S\{(\omega-\omega_o)/|3 \cos^2\theta - 1|, A_{oL}\}/|3 \cos^2\theta - 1|$,
where $2 A_{oL}$ is the width at half-height of the Lorentzian dipolar broadening
function for $\theta_i = 90°$.

Concerning the exact shape $S(\omega, A_o)$ of the dipolar broadening function, its
influence on the resulting overall static line shape is widely suppressed by
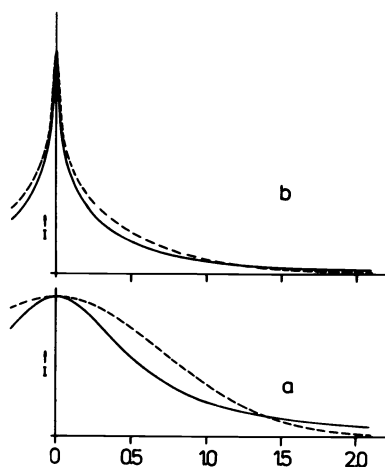the angular dependence of S. This is demonstrated in Fig. 4 for Gaussian and
Lorentzian shape.

Fig. 4. Comparison of Lorentzian (———) and Gaussian (----)
line shapes. a simple; b with angular dependence of width
parameter.

Therefore in our first studies (Refs 3,10), for ease of calculation,
a Lorentzian shape was used for the dipolar broadening function, and only the
characteristic width A_{oL} was adjusted for best fit of measured and calculated
line shape.

With Lorentzian shape of $S_L(\omega, A_{oL})$, $I(\omega)$ can be expressed in explicit form
(Ref. 3)

$$I(\omega-\omega_o) = \int_0^1 \frac{A_{oL}|3\cos^2\theta-1|+B_L}{\pi\{(\omega-\omega_o)^2+[A_{oL}|3\cos^2\theta-1|+B]^2\}} \, d\cos\theta \, ,\qquad (10)$$

where $2B_L$ is the width at half-height of the "narrow" line shape function $R(\omega)$. This equation is suitable for least-squares adjustment procedures with the use of minicomputers. It was applied by us for analyzing static line shapes of swollen polymer networks (Refs 3,10,11). In this analysis we have assumed that in the MAR-NMR experiment, by removal of the near-static dipolar interactions, the shape of the function $R(\omega)$ is revealed. In all cases studied, MAR-NMR lines were very near to Lorentzian and therefore we used the Lorentzian shape of $R(\omega)$, with MAR-NMR line width for $2B_L$ in most cases.

The kind of agreement which can be obtained in this way for swollen cross-linked polystyrene networks (Ref. 11) is demonstrated in Fig. 2. For a one-parameter adjustment procedure, the quality of fit for widely differing line shapes is quite remarkable. A similar quality of fit was obtained by the same procedure for poly(ethylene oxide) networks swollen both in good and poor solvent (Fig. 5), in a broad temperature range (Ref. 10), and for swollen poly(dimethyl siloxane) networks (Ref. 11) (Fig. 6). The success of the described analysis for so widely differing line shapes, and for materials of so varied dynamical properties indicated that the overall static line shape is indeed dominated by the angular dependence of the function S which is expected to be identical for diverse materials, rather than by some other material-dependent distribution function.

Having thus established the functional character of the peculiar line shapes observed in proton NMR spectra of swollen polymer gels, we wished to utilize the characteristic width parameters obtained by their analysis for characterization of the motional restrictions induced by the existence of the crosslink points, in the sense of Eq. (6a). Motional restrictions are best described by the relation of the residual second moment corresponding to the near-static dipolar interactions, averaged over all orientations of $\vec{h}_i$,
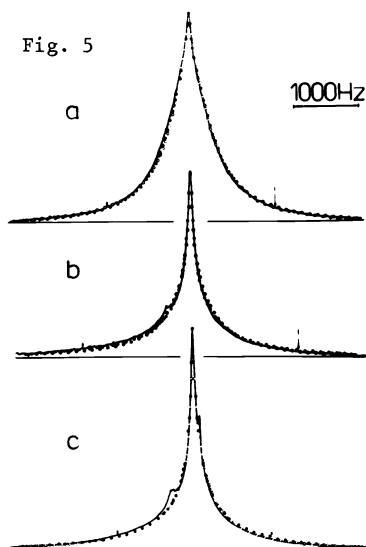
Fig. 5

a

1000Hz

b

c

Fig. 6

a

b

400   200   0   200   400 Hz

Fig. 5. Static ^{1}H-NMR (100 MHz) spectra of crosslinked poly(ethylene oxide) swollen to equilibrium.
a in CCl_4, +23°C; b in $CDCl_3$, -13°C; c in $CDCl_3$, +50°C.
(———) experimental; (●) part of the points of idealized experimental (symmetrized, peaks of crosslinking agent excluded); (o) part of calculated points.
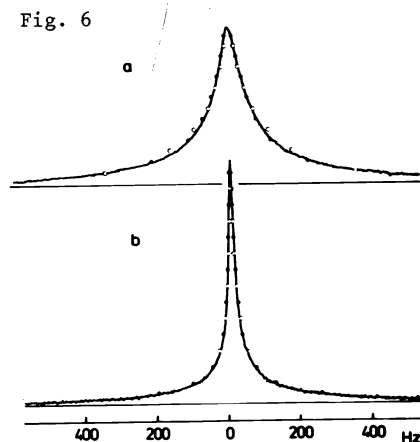
Fig. 6. Static ^{1}H-NMR (100 MHz) spectra of crosslinked poly(dimethyl siloxane) swollen to equilibrium in CCl_4, 23°C. Degree of crosslinking (nominal number of monomer units in chain): a 60; b 600. (———) experimental; (●) part of points of symmetrized digitized spectrum; (o) part of calculated points.

$$\overline{\omega^2_{2bi}} = \omega^2_{2bo}\overline{(3 \cos^2\theta_i - 1)^2} = (4/5)\omega^2_{2bo} \quad ,$$

to the overall rigid lattice second moment, ω^2_2; the width parameter of
a Lorentzian dipolar broadening function S is not suitable for inter-
pretation in terms of second moment. A Gaussian form of S is better suited to
this end, and also is physically more reasonable, as from Eq. (8) and (9),
$S(\omega,\omega_{2bi})$ is expected to be Gaussian in the greatest part of the range of
ω_{2bi}.

For Gaussian shape of the dipolar broadening function, an explicit expression
comprising its angular dependence cannot be written, and line-shape parameters
cannot be obtained by a least-squares fit with the use of a minicomputer.
Therefore we have numerically composed the shape of the dipolar broadening
function from Gaussians of width and population following the angular
dependence of the function S, and the result was numerically folded with
a Lorentzian line shape. In this way model line shapes were calculated for
various values of the ratio of A_{OG} and of the parameter B corresponding to
the width of the Lorentzian function $R(\omega)$. From the values of the widths of
experimental bands measured at several selected fractions of total peak
height, or of total peak area, the parameters A_{OG} and B could be obtained from
the model line shapes by means of a graphical procedure. If the parameter 2B
is identified with the MAR-NMR line width, this corresponds to a one-parameter
adjustment procedure. - A similar procedure was used also for the determi-
nation of the parameter A_{OL} of a Lorentzian dipolar broadening function,
yielding results practically equal to those obtained by the least-squares
adjustment procedure.

ANALYSIS OF SPECTRA

In Fig. 7, several line-shape fitting procedures are compared for a PEO
network swollen to equilibrium in $CDCl_3$. The quality of fit is very good for
Lorentzian shape of the dipolar broadening function S; the correctness of the
fit is sensitively checked by the % of area covered by the shape obtained
from the procedure based on height fractions (101%), and by maximum peak
height reached by the procedure based on area fractions. The fit is not so
good for Gaussian shape of S, where only 86% of spectrum area is accounted
for by the procedure based on height fractions, and peak height is under-
scored by the procedure based on area fractions. The Gaussian shape of the
dipolar broadening function S evidently cannot well describe the behaviour of
$I(\omega)$ near the peak centre. A very perfect fit can be obtained by a linear
combination of Lorentzian shape of S near the peak centre and Gaussian shape
of S in the wings, as demonstrated in Fig. 6e. Contrary to the previous
procedure, this of course is a two-parameter fit; it may be regarded as an
attempt to approximate the correct line shape corresponding to Eq. (8).
The Lorentzian shape of the dipolar broadening function S is evidently better
suited to describe the behaviour of the composite line shape near the peak
centre, thus explaining why in diverse applications a better fit is mostly
obtained with Lorentzian rather than with Gaussian shape of the dipolar
broadening function S. Also the Lorentzian shape, which can be represented as
some distribution of Gaussians, might somewhat relax the simplifying
assumption about the equality of all inter-crosslink chains which certainly
is not fulfilled in real networks.

Similar line-shape fits, for the same PEO network in CCl_4, which is a poor
swelling agent, are compared in Fig. 8. Here the quality of fit is comparable
for Lorentzian and Gaussian shape of the function S. However, the peak height
is not well reproduced by any of the procedures based on area fractions. We
assume that this is caused by the non-ideality of the measured networks.
Generally, even after careful extraction, polymer networks may contain some
amount of linear polymer, and pendant polymer chains cannot be removed at all.
These both would contribute a narrow Lorentzian line hardly affecting total
peak area, but adding markedly to total peak height, even at low contents of
these species. This effect is visually more conspicuous when the spectrum of
the network is broad, therefore it was not noted in Fig. 7. Nevertheless, it
always introduces some error into all analytical procedures normalized to
maximum peak height, and for this reason we prefer parameters based on area
fractions for characterizing the polymer network proper.

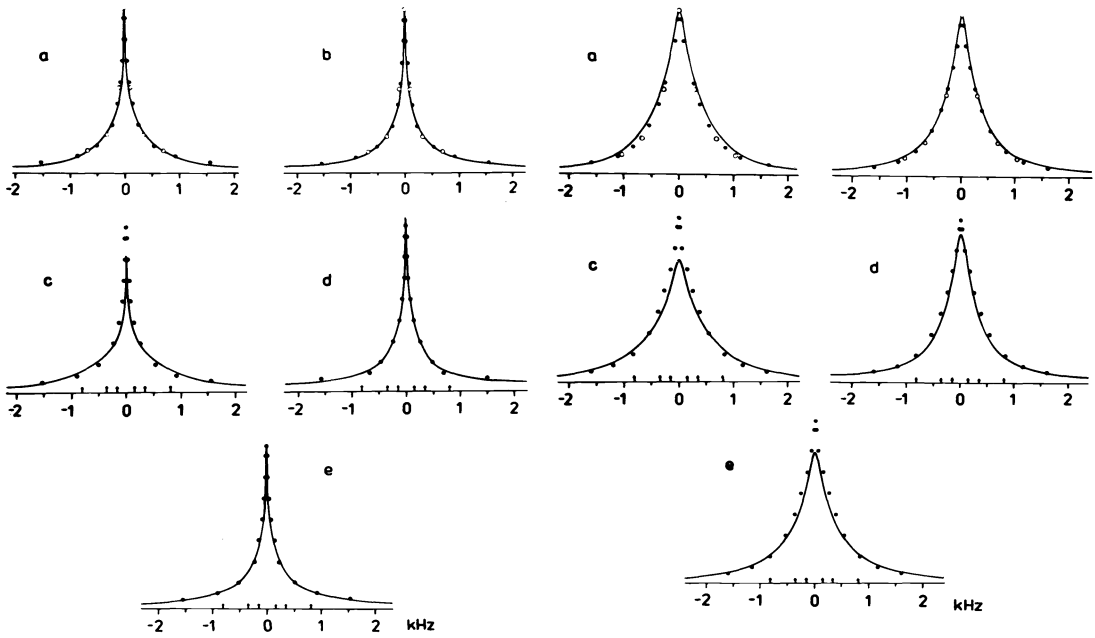The dipolar broadening parameters A_{OL} and A_{OG} obtained from the spectra in

Fig. 7. Comparison of analytical
procedures for crosslinked
poly(ethylene oxide), 22.3% w/w
in CDCl$_3$, +50°C.

Fig. 8. Comparison of analytical
procedures for crosslinked
poly(ethylene oxide), 77.5% w/w
in CCl$_4$, +23°C.

Analysis: a,b from height fractions; c,d,e from area fractions. Shape of
dipolar broadening function: a,c Gaussian; b,d Lorentzian; e linear
combination of Gaussian and Lorentzian. (●) some points of digitized
experimental spectrum; (o) points used for parameter fitting from height
fractions; (↑) points used for parameter fitting from area fractions;
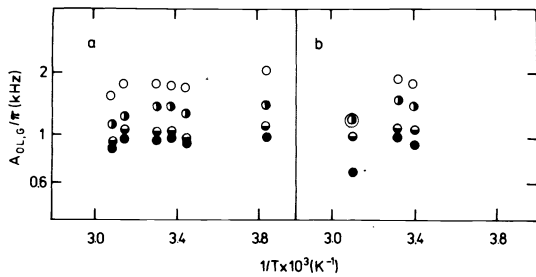(———) calculated.

Fig. 9

Fig. 10

Fig. 9. Temperature dependence of dipolar broadening parameters
obtained by different analytical procedures for crosslinked
poly(ethylene oxide) swollen to equilibrium in CDCl$_3$ (a) and
CCl$_4$ (b). (● o) from area fractions; (◐ ◑) from height
fractions. Shape of dipolar broadening function: (o ◐) Gaussian
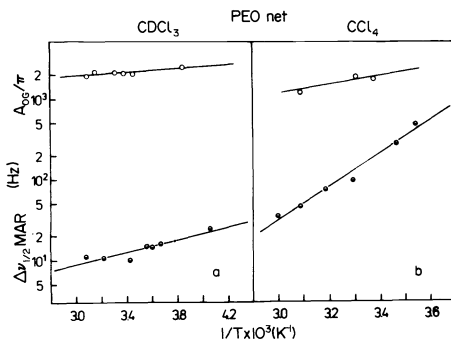(A$_{OG}$); (● ◑) Lorentzian (A$_{OL}$).

Fig. 10. Temperature dependence of Gaussian dipolar broadening
parameters and MAR-NMR line width for crosslinked poly(ethylene
oxide) swollen to equilibrium in CDCl$_3$ (a 22.3% w/w) and
CCl$_4$ (b 77.5% w/w). (o) A$_{OG}$/π; (●) Δν$_{1/2}$, MAR.

the preceding two figures for swollen PEO networks are summarized in Fig. 9. We see that the parameters obtained for the two shapes and by various analytical procedures differ by not more than a factor of 2 (this is to be expected with respect to the definition of A_{OL} and A_{OG}). Even more important, they all exhibit a remarkably identical trend. For reasons discussed above, we choose the parameters obtained with a Gaussian dipolar broadening function, analyzed by means of area fractions, for network characterization. However, for evaluation of a series of materials, Lorentzian parameters, obtained much more easily from peak heights,would serve equally well.

In Fig. 10, the temperature dependence of the Gaussian dipolar broadening parameters from peak areas, corresponding to ω_{2bi} values on frequency scale, for PEO networks swollen in $CDCl_3$ and CCl_4 is presented together with the temperature dependence of MAR-NMR line widths, 2B. We see that the ω_{2bi} values exhibit much less temperature variation than the values 2B, and that for the same network, they do not differ much in the good ($CDCl_3$) and poor (CCl_4) solvent. The temperature trend of the 2B values in the two solvents is completely different. This indicates that rapid segmental motions are most affected by quality of solvent, whereas the motional restrictions caused by network junctions remain practically unchanged. The A_{OG} values shown in this figure correspond to 5.2-6.75% of the square root of the intragroup rigid lattice second moment of the ethylene fragment in $CDCl_3$, and to 3.3-5.0% in CCl_4. The residual second moments are a direct quantitative measure of the motional restrictions induced by crosslinking in swollen networks. Moreover, they can be correlated with standard parameters of molecular mechanics, as indicated e.g. by Gotlib (13) for the relation between residual second moment and the number of statistical segments in the inter-crosslink chain. Reliable methods for obtaining these residual second moments were so far lacking. From the above analysis it is clear that they cannot be obtained simply from overall line shape, because of the folding with the Lorentzian function $R(\omega)$. We hope that in this lecture we have shown one possible approach.

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