

## CHARACTERIZATION OF INTERNAL MOTIONS IN CROSSLINKED POLYMER GELS BY HIGH-RESOLUTION MAR-NMR SPECTROMETRY

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From the temperature dependence of the limiting line widths in high-resolution MAR-NMR spectra, the activation energies of internal motions of  $-\text{OCH}_3$ ,  $\alpha-\text{CH}_3$  and skeletal  $-\text{CH}_2-$  groups were determined in a series of crosslinked poly(methyl methacrylate) gels swollen with chloroform.

It is well known that the line width in NMR spectra of swollen crosslinked polymers is larger than the line width in NMR spectra of analogous linear soluble polymers at equal concentration and temperature<sup>1</sup>. At the same time, the line narrowing effect of increasing temperature is much less pronounced than in linear polymers (Fig. 1).

The increased line width in conventionally measured NMR spectra of crosslinked polymers is due to a number of effects: 1. Insufficient averaging of dipolar interactions in consequence of slow or anisotropic internal motions. 2. 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 so called "magic angle" with respect to the direction of the stationary magnetic field (MAR-NMR) refs<sup>2-8</sup>.

Conditions for the effectiveness of this method in systems that are not quite rigid have been rigorously derived by Andrew and Jasinski<sup>9</sup> and by Haeberlen and Waugh<sup>10</sup>, but they can be simply stated also on the basis of the line width relations introduced by Gutowsky and Pake<sup>11</sup>: The line width of an NMR signal partly narrowed by anisotropic internal motion (*e.g.* rotation or oscillation of proton groups about axes which are more or less fixed in space, or reorientation of molecules or groups of atoms under maintenance of certain intermolecular order) may be described by the relation<sup>11</sup>

$$(\Delta\nu)^2 = B^2 + C^2(2/\pi) \arctg(\alpha\Delta\nu/\nu_c), \quad (1)$$

where  $\nu_c$  is the correlation frequency of the anisotropic motion,  $\alpha$  is a constant of order 1,  $B$  is the line width in case that this motion is very rapid, and the constant  $C$  is defined by the relation  $B^2 + C^2 = A^2$ , where  $A$  is the line width in the corresponding rigid lattice. The residual dipolar interactions summarized in the term  $B$  can be removed by the MAR-NMR technique at technically attainable spinning frequencies  $\nu_r$ , irrespective of the value of the correlation frequency  $\nu_c$ , so that the residual line width is then given by the second member in Eq. (1) (refs<sup>4,6</sup>).

More rigorous treatments indicate that the residual line width in MAR-NMR spectra at sufficiently high spinning speeds is a linear function of the correlation time of "rapid" internal

motions<sup>9,10</sup>

$$(\Delta\nu_r)_{\text{lim}} = K\tau_c.$$

The constant  $K$  is proportional to  $r^{-6}$ , where  $r$  is the distance of the interacting protons; besides that, the constant  $K$  is also a function of the geometrical shape of the corresponding motional mechanism. "Rapid" motions are defined as those for which  $2\pi\nu_r\tau_c < 1$ . "Slow" motions, for which  $2\pi\nu_r\tau_c > 1$ , do not affect the value of  $(\Delta\nu_r)_{\text{lim}}$ . Under these conditions the lines in MAR-NMR spectra are of Lorentzian shape. In the theory of relaxation processes it is usually assumed that the correlation time  $\tau_c$  obeys the Arrhenius relation

$$\tau_c = \tau_{c0} \exp(\Delta E/RT),$$

where  $\Delta E$  is the activation energy of the respective motion. In case of a simple "rapid" motional mechanism, the activation energy of the corresponding motion may be determined from the temperature dependence of the line width.

It is well known that the relaxation times  $T_1$ ,  $T_2$  in polymer solutions conform to the relation  $T_1 > T_2$  (see<sup>12</sup>). This is a consequence of the general anisotropy of motion in polymer solutions, with the slow motions, corresponding mostly to intermolecular interactions, contributing predominantly to  $T_2$ , and the rapid motions, corresponding mostly to intramolecular interactions, determining  $T_1$ . Therefore in a conventional NMR spectrum the line width, which is proportional to  $1/T_2$ , is mostly determined by the slow motional modes. The anisotropy of internal motions is expected to be even more pronounced in swollen polymer networks, leading to an even larger difference between  $T_1$  and  $T_2$ . It could be assumed that in MAR-NMR spectra the effect of slow motional modes (corresponding to intermolecular or intersegmental interactions) upon line width would be suppressed, and the residual line width would be determined by the rapid motional modes only. In this preliminary study we have attempted to obtain high-resolution MAR-NMR spectra of a series of swollen poly(methyl methacrylate) gels of various crosslink density, and to determine the activation energies of the motion of various proton groups by the procedure outlined above.

## EXPERIMENTAL

The measured crosslinked polymers were prepared by radical copolymerization of methyl methacrylate with ethylene-dimethacrylate (0.1; 0.5; 1.0 mol%) in bulk, with isopropyl-percarbonate as initiator (0.5 weight %). The copolymerization components were purified by conventional methods, dried above calcium hydride and distilled directly before copolymerization. All operations were performed in an atmosphere of dried and deoxygenated argon. The glass polymerization apparatus was heated, evacuated and flushed by purified argon. The polymerization components were dosed so that a mixture of methyl methacrylate with isopropyl percarbonate was added to ethylene dimethacrylate. The temperature of copolymerization in the course of the first hour was gradually increased from 30° to 40°C. On this value it was maintained for 18 h, and in the course of the following 2 h it was increased to 65°C where it was maintained for 22 h. The technical material was investigated as such: the samples were prepared from the bulk copolymer by cutting, and

without previous purification they were swollen in  $\text{CDCl}_3$  to the concentration 15% w/w. Conventional NMR spectra were measured on the high resolution NMR spectrometer PS-100 (JEOL) at 100 MHz, the MAR-NMR spectra on the apparatus previously described<sup>13</sup>, at 60 MHz. For variable temperature measurements this apparatus was heated by a stream of warm air.

## RESULTS AND DISCUSSION

Conventional NMR spectra of control poly(methyl methacrylate) (linear PMMA) and of the copolymers of methyl methacrylate with ethylene dimethacrylate (cross-linked PMMA, 0.5% and 1% of crosslinking agent) are compared in Fig. 1. From the figure we see that the spectrum of the sample with lower crosslink density (Fig. 1c) exhibits a number of very narrow lines, superimposed upon a very broad background. In the copolymer prepared with 0.5% of crosslinking agent, the narrow lines represent only about 13% of the total mass of the sample, as determined from the integrated intensities of the bands. The narrow lines correspond partly to signals of normal PMMA, partly to residual monomer. By an increase of temperature (Fig. 1b), a further narrowing of the narrow lines takes place, but the ratio of integrated inten-



FIG. 1

Comparison of Conventional HR-NMR Spectra (100 MHz) of Linear and Crosslinked PMMA (15% w/w in  $\text{CDCl}_3$ )

Concentration of crosslinking agent (mol%): a 0; b, c 0.5; d, e 1. Temperature of measurement ( $^{\circ}\text{C}$ ): a, b, d 60; c, e 22.

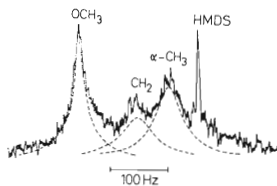


FIG. 2

MAR-NMR Spectrum (60 MHz) of Cross-linked PMMA (1 mol% of crosslinking agent)

15% w/w in  $\text{CDCl}_3$ , 55 $^{\circ}\text{C}$ ,  $\nu_r = 2.5$  kHz.

sities of the narrow lines and of the broad background does not change appreciably. Possible informations 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 (1% of crosslinking agent) the narrow lines disappear completely (Fig. 1e). Indications of narrower lines evident at elevated temperature (Fig. 1d) correspond to the HMDS standard and to residues of unreacted monomer, *i.e.* to low molecular weight components of the system; lines corresponding to various proton groups of the copolymer remain completely unresolved.

In Fig. 2, the spectrum of the sample with 1% crosslinking agent measured with rotation about the magic axis is shown. We see that under these conditions the spectrum exhibits resolved signals of  $-\text{OCH}_3$ ,  $-\text{CH}_2-$  and  $\alpha\text{-CH}_3$  protons, and can be graphically decomposed into lines of Lorentzian shape representing the total mass of the sample.

TABLE I  
Limiting Line Widths in MAR-NMR Spectra of Crosslinked PMMA  
15% w/w in  $\text{CDCl}_3$ , 28°C.

Crosslinking agent, mol. %	$\Delta\nu$ , Hz		
	$-\text{OCH}_3$	$\alpha\text{-CH}_3$	$-\text{CH}_2-$
0	6.3	—	—
0.1	14.7	—	—
0.5	35	63	84
1.0	35	63	91

The room-temperature limiting line widths, obtained as widths at medium height of separated lines of Lorentzian shape in MAR-NMR spectra of copolymers with different crosslink densities, are summarized in Table I. From the temperature dependence of the limiting line widths measured in the temperature interval between room temperature and the boiling point of chloroform, the activation energies of the motion of various proton groups were estimated, and these values are shown in Table II. In this Table, the values  $\Delta E(T_1)$  obtained from the temperature dependence of saturation for benzene solutions of linear PMMA (ref.<sup>14</sup>), as well as the values of  $\Delta E$  obtained from mechanical, dielectric and  $T_1$ -relaxation data for solid PMMA (ref.<sup>15</sup>) are also shown for comparison. From Table II it can be seen that the values of  $\Delta E$  determined from MAR-NMR spectra of crosslinked PMMA are in good agreement with the  $\Delta E(T_1)$  values from saturation measurements of linear PMMA;

TABLE II

Activation Energies of Motion of Various Proton Groups in Crosslinked PMMA  
15% w/w in  $\text{CDCl}_3$ .

Crosslinking agent, mol. %	$\Delta E$ , kcal/mol		
	$-\text{OCH}_3$	$\alpha-\text{CH}_3$	$-\text{CH}_2-$
0.1	2.0	—	—
0.5	2.8	2.8	3.5
1.0	3.2	3.2	4.2
0 <sup>a</sup>	—	1.7	1.7
0 <sup>b</sup>	—	4	50

<sup>a</sup> Linear PMMA, iso- and syndiotactic, 10% w/w in benzene;  $\Delta E$  determined from the temperature dependence of saturation<sup>14</sup>. <sup>b</sup> Solid linear PMMA,  $\Delta E$  determined from various relaxation measurements<sup>15</sup>.

with increasing crosslink densities,  $\Delta E$  increases slightly. In contrast to linear PMMA where  $\Delta E$  is equal for all kinds of proton groups,  $\Delta E$  in crosslinked PMMA increases in the series  $-\text{OCH}_3$ ,  $\alpha-\text{CH}_3$ ,  $-\text{CH}_2-$ . This is not surprising, because a similar, but much more pronounced trend was observed in measurements of the activation energies of solid PMMA.

In conclusion it may be stated that the MAR-NMR method enables us to study separate signals of various proton groups in crosslinked polymers. The line width, determining the best attainable resolution, is limited by the frequency of the internal motion of the respective group in the given polymer; from the temperature dependence of the line width, the activation energy of the corresponding motions can be determined. In crosslinked methyl methacrylate-coethylene dimethacrylate copolymers it was found that activation energies determined in this way, fall reasonably in line with activation energies determined by conventional methods in linear poly(methyl methacrylate).

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