# $^{13}$C n.m.r. chemical shielding tensor elements of solid poly(methyl methacrylate)

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The solid-state non-spinning $^{13}$C nuclear magnetic resonance spectrum of poly(methyl methacrylate) (PMMA) is reassigned. Principal elements of the chemical shielding tensors are obtained for all carbon resonances. The observed anisotropies indicate that the polymer, both with respect to the side chains and the backbone, is essentially rigid at room temperature on the time scale of the experiment (in the millisecond range).

**Keywords** $^{13}$C nuclear magnetic resonance; solids; shielding tensor; polymers; poly(methylmethacrylate)

## INTRODUCTION

Poly(methyl methacrylate) (PMMA) was one of the first polymers to be studied by $^{13}$C nuclear magnetic resonance (n.m.r.) in the solid state[1-3]. As part of our investigations towards the characterization of motions by n.m.r. methods, we have studied the $^{13}$C n.m.r. spectrum of solid PMMA in detail. The spectral assignments made by Schaefer *et al.* for a static sample[1] are only partly correct. Here we report a complete assignment, including new data on the chemical shielding tensors of the carbon resonances in PMMA. This information is essential for an understanding of the n.m.r. spectra observed at various temperatures, which will be reported on another occasion.

## EXPERIMENTAL

All measurements were performed at room temperature with a home-built solid-state n.m.r. spectrometer system, equipped for cross-polarization (CP) and magic-angle spinning (MAS). The $^{13}$C n.m.r. frequency equals 45.26 MHz. Radiofrequency (r.f.) magnetic field strengths equivalent to 62 kHz were used, both for matched CP and for on-resonance proton decoupling. MAS spectra were measured at lower r.f. magnetic fields, equivalent to 32 kHz. MAS spinners of our local design were used[4]. CP n.m.r. spectra (*Figures 1* and *2*) were measured with a CP contact time of 1 ms; the proton spin temperature was alternated[5]. Partially relaxed spectra in a spin–lattice relaxation experiment (*Figures 2e–g*) were measured without saturation of the proton magnetization during the relaxation delay time $\tau$, with the pulse sequence described by Torchia[6]. It should be noted that in this way the partially relaxed spectra decay towards zero for long times $\tau$, instead of approaching the completely relaxed spectrum as is the case in the inversion-recovery method. The spin–echo spectrum (*Figure 2h*) was measured using the sequence ($\mathrm{CP}-\tau-\pi(^{13}\mathrm{C})-\tau-\mathrm{FID}$), where the protons are continuously decoupled during the relaxation delays $\tau$ and during the acquisition of the $^{13}$C free induction decay (FID). The completely relaxed spectrum (*Figure 3*) was obtained from the FID following a $^{13}$C $\pi/2$ pulse, repeated once a minute. This repetition rate is much slower than the $^{13}$C spin–lattice relaxation rates[7]. In all cases, some thousands of FIDs were averaged to obtain the spectra. The PMMA samples studied consisted of rods of commercially available Perspex.

The principal elements of the chemical shielding tensor (*CST*), $\sigma_{11}$, $\sigma_{22}$ and $\sigma_{33}$, are given in parts per million (ppm) relative to TMS. The *CST* will also be given as the isotropic chemical shift $\bar{\sigma}$, the chemical shielding anisotropy $\delta$ and the asymmetry parameter $\eta$[8].

## RESULTS

All five carbon resonances of PMMA can be assigned in the $^{13}$C MAS n.m.r. spectrum (*Figure 1a*); the methylene carbon is partly hidden under the methoxy carbon resonance but is visible as a shoulder[3]. The measured isotropic chemical shifts $\bar{\sigma}$ are given in *Table 1*. The methyl carbon resonance is broadened due to a dispersion of the isotropic chemical shift, which results from different conformations in the solid state[3,7].

The non-spinning spectrum (*Figure 1b*) is not well resolved. As was found before[1-3], only the carboxyl carbon resonance is clearly separated. It shows the powder pattern characteristic of a large anisotropy in the chemical shielding. The principal elements of the carboxyl carbon *CST* are obtained directly from the spectrum. The four remaining resonances show severe overlap, as each of them is broadened by chemical shielding anisotropy.

A careful study of the line shape, of the effect of slowly spinning the sample around the magic axis, and of relaxation differences has enabled us to unravel the composite spectral band into its components.

### *Methyl carbon*

The methyl carbon resonance ($R_1 = 20\,\mathrm{s}^{-1}$) relaxes faster than the other resonances by two orders of magni-

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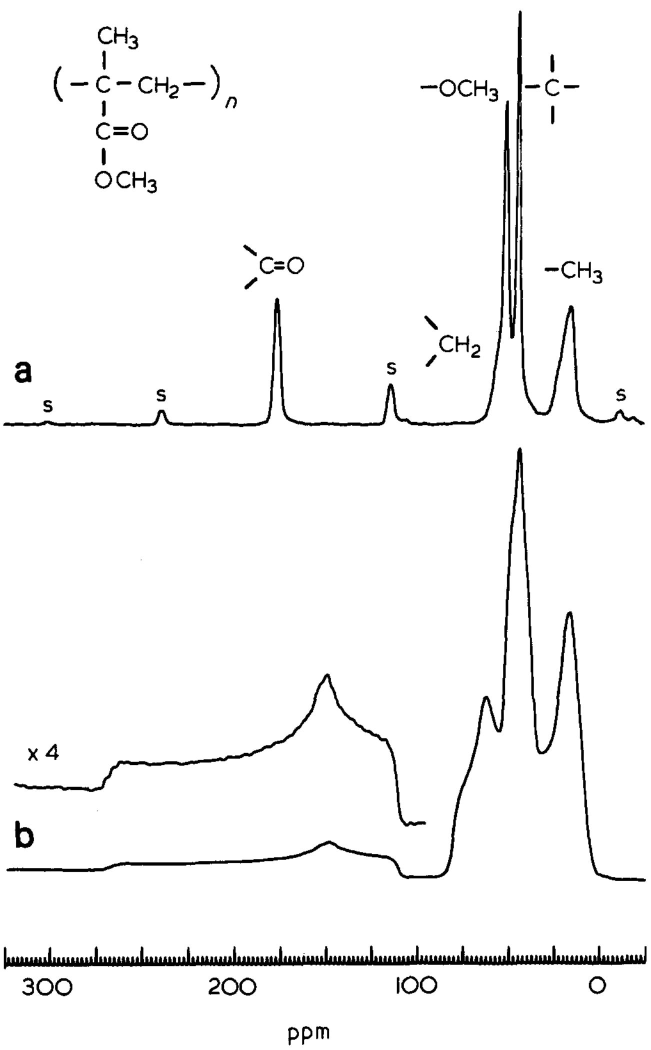

*Figure 1* $^{13}C$ CP n.m.r. spectra of solid commercial PMMA at 45.26 MHz. (a) MAS spectrum, obtained with a sample rotation frequency of 2.82 kHz: the spectral assignments are shown; s denotes a spinning side band. (b) Non-spinning spectrum: the carboxyl chemical shielding powder pattern is also shown with enlarged amplitude

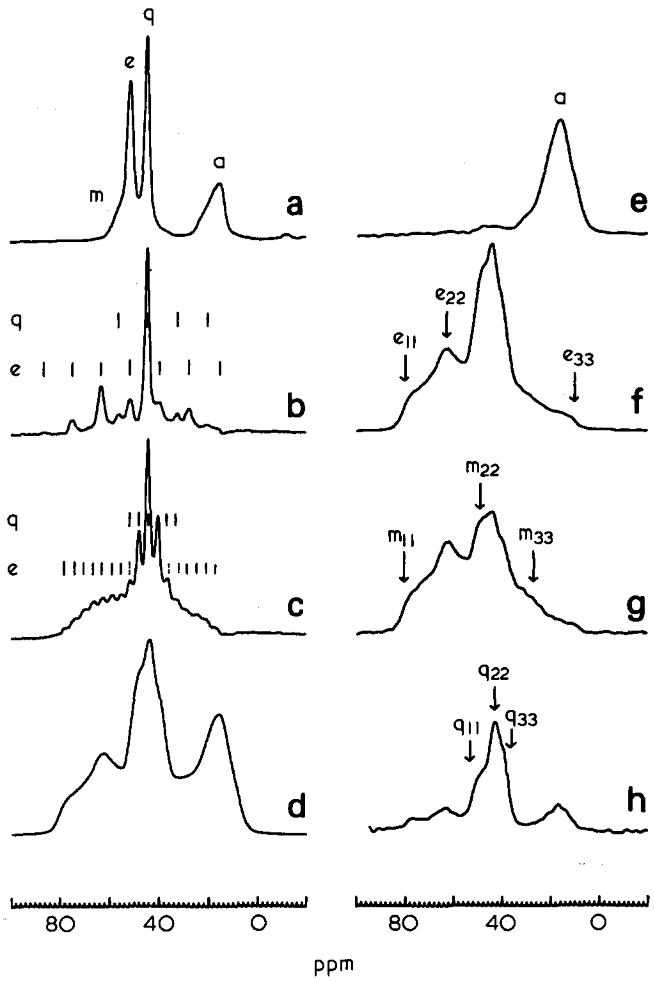

*Figure 2* High-field part of the $^{13}C$ CP n.m.r. spectrum of solid PMMA, observed under various conditions; m=backbone methylene carbon; e=methoxy carbon; q=quaternary carbon; and a=(α–)methyl carbon. (a) to (c) MAS spectra at sample rotation frequencies of 2820, 530 and 170 Hz respectively. In (b) and (c) the methyl resonance has been suppressed by acquiring the spectra in a spin–lattice relaxation experiment with a relaxation delay of 50 ms. The observable spinning side band patterns are indicated. (d) CP non-spinning spectrum. (e) Methyl carbon resonance, selected out by its fast spin–lattice relaxation (see text). (f) and (g) Partially relaxed spectra in a spin–lattice experiment (see text), acquired after relaxation delays of 1 and 10 s, respectively. Arrows point to the positions of the *CST* elements. (h) Quaternary carbon resonance, selected out with a spin–echo sequence (see text) using a delay $\tau$ of 10 ms

tude[7], and can easily be obtained separately. The spectrum shown in *Figure 2e* is obtained from the difference between two partially relaxed spectra, measured in a spin–lattice relaxation experiment with relaxation delays $\tau$ of 1 and 100 ms. Only the fast-relaxing methyl carbon resonance appears. The line is slightly broadened by about 5 ppm in comparison with the MAS spectrum (*Figure 2a*), mainly to the high-field side. This indicates the presence of a rather small chemical shielding anisotropy ($\delta \sim 3$ ppm), which is superimposed on the broader distribution of isotropic chemical shifts ($\Delta\sigma \simeq 10$ ppm). No estimate can be given for the tensor asymmetry because of this small anisotropy.

### *Methoxy carbon*

As was shown by Maricq and Waugh[9], the *CST* can be reconstructed from the intensities of the spinning side bands in a MAS n.m.r. spectrum. Spinning PMMA at rather slow rotation rates clearly shows resolved side bands for the two narrow lines of the methoxy and quaternary carbons (*Figures 2b* and *c*). The side band pattern of the methoxy carbon reveals that this resonance has a rather large chemical shielding anisotropy. Herzfeld and Berger[10] describe a graphical method which enables one to obtain, from the relative intensities of the side bands at a known rotation rate, both the total width $\sigma_{11} - \sigma_{33}$ of the chemical shift powder pattern and the location of the intermediate shielding element, $\sigma_{22} - \bar{\sigma}$. We have applied this graphical method to characterize the methoxy carbon *CST*. From the side band intensities in *Figure 2b* we find a total width $\sigma_{11} - \sigma_{33}$ of $66 \pm 6$ ppm, with $\sigma_{22}$ located at $+15 \pm 5$ ppm from the isotropic chemical shift $\bar{\sigma}$. These figures, together with the measured value of $\bar{\sigma}$ in the MAS spectrum, establish that the shoulder and peak at 80 and 63 ppm in the non-spinning spectrum must be assigned to $\sigma_{11}$ and $\sigma_{22}$ of the methoxy carbon resonance. $\sigma_{33}$ is calculated to be located at 13

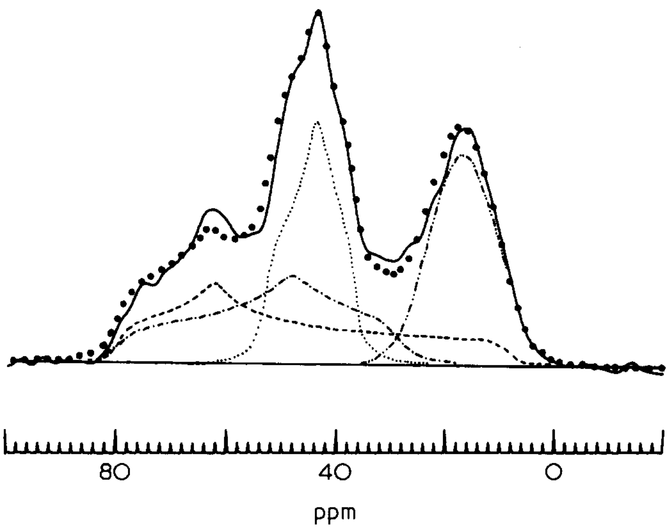

*Figure 3* Completely relaxed $^{13}C$ n.m.r. spectrum of non-spinning PMMA, and the spectrum calculated from the chemical shielding tensor elements (see *Table 1*): ——, measured spectrum; ●●●, simulated spectrum; – – –, methoxy carbon resonance; –·–·–, methylene carbon resonance; ....., quaternary carbon resonance; –··–··–, methyl carbon resonance

$\pm 6$ ppm and so is hidden underneath the methyl carbon resonance. $\sigma_{33}$ can be observed directly in partially spin–lattice relaxed spectra once the methyl resonance has relaxed away. After a relaxation delay of 1 s, the spectrum clearly shows an edge at 10 ppm which is assigned to $\sigma_{33}$ of the methoxy resonance (*Figure 2f*).

### *Quaternary carbon*

The quaternary carbon resonance is broadened by chemical shielding anisotropy, as is clearly indicated by the side bands observed at slow MAS rotation rates (*Figures 2b* and *c*). The total width, $\sigma_{11}-\sigma_{33}$, is small since just a few side bands are observed at the slowest practicable rotation rates. Analysing the side bands as described above, the total width is found to be $15 \pm 5$ ppm; the position of $\sigma_{22}$ cannot be estimated from the side bands. The side band pattern is slightly asymmetric and indicates that $\sigma_{22}$ is close to $\bar{\sigma}$ and lies towards the high-field side.

Additional information is obtained from a spin–echo experiment. The quaternary line is the narrowest one in the MAS spectrum. Therefore, it is expected that it will also have the slowest transverse relaxation rate $R_2$. With a spin–echo experiment we can indeed select the quaternary carbon resonance (*Figure 2h*). A powder pattern with a total width of 16 ppm is observed, with $\sigma_{22}$ at 1 ppm from $\bar{\sigma}$ towards high field; this agrees well with the slow MAS results.

The values found for the *CST* elements (see *Table 1*) identify the peak in the PMMA spectrum (*Figure 2d*) at 43 ppm and the shoulder around 37 ppm as $\sigma_{22}$ and $\sigma_{33}$ of the quaternary carbon. The pronounced shoulder at 48 ppm does not stem from the quaternary carbon resonance.

### *Methylene carbon*

The methylene carbon resonance in the MAS spectrum is too broad to yield identifiable side bands, and the *CST* must be obtained from other spectral features. The resonance must be broadened considerably in the non-spinning spectrum (*Figure 2d*). This follows, for example, from the fact that the isotropic chemical shift coincides with the dip in the spectrum around 53 ppm, where the intensity is much too low to accommodate a relatively narrow methylene resonance. If we compare a completely relaxed spectrum with a simulated spectrum of the three resonances assigned above, we find that intensity is missing across a wide ppm range, mainly in the low-field half of the resonance region (compare *Figure 3*).

The only prominent feature in the spectra not assigned so far is the pronounced shoulder at 48 ppm. This shoulder is assigned to the peak, $\sigma_{22}$, of the methylene resonance. This assignment is supported by other observations. The shoulder is less pronounced when the protons are decoupled by a smaller r.f. magnetic field (32 kHz). We ascribe this to incomplete proton decoupling in the latter case; in this range of r.f. fields, incomplete decoupling affects the methylene carbon the most[11]. Partially spin–lattice relaxed spectra also support the assignment. The methylene resonance has the slowest spin–lattice relaxation rate of the overlapping resonances[7]; it should therefore become more pronounced at long relaxation delays. Spectra obtained after 1 and 10 s relaxation delay clearly show that this is the case for the shoulder at 48 ppm (*Figures 2f* and *g*). In the same spectra a discontinuity is observable at 29 ppm which behaves in a similar way. We assign this spectral feature to $\sigma_{33}$ of the methylene resonance. It then follows that $\sigma_{11}$ is located at 79 ppm and coincides with $\sigma_{11}$ of the methoxy resonance. With these values the missing intensity in the low-field half of the spectrum is explained nicely.

We have tried to differentiate the methylene carbon resonance on the basis of differences in other rate parameters. In MAS spectra we confirmed that both the spin–lattice relaxation rate in the rotating frame ($R_{1\rho}$) and the cross-polarization rate are useful discriminators to separate out the methylene resonance[3], both of them being considerably faster for the methylene resonance than for the other ones. In the non-spinning state the same

*Table 1* Chemical shielding tensor elements of $^{13}C$ in poly(methyl methacrylate). $\sigma$ and $\delta$ are given in ppm relative to TMS. $\bar{\sigma}$ is obtained from the MAS spectrum. (Errors are given relative to $\bar{\sigma}$. The absolute accuracy of $\bar{\sigma}$ is ±0.5 ppm)

| | | $\sigma_{11}$ | $\sigma_{22}$ | $\sigma_{33}$ | $\bar{\sigma}$ | $\delta$ | $\eta$ |
|---|---|---|---|---|---|---|---|
| carboxyl | $-COO-$ | 268 ± 2 | 150 ± 1 | 112 ± 1 | 177 | 91 ± 2 | 0.42 ± 0.03 |
| methoxy | $-OCH_3$ | 80 ± 1 | 63 ± 1 | 10 ± 2 | 51 | –41 ± 2 | 0.41 ± 0.05 |
| methylene | $-CH_2-$ | 79 ± 3 | 48 ± 1 | 29 ± 2 | 52 | 27 ± 3 | 0.70 ± 0.10 |
| quaternary | $-\overset{\vert}{\underset{\vert}{C}}-$ | 52.5 ± 0.5 | 43.0 ± 0.5 | 36.5 ± 0.5 | 44 | 8.5 ± 0.5 | 0.76 ± 0.10 |
| methyl | $-CH_3$ | – | – | – | 12–24 | ~3 | – |

experiments fail to separate out the $CH_2$ resonance for the following reasons. $R_{1\rho}$ is smaller in a non-spinning sample as is common in rigid molecules[12], and its value becomes comparable to those of the other resonances in the spectral band. The rate of $CH_2$ cross-polarization probably still is the faster one, but the analysis of the CP spectra after short contact times (5 to 100 $\mu$s) is troubled by the presence of dipolar oscillations[13], which occur at different frequencies over the chemical shift powder patterns as a result of the dependence on orientation of both the dipolar interaction and the *CST* with respect to the static magnetic field.

### *Spectral simulation*

A final check on the assignments is obtained by calculating a simulated spectrum. This spectrum should be compared with a completely relaxed spectrum of PMMA, in order to have the correct relative intensities. The completely relaxed spectrum and the calculated one are shown in *Figure 3*. The simulated spectrum is calculated from the data in *Table 1*, using line broadening with the line widths given by the MAS spectrum. For ease of calculation, the methyl resonance is represented by a single Gaussian curve. The calculated spectrum reproduces the measured one quite closely. We therefore are convinced that our assignments are correct.

## DISCUSSION

Schaefer *et al.*[1,2] have assigned the $^{13}C$ n.m.r. spectrum of solid PMMA before. The assignment corresponds only partly with the one given here. They assigned the highest peak in the spectrum to the methoxy and quaternary resonances, whereas we identify this peak as being mainly due to the quaternary carbon, with methylene contributing to a lesser extent. The lower-field part of the resonance was assigned to methylene; we find that it reflects mainly the methoxy resonance, but with a sizeable contribution from the methylene resonance.

The chemical shielding tensors obtained for PMMA are collected in *Table 1*. The *CST* elements of the ester side chain carbons are rather similar to those measured in crystalline model compounds such as methylformate or methylacetate[14,15]. This indicates that these *CST*s are not motionally averaged to any extent. The complete side chains are immobile on the time scale defined by the chemical shielding anisotropy, which is of the order of milliseconds.

Data to compare the backbone carbon *CST*s are scarce. The total width of the methylene *CST* (50 ppm) is comparable to those found in crystalline polyethylene (38 ppm)[16] and in crystalline polyoxymethylene (50 ppm)[17]. For a quaternary carbon in an asymmetric environment, no data on other compounds could be found. Since the *CST*s for both backbone carbons are anisotropic as well as clearly asymmetric, we conclude that these tensors show their full widths. The backbone is immobile as well on the same time scale.

The experiments have been performed on commercial atactic PMMA, which, as usual, is mainly syndiotactic. In our assignment we have not taken into account the possibility of different *CST*s for different conformations or configurations. It does not seem that the *CST*s are rather sensitive to such effects. Similar measurements performed on samples of isotactic PMMA indicate very similar anisotropy and asymmetry, although the isotropic chemical shifts may vary by a few ppm[7].

Knowledge of the carbon chemical shielding tensors is a prerequisite for the characterization of motions in PMMA by temperature-dependent n.m.r. measurements. The present study provides the relevant information.

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