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Polymer 43 (2002) 609–614

polymer

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Chemical shift tensors for the aromatic carbons in polystyrene☆

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Abstract

Chemical shift tensors (CST) for the protonated aromatic carbons in polystyrene are presented. Experimental difficulties preclude the direct measurement of these tensors. The values reported are obtained from quantum chemical calculations on 2-phenyl propane using the 6-31G basis set, after testing other basis sets against similar compounds for which the chemical shift anisotropies are known. Corrections for narrowing of the chemical shift anisotropy due to the molecular motions at finite temperatures are also reported. © 2001 Published by Elsevier Science Ltd.

Keywords: Polystyrene; Chemical shift tensors; Quantum chemical modeling

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1. Introduction

Solid-state NMR is an increasingly powerful and popular method for investigating molecular structure in partially disordered polymeric systems [1]. Several NMR techniques, such as DECODER [2] and 2D CP-MAS [3], are based on chemical shift anisotropy where the measured resonant frequencies or the intensities of the spinning side bands are dependent on the orientation of a chemical unit, and the chemical shift tensors (CST) associated with it, with respect to the applied magnetic field. The analyses of the lineshapes acquired from these techniques require accurate knowledge of the principal values of the CST governing the interactions measured in the NMR experiment.

Polystyrene is an ideal candidate for studying the influence of processing on structure since it is a major commodity resin, easily synthesized, and its chain architecture can be readily influenced by choice of polymerization catalysts. Moreover, polystyrene is well suited for solid-state DECODER NMR analysis because of the large chemical shift anisotropy inherent to its aromatic carbons. The chemical shift anisotropy is the difference in the principal values of the chemical shift tensor $\boldsymbol{\sigma}$, where the components σ_{ii} are ordered such that $|\sigma_{yy} - \sigma_{\mathrm{iso}}| \leq |\sigma_{xx} - \sigma_{\mathrm{iso}}| \leq |\sigma_{zz} - \sigma_{\mathrm{iso}}|$ and $\sigma_{\mathrm{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$ [1]. Larger values of the chemical shift anisotropy enable better resolution of the lineshape, and thus a more accurate determination of the underlying molecular order. Aliphatic carbons have relatively small chemical shift anisotropies, in the range of 30–40 ppm. On the other hand, ester groups have chemical shift anisotropies on the order of 150 ppm and phenyl carbons have anisotropies approaching 200 ppm [4].

For analysis of orientational order, a signal free of overlapping chemical shifts from different chemical groups in the chain is desirable, but not essential. Fig. 1 shows the DECODER powder spectrum of polystyrene pellets with a reorientation angle of 180° during the mixing time. The high intensity signal in the range of 5–70 ppm is attributed to the aliphatic carbons in the chain backbone of polystyrene, whereas the diffuse signal covering the range of 15–225 ppm corresponds to the phenyl carbons of the repeat unit. It is evident that the phenyl and the backbone aliphatic carbon signals are completely separated. However, the chemical shift anisotropy of all four chemically distinct carbons in the polystyrene phenyl ring cover roughly the same area.

Fig. 2(a) shows the chemical repeat unit for polystyrene with a label assigned to each chemically distinct carbon. Isotropic chemical shifts of each carbon in the polystyrene repeat unit have been determined by high-resolution CP-MAS experiments [5] and are shown in Table 1. Principal values of the CST of the aromatic carbons of polystyrene are lacking in general compilations of such data [4,6]. The only available polystyrene chemical shift anisotropy data in the literature are for the unprotonated phenyl carbon 3 [7]. In that study, the authors polymerized styrene synthesized from benzoic acid which was isotopically enriched at the unprotonated phenyl carbon site. The principal values of the chemical shift tensor were fit to a 2D proton driven ^{13}C

☆ This paper was originally submitted to *Computational and Theoretical Polymer Science* and received on 31 July 2000; received in revised form on 4 December 2000; accepted on 4 December 2000. Following the incorporation of *Computational and Theoretical Polymer Science* into *Polymer*, this paper was consequently accepted for publication in *Polymer*.

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0032-3861/02/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S1089-3156(00)00029-5

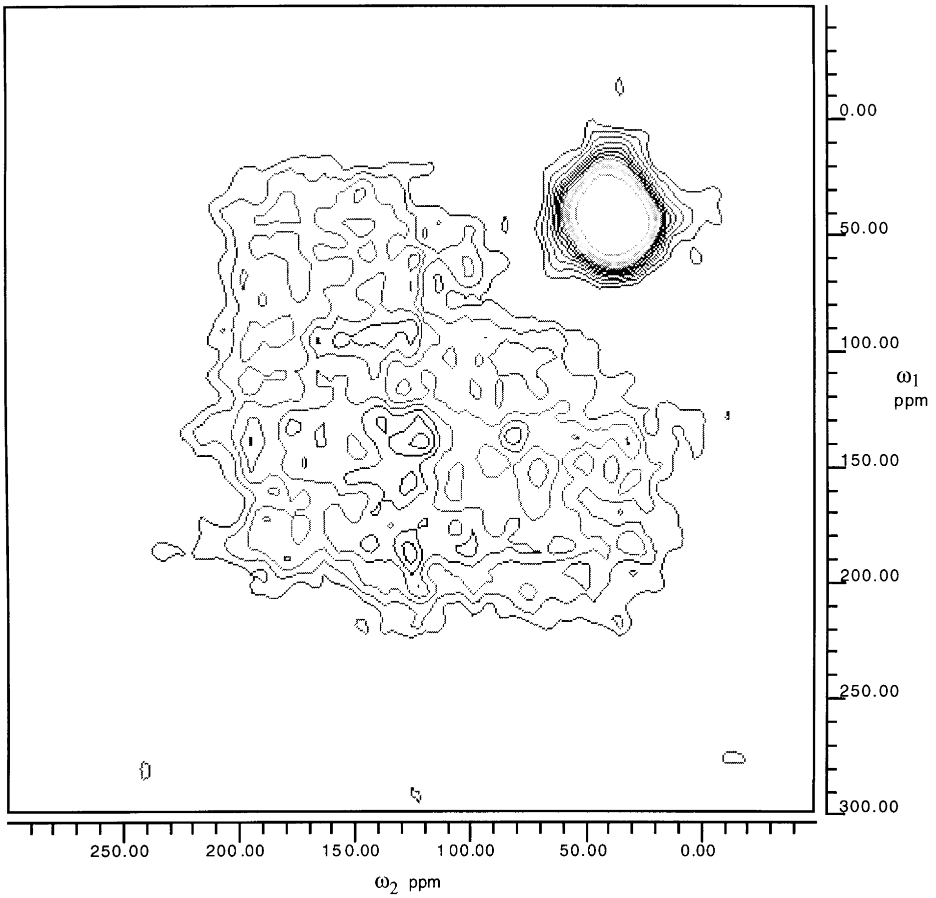

Fig. 1. DECODER NMR powder spectrum of polystyrene pellets with a reorientation angle of 180° during the mixing time.

polarization transfer spectrum with zero mixing time. These components are listed in Table 2. The upfield component (σ_{zz}) is normal to the phenyl ring plane, and the downfield component (σ_{xx}) is parallel to the C2–C3 bond. The value of the isotropic chemical shift obtained by averaging the principal components of the CST agrees with the value reported in Ref. [5]. From a practical standpoint, the use of isotopically enriched material in polymer processing studies requiring an appreciable amount of resin is prohibitively expensive.

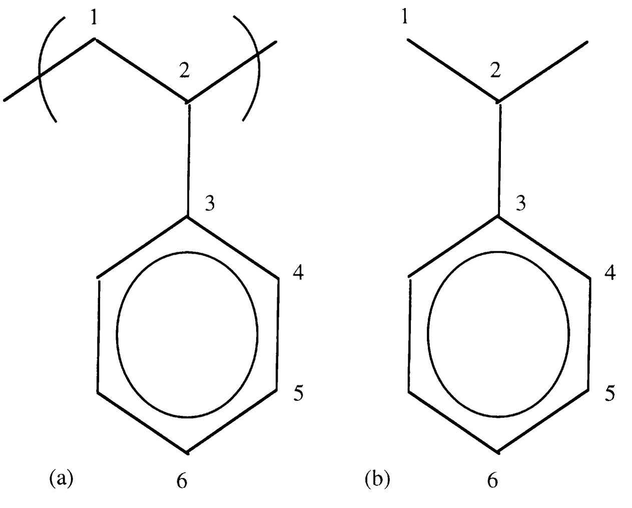

Fig. 2. Chemical structure of: (a) the polystyrene repeat unit; and (b) 2-phenyl propane.

Chemical shift anisotropy data for aromatic carbons in other compounds are reported in the literature, namely for amino acids [8], substituted naphthalenes [9], and various substituted benzenes [4,6]. Whereas the isotropic chemical shifts of some of these carbons agree with the values for the protonated aromatic carbons in polystyrene, the differences in the chemical substituents of the aromatic ring relative to polystyrene render the applicability of the chemical shift anisotropy data from these sources to polystyrene questionable.

Table 1
Isotropic ^{13}C chemical shifts for polystyrene [5]

Carbon number	σ_{iso} (ppm from TMS)
1	42–47
2	41
3	146
4	128
5	128
6	126

Table 2
Chemical shift anisotropy data for the unprotonated phenyl carbon of polystyrene [7]; all values are ppm from TMS

σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}
236	184	18	146

A common method of determining the principal values of CST is the 2D magic angle turning experiment [9]. The signals from the various carbons are separated by their isotropic chemical shifts in one dimension and the fully anisotropic lineshape for each carbon is displayed in the second dimension. The equivalence of the isotropic chemical shifts for carbons 4 and 5 in Fig. 2(a) means that it is impossible to obtain separate signals for these carbons by this method, and the proximity of the isotropic chemical shift of carbon 6 would make its signal difficult to separate experimentally. Similar overlap problems of CST are encountered in the analysis of orientation in HBA/HNA aromatic copolyester fibers [10].

One way to estimate the necessary chemical shift anisotropy information is to calculate the CST for model compounds by using quantum chemical modeling. The remainder of this paper is devoted to the description of calculations used to obtain the CST for the aromatic carbons of polystyrene, and the subsequent modification of those tensors to account for the motional narrowing of the chemical shift anisotropy at finite temperatures.

2. Method

The Turbomole module of the MSI molecular modeling software package [11] was used for the chemical shift tensor calculations. The general method of approach was as follows. The geometry of the test molecule was optimized using the *cvff* force field to obtain a reasonable configuration of low energy. The test molecule was then imported into the Turbomole quantum chemistry module of Biosym. A Hartree–Fock self consistent field ab initio calculation was performed with an appropriate set of basis functions (as described in the next section) to optimize the molecular geometry again and to calculate the electronic energy and electronic density of the molecule. A perturbation calculation was then performed to calculate the secondary magnetic field induced by electronic currents from the application of a static magnetic field [12]. The unperturbed and perturbed electronic density matrices yield the diamagnetic and paramagnetic components of the chemical shift tensor, respectively. The sum of these contributions is reported as the total chemical shift tensor when referenced to the isotropic chemical shift of tetramethylsilane (TMS) calculated in the same manner.

3. Results and discussion

Basis set selection. It is well known that the choice of electronic basis functions is crucial to the accuracy of the results obtained. Several sources [11,13,14] argue the necessity of using a basis set of triple zeta quality to obtain reliable magnetic shielding results. Given the highly polarizable nature of aromatic molecules, it is also likely that a set of polarization functions need to be included in the NMR shielding calculations to obtain accurate results. Nevertheless, in work [14] on naphthalenium and anthracenium ions using the triple zeta basis set with one set of polarization functions on the carbon atoms and a double zeta basis set on the hydrogen atoms (tzp/dz), errors in the isotropic chemical shifts of various carbons of up to 10 ppm were reported; it is reasonable to expect larger errors in the principal components of the CST than in the isotropic value.

Calculation of the carbon chemical shift tensor for benzene was performed with several different basis sets. These results were then compared to experimental data for crystalline benzene [4] to determine the best basis set to use for the current analysis. The data are shown in Table 3. The experimental data correspond to a temperature of 20 K. In the principal axis frame of reference, the *z*-direction corresponds to the ring normal, and the *x*-direction corresponds to the C–H bond direction.

The two basis sets which most accurately reproduce the experimental isotropic chemical shift data are the split-valence 6-31G Gaussian basis functions and the tzp basis set. These two basis sets also minimize the overprediction of the σ_{xx} component of the CST. Calculation of the NMR chemical shift tensor failed to converge in the maximum allowable number of iterations for the 6-31G* set of basis functions, which includes a set of polarization functions. Limitations of the commercial software precluded increasing the number of iterations in the chemical shift tensor portion of the calculation to obtain convergence for this basis set.

Experimental chemical shift anisotropy data are also available for *p*-xylene. This model molecule has both protonated and unprotonated carbons. The CST for both carbons were calculated with both the 6-31G and the tzp basis sets. The results are shown in Table 4 and are compared to experimental data [6].

Again, the results from the 6-31G basis set are in closer agreement to the experimental data than those of the tzp basis set, especially for the σ_{xx} component of the CST.

Table 3
Calculated ^{13}C chemical shift anisotropy data for benzene obtained by using various Hartree–Fock basis sets. Experimental values taken from Ref. [4]; all values are ppm from TMS

H-F basis set	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}
Experimental	234	146	9	130
3-21G	223.9	134.8	3.4	120.7
6-31G	245.0	146.7	3.3	131.7
tz	266.6	152.1	4.9	141.2
tzp	257.9	146.1	4.1	136.0
tzvp	265.7	150.8	3.2	139.9

Table 4
Comparison of calculated and experimental ^{13}C chemical shift anisotropy data for the protonated unprotonated carbons of *p*-xylene. Experimental data taken from Ref. [6]; all values are ppm from TMS

H-F basis set	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}
Experimental	227/232	136/162	21/6	128/133
6-31G	240.2/243.8	138.7/164.8	18.8/4.6	132.5/137.7
tzp	251.8/255.9	138.0/170.0	19.0/4.3	136.3/143.4

This is important since a larger overprediction of the σ_{xx} component will cause calculated spectra in the DECODER analysis to cover a larger domain in frequency space than the experimental data, thus adversely affecting the quality of the fit. Therefore, we considered it appropriate to proceed with the 6-31G basis set in further calculations.

Model compound calculations. It is impractical to perform a quantum chemical calculation of CST on a long chain of polystyrene. Indeed, the calculation is most efficient when it takes advantage of symmetry in the test molecule. The primary requirement is that the electronic environment of the aromatic substituent in the test molecule resemble as closely as possible that observed in polystyrene. To a first approximation, this is determined primarily by chemical bonding. With this in mind, 2-phenyl propane, shown in Fig. 2(b), was used as a model compound to calculate the CST for polystyrene. Intramolecular π-interactions between neighboring phenyl rings are neglected in this analysis.

The results of the Turbomole calculation of the chemical shift anisotropy of 2-phenyl propane with the 6-31G basis set are shown in Table 5, along with experimental data for carbon 3 [7] and the experimental isotropic chemical shifts [5]. The relative magnitudes of the calculated isotropic chemical shifts for the different phenyl carbons are correct, and the differences in these values compared to the experimental data are well within the errors reported for calculations with a tzp basis set [14]. The orientations of the calculated CST for the protonated carbons are in accordance with expectation based on benzene, with the *z*-direction normal to the ring and the *x*-direction along the C–H bond.

Motional averaging of CSTs. There is evidence in polystyrene of a fast motional process active below the glass transition temperature, which is eventually frozen out at approximately 200 K [15,16]. From quasielastic neutron scattering on selectively deuterated polystyrenes, it was concluded that the fast motional process originating at 200 K is associated with phenyl ring rotations [16]. Furthermore, as the observed activation energy of this fast process is nearly zero, the possibility of its being associated with 180° flips of the phenyl ring was excluded. Thus the 25% of rings measured participating in this fast process at 295 K were concluded to be undergoing librational motion [16,17]. Spiess [18] estimated the average amplitude of the librational motion to be 30–40°, whereas simulations put this number at 16 ± 12° [19].

Table 5
Calculated ^{13}C chemical shift anisotropy data for 2-phenyl propane obtained by using the 6-31G basis set. The experimental values correspond to polystyrene: σ_{iso} from Ref. [5] and carbon 3 from Ref. [7]; all values are ppm from TMS

Carbon #	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}	σ_{iso} expt
6	240.6	145.9	5.5	130.7	126
5	247.7	147.4	7.6	134.2	128
4	241.6	137.6	23.0	134.1	128
3	249.6	195.5	14.0	153.0	146
3 expt	236	184	18	146	146

Although several authors have estimated that 20–25% of the rings undergo 180° flips above [18] and below [19] the glass transition temperature (ca. 373 K), only about 3–7% of the rings are estimated to be flipping at room temperature [19,20]. The rings spend negligibly short time in the transition between the two states for 180° flips [21].

Maxwell et al. [22] have proposed a model for the effects of phenyl ring motions on the observed principal components of the phenyl carbon CST in poly(ethylene terephthalate). In particular, for the unprotonated carbon, librations encompassed by the angles $\pm\alpha$ around the unprotonated phenyl carbon–carboxylic carbon bond are considered. For rotation through an angle α about the *x*-axis, the chemical shift tensor is given by:

$$\sigma^{\mathrm{lib}} = R(\alpha)\cdot\sigma\cdot R^{-1}(\alpha) \tag{1}$$

where $R(\alpha)$ is a rotation matrix. The tensor averaged over all permissible values of α is calculated by:

$$\langle\sigma^{\mathrm{lib}}\rangle = \frac{1}{2\alpha}\int_{-\alpha}^{+\alpha}\sigma^{\mathrm{lib}}\,\mathrm{d}\alpha \tag{2}$$

The oscillatory motions leave the σ_{xx} component of the tensor unchanged and provide partial averaging of the σ_{yy} and the σ_{zz} components according to:

$$\begin{aligned}\langle\sigma_{yy}^{\mathrm{lib}}\rangle &= \left(\frac{\sigma_{yy}+\sigma_{zz}}{2}\right) + (\sigma_{yy}-\sigma_{zz})\frac{\sin 2\alpha}{4\alpha}\\ \langle\sigma_{zz}^{\mathrm{lib}}\rangle &= \left(\frac{\sigma_{yy}+\sigma_{zz}}{2}\right) - (\sigma_{yy}-\sigma_{zz})\frac{\sin 2\alpha}{4\alpha}\end{aligned} \tag{3}$$

Ring flips of 180° about the same axis have no effect upon the components of the unprotonated phenyl carbon chemical shift tensor. The rotational motion considered by Maxwell et al. for poly(ethylene terephthalate) is very similar to the rotation of the phenyl group of polystyrene about the bond connecting it to the chain backbone.

This analysis for motional averaging was applied to the calculated chemical shift tensor principal values of carbon 3 listed in Table 5. The value of $\alpha = 20.75°$ for the librational motion in polystyrene gave the best fit to the principal values data [7] for the same carbon. This value is the same order of magnitude as that estimated by other authors [18,19].

Table 6
Explicit effects of librational and flipping motions on the ^{13}C chemical shift tensors for polystyrene; all values are ppm from TMS

	Carbon 4	Carbon 5	Carbon 6
$\langle\sigma_{xx}^{\mathrm{lib}}\rangle/\langle\sigma_{xx}^{\mathrm{flip}}\rangle$	234.6/202.6	240.0/210.1	240.6/240.6
$\langle\sigma_{yy}^{\mathrm{lib}}\rangle/\langle\sigma_{yy}^{\mathrm{flip}}\rangle$	136.4/176.6	145.9/185.0	139.9/145.9
$\langle\sigma_{zz}^{\mathrm{lib}}\rangle/\langle\sigma_{zz}^{\mathrm{flip}}\rangle$	31.2/23.0	16.8/7.6	11.5/5.5

For the protonated carbon numbers 4 and 5, the calculation of motional averaging was slightly more complicated. Rotations of $\gamma = \pm 60°$ and $\pm 120°$, respectively, about the z-axis were required to transform the CST into the frame of reference in which the averaging of the angle α occurred. The effect of the 180° ring flips on the CST for these carbons was also calculated. The results were then rotated back into the original principal axis system frame of reference. The effects of either librational or flipping motion on the CST of carbons 4–6 are illustrated in Table 6.

Finally, motionally averaged CST were calculated for each phenyl carbon with a weighted average according to fractions of each type of motion listed above:

$$\langle\sigma\rangle = 0.25\langle\sigma^{\mathrm{lib}}\rangle + 0.07\langle\sigma^{\mathrm{flip}}\rangle + 0.68\sigma \qquad (4)$$

The results for carbons 4–6 are given in Table 7. The experimentally determined chemical shift tensor for carbon 3 [7] is quoted in preference to the one calculated because of its more accurate isotropic chemical shift. These motionally averaged CST are thus useful in performing lineshape analyses on spectra obtained at room temperature of deformed polystyrene [23].

Sensitivity analysis. As the weighting fractions used in Eq. (4) are subject to error, a sensitivity analysis of $\langle\sigma\rangle$ on the value of the weighting fractions was performed. If the fraction of rings undergoing librational motion changes by 1%, σ_{xx} and σ_{zz} for carbons 4 and 5 change by approximately 0.06 ppm and σ_{yy} changes by about 0.01 ppm, while for carbon 6, σ_{xx} is unchanged and σ_{yy} and σ_{zz} vary by 0.06 ppm. If the fraction of rings flipping changes by 1%, σ_{xx} and σ_{yy} for carbons 4 and 5 change by approximately 0.38 ppm, while σ_{zz} for carbons 4 and 5 and all components for carbon 6 are unaffected. Thus, the principal values of the motionally averaged CST are most sensitive to the value of the fraction of rings flipping, but the effect is much smaller than the magnitude of the error inherent in the calculation of the principal components themselves.

Table 7
Motionally averaged ^{13}C chemical shift tensors for polystyrene according to Eq. (4). Values for carbon 3 are taken from Ref. [7]; all values are ppm from TMS

Carbon #	σ_{xx}	σ_{yy}	σ_{zz}
6	240.6	144.4	7.0
5	243.1	149.9	9.9
4	237.1	140.0	25.0
3	236	184	18

4. Conclusions

We have used quantum chemical methods to calculate the CST for the aromatic carbons for polystyrene. The most appropriate basis set (6-31G) was selected by comparing the results of calculations with data available in the literature for small aromatic molecules such as benzene and p-xylene. 2-phenyl propane was selected as a model compound for polystyrene, and the CST for its aromatic carbons were calculated. Finally, the results from the model compound calculation were applied to polystyrene by accounting for the effect of known motions of the phenyl rings of polystyrene present at room temperature.

This method is broadly applicable in cases where knowledge of certain CST that are difficult or impossible to measure experimentally is required for structural or order analyses. It is particularly valuable in cases where the isotropic chemical shifts of multiple carbons are identical, and therefore the separation of the signals in a standard magic angle turning experiment is precluded. This approach also eliminates the need to resort to the expensive synthesis of isotopically labeled compounds to obtain the desired information.

Acknowledgements

This work was funded in part by grants from the 3M Company and by a Young Investigator Award of the National Science Foundation (CTS-9457111). The authors are grateful to MSI for making the Turbomole software available through an educational license to MIT.

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