Conformational Effects on ^{13}C-NMR Chemical Shifts of an Amorphous Polymer: An *ab Initio* Study by the IGLO Method

R. Born and H. W. Spiess*

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, FRG

W. Kutzelnigg, U. Fleischer, and M. Schindler

Fakultät für Chemie, Lehrstuhl für Theoretische Chemie, Ruhr-Universität, D-44780 Bochum, FRG

Received October 8, 1993; Revised Manuscript Received December 8, 1993•

ABSTRACT: The spread in ^{13}C-NMR chemical shifts in solid amorphous polymers is considered as a source of structural information. To this end, ^{13}C chemical shifts are calculated on an *ab initio* level for the central carbons of a tetramer model molecule, employing the IGLO method. Remarkable agreement between experimental and simulated spectra is obtained for polyisobutylene using the conformational statistics as obtained by Vacatello and Yoon. The observed experimental spread of ≈20 ppm for the CH_2 resonance is quantitatively reproduced in the calculations as is the γ-gauche effect. Correlations of the chemical shift with specific geometrical aspects as C–C bond lengths are established.

1. Introduction

The conformational statistics[1] of polymers is an important parameter determining their packing behavior. This is well known for crystalline polymers but should hold also for amorphous polymers in bulk. There in addition, deviations from the ideal chain geometries are expected due to variations of torsional angles around their free chain values, etc. Experimental determination of such parameters would allow a check of the corresponding calculations by Monte Carlo or molecular dynamics (MD) (see, e.g., refs 2–5) techniques and provide important information to be used in computed-aided X-ray studies of amorphous polymers.[6]

Nuclear magnetic resonance (NMR) of polymers in solution is a well-established tool for determining the chain microstructure.[7,8] As far as solids are concerned, many amorphous polymers display ^{13}C CP/MAS solid-state NMR signals much broader than the lines of analogous crystalline samples. This effect is mostly attributed to the inhomogeneous superposition of contributions from different conformations and is thereby related to the "molecular disorder" in the amorphous phase.[9] Though this explanation is widespread, direct evidence for it is scarce. In the simple case of atactic polypropylene, the main features of the observed spectrum could be obtained by comparison with well-characterized crystalline samples of isotactic and syndiotactic polypropylene.[8,10] On the other hand, an influence of the conformational environment on the chemical shift has long been known under the name of "γ-gauche effect"[11] and has been successfully exploited in the investigation of the stereostatistics of various vinyl polymers.[7,8] More recently, a strong correlation of local geometry and observed chemical shift has been reported in inorganic phosphate and silicate samples.[12,13] In the light of these mostly empirical findings, a conformational origin for the observed broad signals is very likely.

Thus we propose to use solid-state ^{13}C-NMR for determining the conformational statistics and local chain conformation. While the recording of CP/MAS spectra of bulk polymers is standard,[14] the quantitative analysis in terms of conformations is not and requires a thorough theoretical investigation. Modern computing power and novel schemes for the calculation of NMR chemical shifts (Individual Gauge for Localized Orbitals (IGLO),[15–18] Gauge Invariant Atomics Orbitals (GIAO),[19] Localized Orbitals/Local Origin (LORG)[20]) now permit treatment of these problems on the *ab initio* level.[21–23] As a first example for the application to polymers, we present an IGLO study of polyisobutylene (PIB), an amorphous polymer where conformational effects are especially pronounced.[3] This then allows us to look for correlations between specific geometric aspects like bond lengths or angles and the chemical shift.

2. ^{13}C-NMR Spectrum of PIB

Polyisobutylene (see Figure 1a) is an amorphous polymer which undergoes a glass transition at $T \approx 200$ K. It is subject to large steric hindrance due to the two side-chain methyl groups. The ^{13}C CP/MAS spectrum in Figure 2a was recorded at $T = 208$ K (near the glass transition) and at a spinning speed of $f_{ROT} = 3.6$ kHz on a Bruker MSL-300 spectrometer.[24] The methylene resonance is richly structured and spreads over a remarkably wide range of >20 ppm. The methyl peak is unusually broad, too. The high spinning speed precludes any broadening due to residual chemical shift anisotropy. Motional broadening can be ruled out by a 2D exchange experiment;[24] motion occurs with a mean correlation time of ≈500 ms and does not affect the line width. Thus, the broadening can be assumed to be of conformational origin, which makes PIB an interesting sample for a theoretical treatment.

3. Calculation of Chemical Shifts

The IGLO Scheme. The IGLO program has been applied to a great number of compounds (see ref 16 and references therein) and has proved to be a valuable tool in the understanding of NMR chemical shifts. This includes geometrical questions like the discrimination between different proposed geometries for a molecule[25] (ref 16, p 227) and the investigation of conformational effects (ref 16, p 220).[17,26] As the IGLO approach has been described in detail elsewhere,[16,18] only a few basics shall be given here. The chemical shift tensor $\sigma_{\alpha\beta}$ is the second-order response property of a molecular system both to the magnetic moment $\tilde{\mu}^K$ of the nucleus in question K and the

• Abstract published in *Advance ACS Abstracts*, February 1, 1994.

0024-9297/94/2227-1500$04.50/0 © 1994 American Chemical Society

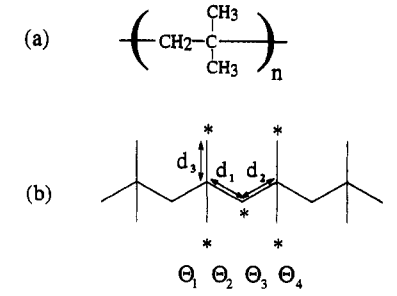

Figure 1. Polyisobutylene (a) and oligomer (b) selected as the model molecule for the calculation. An asterisk denotes the positions of the methyl and methylene carbons for which the end-group effects are small and which are considered typical of the bulk polymer.

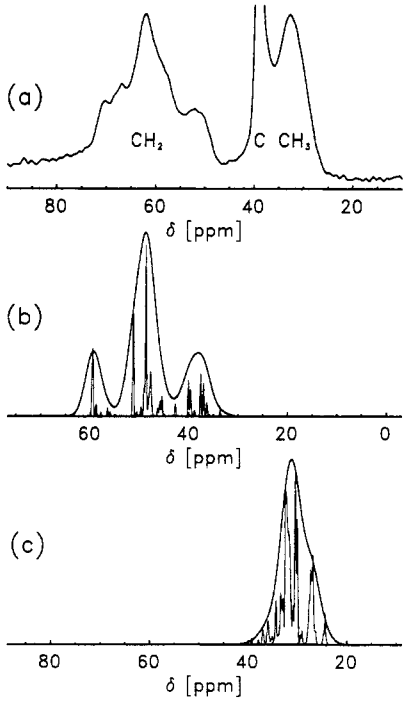

Figure 2. Experimental (a) (taken from ref 24) and simulated (b,c) spectrum of PIB. All values are in ppm from TMS; the theoretical data have been translated from the theoretical scale into the experimental scale by comparison with a calculation of TMS. The displayed range has been selected for both resonances (methyl and methylene) independently. The thin lines in the theoretical spectra indicate the contributions (slightly broadened for typographic reasons) of the various conformations. Note that the more pronounced thin-line peaks are superpositions of many conformations with about the same chemical shift.

applied constant external magnetic field $\vec{B}$

$$\sigma^{K}_{\alpha\beta} = \frac{\partial^2 E}{\partial \mu^{K}_{\alpha} \partial B_{\beta}}, \quad \alpha,\beta = x,y,z \tag{1}$$

where $E = \langle \Psi | \mathcal{H} | \Psi \rangle$ and $\mathcal{H}$ is the *full* Hamiltonian of the system bilinear in the external field $\vec{B}$ and the magnetic moment μ. The Hamiltonian does, however, not contain the magnetic field directly, but the vector potential $\vec{A}$, related to $\vec{B}$ by

$$\vec{B} = \vec{\nabla} \times \vec{A} \tag{2}$$

Though $\vec{B}$ as a physical quantity is unambiguously defined, one may apply a gauge transformation

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \vec{\nabla}\lambda \tag{3}$$

without changing $\vec{B}$. This ambiguity in the choice of $\vec{A}$ can cause considerable errors in the calculation of chemical shifts due to "incomplete cancellation of large terms". Within conventional approaches large basis sets are needed to overcome these difficulties. One thus can only study comparably small molecules. By attributing a special gauge to any *localized* molecular orbital the IGLO method circumvents these problems, and one gets reliable results with small to medium sized basis sets. Then it is possible to study larger systems. (This holds also for the other approaches mentioned before, which use several distributed gauge origins as well. The methods are thus comparable in philosophy although they differ, of course, in detail.) For the detailed deduction, the reader is referred to the literature.[18]

Application to Polymers. The IGLO method has not yet been applied to synthetic organic polymers or models of polymers (but cf. the investigation of zeolithes in ref 27). Thus it is not obvious *a priori* how meaningful results can be obtained for these compounds. Since the chemical shift is mainly a local phenomenon and since the γ-gauche effect is known to dominate the conformational effects of the chemical shift, we simplify the problem and, for the calculation, choose a "tetramer" displayed in Figure 1b as a model for the macromolecule. The terminal backbone carbons have been saturated with methyl groups. The calculations are done for isolated molecules and should thus, in principle, be compared to experimental data in the gas phase at low density. As packing effects are generally small ($\leq$1 ppm),[28] we nevertheless can compare them to the solid-state data.

In a first approximation, the conformation of the molecule can be described by the sequence of the four central dihedral angles $\vec{\Theta} := (\Theta_1,\Theta_2,\Theta_3,\Theta_4)$. The conformational statistics of our model is taken from the advanced Monte Carlo calculation by Vacatello and Yoon.[3] They employ a six-state rotational isomeric state (RIS) model with dihedral angles centered at $\pm$15°, $\pm$105°, and $\pm$130°. For our purposes, we denote $\pm$15° as *trans* (t) states, and the rest as *gauche* (g). In ref 3 the *a priori* probabilities for the dyads (such as described by (Θ_2,Θ_3) in Figure 1) and the interdyads ((Θ_1,Θ_2) and (Θ_3,Θ_4) in Figure 1) are given. If we assume a strictly Markovian behavior of the chain, we can calculate the *a priori* probabilities for the full seqeunce $\vec{\Theta}$. Many of the $6^4 = 1296$ different conformations are almost negligible. In fact, we find that 49 conformations (together with their symmetry-related partners) have an overall probability of >91%. Thus the calculation was restricted to this subset.

Computational Details. For all of the selected 49 conformations, we kept the dihedral angles $\vec{\Theta}$ fixed to the values given by the RIS model. The rest of the molecule was minimized in the Consistent Valence Force Field (CVFF), provided with the INSIGHT/DISCOVER (Version 2.9) package of BIOSYM, Inc. For the optimized geometries, an IGLO calculation was performed with the following basis of *double-ζ* quality (DZ in the notation of ref 16): Carbons were equipped with a (7s,3p) set in the contraction (4,1,1,1;2,1), hydrogens with (3s) contracted to (2,1). Although the DZ basis does not always yield satisfactory results, it works well in saturated hydrocarbons like PIB, especially if the main interest is in the relative chemical shifts (ref 16, pp 190, 212ff). For the quaternary carbons the DZ results would be less reliable than for the primary and secondary ones. As, in addition, the experimental NMR signal of the methine carbons in PIB is not structured and comparably narrow, we do not discuss it here.

The calculations presented here were performed on a Silicon Graphics IRIS INDIGO with a R4000 CPU and

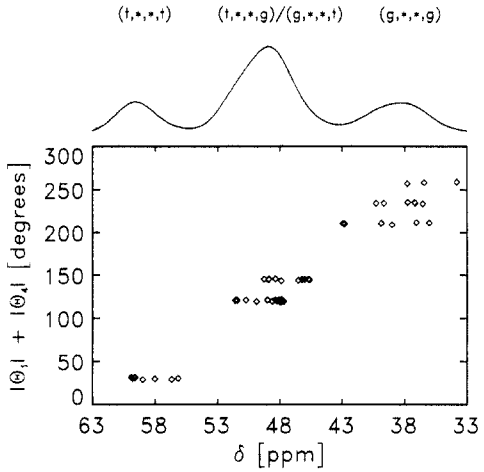

Figure 3. Calculated chemical shift δ vs the sum of the γ-gauche sensitive dihedral angles. The overall decrease of δ with increasing absolute values of the dihedral angles reflects the γ-gauche effect. The variation of δ within clusters of fixed values of $|\Theta_1| + |\Theta_4|$ is due to influences which are not γ-gauche in origin. For a three-state RIS model, only three clusters ((t,*,*,t), (t,*,*,g)/(g,*,*,t), (g,*,*,g)) would show up. With multiple gauche states in a six-state model, the clusters split up into subclusters—another effect which contributes to chemical shift variation.

64-MB core memory. We used the semidirect version of the IGLO program;[29] routinely about 40 million integrals were stored on hard disk. A calculation for a single conformation took roughly 12 h of CPU time in the DZ basis used throughout the calculations. A calculation with the larger, but still medium-sized basis II′ ((9s,5p) contracted to (5,1,1,1,1;2,1,1,1) augmented by a d function for carbon, (3s) in (2,1) contraction for hydrogens) consumes some 65 h on this machine.

To simulate the ^{13}C spectrum, the calculated shifts for all 49 conformations were weighted with their *a priori* probabilities (and the probabilities of the symmetry-related conformations) and any individual value was convoluted with a Gaussian with a width of 1.5 ppm (see below); afterward the various contributions were added. The result is presented in Figure 2b,c.

4. Results and Discussion

As displayed in Figure 2, the qualitative pattern of the experimental spectrum is well reproduced, whereas fine details differ. The widths of both of the methylene and the methyl resonances agree well with experiment. Moreover, the heights of the subpeaks are almost correct except in the region $65 < \delta < 70$ ppm. This is a highly satisfactory finding both for the calculational strategy applied here and the conformational model proposed by Vacatello and Yoon. The leftmost subpeak of the methylene resonance is attributed to $\tilde{\Theta}$ = (t,*,*,t) conformations, the central subpeak to (t,*,*,g)/(g,*,*,t), and the rightmost subpeak to (g,*,*,g) in accordance with the assignment for atactic polypropylene in ref 10. Thus, the γ-gauche effect is essentially confirmed (see also ref 23), as can be seen as well in Figure 3. There, the various clusters with almost constant values of $|\Theta_1| + |\Theta_4|$ correspond to states which are all (t,*,*,t), (t,*,*,g), etc. The decrease of the average δ of the clusters with increasing $|\Theta_1| + |\Theta_4|$ is essentially the γ-gauche effect. However, in addition, a substantial variation within the clusters and a multiple splitting of the clusters are observed. The latter results from the presence of several *gauche* states in the six-state RIS model. Our calculation shows that the ^{13}C chemical shift also depends on the interior dihedral angles (Θ_2,Θ_3) relative to (Θ_1,Θ_4).

This overall agreement between the simulated and the observed ^{13}C-NMR spectrum encourages us to consider specific points of the calculations in more detail in order to check the sensitivity of our approach.

(1) In the amorphous bulk polymer the dihedral angles will be subject to changes due to packing requirements. Therefore, in a separate calculation, we vary the dihedral angles of selected typical conformations by a maximum ±10° from their RIS model value. This induces variations of the chemical shifts of ±(1.5–2.0) ppm for *gauche* states. As expected, the variation of the chemical shift for a *trans* state was found to be smaller (0.5–1.0 ppm). Note, however, that the distortion of the dihedral angles is only one contribution to geometrical variability in the amorphous state, and the values obtained are thus only lower bounds to the overall smearing of the sharp RIS model values. We took account of this disorder broadening by convoluting the calculated sharp values of the chemical shift with a Gaussian function with a width of 1.5 ppm throughout the spectrum (see above). Naturally, this procedure is only an approximation of the computationally unaffordable exact solution (small variations of all geometrical parameters for all conformations).

(2) We have checked for end-group effects by replacing the methyl end groups by an ethyl, propyl, or isobutyl group and found the variation of the chemical shifts of the nuclei in question to be small (<1 ppm).

(3) The calculations yield values on a absolute scale σ, which is related to the experimental value δ by the relation $\delta = \sigma_0 - \sigma$, where σ_0 is the (absolute) shielding of a reference system (e.g., TMS). In the DZ basis used here, the shift difference $\delta_{CH_2} - \delta_{CH_3}$ is too small by about 12 ppm, whereas in the limit of an infinite basis the shift difference should be correctly reproduced. We checked this assertion by a test run on a trial molecule in the larger, but still medium-sized basis II′. As expected, $\delta_{CH_2} - \delta_{CH_3}$ increases by 6 ppm. For an even larger basis, the error in the difference of the shifts is expected to be even smaller. We emphasize again that these values refer to errors when comparing different sites. For the investigation of conformational effects within one resonance there is no problem of this kind. In the figures, the values are given on the experimental scale (in ppm from TMS), obtained by comparison with a calculation of TMS performed with the same basis set. In Figure 2, we adjusted the displayed range for both resonances (methyl and methylene) independently to allow an easy comparison of experimental and theoretical results.

(4) We also analyzed the contributions of the various localized molecular orbitals (LMO). We found that the calculated variation of the chemical shift is mostly due to contributions of the LMOs of the four adjacent bonds. The influence of individual distant valence molecular orbitals is small, whereas carbon 1s orbitals do not depend on molecular geometry at all (cf. ref 16, p 218). This finding agrees well with the small end-group effect mentioned above.

(5) The model of Vacatello and Yoon provides *a priori* probabilities of the conformations at T = 400 K; the experiments, however, were performed at $T \approx 200$ K. This is a major uncertainty as the relative populations depend on the temperature via Boltzmann statistics. Perhaps the remaining deviations of the subpeak heights may be attributed to this difference in temperature.

(6) A noticeable correlation of the combined bond lengths $d_1 + d_2$ with the calculated chemical shift of the methylene resonance has been found as well as an even better correlation of d_3 and δ_{CH_3} (Figure 4a,b). A comparable relationship has been suggested for inorganic

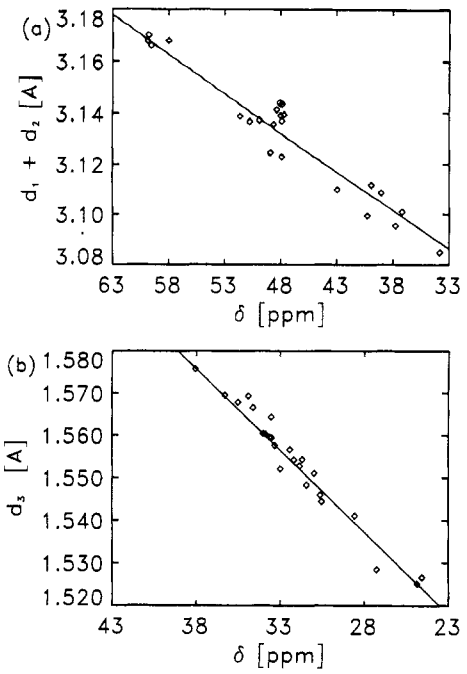

Figure 4. Calculated chemical shift vs the combined length of the adjacent carbon–carbon bonds for the methylene (a) and methyl (b) resonances. A strong correlation is noticable. The solid lines are only guides to the eye and are not meant to suggest fits.

phosphate and silicate samples on the basis of experimental data[13] and a semiempirical approach (PCILO, bond polarization theory).[12] The sensitivity of chemical shifts on local geometries might provide a simple way to check the latter. Further investigations dealing with this question are under way.

(7) The strong dependence of δ on interatomic distances raises, however, the question of the influence of the force field parameters on the results. Empirical force fields are valuable tools in understanding statistics and dynamics of many systems. The quality of geometries obtained by modern force fields is comparable to optimizations done on the *ab initio* level and the computations are much less time-consuming. However, one has to keep in mind that both force field and *ab initio* geometries cannot be expected to be exact in all details. Thus, the influence of subtle changes in the geometries due to force field peculiarities is to be checked. Indeed, preliminary studies with the widespread AMBER force field indicate that the correlation of bond lengths and chemical shifts is less pronounced in this case, though less subtle properties like the γ-gauche effect show up as well as with the CVFF force field. The poorer correlation of bond lengths and chemical shifts with the AMBER force field might be due to the lack of cross terms.

(8) Other RIS models for PIB[30,31] may provide different statistics and thus different simulated spectra. In a later stage of the investigations it might be possible to evaluate the pros and cons of the respective methods by a very direct comparison with experiment.

5. Conclusion and Outlook

In this preliminary study we present a simulation of the experimental ^{13}C CP/MAS spectrum of polyisobutylene, which employs the *ab initio* IGLO method. Based on conformational statistics taken from the literature,[3] a subsequent IGLO calculation of various relevant conformations yields a remarkable qualitative agreement between experiment and theory. The major source of the chemical shift variation is shown to be of conformational origin. For a quantitative analysis some questions raised above (e.g., the influence of the force field, the bias of bond lengths and chemical shift) will have to be solved.

The steady increase in computing power together with refinements of the calculational techniques will make it possible to address more subtle problems; e.g., it will be possible to investigate systems with heteroatoms (which require a larger basis like II′) and take into account specific torsional angles. So far, only isotropic chemical shifts are considered. In the future, we intend to investigate the anisotropic part of the shift tensor already provided by the IGLO method and to explore the structural information available from it.

In the long run it may be possible to circumvent restrictions imposed by lattice theories like RIS models and study the influence of continuous parameter variation. Thus, it is believed that a thorough handling of ^{13}C chemical shifts, both experimentally and an *ab initio* level, will help in the elucidation of local geometries of disordered systems. Specifically, the conformational statistics of amorphous polymers should be accessible through analysis of solid-state ^{13}C-NMR spectra by *ab initio* calculations of chemical shifts.

Further work along these lines is in progress.

References and Notes

(1) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience Publishers: New York, 1969.
(2) Theodorou, D. N.; Suter, U. W. *Macromolecules* **1985**, *18*, 1467–1478. Theodorou, D. N.; Suter, U. W. *Macromolecules* **1986**, *19*, 139–154, 379–387.
(3) Vacatello, M.; Yoon, D. Y. *Macromolecules* **1992**, *25*, 2502–2508.
(4) Catlow, C. R. A.; Parker, S. C.; Allen, M. P., Eds.; *Computer Modelling of Fluids, Polymers and Solids*; Kluwer: Dordrecht, 1991 (NATO ASI Series—Mathematical and Physical Sciences Vol. 293).
(5) Roe, R.-J., Ed. *Computer Simulations of Polymers*; Prentice-Hall: Englewood Cliffs, NJ, 1991.
(6) Blackwell, J.; Biswas, A. In *Developments in Oriented Polymers 2*; Ward, I. M., Ed.; Elsevier Applied Science: London, 1987; Chapter 5, pp 153–198.
(7) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982.
(8) Tonelli, A. E. *NMR Spectroscopy and Polymer Microstructure: The Conformational Connection*; VCH Publishers: New York, 1989.
(9) Voelkel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1468–1483.
(10) Zemke, K.; Chmelka, B. F.; Schmidt-Rohr, K.; Spiess, H. W. *Macromolecules* **1991**, *24*, 6874–6876.
(11) Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315–5318.
(12) Sternberg, U.; Priess, W. *J. Magn. Reson.* **1993**, *A102*, 160–165. Losso, P.; Schnabel, B.; Jaeger, C.; Sternberg, U.; Stachel, D.; Smith, D. O. *J. Non-Cryst. Solids* **1992**, *143*, 265–273.
(13) Grimmer, A.-R. In *Nuclear Magnetic Shielding and Molecular Structure*; Tossel, J., Ed.; Kluwer: Dordrecht, 1993; pp 191–201 (NATO ASI Series).
(14) Komoroski, R., Ed. *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; VCH Publishers: New York, 1986.
(15) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193–200. Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919–1933.
(16) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR Basic Princ. Prog.* **1991**, *23*, 165–262.
(17) Kutzelnigg, W.; Wuellen, C. v.; Fleischer, U.; Franke, R.; Mourik, T. v. In *Nuclear Magnetic Shielding and Molecular Structure*; Tossel, J., Ed.; Kluwer: Dordrecht, 1993; pp 141–161 (NATO ASI Series).
(18) Kutzelnigg, W. *J. Mol. Struct. (THEOCHEM)* **1989**, *202*, 11–61.
(19) Hameka, H. *Mol. Phys.* **1958**, *1*, 203. Hameka, H. *Rev. Mod. Phys.* **1962**, *34*, 87. Ditchfield, R. *J. Chem. Phys.* **1972**, *56*, 5688–5691. Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260.
(20) Hansen, A. E.; Boumann, T. D. *J. Chem. Phys.* **1985**, *82*, 5035–5052.
(21) Ding, J.; Barfield, M.; Combariza, J. E.; Hruby, V. J. *J. Am. Chem. Soc.* **1992**, *114*, 3639–3643. Ding, J.; Barfield, M.; Hruby,

V. J. *Magn. Reson. Chem.* **1993**, *31*, 75–79. Barfield, M. *J. Am. Chem. Soc.* **1993**, *115*, 6916–6928. Barfield, M. In *Nuclear Magnetic Shielding and Molecular Strucutre*; Tossel, J., Ed.; Kluwer: Dordrecht, 1993; pp 523–537 (NATO ASI Series).
(22) de Dios, A. C.; Pearson, J. G.; Oldfield, E. *Science* **1993**, *260*, 1491–1496.
(23) Kuruso, H.; Ando, I.; Webb, G. A. *Magn. Reson. Chem.* **1993**, *31*, 399–402.
(24) Zemke, K.; Schmidt-Rohr, K.; Spiess, H. W. Talk MM 2.4 Presented at the 13th EPS Conference, Regensburg, FRG, March 29–April 2, 1993 (*Europhys. Abstr.* **1993**, *17A*, 1117). *Acta Polym.*, in press.
(25) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020–1033.
(26) Franke, R. Diplomarbeit, Rohr-Universität Bochum, 1990.
(27) Fleischer, U.; Kutzelnigg, W.; Bleiber, A.; Sauer, J. *J. Am. Chem. Soc.* **1993**, *115*, 7833–7838.
(28) Bunn, A.; Cudby, M. E. A.; Harris, R. K.; Packer, K. J.; Say, B. J. *Polymer* **1982**, *23*, 694–698.
(29) Meier, U.; van Wüllen, C.; Schindler, M. *J. Comput. Chem.* **1992**, *13*, 551–559.
(30) Suter, U. W.; Saiz, E.; Flory, P. J. *Macromolecules* **1983**, *16*, 1317–1328. DeBolt, L. C.; Suter, U. W. *Macromolecules* **1987**, *20*, 1424–1425.
(31) Boyd, R. H.; Breitling, S. M. *Macromolecules* **1972**, *5*, 1–7.