Theoretical Prediction of ^{13}C NMR Chemical Shifts of Polymers Using Oligomeric Approach

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ABSTRACT: Combined density functional theoretical (DFT) and ab initio methods have been used for the calculation of ^{13}C NMR chemical shifts of some hydrogen-terminated oligomers of ethylene, propylene, isobutylene, ethylene oxide, vinyl alcohol, and acrylonitrile. The ^{13}C isotropic chemical shift (δ_{iso}) values are calculated with respect to theoretical isotropic shielding constant (σ_{iso}) value of the tetramethylsilane (TMS). The average unsigned error in δ_{iso} values of the various oligomers varies between 2 and 5 ppm. The error of ca. 5.22 ppm for acrylonitrile arises mainly due to the cyano carbon. Oligomeric approach has been employed to calculate the δ_{iso} values of the corresponding polymers. This approach is validated by the excellent correlation obtained for the linear fits. These calculated δ_{iso} values for the polymers are in good agreement with the experimental values.

1. Introduction

The ^{13}C NMR chemical shifts of polymer systems have been studied with a view to understand the structure of polymers. Numerous structural applications of NMR spectroscopy of polymers have dealt with one or several of the following details viz., branching, thermal oxidation, stereoregularity (tacticity), directional isomerism, and copolymer structure. Theoretical prediction of NMR chemical shifts of molecules complements the experimental results and helps in synthesis.[1] Chemical shifts arise from changes in the electronic structure of molecules including changes in the dihedral angles of the skeletal bonds and intermolecular interactions. Information regarding the electronic structure of the polymer, which is required to calculate the chemical shift, can be obtained by using dimers, trimers etc., as representative fragments of the polymer under consideration. Such calculations are very useful as a means of analyzing the structure and conformation of polymers.[2−4] The approach of extending the data of oligomers to polymers had been widely applied in the study of optical properties of oligomers. The transition energies of oligothiophenes has been shown to vary linearly with respect to the inverse number of thiophene rings.[5] Similarly, in the study of photoluminescence of oligo(*p*-phenylenevinylenes), a linear variation between the vertical transition energies and the inverse number of bonds along the backbone had been reported.[6] In the previous work, the variations in the properties of oligomers have been used to extrapolate and estimate the properties of the concerned polymer.[5,6] The method is termed the oligomeric approach, and in this study, an attempt has been made to evaluate the chemical shift values of a few polymers.

Several methods have been developed to calculate the molecular second-order magnetic response properties. One accurate way of prediction of these properties is by the use of gauge-invariant procedures.[7,8] The gauge-including (or invariant) atomic orbital (GIAO) method was first utilized for quantum chemical NMR shift calculations by Ditchfield.[9] A recent NMR chemical shielding constant calculation by ab initio GIAO−CHF and DFT methods indicates the usefulness of the 6-311+G(2d,p) basis set both at the HF and DFT levels.[10] Cheeseman et al have carried out extensive calculations on several organic molecules to compare the GIAO and CSGT (continuous set of gauge transformations) methods of finding nuclear magnetic shielding tensors.[7] They have compared the HF and DFT level of calculations also. It should be noted that the MP2 method, which is computationally demanding, predicts the chemical shifts of several small organic molecules more accurately than the HF or any of the DFT functionals.[8] It is noteworthy to mention that CH_4 was used as reference by Gauss against tetramethylsilane (TMS), the conventional standard.[8] In the individual gauge localized orbital (IGLO) and the localized orbital/local origin (LORG) methods, the gauge factors have been applied only to the localized molecular orbitals instead of being applied to every atomic orbitals as in GIAO.[8,11,12] Also it has been noted that the convergence of the calculated chemical shielding is faster with the GIAO method in comparison with the localized (IGLO and LORG) methods.[13]

The aim of the present study is to predict nuclear magnetic shielding constants and chemical shifts of polymers based on the oligomeric approach. For this study we have chosen some known polymeric systems viz. polyethylene (PE), polypropylene (PP), and polyisobutylene (PIB). Other systems containing heteroatoms, such as poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA) and polyacrylonitrile (PAN) have also been selected to probe the predictive power of the method considered here. All these polymeric systems have been considered only in their isotactic form wherever applicable. In all cases the studies have been carried out up to the trimer of each system (except for PE where tetramer was also considered).

2. Theoretical Background

The energy associated with the nuclear magnetic moment μ, in the presence of an external magnetic field **B**, is given by

$$E_\mu = -\mu\mathbf{B} + \mu\sigma\mathbf{B} \qquad (1)$$
$$= -\mu(1 - \sigma)\mathbf{B}$$

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where the first term $\mu\mathbf{B}$ represents the coupling of the bare moment μ to the external magnetic field, while the second term containing the shielding tensor σ is the effective coupling provided by the electronic cloud between **B** and μ. Thus, the electron cloud provides an additional effective magnetic field of $-\sigma\mathbf{B}$. If σ is positive, then the effective field opposes the external field and the nucleus is said to be shielded which is a diamagnetic effect. If σ is negative, then a deshielding or paramagnetic effect results. It should be noted that the shielding tensor σ is an asymmetric second rank tensor. This is because it couples two physically distinct quantities namely the nuclear moment and the external field.

From (1) the components $\sigma^N{}_{ji}$ of the nuclear magnetic shielding tensor of a particular nucleus N can be expressed as the mixed second derivative of the energy with respect to the external magnetic field **B,** and the magnetic moment μ_N of nucleus N, as

$$\sigma^N{}_{ji} = \frac{\partial^2 E}{\partial B_i \, \partial \mu_{Nj}}$$

Here the suffixes i and j correspond to the components of the external magnetic field and the induced magnetic field, respectively. The energy E and its derivatives are derivable from the Hamiltonian H of the molecular system that can be written as

$$H = \sum_k (\mathbf{p}_k + \mathrm{e}\mathbf{A}_k)^2/(2\mathrm{m}) + V$$

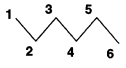
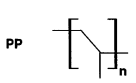
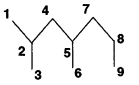
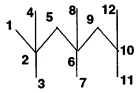
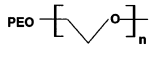
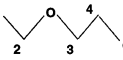
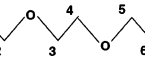
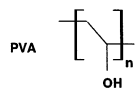
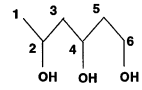
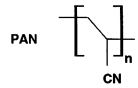
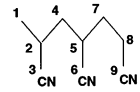
where V is the potential, $\mathbf{A}_k$ is the vector potential experienced by the kth electron and is made up from the contributions of the external field **B** and nuclear magnetic moment μ. Therefore, $\mathbf{A}(\mathbf{r}) = \mathbf{A}_\mathrm{B}(\mathbf{r}) + \mathbf{A}_\mu(\mathbf{r})$ where $\mathbf{A}_\mathrm{B}(\mathbf{r})$ is the vector potential from the magnetic field **B** which is written in a standard form with respect to an arbitrary origin as, $\mathbf{A}_\mathrm{B}(\mathbf{r}) = {}^1/_2(\mathbf{B} \times \mathbf{r})$. The contribution to **A** from the magnetic moment is more specific with distances being measured relative to the nuclear moment located at $\mathbf{R}_N$, as

$$\mathbf{A}_\mu(\mathbf{r}) = (\mu_\mathrm{o}/4\pi)\frac{\mu \times \mathbf{r}_N}{r_N}; \quad \mathbf{r}_N = \mathbf{r} - \boldsymbol{R}_N$$

The idea of vector potential **A** used above arises from the fact that the divergence of the magnetic field **B** vanishes as per Maxwell's equations, and is given by $\mathbf{B} = \nabla \times \mathbf{A}$. But, as the curl of the gradient of an arbitrary scalar function vanishes, the vector potential is not unique and can be written as $\mathbf{A}' = \mathbf{A} - \nabla f$, where f is an arbitrary scalar potential. As the choice of the origin can be seen to affect this physically observable quantity **A**, the nonuniqueness of vector potential **A** leads to "gauge dependence". One of the methods of avoiding gauge dependence is to select an optimum gauge to minimize the problem. Another way is to choose a sufficiently large (or complete) basis so that the effects of the choice of origin are minimal. One can as well use London orbitals or GIAO, instead of using the usual real atomic orbital ϕ_N, located at $\mathbf{R}_N$.[14] This complex orbital χ_N is given by $\chi_N = \phi_N \exp[-(ie/\hbar)\mathbf{A}(\mathbf{R}_N).\mathbf{r}]$. The use of such orbitals in coupled HF theory leads to translational gauge independence.

σ_{ij}, the components of the shielding tensor, will in general not be the same as σ_{ji}. The values of the isotropic shielding constants are obtained by $\sigma_\mathrm{iso} = {}^1/_3(\mathrm{Tr}\ \sigma)$ as σ is represented by a 3×3 matrix. The corresponding isotropic chemical shift (δ_iso) with respect to a particular reference can be obtained using the formula $\delta_\mathrm{iso} = \sigma_\mathrm{ref} - \sigma_\mathrm{iso}$.

Table 1. Hydrogen-Terminated Oligomers Considered for the Present Study[a]

Poly-mer	Polymeric-structure	Oligomer n = 1	Oligomer n = 2	Oligomer n = 3
PE				
PP				
PIB				
PEO				
PVA				
PAN				

[a] Numbers indicated (1 to 12) are the carbon atom labels in the oligomers.

3. Computational Details

To represent the structure of the polymer, the corresponding oligomers have been terminated with hydrogen. The geometries of all hydrogen-terminated oligomers obtained after energy minimization using B3LYP/6-31G* method were used for computation of isotropic shielding constants employing HF/6-311+G(2d,p) method as described earlier by Cheeseman.[7] All calculations were performed using Gaussian 98W suite of package.[15] GIAO method as implemented in the G98W package has been used in this study. Shielding constants for the conventional standard molecules, tetramethylsilane (TMS) and methane were also calculated adopting the same procedure. The calculated isotropic shielding constants have been extrapolated to yield the value for long polymer chain using oligomeric approach.

4. Results and Discussion

Structures of the oligomers considered for the present study are given in Table 1. In Table 2 we present the calculated ^{13}C NMR absolute isotropic shielding constants (σ_iso) for the hydrogen-terminated oligomers of ethylene (OE), propylene (OP), and isobutylene (OIB). The labeling of the carbon atoms in Table 2 is as per the numbering in Table 1. The isotropic chemical shift (δ_iso) values are in general evaluated from the experimental σ_iso values with reference to TMS. Our present calculated σ_iso value for the conventional TMS is 192.7 ppm. It was found from various theoretical calculations that chemical shift values for TMS ranges from 187 to 195 ppm.[7,10,16] In the previous theoretical calculation of chemical shift, methane has also been used as a

Table 2. Calculated ^{13}C NMR Absolute Isotropic Shielding Constants (σ_{iso}) for the Hydrogen-Terminated Oligomers of Ethylene (OE), Propylene (OP), and Isobutylene (OIB)

carbon label[a]	σ_{iso}(ppm)									
	OE				OP			OIB		
	$n=1$	$n=2$	$n=3$	$n=4$	$n=1$	$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
C1	183.1	176.5	176.6	176.5	175.4	168.4	167.3	168.8	158.7	157.4
C2	183.1	166.1	167.4	167.3	173.9	161.5	165.5	168.3	161.6	162.0
C3		166.1	159.3	159.3	175.4	171.4	168.5	168.8	164.4	164.4
C4		176.5	159.3	160.5		156.5	149.6	168.8	164.4	164.4
C5			167.4	160.5		170.5	155.6		145.5	137.5
C6			176.6	159.3		175.5	174.9		162.8	156.5
C7				167.3			156.7		169.9	166.8
C8				176.5			170.9		169.9	166.8
C9							175.3			142.7
C10										162.5
C11, C12										169.4

[a] Carbon label is as per the numbering in Table 1.

Table 3. Isotropic Chemical Shift (δ_{iso}) Values of Oligoethylene (OE) in ppm

n	functional group	δ_{iso} calcd	δ_{iso} expt[a]
1	CH_3(C1,C2)	9.6	5.7
2	CH_3(C1,C4)	16.2	13.0
	CH_2(C2,C3)	26.6	25.0
3	CH_3(C1,C6)	16.1	14.2
	CH_2(C2,C5)	25.4	22.9
	CH_2(C3,C4)	33.4	31.9
4	CH_3(C1,C8)	16.2	14.2
	CH_2(C2,C7)	25.4	22.9
	CH_2(C3,C6)	33.4	32.2
	CH_2(C4,C5)	32.2	29.5
av unsigned error		2.32	-

[a] Experimental values from ref 17.

Table 4. Isotropic Chemical Shift (δ_{iso}) Values of Oligopropylene (OP) in ppm

n	functional group	δ_{iso} calcd	δ_{iso} expt[a]
1	CH_3(C1,C3)	17.3	15.8
	CH_2(C2)	18.8	16.3
2	CH_3(C1)	24.3	22.7
	CH (C2)	31.2	27.9
	CH_3(C3)	21.3	22.7
	CH_2(C4)	36.2	41.6
	CH_2(C5)	22.2	20.6
	CH_3(C6)	17.2	14.4
3	CH_3(C1)	25.4	23.5
	CH (C2)	27.2	25.4
	CH_3(C3)	24.2	22.4
	CH_2(C4)	43.1	47.0
	CH (C5)	37.1	30.1
	CH_3(C6)	17.8	19.8
	CH_2(C7)	36.0	39.9
	CH_2(C8)	21.8	20.1
	CH_3(C9)	17.4	14.4
av unsigned error		2.44	
error excluding C4 values		2.09	

[a] Experimental values from ref 17.

Table 5. Isotropic Chemical Shift (δ_{iso}) Values of Oligoisobutylene (OIB) in ppm

n	functional group	δ_{iso} calcd	δ_{iso} GC[a]
1	CH_3(C1)	23.9	24.3
	CH (C2)	24.4	25.0
	CH_3(C3,C4)	23.9	24.3
2	CH_3(C1)	34.0	30.1
	C (C2)	31.1	31.2
	CH_3(C3,C4)	28.3	30.1
	CH_2(C5)	47.2	53.4
	CH (C6)	29.9	24.9
	CH_3(C7,C8)	22.8	25.3
3	CH_3(C1)	35.3	32.2
	C (C2)	30.7	36.3
	CH_3(C3,C4)	28.3	32.2
	CH_2(C5)	55.2	57.6
	C (C6)	36.2	33.6
	CH_3(C7,C8)	25.9	28.2
	CH_2(C9)	50.0	51.7
	CH (C10)	30.2	21.7
	CH_3(C11,C12)	23.3	24.0
av unsigned error		2.6	

[a] ^{13}C NMR chemical shift values obtained using group contribution or empirical additivity method.

standard.[8] In the present study, model chemistry employing the B3LYP/6-31G* optimization and followed by HF/6-311+G(2d,p) NMR calculations provide a σ_{iso} value of 194.3 for CH_4 carbon. Since the most preferred standard reference system is TMS, we have evaluated the chemical shift values with respect to the σ_{iso} value of 192.7 ppm throughout this article.

To start with, the individual oligomers have been treated as typical organic molecules and their calculated δ_{iso} values have been compared with available experimental data.[17] Tables 3−5 give the isotropic chemical shift (δ_{iso}) values of OE, OP, and OIB systems respectively with reference to the standard values of TMS considered in this study. Hydrogen-terminated ethylene in its oligomeric form represents a linear alkane. Therefore, comparison is made with experimental data for ethane, butane, etc. In the same way, calculated values for propylene and isobutylene oligomers were compared with available experimental data or with values obtained from empirical calculations of corresponding organic molecules. It is known that group contribution method or empirical additivity relation is well-developed, and possible ^{13}C NMR chemical shielding values for several organic molecules, which are in close agreement with experimental values, can be estimated. From the data for oligoethylene (OE) given in Table 3, it can be found that the δ_{iso} values obtained are larger than the experimental values. The average unsigned error in δ_{iso} values of our present calculations for the four oligomers of ethylene ($n = 1-4$) is 2.32 ppm.

The δ_{iso} values for oligopropylene (OP) are presented in Table 4. A trend similar to that of oligoethylene has also been observed in the case of oligopropylene. The corresponding average unsigned error is 2.44 ppm. The δ_{iso} values of the CH_2 group calculated from this study

Table 6. Calculated ^{13}C NMR Absolute Isotropic Shielding Constants (σ_{iso}) for the Hydrogen-Terminated Oligomers of Ethylene Oxide (OEO), Vinyl Alcohol (OVA), and Acrylonitrile (OAN)

carbon label[a]	σ_{iso} (ppm)								
	OEO			OVA			OAN		
	$n = 1$	$n = 2$	$n = 3$	$n = 1$	$n = 2$	$n = 3$	$n = 1$	$n = 2$	$n = 3$
C1	174.5	175.4	175.3	174.5	167.9	168.4	179.3	173.4	172.4
C2	137.0	130.4	130.8	137.1	133.1	129.3	181.3	170.2	172.5
C3		124.9	126.3		152.1	152.2	62.2	60.8	59.2
C4		134.3	126.4		137.8	134.2		161.3	157.2
C5			126.0			150.7		178.3	165.8
C6			132.7			137.8		63.3	61.8
C7									163.8
C8									178.1
C9									63.1

[a] Carbon label is as per the numbering in Table 1.

Table 7. Isotropic Chemical Shift (δ_{Iso}) Values of Oligo(ethylene oxide) (OEO) in ppm

n	functional group	δ_{iso}	
		calcd	expt[a]
1	CH_3 (C1)	18.2	18.1
	CH_2 (C2)	55.7	57.8
2	CH_3 (C1)	17.3	15.0
	CH_2 (C2)	62.3	66.6
	CH_2 (C3)	67.8	71.9
	CH_2 (C4)	58.1	61.6
3	CH_3 (C1)	17.4	15.1
	CH_2 (C2)	61.9	66.6
	CH_2 (C3)	66.4	69.9
	CH_2 (C4)	66.3	70.5
	CH_2 (C5)	66.7	72.8
	CH_2 (C6)	60.0	61.6
av unsigned error		3.21	

[a] Experimental values from ref 17.

Table 8. Isotropic Chemical Shift (δ_{iso}) Values of Oligo(vinyl alcohol) (OVA) in ppm

n	functional group	δ_{iso}	
		calcd	expt or GC[a,b]
1	CH_3 (C1)	18.2	18.1
	CH_2 (C2)	55.6	57.8
2	CH_3 (C1)	24.8	25.2
	CH (C2)	59.6	68.3
	CH_2 (C3)	40.6	40.6
	CH_2 (C4)	54.9	60.0
3	CH_3 (C1)	24.3	27.5
	CH (C2)	63.4	68.2
	CH_2 (C3)	40.5	46.5
	CH (C4)	58.5	67.2
	CH_2 (C5)	42.0	37.8
	CH_2 (C6)	54.9	59.6
av unsigned error		4.01	
error excluding CH values		2.29	

[a] Experimental values from ref 17. [b] ^{13}C NMR chemical shift values for $n = 2$, 3 are obtained using the group contribution or empirical additivity method.

is on the lower side compared to the experimental value. For $n = 3$ (i.e., 2,4-dimethylheptane), the predicted value for the central CH group is higher than the experimental one. It can be observed that for the methyl carbons, C3 in $n = 2$ and C3, C6 in $n = 3$, the calculated chemical shift values are closer to the experimental values. Excluding the CH_2 values, the overall average unsigned error decreases to 2.09 from 2.44 ppm

The δ_{iso} values for the hydrogen-terminated oligoisobutylene are presented in Table 5. The overall average unsigned error is 2.6 ppm. When $n = 1$, the hydrogen-terminated oligoisobutylene is isobutane. It is evident from the results that for isobutane, the average error observed is only 0.6 ppm. When $n = 2$ the molecule is isooctane or 2,2,4-trimethylpentane. The values computed for the CH_2 (C5) group are quite lower when compared to the value obtained by group contribution technique. For $n = 3$, the molecule represents 2,2,4,4,6-pentamethylheptane.

The calculated ^{13}C NMR absolute isotropic shielding constants (σ_{iso}) for the hydrogen-terminated oligomers of ethylene oxide (OEO), vinyl alcohol (OVA), and acrylonitrile (OAN) are given in Table 6. The isotropic chemical shifts (δ_{iso}) for the oligomers OEO, OVA and OAN are presented in Tables 7−9. Comparison has been made with either available experimental values or with the values obtained by group contribution methods.

For $n = 1$, 2, and 3, the hydrogen-terminated ethylene oxide represents ethanol, ethylene glycol monoethyl ether, and 2-[2 ethoxyethoxy]ethanol, respectively. From Table 7, it can be noted that the chemical shift values obtained are much closer to the experimental values. Also it can be seen that except for the terminal CH_3 values, other predicted values are lower than the experimental values. It is notable that for the inner carbons representing the CH_2 group, for both $n = 2$ and 3, the deviation from the experimental values has been found to be almost constant at about 4.5 ppm.

When $n = 1$, hydrogen-terminated vinyl alcohol represents ethanol just like ethylene oxide. Except for the predicted value of chemical shift of the CH_2 group (C5), other values are on the lower side compared to the experimental or empirically estimated chemical shift values. It can be noted that the largest difference of about 9 ppm occurs for the chemical shift values of CH group attached to OH (C2 for $n = 2$ and C4 for $n = 3$). The terminal CH_3 values for both $n = 1$ and 2 are in good agreement with the experimental value, while for $n = 3$ the error is about 3 ppm. In the case of non-hydroxy CH_2 groups the error is negligible for $n = 2$. For $n = 3$, of the two CH_2 groups, the value corresponding to C3 is on the lower side compared to that of C5. The terminal CH_2 groups (with hydroxy attachment) in both $n = 2$ and 3 have the same order of error at about 5 ppm, while for $n = 1$ it is about 2 ppm only.

The calculated δ_{iso} values for oligomers of acrylonitrile are given in Table 9. The results clearly indicate that excluding the CN group the chemical shift values are predicted with an overall error of about 1.2 ppm. It can be noted that the chemical shift values for terminal CH_3 have been predicted quite accurately in the cases of n

Table 9. Isotropic Chemical Shift (δ_{Iso}) Values of Oligo(acrylonitrile) (OAN) in ppm

		δ_{iso}	
n	functional group	calcd	expt or GC[a,b]
1	CH_3 (C1)	13.4	10.6
	CH_2 (C2)	11.4	10.9
	CN (C3)	130.5	121.0
2	CH_3 (C1)	19.3	19.1
	CH (C2)	22.5	23.7
	CN (C3)	131.9	118.9
	CH_2 (C4)	31.4	29.3
	CH_2 (C5)	14.4	15.1
	CN (C6)	129.4	116.1
3	CH_3 (C1)	20.3	19.9
	CH (C2)	20.2	23.2
	CN (C3)	133.5	119.2
	CH_2 (C4)	35.5	36.5
	CH (C5)	26.9	26.1
	CN (C6)	130.9	114.6
	CH_2 (C7)	28.9	28.1
	CH_2 (C8)	14.6	15.2
	CN (C9)	129.6	116.1
av unsigned error		5.22	
error excluding CN values		1.18	

[a] Experimental values from ref 17. [b] ^{13}C NMR chemical shift values for $n = 2, 3$ are obtained using group contribution method.

$= 2$ and 3. Also all other chemical shift values are within a maximum deviation of about 3 ppm. One intriguing point is the positive deviation of about 13 ppm in the shift value of the CN group.

To evaluate the isotropic shielding constants (σ_{iso}) for the various functional groups in a polymer the oligomeric approach as described earlier has been employed. In Table 10 the cumulated σ_{iso} values for the various oligomers are presented. These values have been obtained using σ_{iso} values of the oligomers given in Tables 2 and 6 and employing the procedure outlined below. In the case of polyethylene (PE) there is only one functional group, namely the CH_2 group. However, the hydrogen-terminated $n = 1$ oligomer contains just two methyl groups. Therefore, these two methyl groups have been considered to be the building blocks of the CH_2 group and the average value is taken for consideration. Similarly, for $n = 2$ and 3, all the σ_{iso} values have been averaged to arrive at the values of 171.3 and 167.8 ppm, respectively. Thus, the terminal groups have also been considered in the estimation of the cumulated value, though they may look quite different from the actual functional group under consideration. This procedure is necessary, for otherwise one will have to summarily reject the values obtained for $n = 1$, as in general these values seem to rarely represent the value corresponding to the polymer. Rejection of these values would lead to very few values to be extrapolated to arrive at the σ_{iso} value of the polymer. Though it may be desirable to evaluate σ_{iso} values for higher oligomers like tetramer etc., the computation becomes prohibitively expensive. As another example we consider the OIB dimer ($n = 2$). To obtain the value of σ_{iso} for the C-functional group (methine carbon), σ_{iso} values of the C2 and C6 carbon atoms (Table 2) were averaged to arrive at the value of 162.2 ppm. This procedure has been applied to every carbon atom in a given oligomer, to arrive at the cumulated σ_{iso} value for each functional group in the corresponding polymer.

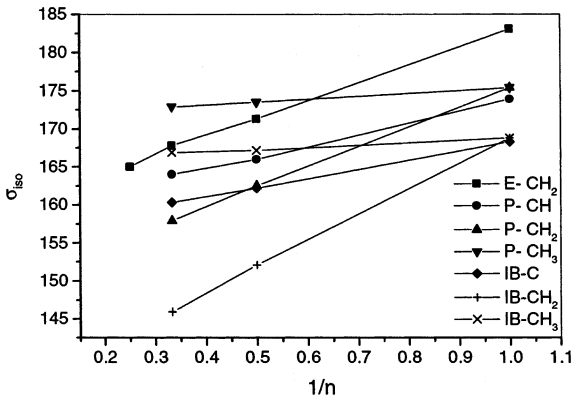


Figure 1. Plot of $1/n$ vs σ_{iso} for ethylene, propylene, and isobutylene oligomers.

The plots in Figures 1 and 2, and the correlation coefficients obtained for the straight line fit to these plots as given in Table 10, clearly vindicate the validity of the oligomeric approach. A linear fit of $1/n$ vs σ_{iso} values leads to the extrapolated value of σ_{iso} at $1/n = 0$ (or $n = \infty$), which can be considered to be the value corresponding to that of the polymer. Such extrapolated

Table 10. Cumulated ^{13}C σ_{iso} Values of the Oligomers and the Extrapolated σ_{iso} Values for Various Functional Groups of the Polymers ($n = \infty$)[a]

		σ_{iso}[b]					δ_{iso} for the polymer		
oligomer	functional group	$n = 1$	$n = 2$	$n = 3$	$n = \infty$[c] (polymer)	R[d]	calcd	expt[e]	expt-oligo[f]
OE	CH_2	183.1	171.3	167.8 165.9 ($n = 4$)	160.1	0.999	32.6	32.7	31.4
OP	CH	173.9	166.0	164.0	158.8	0.998	33.9	26.7	30.4
	CH_2	175.4	162.5	157.9	149.3	0.999	43.4	44.4	47.7
	CH_3	175.4	173.5	172.9	171.6	0.999	21.1	21.9	20.8
OIB	C	168.3	162.2	160.3	156.2	0.999	36.5	33.6	32.6
	CH_2	168.8	152.1	145.9	134.8	0.999	57.9	57.6	58.8
	CH_3	168.8	167.2	166.9	165.8	0.995	26.9	28.2	30.4
OEO	CH_2	137.0	129.9	128.4	123.7	0.997	69.0	71.1	74.2
OVA	CH	137.0	135.5	133.8	132.8	0.950	59.9	65−70	69.2
	CH_2	174.5	160.2	157.1	147.1	0.996	45.6	44.8	47.1
OAN	CH	181.3	174.3	172.1	167.4	0.999	25.3	27−30	27.1
	CH_2	179.3	167.4	164.5	156.6	0.998	36.1	32−34	37.2
	CN	62.21	62.05	61.39	61.26	0.814	131.44	117−122	114.3

[a] Corresponding isotropic chemical shift (δ_{iso}) values are also given. [b] Cumulated σ_{iso} values; see text for description. [c] Values obtained for the polymer by extrapolation using oligomeric approach. [d] Correlation coefficients for the linear fit of $1/n$ vs σ_{iso}. [e] Experimental values from refs 18 and 19. [f] Values obtained by cumulation and extrapolation from experimental (or GC) δ_{iso} values for oligomers given in Tables 3−5 and 7−9.

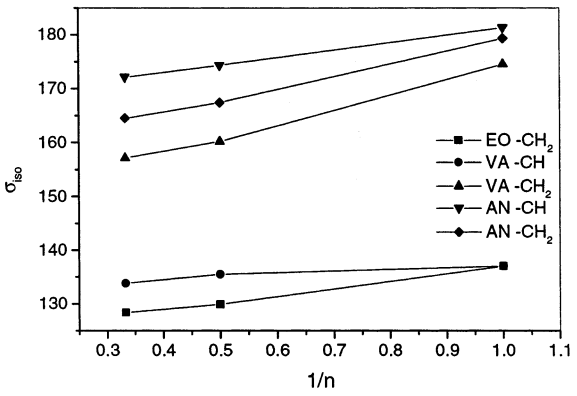


Figure 2. Plot of $1/n$ vs σ_{iso} for ethylene oxide, vinyl alcohol, and acrylonitrile oligomers.

σ_{iso} values and the corresponding δ_{iso} values along with experimental values are given in Table 10. Only the plot for cyano carbon of the acrylonitrile (not shown in Figure 2 due to variation in scale) deviates from linearity to a large extent that the correlation coefficient value is only 0.814. Next to that in PVA, the linear fit for the carbon in CH attached to the hydroxy group has a coefficient of about 0.95. It is notable that all other fits for the various carbon atoms yield correlation coefficient values above 0.99.

To confirm the reliability of the present approach, experimental NMR chemical shift for oligomers have been extrapolated to obtain the same for polymers. The extrapolated values are presented in Table 10. It can be noted that these values agree reasonably with the experimental as well as the theoretically predicted values for polymers. The correlation coefficients of the linear fits used were found to be about 0.99. Furthermore, these extrapolated values estimate, in general, higher δ_{iso} values than the experimental values for the polymers.

In the case of polyethylene, which has identical methylene carbons the δ_{iso} value obtained from the extrapolated σ_{iso} value has been found to agree well with the experimental value. For this, the σ_{iso} values for oligoethylene up to $n = 4$ have been used in the prediction. For polypropylene, the δ_{iso} values of the CH_2 and the CH_3 side chain agree very well with the experimental values, whereas the calculated value for CH is 33.9 ppm, which is very high when compared with the experimental value of 26.7 ppm. In the case of PIB, the experimental δ_{iso} values specified in Table 10 have been obtained from group contribution methods for a longer ($n = 12$) oligoisobutylene. The innermost δ_{iso} values for C, CH_2 and CH_3 groups were considered to represent the values of the isobutylene polymer. The above-mentioned data are chosen even though the experimental values of 40.0, 61.9, and 33.3 ppm were available for the respective C, CH_2, and CH_3 groups of PIB, as these values are not of recent origin, and also the details of the structure of the polymer are not available.[20] Comparison of the extrapolated and empirically evaluated δ_{iso} values of PIB given in Table 10 indicates that the largest variation of 2.9 ppm occurs for the methine carbon, while for the CH_2 and the side chain methyl groups the variations are only 0.3 and -1.4 ppm, respectively.

Born et al have studied the ^{13}C chemical shifts for polyisobutylene using ab initio methods.[3] They have employed the IGLO method and studied conformational effects. In their study, the difference in the chemical shift values between the CH_2 and CH_3 groups is only about 12 ppm,[3] whereas the experimental difference is about 28.6[20] ppm and about 29 ppm in the case of values obtained through group contribution calculations (Table 10). Our present calculation leads to a difference of 31 ppm, which is in very good agreement with the experimental variation.

PP and PIB can be considered as single and double methyl substitution of PE along the backbone, on alternate CH_2 groups. Comparing the δ_{iso} values for the polymers PE, PP and PIB (Table 10) we find that the values for the unmodified CH_2 increase with methyl substitution on its neighbor. This variation agrees well with the experimental data. The δ_{iso} values for the substituted methyl groups on PP and PIB also agree closely with the experimental value. It can be noted that the modified CH_2 group, which turns out to be CH and C in PP and PIB, respectively, shows a variation in δ_{iso} values, which does not agree well with the experimental variation.

The data for PEO indicate a difference of about 2.1 ppm between the predicted and experimental δ_{iso} values. In the case of PVA, the predicted values for the backbone CH_2 agree very well with the experimental value, whereas the value for the CH group in PVA, to which the hydroxy side chain is attached, shows a deviation of more than 5 ppm. The extrapolated δ_{iso} values for PAN indicates that the values for backbone CH and CH_2 groups differ from the experimental value by about 2−4 ppm only. In the whole of our present study, the highest δ_{iso} value encountered is for the CN group in PAN. A possible reason for the large variation in δ_{iso} value of the cyano carbon(CN) is that it involves a triple-bonded system. For atoms involved in multiple bonded systems, large influence of electron correlations is expected. Therefore, the large discrepancy in the case of cyano carbon is probably due to the relatively limited basis set used in geometry optimization and the shielding tensor calculation at the HF level. Use of larger basis sets for geometry optimization and DFT or MPn methods for the calculation of shielding tensor could be expected to lead to much better values of chemical shifts for such carbons in particular and for all other carbons in general.

5. Concluding Remarks

The salient outcomes of the present work are as follows.

The combined use of DFT calculation for geometry optimization at the B3LYP/6-31G* level and ab initio calculation for estimating the chemical shifts at the HF/6-31+G(2d,p) level is able to predict the chemical shift values of oligomers reasonably close to the experimental values.

The oligomeric approach has been found to predict the chemical shift values of the polymers to a good accuracy, thus indicating the usefulness of this approach.

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