of lateral terminal interactions is often difficult to estimate. Structural data available to date support the view that the ordering of side groups in polymers with side group structure related to mesogenic behavior is subjected to laws similar to those governing the mesophase formation in low molecular weight thermotropic liquid crystals.

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# Communications to the Editor

## Correlation between $^{13}$C NMR Chemical Shifts and Conformation of Polymers. I. The Methyl Spectrum of 3,5,7,9,11,13,15-Heptamethylheptadecane[1]

The $^{13}$C NMR spectrum of the central methyl carbon of 3,5,7,9,11,13,15-heptamethylheptadecane (compound I) was interpreted by Zambelli et al.[2a] The nine chemical shifts observed at high temperature were assigned to the ten possible pentad configurational sequences of I. Since the nine peaks coincide with those found in stereoirregular polypropylene, that work allowed pentad assignments in the methyl spectrum of polypropylene.

The purpose of this work is to investigate whether the stereochemical shifts in the resonance peaks can be ascribed to differences in the conformations of the various stereoisomers. If this is the case, then conformational statistics could be employed to interpret the spectra of other (similar) systems or, vice versa, the NMR spectra could provide information on the conformational (not only configurational) characteristics of polymers. The correlation between $^{13}$C chemical shifts and conformer populations in polymers was first suggested by Carman[2b] for poly(vinyl chloride) and then by Bovey[3] for poly(vinyl chloride) and polypropylene.

It is well known[4,5] that the gauche arrangement of a carbon atom with respect to a nonhydrogen substituent in the $\gamma$ position produces an upfield shift relative to the shielding of the same carbon atom in the trans-planar arrangement. The magnitude of this effect varies significantly in different systems,[5] probably because of distortions from a "normal" gauche conformation in some cases, or because of lack of additivity when several gauche interactions affect the observed atom. Also corrections included to account for distortions are unable to determine a unique value for the $\gamma$ effect, ranging approximately from $-6.5$ to $-3.5$ ppm per gauche contact.[3,5] By adopting a value of $-4.3$ ppm and taking quantitative account of the gauche interactions, Bovey[3] has approximately reproduced the triad structure of the methyl spectrum of atactic polypropylene. However, he has not attempted to predict the fine structure of the spectrum.

The interaction of a methyl carbon with a substituent in the $\delta$ position and in the syn-axial (i.e., GG′) conformation has been found[6] to produce a downfield shift of about 2–3 ppm relative to the other conformations, in contrast to the upfield $\gamma$ effect. In flexible molecules such as polypropylene, syn-axial interactions, being more repulsive than gauche interactions, have low probability of occurrence, so that it is reasonable to expect that the $\delta$ effect will give a minor contribution to the chemical shifts of compound I.

Since the various conformers are separated by relatively low energy barriers, the chemical shift for a carbon atom of a given stereoisomer is the Boltzmann average over all the conformations. We base the calculation of the methyl chemical shifts of a chain molecule such as I on the following two assumptions: (a) each torsional angle can assume three conformations T, G, and G′ (three-state model); (b) the chemical shift of a given conformer is a linear function of the numbers of gauche $\gamma$ interactions and syn-axial $\delta$ interactions in which the observed carbon is involved. The calculated chemical shift for a stereoisomer is then given by

$$\nu = \nu_0 + \gamma P_G + \delta P_\omega \qquad (1)$$

where $\nu_0$ depends on the chemical constitution, not on the configuration of the stereoisomer, and corresponds to the chemical shift of any stereoisomer in a conformational arrangement such that $P_G = P_\omega = 0$. The parameters $\gamma = \nu_G - \nu_T$ and $\delta$ represent respectively the $\gamma$ and $\delta$ effects per interaction; $P_G$ and $P_\omega$ are the sums of the probabilities that the observed carbon is respectively in the conformations gauche with respect to the carbons three bonds apart and syn-axial relative to the carbons four bonds apart.

The probabilities $P_G$ and $P_\omega$ are calculated with the usual methods of the rotational isomeric state theory, using the simple three-state model. Results of nonbonded energy calculations[7,8] have shown that the conformational energy of the polypropylene chain can be expressed approximately as the sum of simple interactions, namely chain–chain and methyl–chain gauche interactions ($E_g$ and $E_{SK}$, respectively) and syn-axial interactions ($E_\omega$). We have followed Boyd and Breitling[7] in their statistical treatment of the polypropylene chain, with the minor exception that we do not exclude conformational sequences of the type XG|G′Y for two adjacent dyads unless either XG or G′Y imply another $\omega$ (syn-axial) interaction within either dyad. Therefore our treatment, which is more rigorous but consistent with Boyd and Breitling's energy calculations, requires statistical weights which are functions of three adjacent torsional angles. The partition function is then given by the expression

$$Z = \sum_{\chi_1}\sum_{\chi_2}\ldots\sum_{\chi_N} W(\chi_1,\chi_2,\chi_3)W(\chi_2,\chi_3,\chi_4)\ldots W(\chi_{i-2},\chi_{i-1},\chi_i)\ldots W(\chi_{N-2},\chi_{N-1},\chi_N) \qquad (2)$$

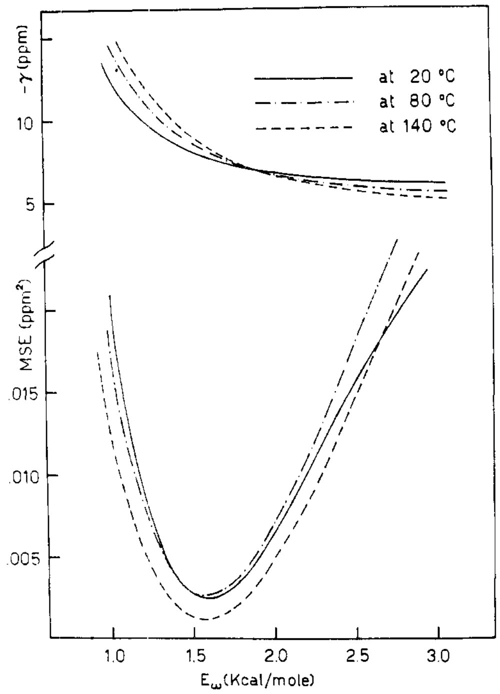

**Figure 1.** Bottom: Mean-square error of calculated with respect to observed methyl chemical shifts, plotted as a function of $E_\omega$, assuming $E_g = 0.4$ and $E_{SK} = 0.6$ kcal/mol. The theoretical $\nu$'s were calculated for compound II, while the observed values refer to I. Top: the corresponding curves of the parameter $\gamma$, calculated by the least-squares method.

where each three-dimensional statistical weight matrix $W$ depends on the configuration of four consecutive chain atoms and is built on the basis of three-bond ($E_g$, $E_{SK}$), four-bond ($E_\omega$), and five-bond energies ($E = \infty$ if the five bonds show two $\omega$ interactions, e.g., GG′G; otherwise $E = 0$). End effects are included in the first and last matrices. Since the statistical methods[7,8] based on nearest neighbor correlation differ from our treatment only with respect to highly unfavored conformational states, it is possible that use of such methods[7,8] would yield quite similar results.

Since the chemical shifts of the central 9-methyl carbon in compound I were assigned[2a] to pentad configurational sequences, we first neglected the effect of the two terminal methyl groups and calculated $P_G$ and $P_\omega$ for the central 8-methyl carbon of 2,4,6,8,10,12,14-heptamethylpentadecane (compound II). Given the present uncertainty about the value of $\gamma$, we have determined it by least-squares fitting of eq 1. Since $P_G$ and $P_\omega$ are highly correlated, we have not tried to fit both $\gamma$ and $\delta$ but have assumed $\delta = 3$; the calculations were also repeated neglecting the $\delta$ effect. Starting with the values of $E_g$, $E_{SK}$, and $E_\omega$ proposed by Boyd and Breitling,[7] we have examined the validity of the linear relationship (eq 1) and the behavior of $\gamma$ upon varying the energy parameters. It is found that in the range of values of $E_\omega$ proposed in recent work,[7,8] the order of the peaks is predicted correctly and the points of the plot of $(\nu^{\text{obsd}} - 3 \times P_\omega)$ vs. $P_G$ lie approximately on a straight line.

The mean-square error $\frac{1}{10}\,\Sigma_i(\nu_i - \nu_i^{\text{obsd}})^2$ is plotted vs. $E_\omega$ in the lower part of Figure 1. The value of $E_\omega$ corresponding to the minimum error ($E_\omega \sim 1.6$ kcal/mol) is only slightly sensitive to changes in temperature and also to changes in the other two energy parameters. The calculated $\gamma$ (upper part of Figure 1) shows a marked dependence on $E_\omega$; so we observe that for the value of $E_\omega = 1.3$ kcal/mol given by Boyd and Breitling[7] the calculation shows a reasonably good fitting but an exceedingly large value of $\gamma$. On the other hand, values of

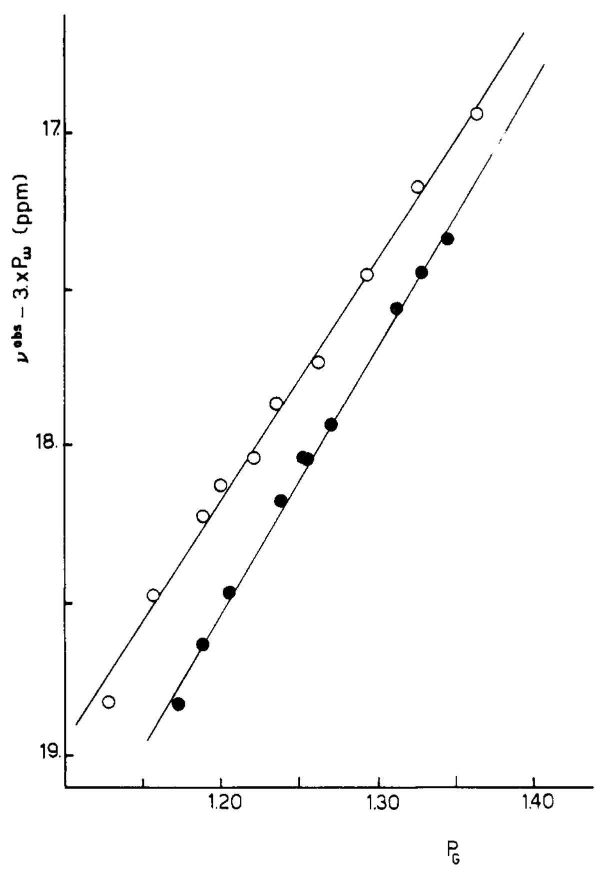

**Figure 2.** Plot of $(\nu^{\text{obsd}} - 3 \times P_\omega)$ vs. $P_G$, calculated for compound II assuming $E_g = 0.4$, $E_{SK} = 0.6$, and $E_\omega = 1.6$ kcal/mol. Open circles: $T = 20$ °C, best-fitting parameters $\gamma = -7.697$, $\nu_0 = 27.418$ ppm. Full circles: $T = 140$ °C, $\gamma = -8.442$, $\nu_0 = 28.669$ ppm.

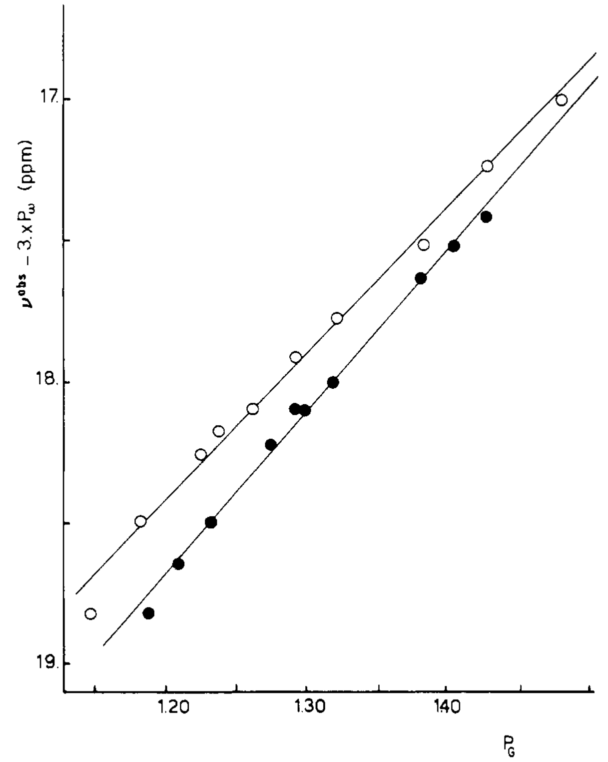

**Figure 3.** Plot of $(\nu^{\text{obsd}} - 3 \times P_\omega)$ vs. $P_G$, calculated for compound II assuming $E_g = 0.45$, $E_{SK} = 0.5$, and $E_\omega = 1.7$ kcal/mol. Open circles: $T = 20$ °C, $\gamma = -5.179$, $\nu_0 = 24.645$ ppm. Full circles: $T = 140$ °C, $\gamma = -5.733$, $\nu_0 = 25.566$ ppm.

**Table I**
**Experimental and Calculated $^{13}C$ NMR Chemical Shifts for the 9-Methyl Carbon of Compound I at Three Different Temperatures**

| | 20 °C | | | 80 °C | | | 140 °C | | |
|---|---|---|---|---|---|---|---|---|---|
| Configuration | Exptl[a] | Calcd I | Calcd II | Exptl | Calcd I | Calcd II | Exptl | Calcd I | Calcd II |
| mmmmmr | 19.367 | 19.280 | 19.260 | 19.658 | 19.569 | 19.563 | 19.798 | 19.738 | 19.740 |
| rmmmrr | 18.978 | 19.006 | 18.986 | 19.356 | 19.348 | 19.334 | 19.582 | 19.574 | 19.564 |
| mrmmrr | 18.687 | 18.728 | 18.726 | 19.064 | 19.129 | 19.116 | 19.388 | 19.411 | 19.394 |
| mmmrrr | 18.568 | 18.642 | 18.667 | 18.892(?) | 18.896 | 18.915 | 19.043 | 19.076 | 19.092 |
| rmmrrm | 18.568 | 18.619 | 18.606 | 18.827 | 18.884 | 18.884 | 19.043 | 19.070 | 19.077 |
| rmmrmr[d] | 18.460 | 18.415 | 18.449 | 18.698 | 18.709 | 18.735 | 18.892 | 18.934 | 18.951 |
| rrmrrr[d] | 18.277 | 18.319 | 18.327 | 18.616 | 18.654 | 18.657 | 18.892 | 18.903 | 18.904 |
| rrmrmm | 18.115 | 18.093 | 18.142 | 18.482 | 18.470 | 18.494 | 18.762 | 18.763 | 18.771 |
| mrmrmr | 18.115 | 18.083 | 18.118 | 18.482 | 18.466 | 18.483 | 18.762 | 18.762 | 18.767 |
| mrrrrr | 17.834 | 17.836 | 17.798 | 18.115 | 18.127 | 18.110 | 18.352 | 18.364 | 18.360 |
| rmrrrr | 17.543 | 17.564 | 17.551 | 17.910 | 17.921 | 17.916 | 18.223 | 18.215 | 18.213 |
| mmrrmr | 17.295 | 17.259 | 17.260 | 17.759 | 17.702 | 17.700 | 18.104 | 18.062 | 18.057 |
| $\gamma$[b] | | −7.700 | −5.185 | | −8.068 | −5.472 | | −8.443 | −5.738 |
| $\nu_0$[b] | | 27.423 | 24.654 | | 28.073 | 25.160 | | 28.670 | 25.573 |
| $E_g$[c] | | 0.4 | 0.45 | | 0.4 | 0.45 | | 0.4 | 0.45 |
| $E_{SK}$ | | 0.6 | 0.5 | | 0.6 | 0.5 | | 0.6 | 0.5 |
| $E_\omega$ | | 1.6 | 1.7 | | 1.6 | 1.7 | | 1.6 | 1.7 |

[a] Reference 11, in ppm from hexamethyldisiloxane (HMDS). [b] Best fitting parameters obtained with the given sets of energies. [c] Energies expressed in kcal/mol. [d] The chemical shifts corresponding to these two configurations were unequivocally assigned[11] at low temperature on the basis of the relative peak intensities and of the known composition of the stereoisomers mixture.[2a] This assignment coincides with that proposed earlier by Randall.[12]

$E_\omega$ larger than 2 kcal/mol, suggested in early statistical studies of polypropylene[9] and more recently reproposed by Tonelli,[10] yield much poorer fitting and lower $\gamma$. Also adjustments of $E_g$ and $E_{SK}$ by 0.1 or 0.2 kcal/mol appear to change $\gamma$ by some ppm, without much affecting the accuracy of the fitting. For example, the several sets of energy parameters (with $E_\omega$ from 1.5 to 1.8) recently given by Suter and Flory[8] yield values of $\gamma$ in the range of −4.7 to −6.8 ppm with mse slightly higher than the minimum of Figure 1.

It appears clear that we cannot determine a unique value of $\gamma$. However, having much restricted the range of the energy parameters which reproduce the observed chemical shifts satisfactorily, we can consider $\gamma$ just as a "best fitting" parameter to be used consistently with the chosen set of energies. Figures 2 and 3 show the results obtained with two such sets of energies: the first one corresponds to the minimum error in Figure 1, while in the second case the energies are intermediate among the values given by Suter and Flory.[8] In both cases the major defect of these calculations seems to be the inability to give wider isotactic than syndiotactic bands at all temperatures. On the other hand, the temperature dependence of the observed chemical shifts[11] is reproduced by the calculation to a good approximation. As observed experimentally, the two central peaks corresponding to the heterotactic mmrm and rmrr pentads are resolved at low temperatures, while they coincide at 140 °C. Moreover it is correctly predicted that the pentad split is larger at lower temperatures, so that the three iso-, hetero-, and syndiotactic bands are less clearly separated. However, the overall shrinking of the spectrum at high temperature is somewhat exaggerated by $P_G$, so that $\gamma$ increases in absolute value by ~10% in the 120 °C interval.

This moderate temperature dependence of the best-fitting parameter $\gamma$ may arise from the oversimplifications of the statistical treatment inherent to the three-state model and from errors in the energy parameters. Figure 1 shows that the temperature dependence of $\gamma$ vanishes for $E_\omega$ just 0.3 kcal/mol higher than the value of minimum mse.

When the $\gamma$'s are calculated omitting the $\delta$ term in eq 1, a poorer fitting is found whatever energies are used; moreover, one obtains values of $\gamma$ larger by about 1 ppm. However, the major features of the plots of Figures 1 and 2 are maintained, so that we can conclude that the $\gamma$ effect is the main factor in determining the stereochemical shifts.

Finally we have checked the validity of our assumption that compounds I and II were equivalent for our purposes by calculating the chemical shifts of the central 9-methyl carbon of I with the two above mentioned sets of energies: Since the terminal ethyl and methyl groups are not equivalent, there are 36 possible heptad configurational sequences in compounds I; of these, only 12 were present in the observed mixture of stereoisomers.[2a] The calculated heptad split is negligible at high temperature, while at 20 °C each pentad signal of II is replaced in I by a heptad band ~0.10–0.15 ppm wide, with some overlaps between adjacent pentads. However, since the 12 observed stereoisomers correspond to the center of each band, the agreement between calculated and observed $\nu$'s is just as good as with compound II, so that our assumption turns out to be valid. It remains to be seen whether the predicted heptad effect at low temperature is physically meaningful. The experimental and calculated chemical shifts of compound I are listed in Table I.

The conclusion reached by this work is that the fine structure of the methyl $^{13}C$ spectrum of stereoirregular polypropylene can be explained by the average conformational changes induced on the central triad by the configuration of the rest of the chain, without invoking shielding effects due to interactions between the observed methyl group and atoms farther than in the $\delta$ position. The three-state model gives satisfactory results; on the other hand, more sophisticated statistics would require the knowledge of the $\gamma$ and $\delta$ parameters as continuous functions of the torsional angles. We have applied the present scheme and the parameters derived from compound I to several other model compounds of polypropylene with chemical defects; the results will be presented elsewhere.

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**A. Provasoli and D. R. Ferro***

*Istituto di Chimica delle Macromolecole del CNR*
*12-20133 Milano, Italy*

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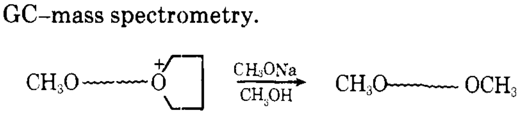
## Macrocyclic Tetrahydrofuran Oligomers

Formation of macrocyclic oligomers is a well-known side reaction in the ring-opening polymerization of three- and four-membered cyclic ethers. Under certain conditions the macrocyclic ethers are the predominant products of the polymerization of ethylene oxide[2] and may account for as much as 35% by weight of the polymerization products of oxetane.[3] No corresponding macrocycles however have been found in the polymerization products of the next higher homologue tetrahydrofuran (THF).[4]We wish to report the identification of a series of macrocyclic oligomers formed during the polymerization of tetrahydrofuran.

The polymerizations were initiated with $Me_3O^+BF_4^-$ or $CF_3SO_3Me$ in nitromethane. Samples of the polymerization mixture were quenched with MeONa/MeOH to give dimethoxy poly(tetramethylene) ether. The neutralized solutions of the polymer products were analyzed by gas chromatography and GC–mass spectrometry.



The gas chromatograph used was a Varian Aerograph Series 2700 model with flame ionization detectors. The columns were 60 cm long, packed with 10% SE-30 on Chromosorb W-HP. The injection port had exchangeable glass inserts. Column temperature was programmed at 20 °C/min from 100 to 275 °C. BHT (2,6-di-*tert*-butyl-4-methylphenol) was used as internal standard. Electron impact (EI) mass spectra were obtained with a Du Pont 21-490 GC/MS system. Chemical ionization mass spectra were obtained on a Du Pont 21-491 GC/MS system with isobutane as the reagent gas.

Computer reconstructed total ion chromatograms of the low molecular weight oligomers which are volatile under these conditions are shown in Figure 1. Electron impact mass spectra of the individual peaks indicate two homologous series of fragmentation patterns. For the series of peaks designated 2, 3, 4, etc. (Figure 1), there are two predominant fragments in the mass spectra, *m/e* 87 and 45. They are attributed to fragments containing a methoxy group:

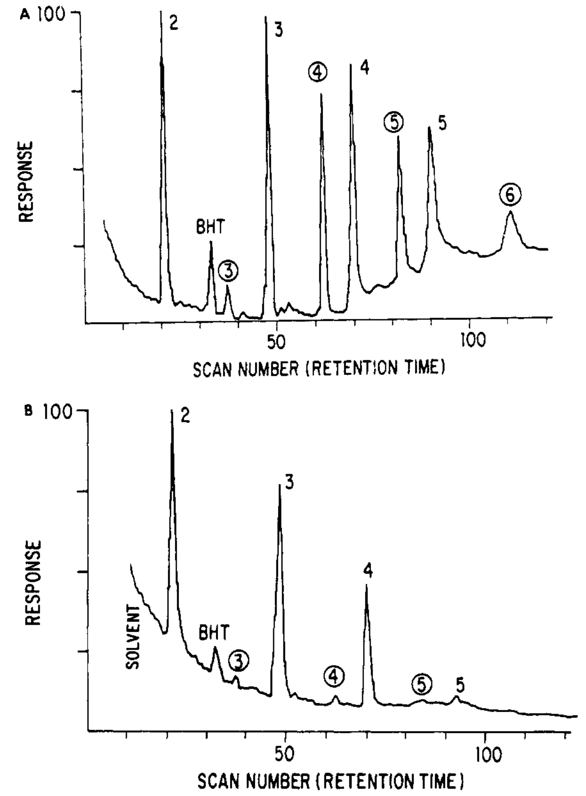
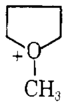


**Figure 1.** Total ion chromatograms of tetrahydrofuran oligomers. $THF/CH_3NO_2/Me_3OBF_4$ = 45.5/53.4/1.1 mol %; polymerization time = 24 h: (A) polymerization temperature = 25 °C; (B) polymerization temperature = 50 °C; 2, 3, etc. = linear oligomers; ③, ④, etc. = macrocyclic oligomers.

m/e 45: $CH_3OCH_2^+$

m/e 87: $CH_3OCH_2CH_2CH_2CH_2^+ \longleftrightarrow$



This series of peaks was therefore assigned to the linear dimethoxy oligomers (dimer, trimer, tetramer, etc.). The mass spectra of the other series of peaks designated ③, ④, etc. (Figure 1A), show five major fragments of *m/e* 71, 43, 41, 55, and 73, in order of decreasing intensity. Although much more complex, these spectra contain all the fragments of the monomeric THF ring. In contrast to the previous series, the strong peaks at *m/e* 87 and 45, corresponding to the fragments with methoxy groups, are not observed here. The absence of methoxy end groups suggests macrocyclic structures.

Due to extensive fragmentation of the molecular ions (M) under electron impact (EI) conditions, molecular weights cannot be determined. However, the molecular weights of the oligomers corresponding to the individual GC peaks can be obtained from the recently developed chemical ionization (CI) mass spectrometry. This technique uses a lower energy ionizing plasma to protonate the parent compounds, thus preventing complete fragmentation of the molecular ions.[5] Examples of a CI spectrum and a corresponding EI spectrum are shown in Figure 2.

Figure 2A illustrates the EI fragmentation pattern of the compound corresponding to GC peak ④, which is the strongest peak of the series without the abundant *m/e* 87 and 45 fragments. The corresponding CI spectrum is seen in Figure 2B. The highest *m/e* observed here are 289 and 290, representing ($M$ + 1) and ($M$ + 2). The molecular weight of the compound corresponding to GC peak ④ is therefore 288 and was assigned the structure of a cyclic tetramer of THF. Similarly, the molecular weights of the compounds corresponding to GC peaks ③, ⑤, and ⑥ were found to be 216, 360, and 432,