

Notes and Communications

NMR Studies of Polymer Solutions VIII. A Further Study of Conformational Changes of Oligomeric Polymethylenes with Chain Length

RECENTLY, we pointed out that any structural variation of polymeric chain segments that affects polymer-solvent interaction may be examined by high resolution NMR measurements¹. Investigating this proposition, we found that *n*-alkanes, i.e. oligomers of polymethylene, exhibit a sharp conformational transition as a function of chain length in certain bulky aromatic solvents^{2, 3}. For example, the internal methylene peak² was found to be split in two in *α*-chloronaphthalene at 35°C if, and only if, the number of carbon atoms (*n*) in the paraffin chain is greater than 16. The aromatic solvent effect⁴ produces clearly different chemical shifts on segments of the solute which have different average conformations. The internal methylene segments appear to reside in a single average environment when $n \leq 16$. From analysis of the Raman spectra of *n*-alkanes, Schaufele has reported very recently that, unlike the fully extended *trans* chains of the solid, the abundance of the *trans* conformation in the liquid polymethylene is vanishingly small for $n \geq 9$, in favour of chain shortened forms⁵. This peculiar conformational change observed by Schaufele, for $n \geq 9$, was not noted in our previous high resolution NMR studies on hydrocarbons^{2, 3}. The question, then arises, what evidences may one obtain from NMR measurements as a consequence of the particular conformational change of polymethylene reported by Schaufele? In the present work, the single averaged environments of the internal methylene segments and the end methyl protons of the low alkanes ($n = 5$ to 16) were carefully examined by high resolution NMR, and the results are reported here.

Highly purified linear hydrocarbons used in this study were the materials described previously². The solvent benzene (spectro-quality) was purified by distillation. High resolution NMR spectra of the pure hydrocarbons and their benzene solutions were measured at 35°C with a Varian A-60 spectrometer (Varian Associates, California). All the chemical shifts of the internal methylene peaks are expressed in cycles per second (c/s) relative to the chemical shift of an internal reference, hexamethyl disilane (1%). The results of chemical shifts can easily be reproduced within 0.1 c/s uncertainty.

Chemical shifts of the end methyl (δ_1) and the internal methylene (δ_2) peaks of *n*-alkanes in their pure states (δ_1 and δ_2) or in 5% benzene solutions (δ_1' and δ_2') are shown in *Figure 1*. In the pure liquid, δ_2 progressively increases from $n = 5$ to $n = 9$, and remains virtually constant when $n \geq 9$, whereas the chemical shift of the end methyl protons, δ_1 , remains constant for all the hydrocarbons studied ($n = 5$ to 16). In 5% benzene solution, both δ_1' and δ_2' increase with chain length ($n = 5$ to 16), although the increasing rates change in some peculiar ways (see below).

The present NMR results of pure liquid alkanes suggest that the environment of the end methyl protons is insensitive to the chain length for the

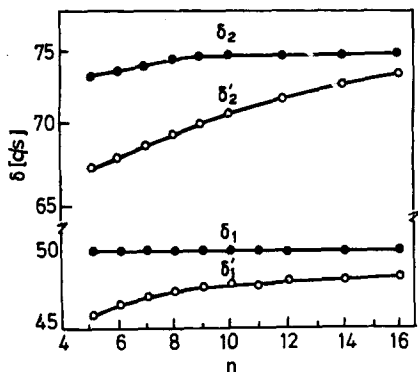


Figure 1—Chemical shifts of the end methyl (δ_1) and the internal methylene (δ_2) peaks of n -alkanes in their pure states (δ_1 and δ_2) and in 5% benzene solutions (δ_1' and δ_2') at 35°C. Hexamethyl disilane, 1%, was used as an internal reference

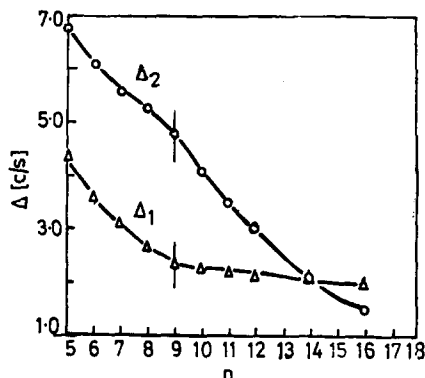


Figure 2—A plot of Δ , the relative solvent effect on the chemical shifts, ($\Delta_1 = \delta_1 - \delta_2'$, $\Delta_2 = \delta_2 - \delta_2'$) as a function of carbon number (n) in polymethylene

whole range studied, but that the environment of the internal methylene protons varies from $n = 5$ to 9, and remains constant when $n \geq 9$. This indicates that, in the sense of high resolution NMR, the averaged environment of the internal methylenes of an n -alkane is sensitive to chain length if, and only if, $n < 9$. It may also be seen that the δ_2 in pure liquid does not change with the chain length in a gradual way to approach an asymptotic value. For example, the differences in δ_2 between $n = 5$ and 7, $n = 6$ and 8, $n = 7$ and 9, $n = 8$ and 10, and $n = 9$ and $n > 9$ are, respectively, 0.5, 0.8, 0.7, 0.2 and 0 c/s. Therefore, it seems reasonable to interpret the present results on δ_2 as a consequence of a peculiar conformational change of the paraffin chain at $n = 9$ as reported very recently by Schaufele⁵.

The presence of the conformational transition at $n = 9$ was further examined in solution. A structural transition in n -alkanes may also be expected to appear as an abrupt change in its solvation behavior. It is known that aromatic solvent effect causes the chemical shift to move to higher magnetic field⁴. The present results as also shown in Figure 1 (δ_1') indicate that, even on the end methyl protons in polymethylene, this effect is quite sensitive to the chain length when $n < 9$, and becomes very small for any further increase of chain length. Its effect on the internal methylene protons (δ_2) decreases with the growth of chain length. In order to compare quantitatively the solvent effect on the chemical shifts of δ_1 and δ_2 , the amount of change in chemical shifts (Δ), which is evidently the difference between the corresponding δ_1' and δ_1 (Δ_1), or δ_2 and δ_2' (Δ_2), is plotted as a function of n in Figure 2. Again, it can be seen that there are two modes of variations for those $n < 9$ and $n > 9$. We believe that this is also a consequence of an abrupt conformational change of the paraffin chain at $n = 9$.

It may also be noted in Figure 2 that the Δ_2 of the internal methylene protons is larger than Δ_1 of the end methyl protons when $n < 14$, but becomes less than Δ_1 when $n > 14$. These results indicate that the relative solvent effect on chemical shifts of polymethylene is larger for the internal

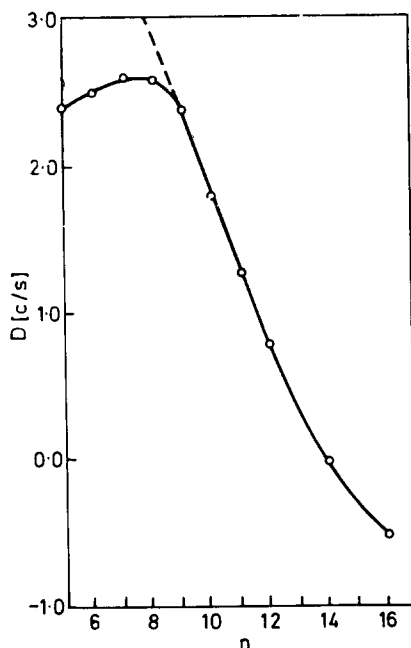


Figure 3—A plot of the differences between the relative solvent effects on chemical shifts of the internal methylenes and of the end methyls ($D = \Delta_2 - \Delta_1$) as a function of carbon number (n) in polymethylene

methylenes than for the end methyl as $n < 14$. For further increase of chain length ($n > 14$), the solvent effect on the internal methylene protons becomes so small that it is even less than that of the corresponding end methyl protons. A systematic presentation of these differences ($D = \Delta_2 - \Delta_1$) as a function of chain length (n) is shown in Figure 3.

Alternatively, this plot is equivalent to the plot of Δ_2 shown in Figure 2, if the chemical shift of the end methyl protons is used as an internal reference. This is a good presentation of the chain-length effect on the relative difference in the solvent effect on the end methyls and internal methylenes of the same hydrocarbon. When the chain length is greater than 8, the relative solvent effect, as reflected by D , decreases normally with increasing chain length as would be expected^{2, 6}. This chain length effect on the solvent-polymer interaction also explains why the Δ_2 of the internal methylenes becomes even less than the Δ_1 of the end methyls when the polymer chain is sufficiently long, i.e. $n > 14$ (Figure 2). However, it is surprising to observe that the change of the relative solvent effect (D) with respect to n drastically deviates from the expected behavior, when $n < 9$. When n increases from 5 to 8, the D value, instead of decreasing, actually increases. This peculiar solvation behavior of polymethylene is again believed to be a consequence of an abrupt conformational change of the averaged environments of the

internal methylenes of *n*-alkane chains, i.e. a conformational transition with chain length occurs, which is superimposed on the ordinary chain length effect on the solvation behavior of *n*-alkanes.

In conclusion, in addition to the previously reported conformational change of *n*-alkanes in certain bulky aromatic solvents at $n = 17$, our NMR results, in agreement with those Raman results reported by Schaufele, also present evidences of the existence of a particular conformational change for *n*-alkanes in their pure states, as well as in their benzene solutions, at $n = 9$.

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(Received August 1969)

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