Interaction of Cycloalkanes with Polymers

By IAN T. HARRISON

(*Syntex Research, Stanford Industrial Park, Palo Alto, California* 94304)

Summary A homologous series of cycloalkanes showed delayed g.l.c. elution times owing to polymer–polymer interactions through the ring of the larger homologues.

THE feasibility of threading macrocycles on to relatively short aliphatic chains has been clearly demonstrated previously by the synthesis of rotaxanes[1]. We have now attempted to show that macrocycles can be threaded on to polymer chains. Although proof of such threading has eluded us, a novel effect ascribed to polymer–polymer interactions through the macrocycle ring has been discovered.

G.l.c. provides a convenient method for the investigation of the vapour pressure of macrocyclic hydrocarbons. In the absence of threading, the macrocycle will be present in the gas phase A (Figure 1) in equilibrium with the solution phase B. Threading of the macrocycle on to the polymeric stationary phase will give rise to non-volatile forms C and D which will decrease the macrocycle vapour pressure, resulting in increased retention times.

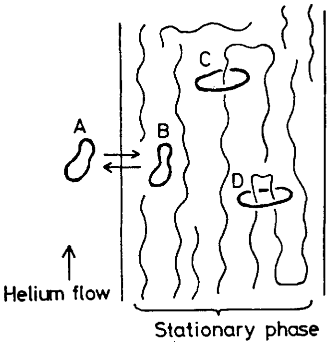

FIGURE 1. Gas chromatography of macrocycles.

A plot of the logarithm of retention times against the number of methylene units for a homologous series of cycloalkanes was found to be linear from $C_{14}H_{28}$ to $C_{33}H_{66}$ when a non-polar silicone (OV101) stationary phase was used. This linearity is a well known result and is supported theoretically.[2] However, when g.l.c. was performed on polyethylene glycol (Carbowax 20M), a polar phase, marked deviations from linearity were evident. Cycloalkanes with more than 25 methylene units were delayed (Figure 2). A homologous series of n-alkanes led to normal linear plots from n-$C_{16}H_{34}$ to n-$C_{34}H_{70}$ on either polar or non-polar stationary phases.

These results are consistent with the predicted effects of threading; only macrocycles with more than about 24 methylene units would be expected[1] to thread and thereby show increased retention times. The magnitude of the effect (up to 33% increase in retention time) was, however, surprisingly large in view of the low statistical yields (<2%) of threaded compounds obtained previously in synthetic experiments.[1] Distortion of the peak shape due to the finite time required for diffusion of the threaded macrocycle along the polymer chain was expected but not observed.

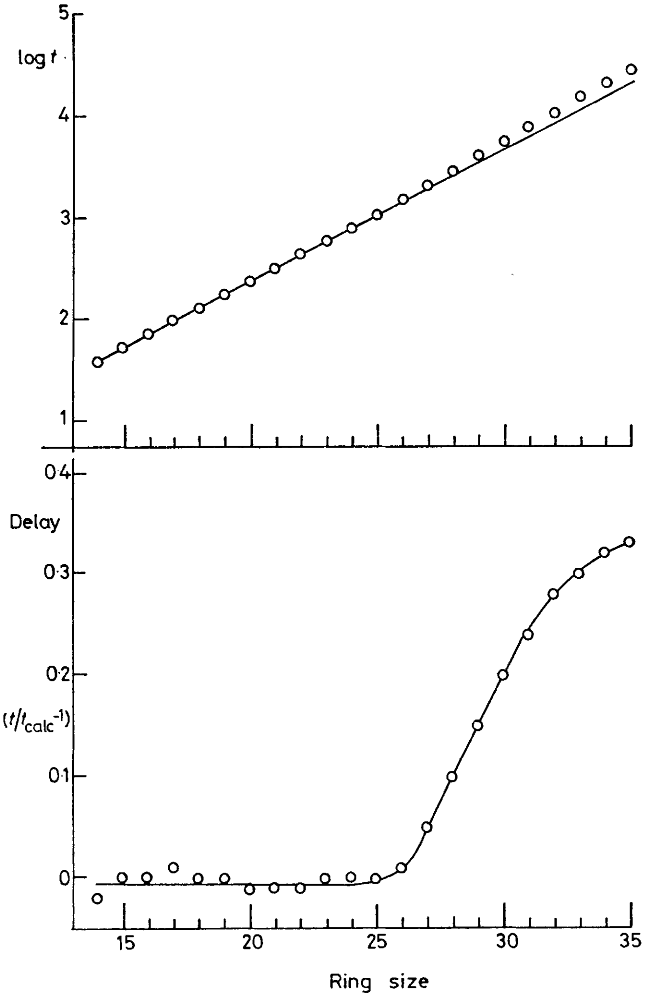

FIGURE 2. G.l.c. of cycloalkanes. Upper curve: logarithm of retention time t (in s from leading edge of solvent peak) plotted against ring size (number of methylene units). Lower curve: delay (fractional increase in retention time) plotted against ring size. Column, 92 ft, 0·03 in diameter, coated with Carbowax 20M, temp. 180 °C, helium flow *ca.* 10 ml min^{-1}.

We consider that the above results are best explained as a conformational effect. Cycloalkanes larger than *ca.* C_{25} can adopt an open conformation in which the central hole is sufficiently wide to allow solvent–solvent polar interaction through the ring. These open conformers have an increased solubility and correspondingly longer retention times.

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[1] I. T. Harrison, *J.C.S. Perkin I*, 1974, 301.

[2] L. S. Ettre, in 'The Practice of Gas Chromatography,' eds. L. S. Ettre and A. Zlatkis, Interscience, New York, 1967, ch. 7.