Note

Correlation of the response factors of thermal-conductivity detector with molecular weight for methylsiloxanes

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In studies on the kinetics of the polymerization of hexamethylcyclotrisiloxane (D_3) we used gas–liquid chromatography (GLC) for determining the extent of conversion of the monomer as well as the concentrations of oligomers formed during the polymerization:

$$D_3 \rightarrow polymer + D_x \tag{1}$$

where D denotes the $(CH_3)_2SiO-$ unit, and x has a value between 4 and 30.

As we had only a limited number of pure compounds of the poly(dimethyl-cyclosiloxane) homologous series (x = 3–9, and 12) it was necessary to determine the response factors for higher homologues by extrapolation. The response factor for a flame ionization detector was recently found to be independent of the number of siloxane units in the polymer[1,2], but quantitative analysis is difficult because of the poor linearity of response of the flame ionization detector, and because of the peak inversion that has been frequently observed in the analysis of organosilicon compounds[3,4]. These disadvantages may be partly avoided if only a small concentration of the silicon compound appears in the eluate (the best results may be attained by using capillary columns).

Quantitative analysis with a thermal-conductivity detector (TCD) is more reliable, but the determination of response factors for higher homologues constitutes a problem. We have established a correlation that may serve to overcome this difficulty.

EXPERIMENTAL AND RESULTS

A mixture of cyclic dimethylsiloxanes (D_x; x = 3–9, and 12) containing an internal standard was submitted to GLC on a JEOL 1100 gas chromatograph, with a TCD and a digital integrator (TR 2215A); the stainless-steel column (2 m × 3 mm) was packed with 10% OV-101 on Varaport 30 (80–100 mesh) and its temperature was programmed from 40° to 250° at 10°/min; the injector and detector temperatures were 250° and 270°, respectively, the carrier gas was hydrogen (40 ml/min), and the TCD current was 90 mA.

TABLE I

MOLAR RESPONSE FACTORS (f) FOR DIMETHYLCYCLOSILOXANES*

n-Undecane is used as internal standard.

Parameter	Number of $(CH_3)_2SiO$ units in test compound							
	3	4	5	6	7	8	9	12
f^*	0.975	0.778	0.671	0.592	0.534	0.476	0.440	0.352
M_x	222.46	296.61	370.77	444.92	519.07	593.22	667.38	889.84

* Each value is the mean from 10 determinations.

The molar response factors, f, were determined from the relationship in eqn. 2 and are shown in Table I.

$$f = \frac{n_{Si}\, S_{IS}}{n_{IS}\, S_{Si}} \tag{2}$$

where n and S indicate amount (moles) and peak area, respectively, and the subscripts IS and Si refer to the internal standard and the siloxane, respectively.

Some years ago, Messner et al.[5] defined the relative molar response (RMR) as the area obtained from an amount of a given substance compared with that for an equimolar amount of benzene, the value for which is taken to be 100. They showed that the RMR within a homologous series was linearly dependent on the molecular weight of the substance being determined. The RMR values were independent of
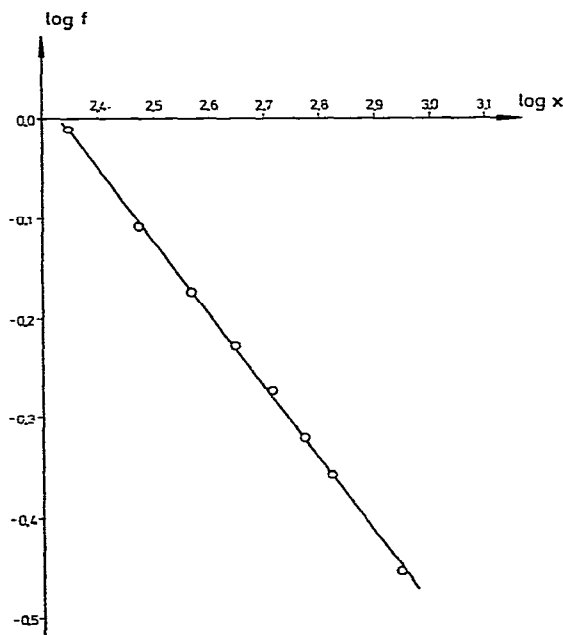

Fig. 1. Graph showing linear correlation of response factors with molecular weight for dimethyl-cyclosiloxanes in a double logarithmic plot (n-undecane as internal standard).

the type of TCD, the temperature and the hydrogen flow-rate. On the basis of this definition and eqn. 2:

$$RMR = 100f \tag{3}$$

It is evident from eqn. 3 that the use of another internal standard would also give a linear correlation between RMR and molecular weight. This dependence is not fulfilled for all homologous series; it is not observed, for example, with halogenated hydrocarbons[6]. The results in Table I indicate that there is no linear correlation for cyclic dimethylsiloxanes either. However, by making a double logarithmic plot, we were able to establish a good linear correlation between the f value and the molecular weight for these homologues, as shown in Fig. 1.

For cyclic siloxanes, the following equation may be written:

$$\log f_x = A \log M_x + B \tag{4}$$

where M_x is the molecular weight of cyclic siloxane D_x and A and B are constants. We subsequently found that the f values and molecular weights for a homologous series of linear methylsiloxanes, $Me_3SiO(Me_2SiO)_xSiMe_3$ ($x = 0-10$), exhibited an analogous relationship. The values of A and B in eqn. 4 for cyclic and linear siloxanes, and for various internal standards, are shown in Table II.

TABLE II

VALUES OF THE CONSTANTS A AND B FOR CYCLIC AND LINEAR METHYLSILOXANES

Internal standard	Cyclic compounds		Linear compounds	
	A	B	A	B
Toluene	−0.713	1.420	−0.757	1.481
n-Heptane	−0.712	1.488	—	—
n-Undecane	−0.725	1.690	—	—
n-Tridecane	−0.713	1.719	−0.768	1.817
n-Pentadecane	—	—	−0.766	1.875

We believe that the linear correlation between $\log f$ and $\log M$ is also valid for higher homologues. On the basis of eqn. 4, we could determine, by extrapolation, the f values for the higher members of homologous series of dimethylcyclosiloxanes[7]. Thus, we could calculate the concentration of cyclic oligomers (with values of x up to 30) formed in the polymerization of hexamethylcyclotrisiloxane.

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