Infra-red detection in gel permeation chromatography

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As part of a programme characterizing oligomers in unsaturated polyester resins[1], we have been using an infra-red spectrometer on line with a gel permeation chromatography (g.p.c.) column. Although the detection of eluting solutes by infra-red spectroscopy has been mentioned in the literature, see for example the references cited elsewhere[2], a quantitative treatment of the detector response in terms of transmittance has not been reported.

In a g.p.c. separation the spectrometer is operated at a fixed wavelength where only solute absorbs. The generation of a chromatogram may be regarded as the result of a series of separate infra-red experiments in which the spectrometer cell is filled with solutions having various solute concentrations. The baseline for the pure eluent corresponds to zero absorbance, A, or to 100% transmittance, T. The parameters A and T are related to solute concentration, c (mol/dm^3), according to Beer's law:

$$A = \log \frac{1}{T} = \epsilon_\lambda l c \qquad (1)$$

in which the extinction coefficient, ϵ_λ, at a particular wavelength, λ, and the path length l of the detector cell are constants. The detector response in terms of transmittance is therefore given by:

$$T = e^{-kc} \qquad (2)$$

where k is the product of ϵ_λ and l. This leads to difficulties when chromatogram areas are used to monitor the concentration of oligomers because the maximum on the linear transmittance scale corresponds to zero solute concentration.

Therefore, the relevant linear expression for the calculation of the chromatogram height in terms of a chart scale is $(1 - T)$ which is related to concentration by

$$(1 - T) = 1 - e^{-kc} \qquad (3)$$

By expanding the exponential factor,

$$(1 - T) = 1 - \left(1 - kc + \frac{k^2c^2}{2!} - \frac{k^3c^3}{3!} \ldots\right) = kc - \frac{k^2c^2}{2!} + \frac{k^3c^3}{3!} \qquad (4)$$

If the concentration is low enough for the second and third terms to be disregarded, then:

$$(1 - T) = kc \qquad (5)$$

This implies that the spectrometer pen deflections, measured in cm, for example, are linearly proportional to the solute concentration in the cell. It follows that the area, S, under a chromatogram will be represented by the sum of these deflections, each being the result of an independent experiment, i.e.:

$$S = kc_1 + kc_2 + kc_3 + \ldots = k\Sigma c_i \qquad (6)$$

and this total area is proportional to the concentration of an oligomer.

The application of the above treatment depends on the validity of Beer's law. It is, therefore, important to estimate the range of concentration over which equation (5) is obeyed. For a fixed wavelength, with $\epsilon_\lambda l$ a constant, the dependence of $(1 - T)$ on relative concentration may be calculated for particular values of A. From *Figure 1*, it is clear that equation (5) is obeyed in the absorbance range 0 to 0.035. Hence, provided the concentration of the solute or the maximum of its chromatogram curve is restricted to this absorbance range, the area of the chromatogram is proportional to the solute concentration. The view that a detec-

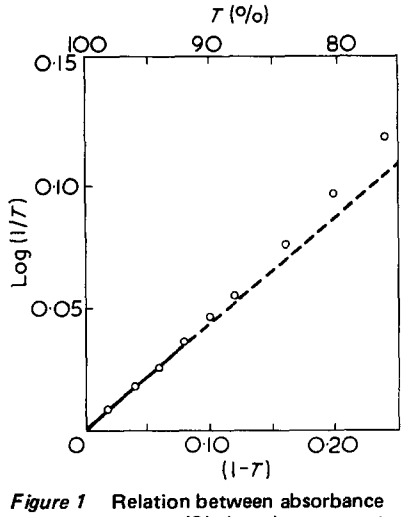

Figure 1 Relation between absorbance and transmittance (○); (——), linear region

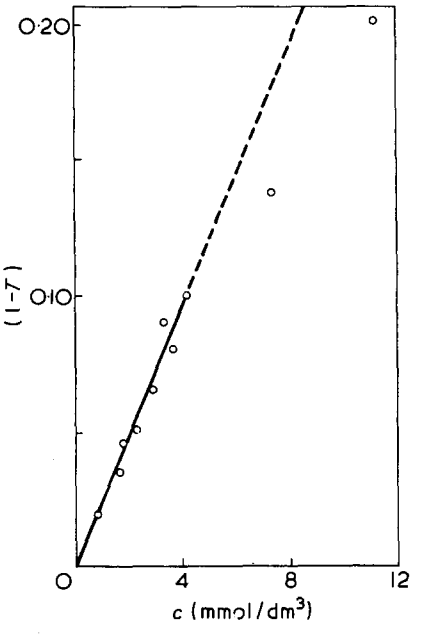

Figure 2 Experimental dependence of $(1 - T)$ for the carbonyl band (1715 cm^{-1}) on the concentration of bis(2-hydroxypropyl)terephthalate (○); (——), linear region

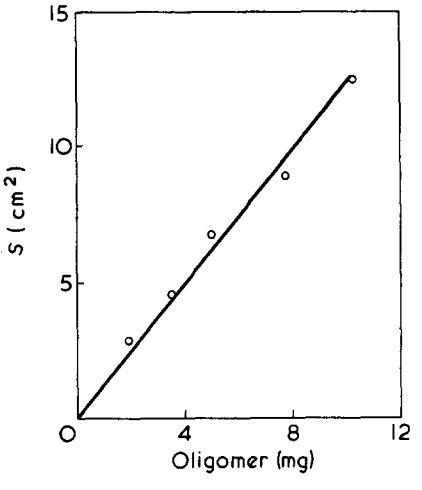

Figure 3 Experimental dependence of chromatogram area for the carbonyl band (1715 cm^{-1}) on the concentration of bis(2-hydroxypropyl)terephthalate

tor response in terms of transmittance may be used for accurate determinations of oligomer concentrations has been confirmed experimentally. The validity of equation (5) has been verified with dilute chloroform solutions of bis(2-hydroxypropyl)terephthalate (*Figure 2*). Further, a linear relationship between the quantity of oligomer applied to the g.p.c. column and the corresponding chromatogram areas has been obtained (*Figure 3*).

Acknowledgements

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References

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Photometric determination of gel point in PVC thermal degradation

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INTRODUCTION

In the thermal degradation of PVC in parallel with the primary process of allyl-activated dehydrochlorination, secondary reactions also take place[1–3]. One of them is crosslinking: as a consequence of this, even at an early stage of HCl elimination, the thermally degraded PVC becomes partly insoluble[4,5]. The crosslinking process can be characterized by the gel point, i.e., the first appearance of insoluble polymer in the course of degradation, an important parameter also from the practical point of view.

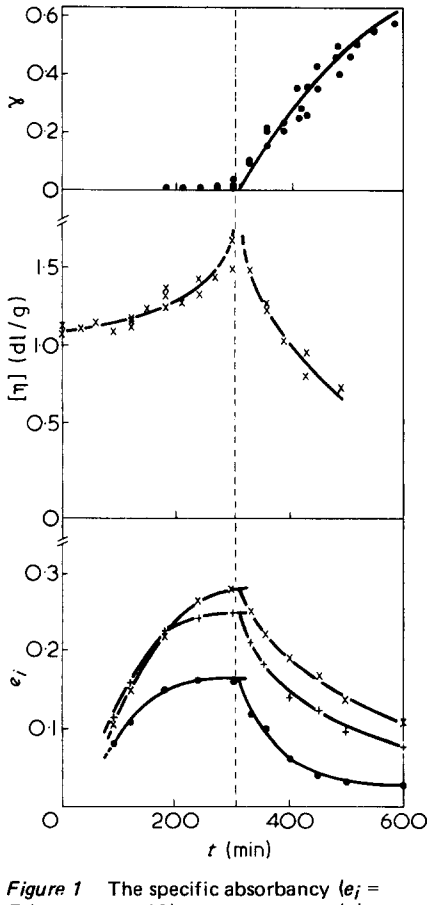

Figure 1 The specific absorbancy ($e_i = E_i/cd$, i = 5, 7, 10), the gel fraction (γ), and the intrinsic viscosity, [η], as a function of degradation time. (K = 69, 180°C, Ar; (– – –), gel point)

EXPERIMENTAL

PVC powder samples of different Fikentscher K values were degraded at 180°C in an argon atmosphere. The insoluble part of the treated samples was determined by gravimetry. Viscosity measurements were made at 25°C in cyclohexanone with an Ubbelohde viscometer. Solution spectra of degraded PVC in THF were registered on Specord UV–VIS spectrophotometer (Zeiss/Jena). Freshly distilled, peroxide-free THF was used.

Photometric determination of gel point

In the primary process of thermal PVC degradation hydrogen chloride splits off from the polymer backbone, producing conjugated unsaturated structures. The collective absorption of these polyenes gives a characteristic absorption spectrum, which may also be used for quantitative determination[2,6–12]. The maxima can be assigned to polyenes having different numbers of double bonds.

In studying the solution spectra of thermally degraded PVC powder samples, we have found that for the polyene with i double bonds the quantity

$$e_i = \frac{E_i}{cd} \qquad (1)$$

(i.e. the specific absorbance for unit concentration of PVC and unit path length) changes as a function of degradation time according to a kinked curve (E_i is the absorbancy, c is the concentration of polymer solution and d is the optical path length). The time corresponding to the inflexion point is practically independent of the wavelength, i.e., from the double-bond number of the polyene investigated. The decrease of specific absorbance of the solution is a consequence of gel formation as the non-soluble phase contains a continually increasing part of polyenes.

On the *Figure 1* the gel fraction (γ), the intrinsic viscosity, [η], and the specific absorbance for different i values (e_i) are plotted as a function of degradation time (t) for the same PVC sample. The time of discontinuous change is very nearly the same in all cases and corresponds to the gel point of the system.

The reliability of the photometric gel point determination described above may be improved by plotting the log e_i values as a function of degradation time, as in this case the curve after the gel point becomes nearly linear (*Figure 2*).

Table 1 shows gel point values determined by gravimetry and by the photometric method, respectively, for

Table 1 Gel point of different PVC powder samples degraded at 180°C in argon atmosphere

	t_g (min)	
K	From gel fraction	Photometrically determined
38.3	240	245
49	250	248
62.6	114	116
69	310	310
79.5	181	183