

CHARACTERISATION AND EVALUATION OF PYE LIQUID CHROMATOGRAPH

C. BOOTH*, A. DAVIS, AND N. F. SCILLY

Ministry of Technology, Explosives Research and Development Establishment, Waltham Abbey, Essex (Great Britain)

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INTRODUCTION

The Pye Liquid Chromatograph has been developed as a detector for liquid chromatography from the system described by James *et al.*¹. The principle of the detector is that a clean wire passes through the liquid stream to be monitored into a solvent evaporator, thence into a pyrolysis chamber, from where the volatile products of pyrolysis are swept by a stream of argon to a flame ionisation detector. The instrument has potential as a detector in a determination of a molecular size distribution of polymers by gel permeation chromatography. It may also be used to study the kinetics of pyrolysis of thin films of polymers. Here a study on the pyrolysis of several polymers, principally of poly- α -methylstyrene, which throws light upon the use of the instrument in these related fields is reported.

EXPERIMENTAL

Materials

The solvent was tetrahydrofuran which had been distilled from sodium wire and filtered.

Poly- α -methylstyrene and polystyrene samples were prepared by Richards and Salter² by means of anionic initiators. The poly- α -methylstyrene samples had viscosity average molecular weights in the range 2×10^4 to 2×10^5 (Ref. 3); the polystyrene sample had viscosity average molecular weight of 6×10^5 (Ref. 4). The polymethyl methacrylate was Diakon MG 100, an I.C.I. product (viscosity average molecular weight 1×10^5) (Ref. 5).

All solutions of polymers were filtered before use.

Apparatus and performance

A schematic diagram of the Pye Liquid Chromatograph (system 2)^{1, **} used in this work is shown in Fig. 1. The apparatus required some four hours to equilibrate. Usually the furnaces were left on continuously and about one hour allowed for the

*Permanent address: Department of Chemistry, University of Manchester, Manchester, England.

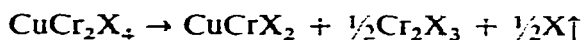
**W. G. Pye and Co. Ltd., York Street, Cambridge, England.

The results obtained for the decomposition temperature, final products, volatile and deposited materials, probable decomposition processes, and molecular weights of the final products for each of the samples studied are summarized in Table I. In the second column of this table, the decomposition temperature is given as the temperature interval from the initial temperature at which a change in weight was observed to that temperature at which no further appreciable change was observed.

Using the minimum TGA dissociation temperature as the criteria for determining thermal stability, the thermal stability of CuCr_2X_4 ($\text{X} = \text{S}$ or Se) was observed to increase from S to Se . That of the halogen derivatives, $\text{CuCr}_2\text{Se}_{3.2}\text{Y}_{0.8}$ ($\text{Y} = \text{Cl}$ or Br), increased in the order of $\text{CuCr}_2\text{Se}_{3.2}\text{Cl}_{0.8}$, $\text{CuCr}_2\text{Se}_{3.2}\text{Br}_{0.8}$, and CuCr_2Se_4 . In the case of the sulfide and selenide homologues of MCr_2X_4 ($\text{M} = \text{Zn}$, Cd or Hg , $\text{X} = \text{S}$ or Se), the thermal stability increased in the order of Hg , Cd and Zn . Among these spinels, HgCr_2Se_4 was thermally the most unstable, and started to decompose at 300°C . Lehmann and Emmenegger⁹, however, found thermogravimetrically that in an argon atmosphere this compound decomposes into Cr_2Se_3 and HgSe above 450°C . Attempts at annealing HgCr_2Se_4 between 300°C and 600°C under a Se atmosphere failed due to decomposition of the compound into HgSe and Cr_2Se_3 , and in a Hg atmosphere, however, the sample did not decompose, regardless of the pressure of Hg in the ampoule¹⁰. It was found in the present study that CdCr_2Se_4 decomposed into CdSe and Cr_3Se_4 at about 560°C in vacuum. Wehmeier¹¹ observed in an annealing study that an excess of selenium vapor (20 mg/ml ampoule volume) prevents CdCr_2Se_4 from decomposing into CdSe and Cr_2Se_3 at temperatures less than 870°C .

The ternary chalcogenides BaCr_2S_4 , PbCr_2Se_4 and EuCr_2Se_4 , which have a hexagonal structure, were also subjected to thermogravimetric analysis. The thermograms of BaCr_2S_4 and EuCr_2Se_4 monotonically decreased over the entire temperature range from 200 to $1,000^\circ\text{C}$ and were poorly defined. Accordingly, the decomposition temperatures of these materials could not be determined although the thermal stability of PbCr_2Se_4 was observed to be comparable to that of CdCr_2Se_4 .

The final products, after completion of decomposition, were weighed with an analytical balance. The final products and also the intermediate products obtained by heating the sample up to a given intermediate temperature and then cooling to room temperature were identified qualitatively by X-ray powder diffraction. The material deposited on the vessel wall was subjected to qualitative chemical analysis. The analytical results obtained are tabulated in Table II. From these measurements the major decomposition processes and final products for each sample were deduced and these are shown in the third and fourth columns of Table I. As is seen in Table I, the decomposition process of the CuCr_2X_4 ($\text{X} = \text{S}$ or Se) spinels was determined to be



For the halogen derivatives of the copper-spinels, $\text{CuCr}_2\text{X}_{3.2}\text{Y}_{0.8}$ ($\text{X} = \text{S}$ or Se ; $\text{Y} = \text{Cl}$ or Br), the formation of CuCrX_2 and of the chromium chalcogenides as final products is similar to that for CuCr_2X_4 . However, the data obtained for the com-

Under conditions where pyrolysis of the polymer on the wire is complete, *i.e.* at low wire speeds and high temperatures, the response is found to vary directly as the five-thirds power of the wire speed (see Fig. 2). This is the expected result: the film of liquid adhering to the wire will have a thickness which is proportional to the two-thirds power of the wire speed⁷, while the length of wire exposed to the solution as it passes the coating block will be proportional to the first power of the wire speed.

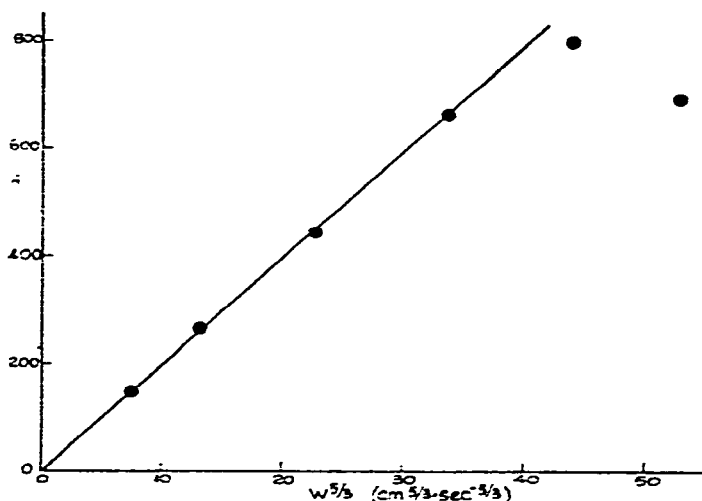


Fig. 2. Dependence of detector response (A) upon wire speed (W) for the pyrolysis of poly- α -methylstyrene at furnace temperature $T = 650^\circ\text{C}$.

At low temperatures and high wire speeds pyrolysis of the polymer on the wire is incomplete. In what follows we present the results of the partial pyrolysis of the polymers we have studied.

RESULTS AND DISCUSSION

Pyrolysis of poly- α -methylstyrene

Table I shows the results of typical experiments in which the temperature of the pyrolyser furnace (T , $^\circ\text{C}$) and the residence time in the pyrolyser furnace (t , sec) were varied. The fraction of polymer remaining on the wire when it leaves the furnace (P/P_0) is calculated from the area of the peak obtained at high temperatures when pyrolysis is complete (A_0) and that at the lower temperature (A) by the relation

$$P/P_0 = (A_0 - A)/A_0$$

Values of A_0 for a given wire speed were calculated from the known dependence of A_0 on $W^{5/3}$ (wire speed; Fig. 2). It was shown in another experiment, that the response of the apparatus under conditions leading to partial pyrolysis is independent of the weight or concentration of polymer injected into the solvent stream. This is expected for thin films⁸: our estimate of the thicknesses of the polymer films formed on the wire under the conditions of our experiments is 700 Å or less.

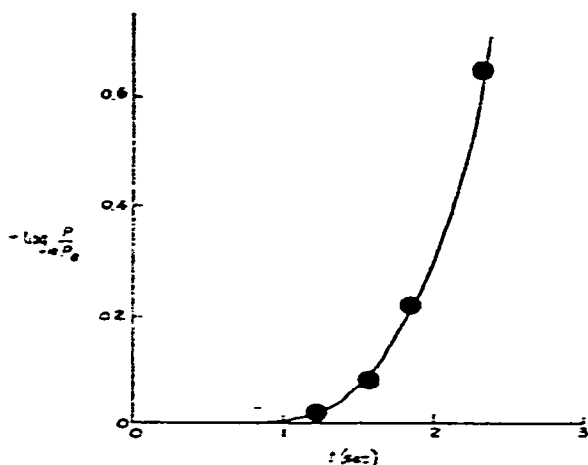


Fig. 3. First order plot for the pyrolysis of poly- α -methylstyrene. Furnace temperature $T = 500^\circ\text{C}$.

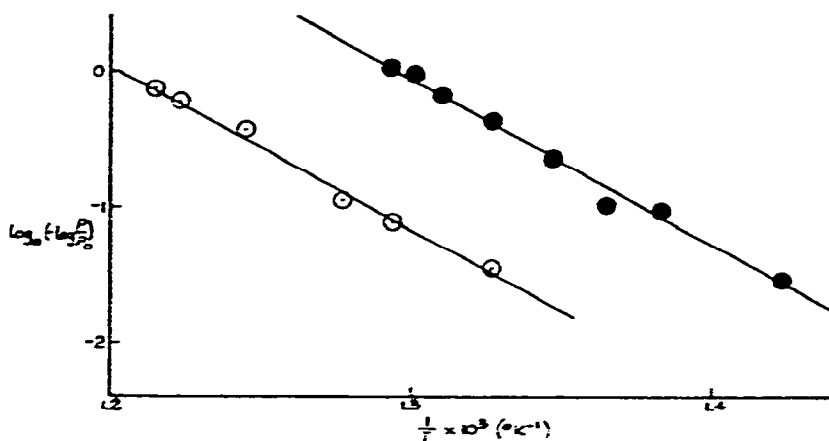


Fig. 4. Arrhenius plots for the pyrolysis poly- α -methylstyrene of molecular weight $M_w = 195,000$. Residence times of 1.50 sec (○) and 2.41 sec (●).

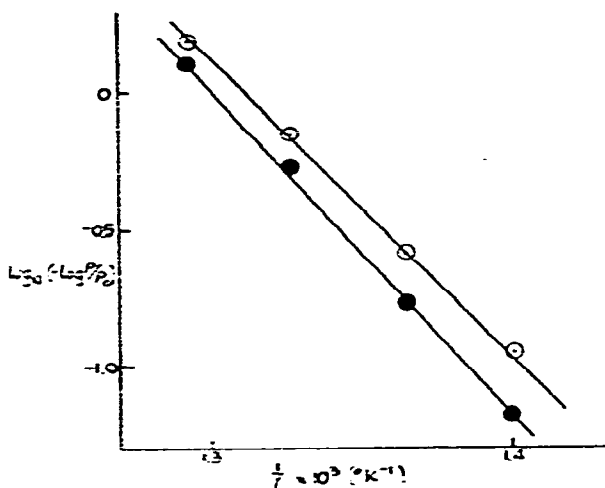


Fig. 5. Arrhenius plots for the pyrolysis of poly- α -methylstyrene with a residence time of 2.52 sec. Molecular weights $M_w = 155,000$ (○) and 23,000 (●).

TABLE I

THE PYROLYSIS OF POLY- α -METHYLSTYRENE, MOLECULAR WEIGHT 195,000

$t = 2.41 \text{ sec}$		$T = 500^\circ\text{C}$	
$T(^{\circ}\text{C})$	P_i/P_0	$t(\text{sec})$	P_i/P_0
650	0	2.31	0.22
600	0	1.85	0.62
550	0	1.56	0.82
510	0	1.21	0.95
500	0.08		
490	0.22	1.04	0.98
480	0.37		
470	0.59		
460	0.78		
450	0.81		
430	0.94		
400	0.97		

The mechanism of pyrolysis of low molecular weight poly- α -methylstyrene has been investigated by Richards and Salter². Their reaction scheme comprises random homolytic scission followed by complete depolymerization of the polymeric radicals (provided the molecular weight of the original molecule is less than 60,000) and by diffusion of the terminal monomeric radicals out of the system. This scheme leads to the rate equation

$$\frac{-dP}{dt} = k_1 P \quad (1)$$

where P is the weight of polymer remaining after time t , and

$$k_1 = 2k_i x \quad (2)$$

where k_i is the rate constant for scission and x is the degree of polymerization of the original molecules ($x < 500$). Integration of Eqn. (1) gives

$$-\log_{10}(P/P_0) = \frac{k_1 t}{2.3}$$

Thus, provided the same mechanism operates under the conditions of our experiments, we expect a plot of $-\log_{10}(P/P_0)$ against residence time to be a straight line of slope $k_1/2.3$, and a plot of $\log_{10}[-\log_{10}(P/P_0)]$ against $1/T$ to be a straight line of slope $E_2/2.3R$, where E_2 is the activation energy for the degradation (scission) process.

The appropriate plots are shown in Figs. 3 to 5. The first order plot (Fig. 3) is not a straight line. This is ascribed to the fact that the effective temperature of pyrolysis decreases as the wire speed increases. The Arrhenius plots are straight lines and give values of the activation energy around $230 \text{ kJ} \cdot \text{mol}^{-1}$. This value compares well with the values in the literature of $270 \text{ kJ} \cdot \text{mol}^{-1}$ (Ref. 2) and $230 \text{ kJ} \cdot \text{mol}^{-1}$ (Ref. 9).

Richards and Salter have determined values of k_i in the temperature range 260–290°C. We have used these values, together with their value of the activation energy, to extrapolate k_i , for poly- α -methylstyrene of molecular weight 23,000, into the range of temperatures we have studied. Comparison of the two sets of data is made in Fig. 6 where we have plotted $\log_{10} k_i/2.3$ against $1/T$. It can be seen that a

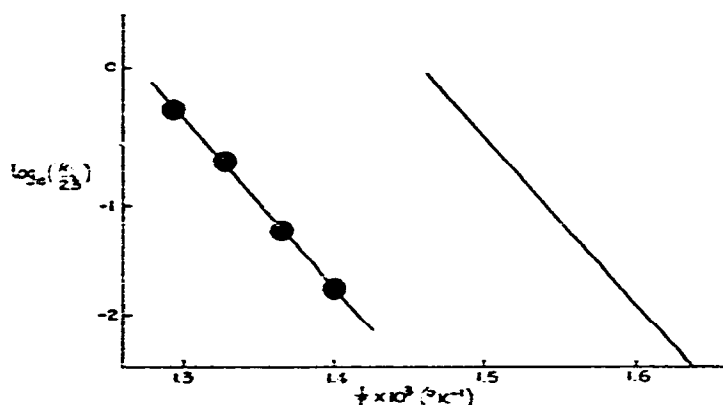


Fig. 6. Arrhenius plots for the pyrolysis of poly- α -methylstyrene of molecular weight $M_v = 23,000$. Data from Pye Liquid Chromatograph (●) and from results of Ref. 2 (—).

lateral shift of some $2 \times 10^4 \text{ deg}^{-1}$ is necessary in order to bring the two lines into coincidence. In other words, with a residence time of 2.5 sec and furnace temperatures in the range 500–440°C, the effective temperatures of pyrolysis (T^*) are in the range 400–360°C.

Correlation of data at other residence times and temperatures can be made in a similar way. Values of T^* obtained are listed in Table II.

TABLE II

EFFECTIVE TEMPERATURES OF PYROLYSIS (T^*) FOR POLY- α -METHYLSTYRENE, FURNACE TEMPERATURE $T = 500^\circ\text{C}$

Residence time, t (sec)	Effective temperature, T^* (°C)
2.52	400
2.31	380
1.85	370
1.56	355
1.21	335
1.04	325

T^* has also been estimated by considering the conditions of heat transfer in the pyrolyser (details are given in the Appendix to this paper). Values of T^* are in good agreement with those found by comparison of rates of degradation. It was noted that T^* is only slightly dependent upon the activation energy of the polymer (see Appendix); values of T^* obtained for poly- α -methylstyrene can also be used for other polymers.

Pyrolysis of polymethyl methacrylate

Lehrle *et al.*¹⁰ have shown that the degradation of polymethyl methacrylate follows a rate equation of the form of Eqn. (1). Accordingly, in Fig. 7, we plot $\log(k_1/2.3)$ against $(1/T)$. The temperature shifts necessary to bring these curves into

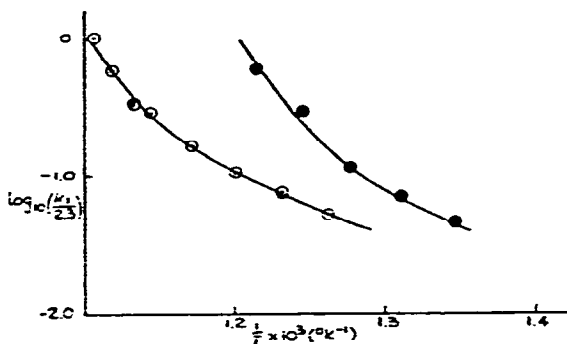


Fig. 7. Arrhenius plots for the pyrolysis of polymethyl methacrylate. Residence times of 1.33 sec (○) and 2.68 sec (●).

coincidence are substantially those predicted from the results for poly- α -methylstyrene. We estimate that our measurements cover a range of effective temperatures from 370 to 450°C. However, the Arrhenius plots are curved. This is in keeping with the results of Lehrle *et al.*, who have shown that at temperatures below 400°C the mechanism of depolymerisation is almost wholly end initiated and bimolecularly terminated, whereas at temperatures above 400°C random scission and complete depolymerisation of polymeric radicals predominates.

Pyrolysis of polystyrene

The mechanism of degradation of polystyrene is complex¹¹ and the rate equation is not simple. Consequently it is not possible to analyse kinetically the data available from our technique. However in Fig. 8 the fraction of polymer volatilized in about 2.5 sec at various values of T^* , is plotted for polystyrene, poly- α -methylstyrene and polymethyl methacrylate. These may be compared with conventional plots of weight loss against temperature¹².

CONCLUSIONS

The maximum effective temperature of pyrolysis in the Pye Liquid Chromatograph is little more than 500°C. Consequently polymers of thermal stability greater than (say) polystyrene will not volatilize completely in the three seconds or less residence time in the pyrolysis furnace. For example, a sample of polysulphone (reprecipitated Bakelite polysulphone, P1700 Union Carbide Corporation) could not be pyrolysed completely in the apparatus. Since the rate of degradation, and therefore the response of the apparatus may depend upon the molecular weight when pyrolysis is incomplete [see, for example, Fig. 5 or Eqn. (1)] this represents a limitation to the use of the apparatus as a detector in gel permeation chromatography.

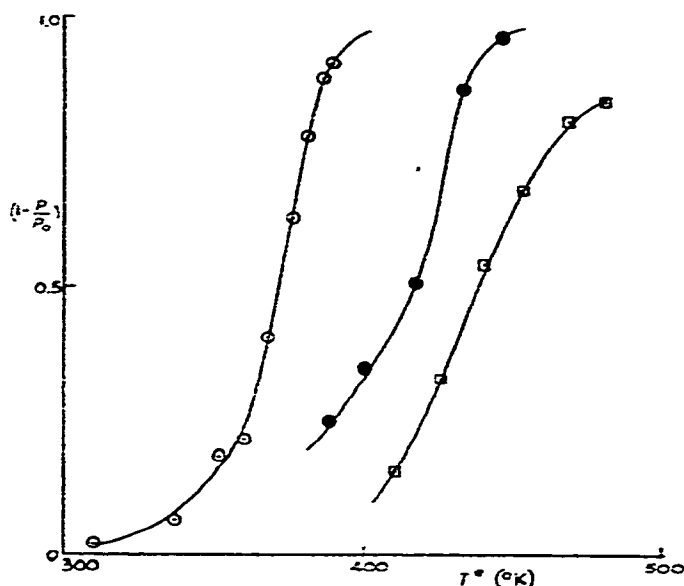


Fig. 8. Volatilization vs. effective temperature of pyrolysis for poly- α -methylstyrene (○), polymethyl methacrylate (●), and polystyrene (□).

It is possible, under favourable circumstances, to use the apparatus to obtain basic information about polymer degradation processes. For example we have shown here that the mechanism of degradation of poly- α -methylstyrene is unchanged over the temperature interval 220–400°C, whereas previous studies were restricted to temperatures less than 300°C.

APPENDIX

Calculation of the effective temperature of pyrolysis

The equation for overall heat transfer from the furnace to the wire can be written^{1,3}

$$q = UA_m \Delta T_m t / l \quad (\text{A1})$$

where q is the heat transferred to one cm of wire, A_m is the log mean area through which heat is transferred, ΔT_m is the log mean temperature difference between wire and furnace, t is the time of heat transfer, l is the distance over which heat is transferred and U is the overall heat transfer coefficient. If we further write

$$q = c(T_0 - T_t) + c(\Delta T_0 - \Delta T_t) \quad (\text{A2})$$

and

$$\Delta T_m = (\Delta T_0 - \Delta T_t) / 2.3 \log_{10}(\Delta T_0 / \Delta T_t) \quad (\text{A3})$$

where c is the heat capacity per centimetre of wire, T_0 and T_t are the temperatures of the wire after time $t = 0$ and $t = t$ in the furnace, and ΔT_0 and ΔT_t are the corresponding temperature differences between furnace and wire, we obtain

$$\log_{10} \Delta T_t = \log_{10} \Delta T_0 - (UA_m t / 2.3 cl) \quad (\text{A4})$$

The effective temperature of pyrolysis of a polymer on the wire is given by

$$T^* = \frac{\int_0^t T_i e^{-E_a/RT_i} dt}{\int_0^t e^{-E_a/RT_i} dt} \tag{A5}$$

In our apparatus the furnace tube diameter (0.30 cm) and the wire diameter (0.012 cm) are such that A_m is 0.29 cm², the distance between the tube and wire (b) is 0.15 cm and the heat capacity (c) is 5×10^{-4} J·deg⁻¹. We take T_0 to be 200 °C (the wire emerges from the evaporator oven immediately before entering the pyrolysis furnace) and we choose U to be 1.25×10^{-4} J·cm⁻¹·deg⁻¹·sec⁻¹ in order to bring this calculation into approximate coincidence with our finding that $T^* = 400$ °C when $T = 500$ °C and $t = 2.5$ sec. Approximate numerical evaluation of the integrals of Eqn. (A5) with $E_a = 270$ kJ·mol⁻¹ gives the result

$$T^* \sim T_i - 10$$

and these values, listed in Table A1, may be compared with those obtained earlier (Table II). The agreement is satisfactory, bearing in mind the approximations made concerning T_0 and U .

TABLE A1
CALCULATED VALUES OF THE EFFECTIVE TEMPERATURE OF PYROLYSIS OF POLY- α -METHYLSTYRENE

Furnace temperature, T (°C)	Residence time, t (sec)	Effective temperature T^* (°C)
500	2.5	400
500	2.0	380
500	1.5	350
500	1.0	310
600	2.5	470
400	2.5	330

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