

Sample size dependence in pyrolysis: an embarrassment, or a utility?

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ABSTRACT

Product ratios, fractional conversions, and rates of pyrolysis may show confusing variations with sample size or thickness. There are several reasons for this, amongst which heat transfer and temperature gradients across the sample are important. To obtain meaningful results, a suitable approach is to reduce sample size to find a sample thickness range over which the reaction parameters are independent of the size. The objective in this approach is thereby to eliminate any effects of sample size. Recent work however has shown that investigations of the dependence of reaction parameters on sample size may reveal mechanistic features of the pyrolysis process itself. Two such features are: (a) secondary reactions which occur during the residence time of primary products in the melt, and (b) diffusion-restriction of the interaction of long-chain radicals, when the thickness of the degrading film is comparable with the diameter of the hydrodynamic volume of the polymer molecules. Both types of study have been performed on a range of polystyrene and PMMA samples.

Poly(methyl methacrylate); polystyrene; pyrolysis; sample size.

INTRODUCTION

For many years it has been recognised that results from polymer pyrolysis studies may show confusing variations with sample size or thickness [1]. The reasons for this can broadly be classified into (a) those depending primarily on physical factors, and (b) those depending on chemical factors.

Physical factors

Sample size can have a pronounced effect on the mean temperature which is attained by a sample, the temperature gradient across a sample, and the time taken for the sample to reach a steady temperature. These statements apply whether the sample is heated by pushing/dropping it into a furnace,

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or by coating it on a filament which is rapidly heated. The underlying reason for this situation is that synthetic and natural polymers are rather poor conductors of heat; this means that pronounced temperature gradients may exist across samples even when their thickness is much less than a micron. Moreover, the temperature of such 'thick' samples of poor conductivity may rise rather slowly to the steady value, i.e. the time-scale of the temperature rise may be quite comparable with that during which substantial degradation of the sample occurs. Since pyrolysis product ratios and pyrolysis rates generally show pronounced temperature-dependence, it is not surprising that the observed values of these reaction parameters are found to depend on sample thickness if this has such effects on temperature. The unknown and uncontrolled temperature effects associated with sample thickness also influence another physical factor which is important in pyrolysis: the diffusion of molecules and other species through the sample. The viscosity of the melt and the diffusivities of the molecules within it are temperature-dependent, and insofar as these can influence rates or mechanisms of pyrolysis, these will again be affected by sample thickness.

It is not easy, or perhaps not even possible, to eliminate all of these problems when studying the pyrolysis of thick samples. Indeed the thermal degradation characteristics of interest with large samples may be determined by the way in which the sample size/shape and the method of heating, influence the temperature rise, temperature gradients, and mean temperature.

However, when it is desired to measure kinetic parameters of the pyrolysis at specified sample temperatures, the only practical approach is to study such parameters as a function of sample thickness, and accept results only if they lie within a region where there is no anomalous thickness dependence. Thus for kinetic measurements on poly(methyl methacrylate) [1-3] sample thicknesses as small as 20 nm (200 Å) were found to be necessary, and with polystyrene [4,5], samples of 20-45 nm, and with polyacrylonitrile [6,7], samples of 75-1000 nm, were used on the basis of thickness studies *.

Chemical factors

In the previous section the total objective could be defined as the elimination of the undesirable effects of temperature uncertainties arising

* These sample thickness figures, and others quoted subsequently in the present paper, are calculated on the basis of the uniform spreading of a known volume of sample, deposited from solution, on a defined area of filament. With filaments used by the authors this area is 1 mm × 3 mm. Considerable care is necessary in depositing the sample, since it is notoriously difficult to produce uniform films. The procedure has been refined by the present authors and their co-workers by using electron microscopy to assess the procedure. Details of these sample deposition studies will be published shortly.

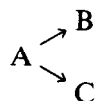
from sample thickness effects. If the chemistry of the pyrolysis changes with sample thickness, the situation is less clear; our target must be to investigate such effects and try to understand them on a molecular basis. This is the principal concern of the present paper: we attempt to assess contributions to thickness dependence which would be expected even in the absence of temperature uncertainties. The mechanistic implications of these will be considered, and evidence for them will be sought in the precise measurements of thickness dependence made in the laboratories of the authors.

MECHANISMS FROM SAMPLE SIZE EFFECTS

Dependence of product ratios on sample thickness

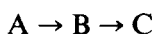
Suppose we observe volatile products B and C to be evolved from a heated melt of substance A. We may propose two basic mechanisms:

(i) B and C are both primary products, i.e. they are both formed directly from A:



With this mechanism there is no reason to suppose that the B/C product ratio depends on the sample size chosen.

(ii) Either B or C is a secondary product, by which we mean that C (for example) is formed consecutively from the primary product B:



If in this case the $B \rightarrow C$ process is favoured in the melt environment (or at the melt temperature), then the longer the time B spends in the melt, the smaller will be the B/C ratio in the observed products. Since we expect a longer residence time for B if the melt is thicker, the B/C ratio may be expected to decrease when the sample size is increased.

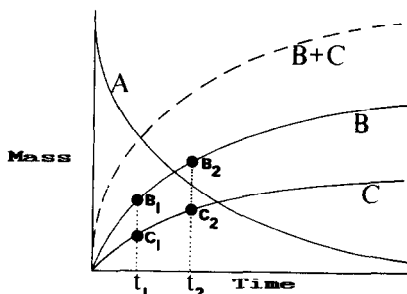


Fig. 1. Parallel reaction mechanism. t_1 and t_2 represent different reaction times. $B_1/C_1 = B_2/C_2$.

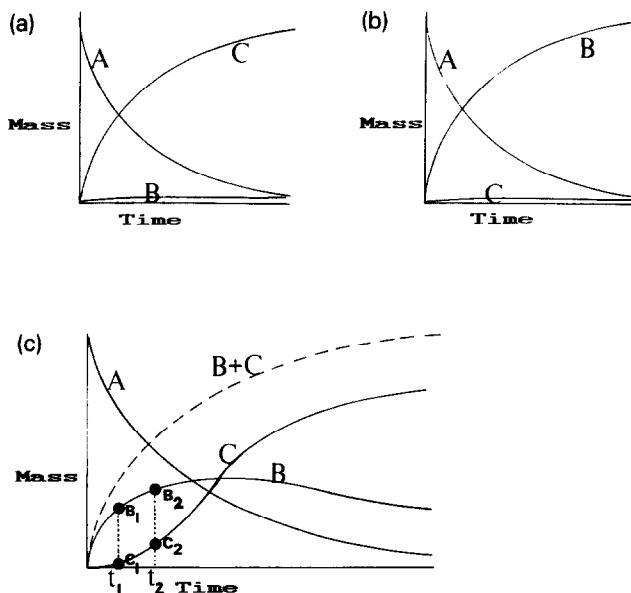


Fig. 2. Consecutive reaction mechanism. t_1 and t_2 represent different reaction times. $B_1/C_1 \neq B_2/C_2$.

These basic proposals about the B/C product ratio can be understood with reference to conversion vs. time curves as shown in Figs. 1 and 2, the essential mathematical background for which can be found in standard physical chemistry texts (e.g. ref. 8).

Mechanism (i), the parallel reaction mechanism, is shown in Fig. 1. It is a feature of this mechanism that, provided that the processes giving B and C are of the same order, the B/C product ratio is independent of the time of reaction, i.e. $B_1/C_1 = B_2/C_2$. Now if we think of a greater residence time in the high-temperature melt as being somewhat analogous to an extended reaction time, we expect no change in the B/C ratio with sample thickness.

Mechanism (ii), the consecutive reaction mechanism, is illustrated in Fig. 2(a) for a situation where the rate of the $B \rightarrow C$ process is very fast (i.e. B is an unstable intermediate), and in Fig. 2(b) if the $B \rightarrow C$ process is very slow. Figure 2(b) will also represent the situation where the $B \rightarrow C$ process is of moderate speed in the melt, but where this conversion cannot occur because B distills directly out of the melt as soon as it is formed. This might be expected if the thickness of the melt is very small. On the other hand if the $B \rightarrow C$ process is of moderate speed in the melt, and the residence time of B in the melt is prolonged because of the thickness of the melt, then the situation corresponding to Fig. 2(c) will pertain. Here the B/C ratio depends on both the reaction time and the residence time; as either of these increases we expect the B/C product ratio to decrease. Hence if a decrease in the B/C

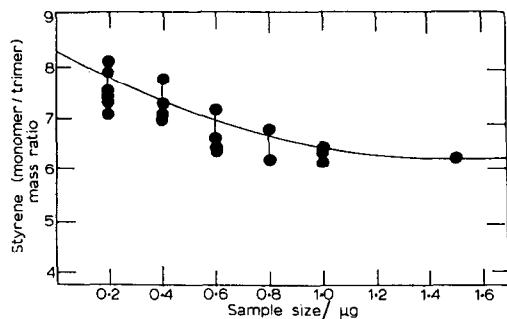


Fig. 3. Sample size dependence of the monomer/trimer ratio from polystyrene pyrolysed at 530 °C, [10].

product ratio is observed as sample size is increased, we may take this as evidence for a consecutive mechanism.

As an illustration of this general approach we may consider the pyrolysis of polystyrene to yield monomer and oligomeric products. If the latter are formed by intramolecular processes during depropagation [5], all products are effectively primary products, and no dependence of product yield ratios on sample size is expected. On the other hand, if some or all of the oligomers are formed by monomer recombination within the melt [9], then monomer/oligomer yields should decrease with increasing sample size. Results [10] for such investigations of the monomer/trimer ratio and the monomer/dimer ratio are shown in Figs. 3 and 4. For sample sizes less than 1 μg (thickness ca. 0.1 μm or 1000 Å) there is some decrease of the monomer/trimer ratio with increasing sample thickness, and this provides some indication of the existence of a monomer recombination reaction to

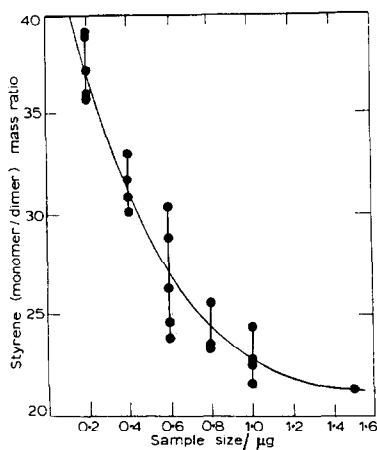


Fig. 4. Sample size dependence of the monomer/dimer ratio from polystyrene pyrolysed at 530 °C, [10].

form a trimer. In the same sample size range there is a dramatic decrease of the monomer/dimer ratio, and this strongly suggests that monomer recombination is a very important source of dimer formation. On this basis, it is concluded that under the conditions used, dimers may be formed almost exclusively as a result of secondary reactions, and trimers at least partially so.

The proposals made throughout this section (about the independence or dependence of product yield ratios on sample thickness) are applicable whether we are considering a partial pyrolysis of a sample under specified degradation conditions, or a total pyrolysis to give the complete available yield of all products. In the next section, we consider how the fractional yield of a given product should depend upon sample size, when the specified time and temperature of degradation lead to incomplete pyrolysis.

Dependence of individual product yields on sample thickness

In this section we again exclude the physical factors discussed in the introduction, i.e. we consider chemical contributions to thickness dependence which could exist even in the absence of temperature uncertainties with sample thickness. Furthermore, we will assume that reaction times are sufficiently short for the conversion to be occurring in an 'initial rate' period where first order decay of reactant mass (or first order growth of product mass) is observed.

For the first order decay of mass m_0 with time t , if m^* is the mass remaining at any time,

$$m^* = m_0 \exp(-kt) \quad (1)$$

where the constant k characterises the rate of the decay at a specified temperature. If we define m as the mass of product formed at time t , we can replace m^* by $(m_0 - m)$, and eqn. (1) then becomes

$$\left\{1 - \frac{m}{m_0}\right\} = \exp(-kt)$$

or $\frac{m}{m_0} = 1 - \exp(-kt).$ (2)

m/m_0 is the yield (m) of product expressed as a fraction of the total available yield (m_0) of that product. This is the parameter which is usually measured in kinetic pyrolysis work. Equation (2) shows that within the assumptions stated, this fractional yield should be a constant if the time and temperature of a pyrolysis are specified. If the value of this constant (the R.H.S. of eqn. 2) is written as K ,

$$\text{Then } \frac{m}{m_0} = K \quad (3a)$$

$$\text{or } m = Km_0 \quad (3b)$$

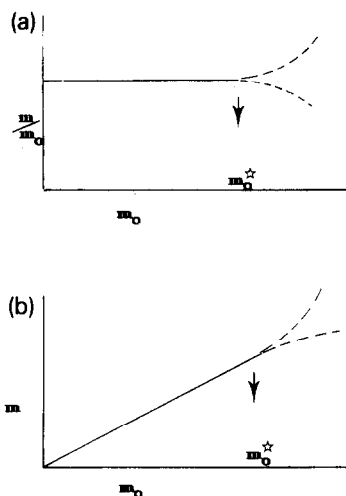


Fig. 5. Anticipated anomalous size-dependences are shown by dotted lines. Samples of sizes up to m_0^* are suitable for kinetic studies.

Equation (3a) implies that if fractional conversion is plotted against m_0 (initial sample size), a horizontal line should be obtained. Equation (3b) implies that a plot of sample yield against initial sample size should be a straight line through the origin. The extent to which such plots are linear defines the acceptable size range in kinetic work; deviations are of course expected for thicker samples, for the reasons stated in the introduction. We can therefore say that plots similar to Figs. 5a or 5b are anticipated for product yields if the products are primary and do not decompose or combine. Curvature of the complete plot may reveal the possibility of a complex pyrolysis mechanism.

Before examining pyrolysis data from this standpoint, it must be noted that plots according to eqn. (3b) are more helpful in indicating anomalous thickness dependence than those according to (3a). This is because a small ordinate intercept on a linear type 3b plot confers hyperbolic curvature on to type 3a. This can be understood if the intercept is represented by i ; eqn. (3b) becomes $m = i + Km_0$, but if we now divide by m_0 we obtain instead of eqn. (3a) the equation

$$\frac{m}{m_0} = \frac{i}{m_0} + K$$

The i/m_0 hyperbolic curvature is present over the whole plot, and becomes very pronounced for small values of m_0 . For this reason, sample thickness-dependence will be assessed according to eqn. (3b) in the remaining part of this section.

The pyrolysis of PMMA is a convenient system for preliminary assessment of the thickness-dependence proposals in the present section. As noted

in the introduction, it has been found to display anomalous thickness dependence unless very thin films are used, but nevertheless it is uncomplicated in that there is a single pyrolysis product (monomer) observed, provided excessively high pyrolysis temperatures are avoided. The results obtained (for experimental details see Appendix I) when monomer yields were plotted against sample size were rather surprising. Although satisfactory linearity was obtained over the sample range from several micrograms down to $0.5 \mu\text{g}$, anomalous behaviour was observed for sample sizes below

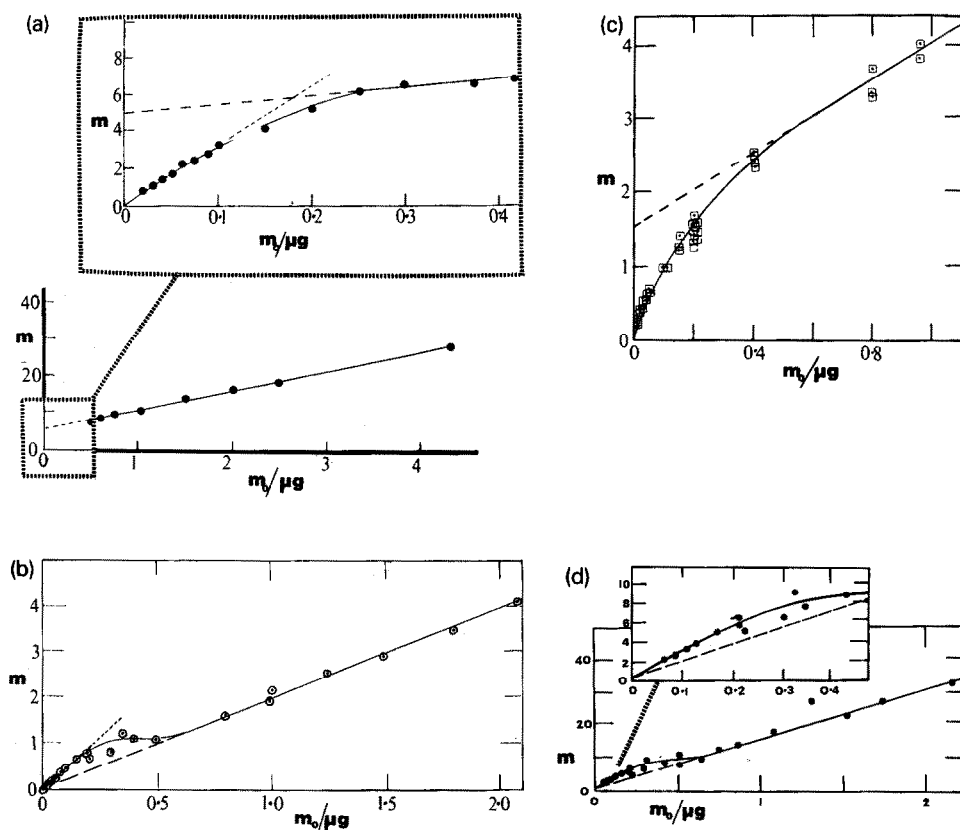


Fig. 6(a). Dependence of sample yield, m (arbitrary units), on initial sample size, m_0 , for pyrolyses of PMMA at 367°C for 6.1 s. The behaviour at the smallest sample sizes is shown in detail on the upper plot. [Sample GTP 31400].

Fig. 6(b). Dependence of sample yield, m (arbitrary units), on initial sample size, m_0 , for pyrolyses of PMMA at 353°C for 5.3 s. [Sample GTP 16000].

Fig. 6(c). Dependence of sample yield, m (arbitrary units), on initial sample size, m_0 , for pyrolyses of polystyrene at 420°C for 9.5 s. [Sample BASF/RPPTD].

Fig. 6(d). Dependence of sample yield, m (arbitrary units), on initial sample size, m_0 , for pyrolyses of polybutadiene at 436°C for 1.6 s. [Sample IE].

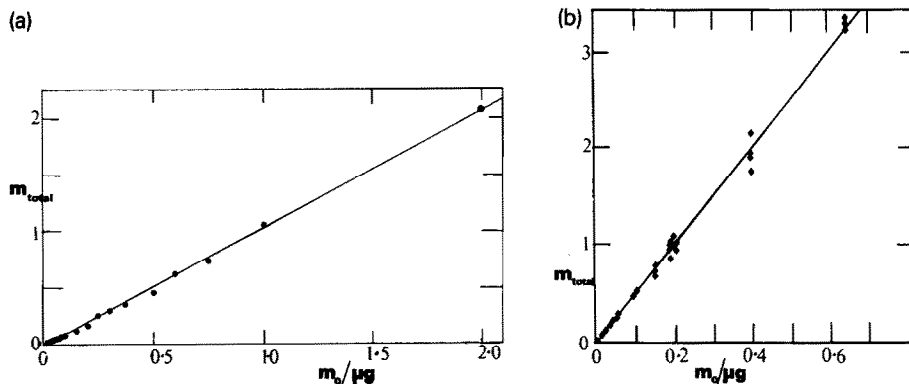


Fig. 7(a) Dependence of total available monomer yield (arbitrary units) on initial sample size, for PMMA pyrolyses at 353°C. [Sample GTP 16000].

Fig. 7(b) Dependence of total available monomer yield (arbitrary units), on initial sample size, for polystyrene pyrolyses at 420°C. [Sample BASF/RPPTD].

this value. Two distinct types of behaviour were observed. In the more common type, illustrated by Fig. 6(a), the main plot extrapolated to give an apparent ordinate intercept, but studies on the small samples revealed a change to steeper gradient which takes the line through the origin. In the less common type it was observed that for a sample where the main plot did extrapolate through the origin, a deviation to another line of steeper gradient still occurred for the smallest samples (Fig. 6(b)). Figures 6(c) and 6(d) show that these effects are not confined to PMMA pyrolyses. When the total available yield of monomer was plotted against sample size over an equivalent range however, a straight line through the origin was obtained (Figs. 7(a) and 7(b)). This indicates that the anomalies observed at small sample size in fractional yield experiments must be associated with a kinetic effect, since such an effect would be absent when measuring total available yield. The following possible explanations of the observations were therefore proposed: (a) Temperature gradient across the sample. (b) Catalysis by the filament surface. (c) Diffusion control of rate processes.

These ideas are assessed in the subsections below.

(a) Temperature gradient across the sample

The anomalies observed for small sample sizes could be explained if it is assumed that the layer of sample close to the filament surface has an enhanced rate, i.e. that it produces a higher pro rata yield of product in a given time. If such an effect existed because of the variation of any temperature gradient across the sample with sample thickness, then varying any experimental parameters which would affect any temperature gradient should influence the observed anomaly. A detailed investigation of this kind has been performed on PMMA by Suggate [11]. In his work the following

ranges were explored throughout the whole range of sample size in order to influence any temperature gradient across the sample: (i) Pyrolysis chamber diameter increased by 33%, (ii) Pyrolysis chamber temperature reduced from 150 °C to 20 °C, and (iii) Carrier gas flow rate increased by 300%. In none of these cases was any change in the low-thickness anomaly detected. The idea that the latter could be caused by temperature gradients across the sample was therefore discarded.

(b) Catalysis by the filament surface

If the filament surface had a positive catalytic effect on the degradation process, this could provide the enhanced rate which could explain the low-thickness anomaly. In an early publication from these laboratories [12] it was mentioned that experiments in which resistive nichrome filaments were plated with gold to change the surface characteristics had demonstrated that no surface-catalysed degradation was detectable under the conditions used. Further experiments of this kind have now been performed. A thermocouple-feedback filament [7] was constructed by spotwelding the thermocouple to a nichrome ribbon which had been gold-coated using an Edwards 12 EA vacuum evaporator. The results obtained using this filament are shown in Fig. 8, where it can be seen that the low-thickness anomaly is still evident, and indeed the intercept by extrapolating the final line is within experimental error the same as that obtained using an uncoated nichrome filament. Figure 8 also includes results from experiments designed to test whether the filament cleaning procedure could contribute to any surface activation. The filament is normally heated to dull red heat (ca. 700 °C) between runs to degrade any residues which may be remaining after pyrolysis. Several runs were carried out in which this procedure was omitted, i.e. the undegraded

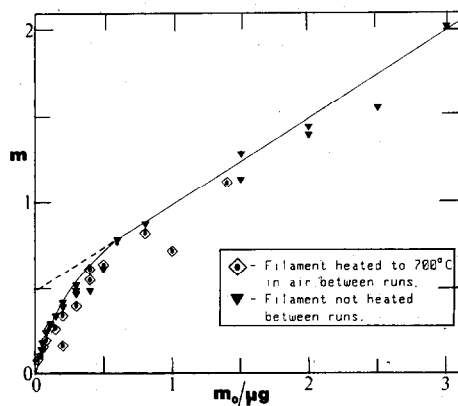


Fig. 8. Dependence of sample yield, m (arbitrary units), on initial sample size, m_0 , for pyrolyses of PMMA on a gold-coated filament, with and without high-temperature cleaning. Pyrolysis conditions: 370 °C for 6.5 sec.

polymer being removed by prolonged heating at the pyrolysis temperature. The results indicate that this had little, if any, detectable effect on the low-thickness anomaly. It must also be noted that earlier work by Suggate [11] in which the filament surface was subjected to abrasion in various ways again produced no detectable effect on the low-thickness anomaly. On the basis of all of this evidence, it is concluded that no convincing evidence has been obtained for the idea that the anomaly is caused by filament surface catalysis.

(c) Diffusion control of rate processes

If it is borne in mind that monomer is evolved from PMMA as a result of a chain depropagation reaction, then the overall rate of this process will be enhanced if the chain termination process is discouraged in some way. This could occur if there is more severe diffusion restriction of the chain termination reaction when the film thickness approximates to the macroradical hydrodynamic diameter in the melt. Such 'two-dimensional diffusion' effects are illustrated in Figs. 9(a) and 9(b). In Fig. 9(a) it is assumed that diffusion restriction of macroradicals will always occur in a layer close to the filament surface; in Fig. 9(b) it is assumed that the diffusion restriction becomes pronounced only if the film itself is of a thickness comparable with this layer. It can be seen that the low-thickness anomalies predicted in this way correspond to the two types of behaviour observed in Figs. 6 and 7. The fact that both types of behaviour can be explained in terms of diffusion control is an additional reason why this interpretation is preferable to the previous ones. It also fits with the general observation that low-thickness anomalies depend much more on choice of sample than on choice of filament.

In an attempt to confirm this diffusion restriction effect, experiments were performed at two temperatures (463 and 413°C) on a PMMA sample of low molecular weight ($M_n = 3100$). Kinetic experiments [2,3] had demonstrated that at the higher temperature the predominant termination reaction for such a low molecular weight sample is that the molecules depropagate completely to the end of the chain, whereas at the lower temperature there is a more predominant contribution from radical-radical interaction to the termination process. On this basis a greater low-thickness anomaly would be expected at the low temperature than at the higher temperature. (This is a more significant test than simply considering any change in diffusivity with temperature, since such changes would be expected for both thick and thin films.) A pyrolysis time of 0.6 sec was used at each temperature, and sample sizes throughout the range 0.2–3.0 μg were studied. The results are shown in Figs. 10 and 11. The size of the intercept relative to the fractional conversion obtained may be used as an index of the low-thickness anomaly. This ratio is shown in Table 1 for the results obtained at the two temperatures, and it can be seen that the values are consistent with the idea that diffusion restriction of macroradicals is responsible for the anomaly.

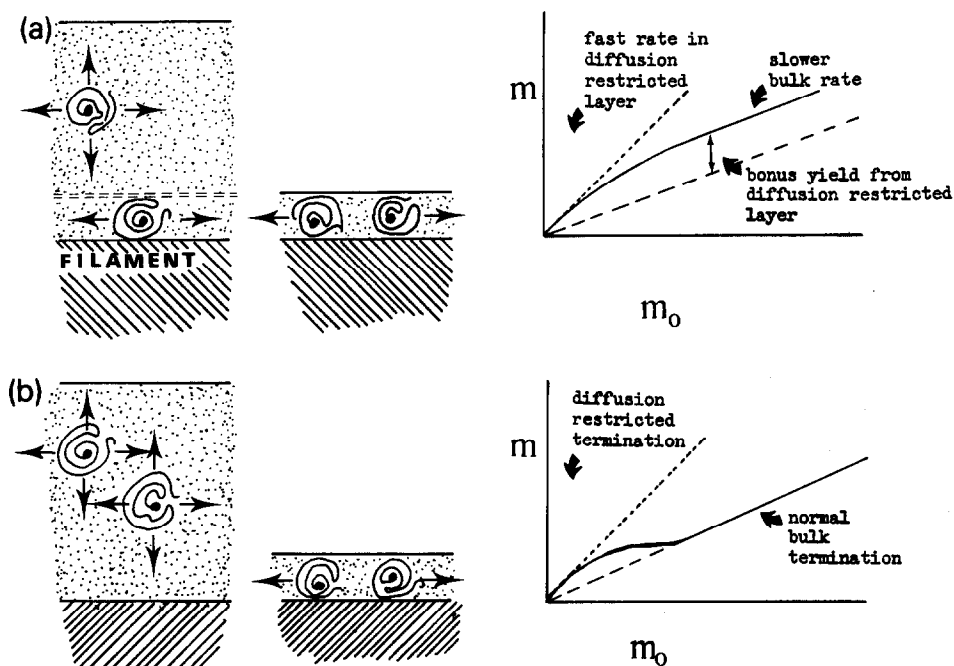


Fig. 9(a). Diffusion restriction of chain termination occurs in a layer of macroradical thickness at the filament surface.

Fig. 9(b). Diffusion restriction of chain termination occurs when the sample thickness becomes comparable with the size of a macroradical.

On the basis of the present work, it is therefore concluded that the existence of more restricted 'two-dimensional' diffusion of macroradicals has been demonstrated to have detectable kinetic effects. It is of course generally accepted that in free-radical polymerisation systems, bimolecular termination reactions may be diffusion controlled [13]. The effects of this have been observed as the autoaccelerative 'gel effect' (Trommsdorf effect) in some polymer syntheses. Radical-radical interaction in polymerisation is believed to occur to a large extent by segmental diffusion of polymer chain ends, and it has been proposed that this picture also applies when depoly-

TABLE 1

Pyrolysis temperature (°C)	Intercept/fractional conversion (arbitrary units)
413	0.54
463	0.13

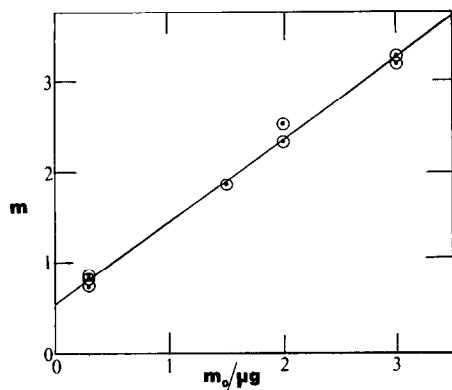


Fig. 10. Dependence of sample yield, m (arbitrary units), on initial sample size, m_0 , for 0.6 second pyrolyses of a low molecular weight PMMA sample. Pyrolysis temperature = 413°C.

merising macroradicals terminate within polymer melts [14]. In experiments on the photolysis of MMA, Cowley and Melville [15,16] and Jellinek et al. [17–19] obtained activation energies for termination of the order of 85 kJ mol⁻¹ which was assumed to be compatible with a bimolecular diffusion-controlled termination. The suggestion in the present work that such effects become more important in thin films is novel, and of interest in that calculations of the film thickness region in which ‘two-dimensional’ diffusion becomes important indicate values in the region 20–50 nm (200–500 Å). This range approximates to the diameter of a coiled polymer molecule within the melt [20]. This might even suggest that movement of the macroradical as a whole may play a greater part in the diffusion-controlled termination process than is generally assumed.

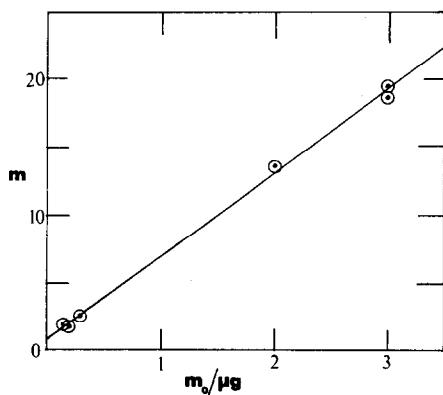


Fig. 11. Dependence of sample yield, m (arbitrary units), on initial sample size, m_0 , for 0.6 second pyrolyses of a low-molecular weight PMMA sample. Pyrolysis temperature = 463°C.

CONCLUSIONS

In any quantitative study of polymer pyrolysis, it is essential to study the reaction parameters of interest as a function of sample size, and to perform any necessary extrapolations of the data to eliminate any anomalous effects of sample thickness.

The results presented in the present paper show that anomalous behaviour of kinetic data as a function of sample thickness may be utilised to reveal mechanistic information. In particular, the thickness-dependence of sample yield ratios can provide clear evidence for a consecutive rather than a parallel reaction mechanism, and thickness dependence of the yield itself has provided evidence that 'two-dimensional' diffusion causes increased diffusion-restriction of the termination process in chain depropagation.

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APPENDIX

GTP-PMMA samples

These group-transfer synthesised samples of PMMA were kindly supplied by Dr. N.C. Billingham (University of Sussex). They were prepared using methyl silyl ketene acetal as the initiator, with trimethyl aminosulphonium fluoride $[(\text{Me}_3\text{N})_2\text{SHF}_2^-]$ as the nucleophilic catalyst, present at a concentration 1% of that of the initiator. All polymerisations were taken to 100% conversion, and MeOH was used to quench the reaction. Of the samples in the present work, that used in Fig. 6(a) had a number-average molecular weight of 31 400, and that in Figs. 6(b) and 7, of 16 000.

Pyrolysis conditions

The samples were deposited on to a thermocouple-feedback filament [7] from toluene solution in volumes of 1.5 to 2.5 μl . The smallest sample size studied was 20 ng, which corresponds to a sample thickness of ca. 40 Å. The pyrolysis products were passed directly into a Varian 1860 glc apparatus equipped with a flame ionization detector. A Spectra-Physics SP4100 computing integrator was used to calculate the peak areas in the pyrograms. In Fig. 6(a) the pyrolyses were performed at 367°C for 6 sec. In Fig. 6(b) the pyrolyses were performed at 353°C for 5.3 sec.

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