Kinetic Measurements by Micropyrolysis–GLC: Thermal Degradation of Polymethylmethacrylate Possessing Lauryl-mercaptyl End Groups

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A sample of polymethylmethacrylate possessing lauryl-mercaptyl end groups has been fractionated by gel permeation chromatography, and measurements of the thermal degradation of the fractions have been performed by micropyrolysis–gas-liquid-chromatography. The rates of pyrolysis were measured between 330°C and 463°C by a resistive heating technique incorporating initial boost; between 450°C and 510°C heating by induction ('Curie-point') was attempted. Changes in mechanism with temperature have been deduced from: (a) Trends in specific reaction rate with initial molecular weight at different temperatures, (b) Inflections in the Arrhenius plots for the different fractions, and (c) Trends in molecular weight with conversion, for both fractionated and unfractionated samples. End-initiation is the predominant mechanism at low temperatures, but random scission becomes more important at higher temperatures. The predominating termination process also depends upon temperature; above 400°C the majority of chains unzip to the end provided the initial molecular weight is not too high, but at the lower temperatures termination occurs by a first order process during the unzip.

FROM a study of the degradation kinetics of polymethylmethacrylate prepared in bulk at 60°C (azobisisobutyronitrile initiator), changes in pyrolysis mechanism with increasing temperature (340°–460°C) were postulated[1]. The present work has been performed in order to test whether polymethylmethacrylate possessing lauryl-mercaptyl end groups shows similar changes in mechanism over a comparable range of temperature. Pyrolytic studies of this sample are of interest because the work on the conventional polymer showed that end group initiation is the predominant mode of initiation in the lower temperature region, but is of decreasing importance as the temperature increases.

APPARATUS AND TECHNIQUES

Micropyrolysis–GLC

This technique[2,3] involves the pyrolysis of a sample deposited on a filament in the carrier-gas stream at the head of a GLC apparatus. In quantitative kinetic work[4] two experimental requirements are of special importance: (a) the sample thickness must be small enough (200Å, 5×10^{-8}g, for PMMA) to ensure that the specific rate is independent of size, and (b) to achieve the degradation the sample must be subjected to a 'rectangular' temperature/time profile. The latter requirement is most conveniently satisfied by using the 'boosted filament' method[4]; this resistive-heating approach has been largely used in the present work, though attempts have been made to use the alternative 'Curie point' induction-heating method[3] at the highest pyro-

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lysis temperatures (450°–510°C). At the present stage, however, the Curie point method is not sufficiently well-developed to be reliable for quantitative kinetic work[3, 5].

Large-scale filament apparatus

A pyrolysis apparatus employing a ribbon filament 2m long was devised in order to provide sufficient sample residue for molecular weight analysis by gel permeation chromatography (GPC). This apparatus and the operating technique have been described elsewhere[6].

MATERIALS

LMTS-PMMA

The initial sample of lauryl mercaptan transfer-synthesized polymethylmethacrylate (LMTS-PMMA) was supplied by I.C.I. Plastics Ltd. It was prepared at 85°C by a suspension process in the presence of 0·28 per cent lauryl mercaptan (transfer agent) and 0·2 per cent azobisisobutyronitrile (initiator). The transfer control of molecular weight implies that the fraction of unsaturated ends formed by disproportionation-termination must therefore be smaller than in conventional samples. GPC analysis showed that the molecular weight dispersity was close to two as expected; the number-average molecular weight estimated by this technique was 53 000.

LMTS-PMMA fractions

12 mg of the LMTS-PMMA sample was fractionated by making use of a conventional analytical GPC apparatus. The details of this microfractionation method are published elsewhere[7]. Seven fractions, covering the molecular weight range 11 000 to 300 000, were obtained.

RESULTS AND DISCUSSION

Dependence of the specific rates of the fractions on their initial molecular weight

It has been shown previously[1] that whatever the initiation and termination mechanisms in a depropagation reaction, the initial rates are expected to follow first-order kinetics; the initiation and termination mechanisms influence only the manner in which the specific reaction rate depends upon the initial molecular weight of a fraction. In the work described below, checks were initially performed in order to test that the measured conversions fell within the first order region; initiation and termination mechanisms are then postulated from a consideration of the dependence of specific reaction rate on initial molecular weight.

Overall specific rates (k_0) observed for pyrolyses of the LMTS-PMMA fractions at the lower temperatures (330°, 340°, 400°C) are plotted against the reciprocal square root of the initial degree of polymerization ($1/D_0^{\frac{1}{2}}$) in *Figure 1*. The general upward trends of these plots suggest an end-initiation mechanism with termination occurring during the depropagation[1], but the curvature is not consistent with a termination process involving second-order interaction of depropagating radicals. Furthermore, extrapolation of the low molecular-weight results to infinite molecular weight leads to negative intercepts on the specific rate axis, whereas the

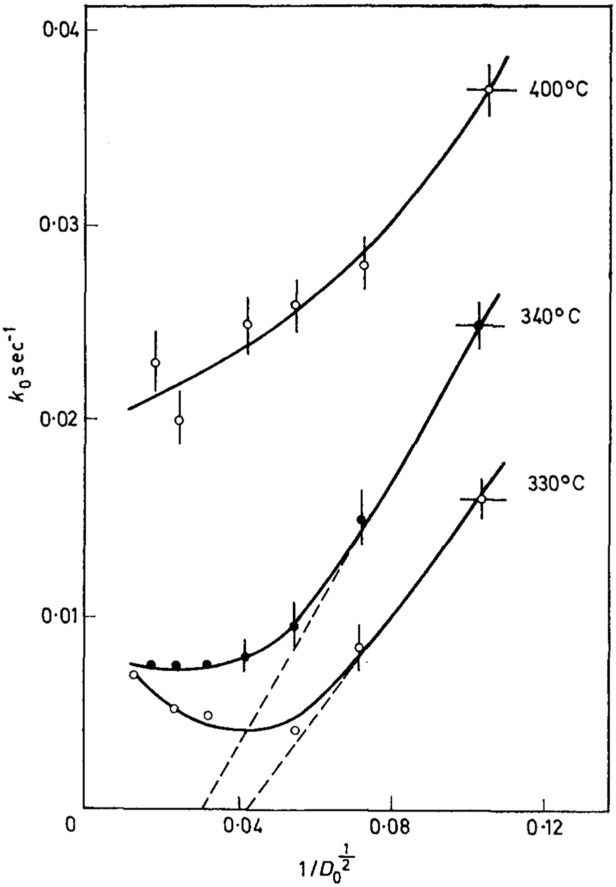

Figure 1—Dependence of initial specific rate on $1/D_0^{\frac{1}{2}}$ at the lower temperatures

intercept should be zero for the mechanism mentioned, or positive if there is a small superimposed scission initiation reaction. In order to assess the possibility of first-order termination during depropagation, the specific rates were re-plotted against $1/D_0$ (see *Figure 2*). An extrapolation of the 330° results through the origin is now quite acceptable, and the 340° (and 400°) results extrapolate to give a positive intercept. The remaining curvature for the high molecular-weight fractions remains unexplained; possible interpretations of this are: (a) diffusion-restriction of the termination process becomes important as the melt-viscosity of the medium increases with molecular weight, or (b) for some reason higher molecular-weight molecules are more susceptible to scission. Certainly for the lower molecular-weight fractions at 330°C it appears that scission initiation is absent; the initiation occurs at the ends of the molecules, and termination occurs during depropagation probably by a first-order mechanism. The results at 340° and 400° are interpreted in a similar way, but here the positive inter-

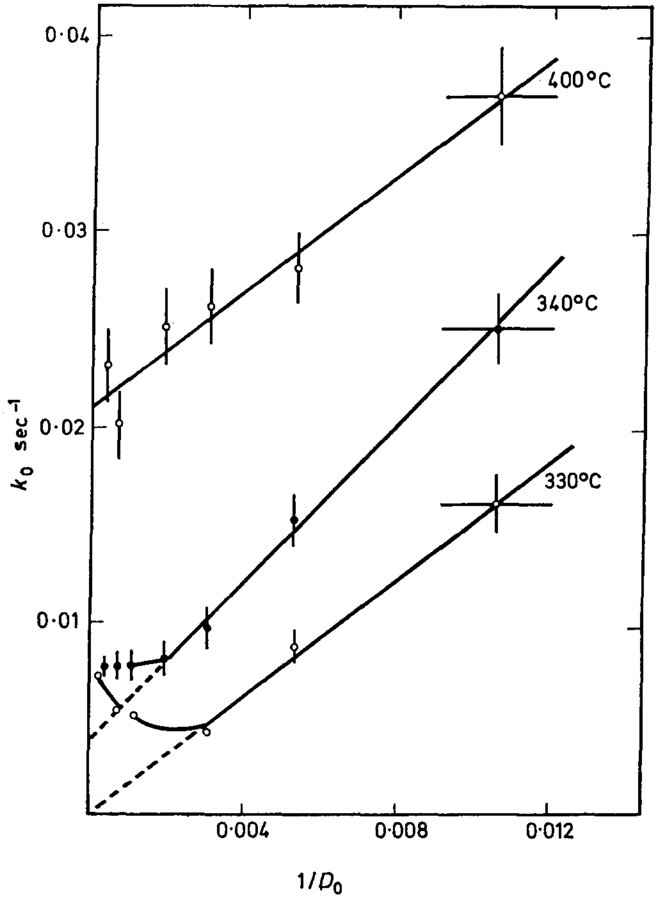

Figure 2—Dependence of initial specific rate on $1/D_0$ at the lower temperatures

cepts suggest an increasing participation of scission initiation as the temperature increases.

There are at least two types of bimolecular reaction which would give rise to first-order kinetics for the termination reaction during depropagation. In the polymer melt there exists a stationary concentration of monomer molecules in process of diffusion out of the liquid phase. If a transfer reaction occurred between the depropagating chain and a monomer molecule, the resulting monomer radical could diffuse out of the system without further reaction. Alternatively 'geminate termination', involving the bimolecular interaction of the depropagating chain with the end-fragment resulting from the initiation, would lead to first-order kinetics for the termination reaction. This would arise if the lauryl-mercaptyl fragments were unable to diffuse away from the locus of depropagation sufficiently rapidly.

The dependence of specific rate on the initial degree of polymerization at intermediate (416°) and high (463°) temperatures is shown in *Figure 3*.

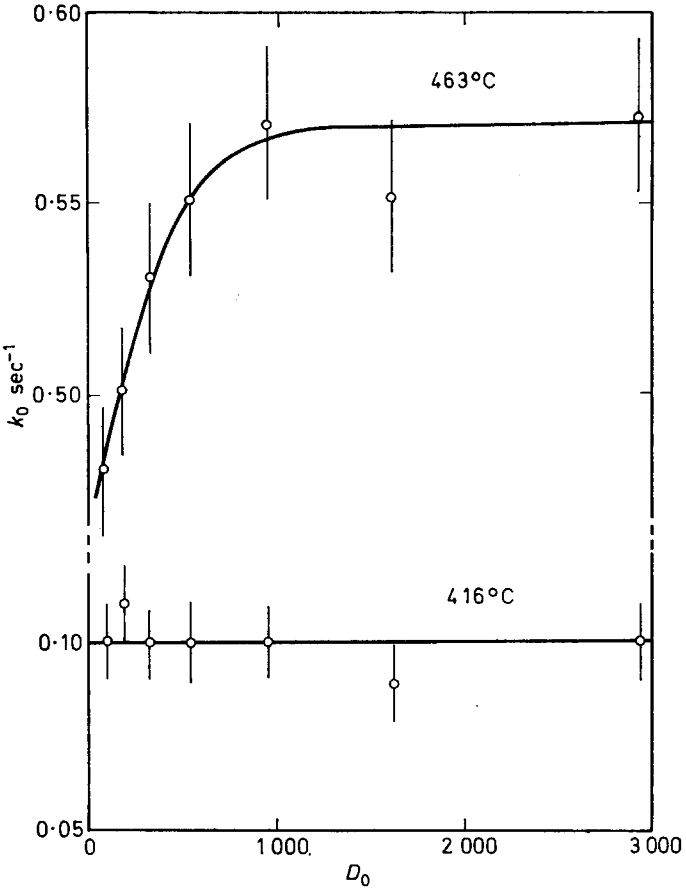

Figure 3—Dependence of initial specific rate on D_0 at intermediate and high temperatures

At 416° the specific rate is invariant over the molecular weight range studied. In view of the fact that some random scission initiation is already evident in the lower temperature results, the most probable interpretation of these results is that scission initiation has now become the predominant initiation mechanism, whilst termination during depropagation occurs as before[1]. (The alternative interpretation of invariance—end initiation and termination by depropagation to the end of the chain—is very improbable not only because of the above evidence for scission initiation at lower temperatures, but also because the first order plots of the 416° results are linear to 90 per cent conversion. If end-initiation were the predominant mechanism, deviation from first order overall kinetics is expected at moderate conversions[1].)

The results at 463°C indicate that k_0 increases linearly with D_0 in the low molecular weight region, but for high molecular weight samples k_0 becomes independent of D_0. The simplest interpretation of this behaviour is that at this high temperature, initiation is predominantly by random scission and that most of the chains depropagate to the end without interaction during the unzip[1]. For the higher molecular weight samples, termination during depropagation becomes increasingly probable, however, and the mechanism is then similar to that observed at intermediate temperatures.

It is of interest that the specific rates observed for the pyrolyses of the LMTS-PMMA fractions are of the same order of magnitude as those previously reported[1] for conventional PMMA samples. The lower-temperature results show that initiation at lauryl-mercaptyl groups must therefore occur with comparable facility as that which occurs at unsaturated terminal groups.

Arrhenius plots for the fractions

Arrhenius plots for the pyrolyses of all the fractions are shown in *Figure 4*. The curvature of the plots is quite consistent with the changes in mechanism proposed in the previous section. It is of considerable interest that all plots converge to a single line at intermediate temperature, since the kinetic interpretation of the intermediate temperature mechanism[1] is that k_0 is then independent of D_0. Even at the highest temperatures only the fractions of

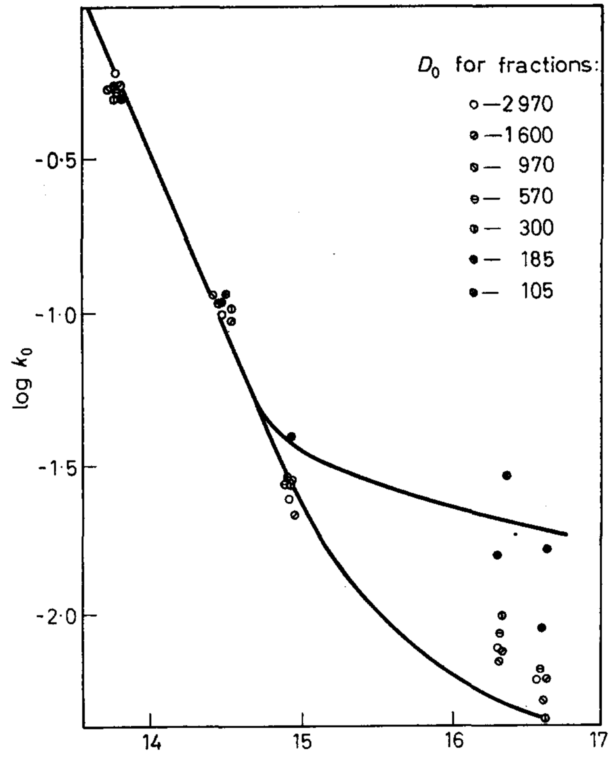

Figure 4—Arrhenius plots for the pyrolyses of the fractions at temperatures over the range 330°–460°C

lowest molecular weight show a detectable dependence of k_0 on D_0 (see *Figure 3*), and the variation is small in comparison with the scale of *Figure 4*. Thus all fractions should display the same Arrhenius plot over the higher temperature range; the fact that this is observed provides further confirmation of the mechanism.

Until reaction times and temperatures can be specified at the higher temperatures with greater precision, it is not possible to attach much significance to the corresponding activation energy. (It appears to lie within the range 60 ± 20 kcal/mole, whereas the overall activation energy values in the low temperature region are *ca.* 30 kcal/mole or less.) In order to explore the 450°–510° temperature region the 'Curie-point' induction-heating technique has been developed, but the control of time and temperature by this technique is poorer than the initial claims[8] would suggest. An appraisal of the technique and the results obtained will be published elsewhere[5].

Trends in molecular weight with conversion

It can be shown[6] that the mechanisms proposed above require that: (a) In the low temperature region, the molecular weight of an unfractionated sample remains invariant with conversion, whilst that for a fractionated sample decreases with conversion, and (b) In the high temperature region, the molecular weight of an unfractionated sample decreases with conversion, the molecular weight of fractions of small D_0 is invariant with conversion, and the molecular weight of fractions of large D_0 decreases with conversion. These trends have all been observed[6], and provide further confirmation of the mechanisms.

CONCLUSIONS

End-initiation is the predominant initiation mechanism at low temperatures for PMMA samples possessing lauryl-mercaptyl end groups; the latter initiate with a facility comparable with that of terminal unsaturated groups. The termination mechanism at low temperatures is unusual in that its rate appears to be first order in chain radical concentration; this may be due to a transfer reaction with monomer, or to geminate recombination involving the radical produced in the end-initiation process. As the temperature increases, initiation by random scission becomes increasingly important, and at 416°C there is evidence that scission has become the predominant initiation mechanism, whilst the predominant termination mechanism still involves interaction before the chain has unzipped to the end of the molecule. At higher temperatures molecules of high molecular weight degrade by the mechanism proposed for 416°C, but the lower molecular weight fractions terminate principally by unzipping to the end of the molecule.

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