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The Use of Model Compounds in Interpreting the Thermal Degradation of Poly(Methyl Methacrylate)

Effect of Groups Produced During Termination of Polymerization

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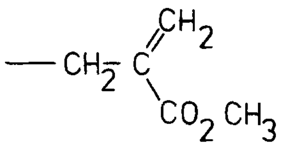
Summary

Methyl methacrylate oligomers have been synthesised and used as models to probe the effect of groups formed during termination of polymerization on the thermal stability of poly(methyl methacrylate). Oligomers containing a head-to-head linkage were found to be the least thermally stable, degrading at temperatures around 190°C. In comparison, oligomers containing unsaturated end groups degrade at 255°C, while models containing saturated terminal units are relatively stable and only degrade at temperatures in excess of 300°C.

Introduction

It has been suggested that groups generated during the termination of the free radical polymerization of methyl methacrylate (MMA) have a profound effect on the thermal stability of the resulting polymer (1). Grassie showed (2) that the thermal degradation of poly(methyl methacrylate) (PMMA) occurs in two distinct stages. Approximately 50% of a PMMA sample degrades between 170-250°C while the remainder requires temperatures well in excess of 300°C.

The two separate phases of the degradation were attributed to the presence of two types of end groups, imparting different thermal stabilities. Thus it was proposed that polymer chains having an unsaturated end group 1 were less stable than those containing a saturated terminus 2 (2). This view has received wide support (3,4) although, until now, there has been no direct evidence for this proposal.



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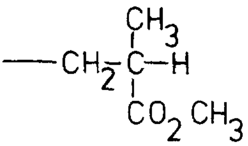
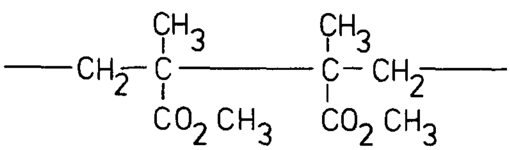


$$—CH_2—\overset{\displaystyle CH_3}{\underset{\displaystyle CO_2CH_3}{C}}—H$$

2



$$—CH_2—\overset{\displaystyle CH_3}{\underset{\displaystyle CO_2CH_3}{C}}——\overset{\displaystyle CH_3}{\underset{\displaystyle CO_2CH_3}{C}}—CH_2—$$

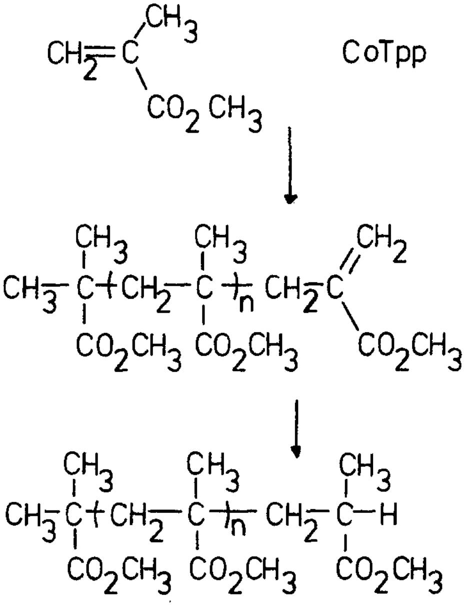
3

In the absence of transfer agents, the termination of MMA polymerization occurs by combination or disproportionation. Disproportionation results in a saturated 1 and an unsaturated end group **2**, while combination of growing radical chains yields a head-to-head (H-H) linkage **3** within the chain.

The thermal behaviour of PMMA containing a H-H linkage has not been reported. If the overall stability of PMMA is to be understood the thermal lability of these linkages must be considered (1) since in some cases polymers containing H-H junctions appear to be less stable than the corresponding head-to-tail polymer (H-T) (5). In order to interpret the thermal properties of PMMA we have synthesised the model oligomers, **4**, **5**, and **7** and their thermal stabilities are described in this report.

Results and Discussion

The unsaturated oligomers **4** were prepared by employing cobalt tetraphenylporphyrin (CoTpp), which yields exclusively unsaturated end groups (6) and variation of the ratio of CoTpp to MMA produced a variety of molecular weights [number average molecular weights ($\overline{M}_n$) of 400, 700, 1500, 5000 and 10000] with relatively narrow distributions ($\overline{M}_w/\overline{M}_n$ = 1.2 - 1.4).

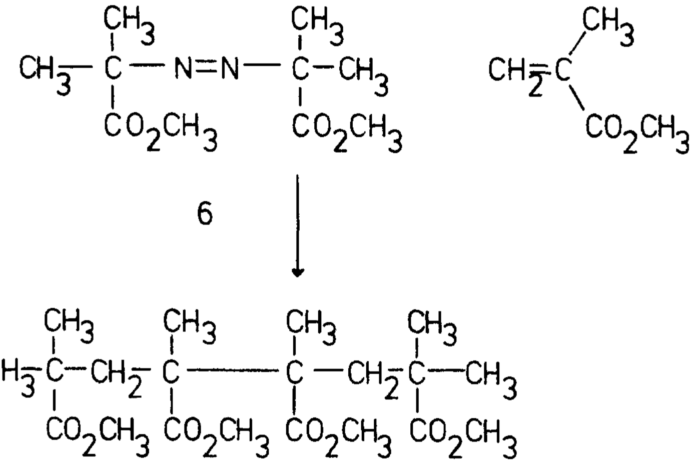


4

5

These mixtures were subsequently hydrogenated using 5% Pd/C to yield the fully saturated oligomers **5**.

The oligomer **7** containing a H-H linkage was prepared by decomposing dimethyl-2,2'-azoisobutyrate **6** (0.2M) in chlorobenzene containing MMA (0.2M) at 80°C for 24 hrs. The reaction mixture was distilled in a Kugelrhor apparatus at 0.01 mm Hg and a fraction collected at 110°C was shown to contain a mixture of structural isomers of tetramer **7**. This fraction, on keeping at room temperature, yielded crystals of a single diastereomer of **7**.



6

7

The oligomers 4, 5, and 7, representing polymers containing end groups or linkages formed by the different termination mechanisms, were individually tested for thermal stability using combined differential scanning calorimetry and thermal gravimetric analysis (DSC/TGA) (heating rate = 20°C/minute). The thermogram of the saturated oligomer (5, $\overline{M}_n$ = 1500) showed that decomposition began at approximately 300°C, and this value for the onset of degradation was the same for oligomers 5 having $\overline{M}_n$ of 700, 5000 and 10000. The breakdown of the unsaturated oligomers 4 commenced at 255°C and was also independent of molecular weight. The tetramer 7 (both diastereomers) decomposed at 195°C, clearly showing that the H-H linkage is the least stable group arising from the termination of polymerization.

Recent work (7) has shown that, within a given sample of PMMA obtained by free radical polymerization, longer chains are more thermally labile than their shorter counterparts. Through our studies we can now offer an explanation for these findings. Most of the higher molecular weight molecules are expected to arise by combination of the growing chains and hence would contain the weak H-H linkage. Degradation of these chains, therefore, will be observed during the early stages of thermolysis.

In the light of these results it would be of considerable importance to be able to determine and, if possible, control the mechanism of termination of the PMMA propagating radical. A survey of the literature on the termination of PMMA shows a wide range of values for the ratio of combination to disproportionation (8). For example, if a value of 1 is taken for this ratio then 75% of the PMMA should contain linkages which undergo homolysis at temperatures below 255°C. Our results also indicate that the use of a suitable chain transfer agent, which would eliminate H-H linkages as well as unsaturated end groups, could substantially increase the overall thermal stability of PMMA.

We are currently investigating the effect of H-H linkages and other defect groups on the thermal stability of various polymers and co-polymers by using model compounds.

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