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Thermal stability of poly(methyl methacrylate)

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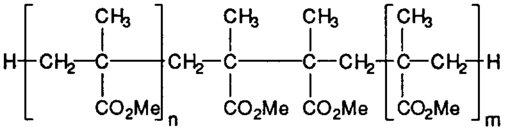
Summary

A series of monodisperse oligo(methyl methacrylates) of well-defined structure has been prepared and used to assess the thermal stability of groups formed in the termination of radical polymerization of methyl methacrylate. The role of head-to-head linkages and unsaturated ends as defect structures in poly(methyl methacrylate) (PMMA) is confirmed and the relative stability of these groups is established. The half-lives for oligo(methyl methacrylate) "decamers" containing head-to-head and unsaturated linkages at 240 °C in nitrogen are 72±3 min. and 19±2 min., respectively. Some limitations on Thermogravimetry when used for the quantitative analysis of PMMA are addressed.

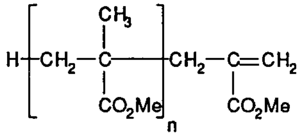
Introduction

In 1984 we reported (1) preliminary findings from our studies on the use of model compounds (**1**-**3**) to interpret the thermal degradation of poly(methyl methacrylate) produced by radical polymerization (2). This work established that both head-to-head and unsaturated linkages are "weak links" in PMMA. More recently, Rae et al. (3,4) have conducted product studies on model compounds. They confirmed lability of these structures and established the chemistry of their decomposition.



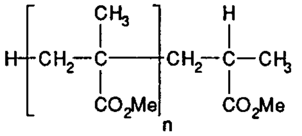
$$H\left[CH_2-\overset{CH_3}{\underset{CO_2Me}{C}}\right]_n CH_2-\overset{CH_3}{\underset{CO_2Me}{C}}-\overset{CH_3}{\underset{CO_2Me}{C}}-CH_2\left[\overset{CH_3}{\underset{CO_2Me}{C}}-CH_2\right]_m H$$

1



$$H\left[CH_2-\overset{CH_3}{\underset{CO_2Me}{C}}\right]_n CH_2-\underset{CO_2Me}{C}=CH_2$$

2



$$H\left[CH_2-\overset{CH_3}{\underset{CO_2Me}{C}}\right]_n CH_2-\overset{H}{\underset{CO_2Me}{C}}-CH_3$$

3

Kashiwagi et al. (5) have conducted a detailed investigation of PMMA degradation by thermogravimetric analysis (TGA). In experiments carried out in inert atmospheres they observed three stages of weight loss for polymers prepared by radical polymerization. They attributed

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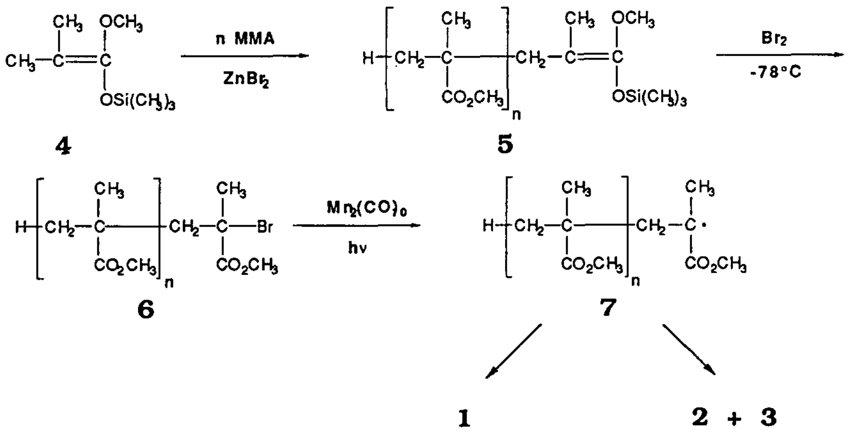
*To whom offprint request should be sent very low temperature weight loss to degradation of chains containing head-to-head linkages and cited our work as precedent for their hypothesis. No direct evidence was provided. This publication has led other workers (6) to use the absence of a low temperature weight loss peak in TGA as evidence for there being no termination of polymerization by combination.

The low temperature weight loss observed by Kashiwagi et al. (5) occurred between 120 and 190 °C with a heating rate of 2 °/min. In our earlier work (1) we reported the relative stabilities in terms of the onset temperatures for decomposition of the MMA oligomers; these being the lowest temperature at which "measurable" weight loss could be observed by TGA with a heating rate of 20 °/min. For the model compound (**1**, n=m=1) this was determined as 195 °C. Kashiwagi et al. suggested that the substantially lower onset temperatures observed in his study on PMMA (ca. 120 °C vs. 195 °C) might reflect the different experimental conditions (a greater heating rate should give rise to a higher onset temperature). Unfortunately, in our earlier work (1) onset temperatures for low heating rates could not be reliably measured for the head-to-head model compound (**1**, n=m=1) because of this compound's low molecular weight and consequent volatility (see later discussion). This fact also prevented studies on isothermal decomposition rates and the measurement of meaningful peak rate decomposition temperatures (T_p). This emphasized the need for higher molecular weight model compounds.

Some preliminary work was carried out with higher molecular weight oligomers presumed to have structure (**1**, n~m~8). These were obtained by the $TiCl_4$ induced coupling (7) of the silylketene acetals (**5**, n~8) generated by the group transfer method. However, recent studies carried out in these laboratories and elsewhere (8) have led us to doubt the nature and homogeneity of the products prepared by this coupling reaction. This has prompted the present study on higher molecular weight oligomers synthesized by unambiguous routes.

Model Compounds



Scheme 1

The terminally unsaturated oligomers (**2**) were prepared as described in the previous work (1,9). The saturated oligomers (**3**) were synthesized by catalytic hydrogenation of **2** or by quenching of the silylketene acetals (**5**) with methanol. The individual oligomers were separated according to molecular weight by preparative HPLC and were fully characterized by spectroscopic analysis.

Oligomers containing head-to-head linkages (**1**) were prepared as outlined in Scheme 1. MMA was oligomerized by the group transfer method at 40 °C using $ZnBr_2$ as catalyst (10) and the ketene acetal (**4**) as initiator. The ketene acetal intermediate (**5**) was quenched with bromine at -78 °C to afford the bromo compounds (**6**) which were separated according to molecular weight by column chromatography on silica gel. Irradiation of the bromo-compound (**6**, n=1-7) at 25-30 °C in the presence of $Mn_2(CO)_{10}$ (11) generated the radicals (**7**), approximately 40% of which underwent the desired coupling process to afford **1**. Because of the two-fold molecular weight increase, these oligomers (**1**) were readily resolved from any unchanged starting material and the concurrently formed disproportionation products by chromatography. It should be noted that potentially troublesome by-products may arise, from the reaction of radicals (**7**) with the unsaturated disproportionation product (**2**), when this reaction is carried to high conversion.

A typical procedure for the coupling is as follows. A solution of the bromo-compound (**6**, n=4) (464 mg, 0.79 mmol) and $Mn_2(CO)_{10}$ (116 mg, 0.30 mmol) in ethyl acetate (3.5 mL) was degassed through three freeze-thaw cycles at 0.1 mmHg. The solution was thermostatted at 25-30 °C and irradiated for 18 h with a 150 W tungsten lamp. The vessel was then opened to air, acetonitrile (1 mL) added, and irradiation then continued until complete decomposition of the catalyst to a brown precipitate which was removed by filtration. The solvent was evaporated from the filtrate and the residue chromatographed on silica gel with light petroleum-ethyl acetate as the eluent. Freeze-drying afforded **1** (n=m=4) as a white powder (156 mg, 39%). The presence and position of the head-to-head linkage was confirmed by ^{13}C NMR and fast atom bombardment (FAB) mass spectrometry (to be subject of a forthcoming communication).

Utilization of the method of radical generation described in this paper may offer a new means of establishing the relative importance of combination and disproportionation during MMA polymerization (12). Since they are uncorrected for unchanged starting material or other by-products, the yields of combination products obtained in the present experiments should be regarded as a lower limit on the percentage of radicals which undergo termination by combination at 25-30 °C. The yields of coupling products obtained in the above experiments are consistent with the findings of Bizilj et al., (13) who established a lower limit of 35% on the amount of combination for the "dimeric" species at 60 °C and showed for the "monomeric" species the ratio of combination to disproportionation to be essentially independent of temperature. Our results also support the work of Bamford et al. (14) who determined 33% combination for PMMA radicals at 25 °C. The recent finding by Kodaira et al. (15) that combination accounts for <10% of oligoMMA radicals at 60 °C should be viewed circumspectly.

Results and Discussion

Peak rate decomposition temperatures (T_p) were found useful for a preliminary measurement of relative stability and volatility of the oligomers (**1**-**3**). Values obtained are given in Table 1. A heating rate of 2 °/min was employed to permit comparison with the findings of Kashiwagi et al. for PMMA (5). The values of T_p increase with the degree of polymerization (DP), then plateau at DP=8 for **1** & **2** and at DP=10 for **3**. This is a consequence of sample volatility shifting T_p to lower temperatures.

Table 1. Degradation of MMA oligomers[a,b]

	T_p(°C) for Oligomer[c]		
DP[d]	**1**	**2**	**3**
4	245	235	235-275
6	260	265	335
8	270	265	370
10	275	265	390
16	270[e]	-	390

[a] A Mettler TA3000 thermoanalysis system incorporating a TG50 thermobalance and a TC10A processor unit was employed. [b] In alumina crucibles and an atmosphere of high purity nitrogen. [c] Peak rate decomposition temperature for heating rate of 2 °/min and sample size 1.5±0.5 mg. T_p are reported to the nearest 5°. [d] DP=n+1 for (**2** & **3**). DP=n+m+2 and n=m for (**1**). [e] A second weight loss peak is observed at ca. 350 °C (see text).

The decomposition of pure head-to-head oligomer (**1**, n=m=7) showed a further weight loss with T_p=350 °C. Analysis (HPLC, NMR) of a partially decomposed sample (at 240 °C) of this material demonstrated the presence of the saturated octamer (**3**, n=7). It is proposed that this material arises by disproportionation of the geminate pair formed on homolysis of the head-to-head linkage. This material (**3**, n=7) is stable and accumulates at temperatures <300 °C but becomes volatile by 350 °C (c.f. Table 1). The concurrently formed unsaturated oligomer (**2**, n=7) degrades under these conditions and is lost (see Table 1). It is notable that no oligomers with n<7 were detected in the degradation of **1** (n=m=7). The oligomers **2** (n=5, 6) are not particularly volatile at temperatures <300 °C (see Table 1) and, if formed, should also accumulate. This finding is consistent with the proposal that compound **3** (n=7) arises largely through a cage process. The analysis of the partially decomposed samples also indicated that the different stereoisomers of **1** have slightly different thermal stabilities.

In the light of these results, it is clear that if weight loss measurements are to be used as a measure of the relative stabilities of the weak links in oligomers **1** and **2**, then the molecular weights of the oligomers must fall within a very narrow window. For DP≤6, sample volatility is a problem, while for DP≥14, incomplete weight loss occurs for the head-to-head oligomers. For these reasons, our isothermal measurements were performed on the decamers, ie. **1** (n=m=4) and **2** (n=9). The rates were measured at 240 °C, a temperature at which pentamers and lower oligomers should be volatile and thus cleavage of the weak link should lead to complete weight loss. The half-lives of **1** (n=m=4) and **2** (n=9) at 240 °C in alumina crucibles under nitrogen are 72±3 min. and 19±2 min., respectively. Oligomer **3** (n=9) is stable under these conditions.

The present work clearly confirms that head-to-head linkages and unsaturated ends are both weak links in PMMA. The weakest link is the bond α to the unsaturated end of **2** which is measurably less stable than the head-to-head linkage of **1**. The results show that the low temperature weight loss peak observed by Kashiwagi et al. (5) is unlikely to be due to the degradation of PMMA chains containing head-to-head linkages. Other workers have attributed weight loss at temperatures <200 °C to occluded monomer (16). We also conclude that, while TGA may be used to demonstrate the presence of weak links (unsaturated ends or head-to-head linkages) in PMMA, it cannot distinguish between these groups. For these reasons, we consider TGA to be generally unsuitable for the quantitative analysis of defect structures in PMMA.

References

1. Cacioli, P., Moad, G., Rizzardo, E., Serelis, A.K., Solomon, D.H., *Polym. Bull.*, 11, 325 (1984).
2. McNeil, I.C., *Eur. Polym. J.* 4, 21 (1968).
3. Holland, K.A., Rae, I.D., *Aust. J. Chem.*, 40, 687 (1987).
4. Morrow, G.R., Rae, I.D., *Aust. J. Chem.*, 40, 1477 (1987).
5. Kashiwagi, T., Inaba, A., Brown, J.E., Hatada, K., Kitayama, T., Masuda, E., *Macromolecules*, 19, 2160 (1986)
6. Giannetti, E., Mazzochi, R., Fiore, L., Visani, F., *J. Polym. Sci., Polym. Chem. Ed.*, 24, 2517 (1986).
7. Sogah, D.Y., Webster, O.W., *J. Polym. Sci., Polym. Lett. Ed.*, 21, 927 (1983).
8. Fallon, G.D., Felsbourg, M.L., Holland, K.A., Rae, I.D., *Aust. J. Chem.*, 40, 501 (1987).
9. Cacioli, P., Hawthorne, D.G., Laslett, R.L., Rizzardo, E., Solomon, D.H., *J. Macromol. Sci., Chem.* 23, 839 (1986).
10. Hertler, W.R., Sogah, D.Y., Webster, O.W., Trost, B.M., *Macromolecules*, 17, 1415 (1984).
11. Bamford, C.H., in "Reactivity, Mechanism and Structure In Polymer Chemisty" (A.D. Jenkins and A. Ledwith, Eds.) p.52, Wiley: London, 1974.
12. Moad, G., Solomon, D.H., in "Comprehensive Polymer Science" ch. 2.8, Pergamon, 1988 (in press).
13. Bizilj, S., Kelly, D.P., Serelis, A.K., Solomon, D.H., White, K.E., *Aust. J. Chem.*, 38, 1657 (1985).
14. Bamford, C.H., Dyson, R.W., Eastmond, G.C., *Polymer*, 10, 885, (1969).
15. Kodaira, K., Ito, K., Iyoda, S., *Polym. Commun.*, 28, 86 (1987).
16 Davidson, R.G., *Aust. J. Chem.*, 34, 1631 (1987).

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