Chain end initiated depolymerization in anionic poly(methylmethacrylate)s

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SUMMARY

The thermal degradation of different Poly(methyl methacrylate) samples prepared by anionic polymerization has been investigated. It is shown that the polymers obtained with Cumyl Cesium as initiator present two stages of degradation: the lower temperature stage is due to a chain end initiated depolymerization. The instability of these polymers is attributed to the initiator residues present as terminal groups in the macromolecules. From the molecular weight dependence of the monomer produced in the first degradation stage the depolymerization length of the process has been evaluated.

INTRODUCTION

It is well known that Poly(methyl methacrylate) (PMMA) prepared via radical polymerization may present two separate steps in his thermal degradation (1,2): the first one is a monomer volatilization process , initiated at the unstable terminal groups present in some of the macromolecules, which proceeds with rates already measurable at $T \simeq 200$ °C; the second step is due to the depolymerization of the radicals resulting from the random scissions of the polymer chains, occurring at $T > 300°C$. The chemical structures which are taken as responsible for the end initiated volatilization process are the vinylidene units which build up in the disproportionation termination reactions of methyl methacrylate radical polymerization (3). Another type of unstable unit, also generated in termination reactions, is that resulting from head-to-head coupling of the propagating macroradicals in the polymerization (4): it has been shown for PMMA that in such structures bond scission takes place with maximum rate at temperatures as low as 165 °C (5).

Polymer samples synthesized by anionic living polymerization do not contain the head-to-head or the unsaturated structures previously described, as the termination reactions are simply a proton addition to the reactive polymeric anion. And, in fact,in the few cases reported up to now, anionically prepared PMMA samples only show the degradation step due to the random chain scissions (5,6). Anionic living polymerization of methyl methacrylate, however, can be performed in different experimental conditions with numerous initiator systems (7). In some cases, these polymerizations may suffer from the occurrence of several secondary

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reactions, like termination with the monomer, chain branching or intramolecular cyclization (8), which can seriously impair the structure and, eventually, the stability of the resulting polymers. But even when these reactions are avoided, it cannot be excluded that polymers obtained with different initiators behave differently, as far as their thermal degradation is concerned.
In this communication the preliminary results are presented of an investigation on the thermal stability of several PMMA samples, most of them anionically prepared. It is shown, for the first time, that the anionic polymers obtained with a particular initiator system are less thermally stable than other types of PMMA, inasmuch they present a first stage of degradation which could be attributed to an end group effect.

EXPERIMENTAL
        The narrow distribution anionic PMMA samples were commercial standards from different suppliers (Polymer Laboratories, England, and Polysciences, USA). Isotactic and syndiotactic polymers were obtained from Polysciences. A radical PMMA prepared in this laboratory with AIBN as initiator has also been employed for comparison.
Molecular weights of the polymers were determined in tetrahydrofuran by Size Exclusion Chromatography (SEC) with a system of $10^5 + 10^4 + 10^3$ Ultrastyragel columns (Waters, USA), and a differential refractive index detector (Erma 7510, Japan). Tacticities of the samples have been measured by NMR. Thermal degradation experiments have been performed on a Du Pont 951 Thermobalance coupled with a Du Pont 1091 Control Unit under nitrogen flow of 60 cm^3/min.

RESULTS AND DISCUSSION
        In Table I are reported the molecular characteristics of the polymers which were investigated. All the samples prepared via living

TABLE I. Molecular characteristics of the PMMA samples

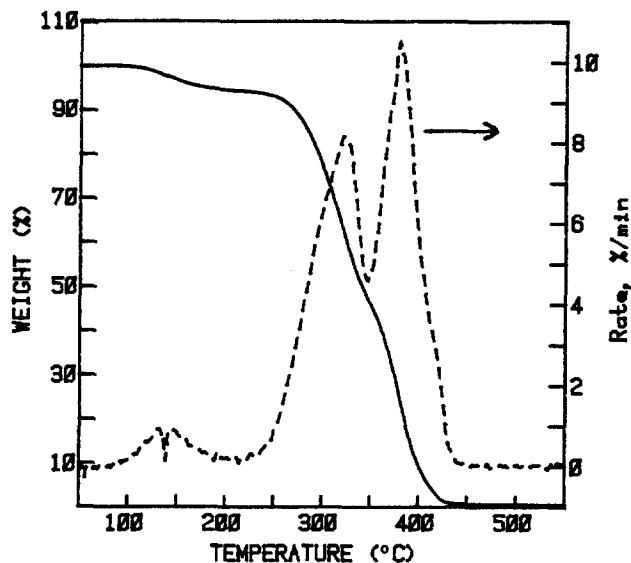| Sample	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Tacticity %		
			I	H	S
A	3400	1.14	22	10	67
B	19700	1.10	6	47	47
C	25000	1.08			
D	41000	1.05	10	44	46
E	53000	1.04			
F	67000	1.08			
G	100000	1.06			
H	506000	1.19	10	41	49
L	50000	5.70	82	10	8
M	27000	1.55	7	31	62
N	97000	1.77	17	41	42

Fig. 1. TG (—————)
and DTG (- - - -) of
radical PMMA.
Heating rate: 10 °C/min;
atmosphere: nitrogen.

polymerizations showed narrow SEC peaks, and therefore good dispersity
indexes. Polymer M presented a broader molecular weitht distribution
whereas polymer L had a very broad bimodal distribution of molecular
weights. Polymer M was supposed to be a nearly pure syndiotactic sample,
and polymer L an isotactic one. Whereas for the latter the quality was
reasonable, the former sample had only slightly more than 60% sindiotactic
units, being not very different from sample A.
The thermal behaviour of the polymers has been determined from the
thermogravimetry (TG) measurements performed with heating rate of 10
°C/min. With such measurements important differences between polymers of
different origin could be emphasized. In Fig. 1 the behaviour of the
radical sample N, as shown by the TG and by the differential curve (DTG),
is reported. Three different steps in weight loss are present, with
maximum rates at T 150, 320 and 380 °C. Whether the first small peak of
the DTG is due to the scission of the head-to-head linkages in the polymer
(5) or to impurities present in the sample has not been investigated: the
polydispersity of the sample indeed indicates that some radical coupling
must have taken place during polymerization. The two other peaks are due
to the depolymerization reactions initiated at the unsaturated chain ends
and at random positions in the polymer molecules, respectively.
In Fig. 2 the TG of polymer A, which is an anionic sample initiated with an
alkali salt of 1,1 diphenylhexane (9) is shown: the thermal behaviour is,
as expected, that of a PMMA which only depolymerizes after main chain
scissions at T>300 °C. The TG curves of the other narrow distribution
polymers, samples B to H, are reported in Fig. 3; all these samples belong
to a same family, as they have been prepared with Cumyl Cesium as
initiator (10). Apart from the high molecular weight sample H, the thermal
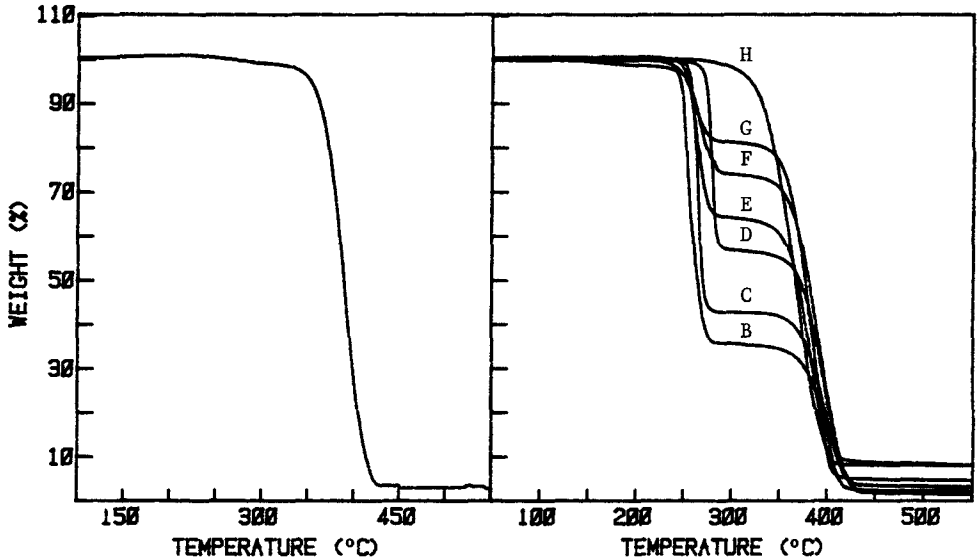
Fig. 2. TG of anionic PMMA A.

Fig. 3. TG 's of PMMA samples prepared with Cumyl Cesium initiator.

characteristics of these polymers are completely unexpected for anionic PMMA, because a low temperature degradation stage is very evident, well separated from the process occurring at higher temperature. The maximum rate of the first volatilization occurs at temperatures between 260 and 280 °C; the second volatilization stage has its maximum at T $\simeq$ 395 °C, and the temperatures slightly decrease with increasing molecular weights. The
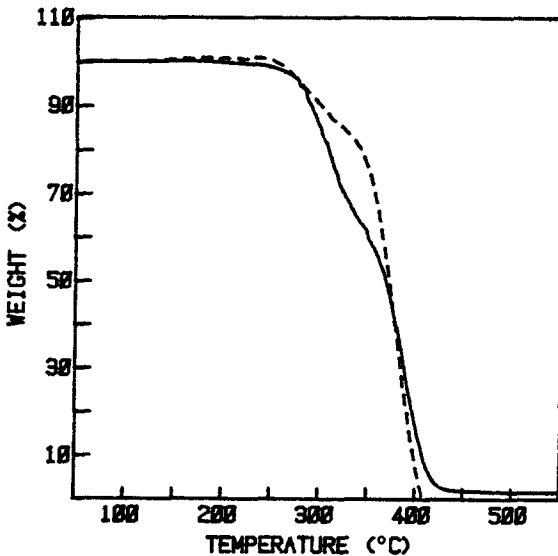

Fig. 4. TG of sample M, syndiotactic (————), and of sample L, isotactic (- - - -).

fractional weight loss of the first stage is inversely proportional to the initial number average degree of polymerization, and this indicates that the process depends on the number of the degrading chain molecules. It was checked whether such a thermal behaviour could be attributed to different tacticities in the samples, but this effect could be disregarded by looking at the data in Table I, and also by comparison with the thermogravimetries of polymers L and M (Fig. 4) which also present a lower temperature degradation process, but at temperatures and with extents different from the previous samples. For the polymers of Fig. 3 the possibility that abnormal, secondary reactions (7,8) had been occurred during the anionic polymerization, leading to the presence of thermally unstable structures in the macromolecules, can be safely excluded as the dispersity indexes of the polymers indicated that the polymerization reaction was indeed a living and clean one. It must be therefore concluded that the instability of these polymers is due to the presence of the initiator residues as terminal groups of the chains. The degradation reaction initiates from the scission of these groups and proceeds, giving rise to monomer, for a given number of units through each macromolecule. This number, the depolymerization length λ, is lower than the initial number average degree of polymerization $\bar{X}_{n,o}$ of the samples investigated, and therefore the degradation does not go to completion in this stage. The amount of monomer generated, however, increases with the decreasing polymer molecular weight, because the number of molecules, and of chain ends, per unit weight also increases. On the other extreme, when the polymer molecular weight is very much higher than λ, the first degradation stage is not visible any more, as it happens in sample H.

If all the macromolecules in a degraded sample are end initiated, the depolymerization length λ can be simply calculated by knowing the initial molecular weight of the polymer and the amount of monomer produced in the process. Let n_o be the number of initial molecules, which also corresponds to the number of degraded molecules. The total number of monomer molecules, m_o, constituting a given sample will be $m_o = n_o * \bar{X}_{n,o}$. The number of monomer molecules, m_i, generated in the depolymerization is given by

$$m_i = \lambda * n_o = \lambda * m_o / \bar{X}_{n,o} \qquad (1)$$

and therefore

$$m_i / m_o = \lambda / \bar{X}_{n,o} \qquad (2)$$

A plot of the fractional conversion, m_i / m_o, obtained in the first degradation stage of polymers B to H against the respective $1/\bar{X}_{n,o}$ values is shown in Fig. 5.

With the exception of samples B and C, all the other polymers lie on a straight line, from whose slope an average depolymerization length $\lambda = 180$ is obtained. For the polymers B and C, their $\bar{X}_{n,o}$ values are quite close to this value of λ, and as the samples are not exactly monodisperse, it happens that some molecules, having $\bar{X}_o < \lambda$, will depolymerize completely. The monomer fraction which is measured in these
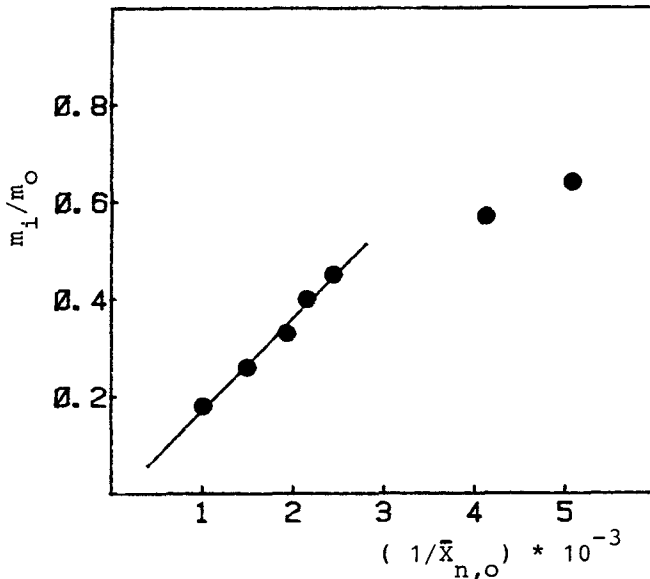
Fig. 5. Fractional monomer conversion vs. reciprocal initial degree of polymerization for the polymers of Fig. 3.

cases is then lower than that obtained for the samples where all the molecules have $\bar{X}_o > \lambda$, and that is the cause of samples B and C not falling on the same line with the other polymers.

In conclusion, it is clearly shown by these results that chain end initiated depolymerization of PMMA may occur not only with radical polymers, but also with some types of anionically prepared polymers. The investigation on the thermal behaviour of anionic PMMA samples is continuing and further results will be reported later.

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