

## Stabilizing effect of oxygen on thermal degradation of poly(methyl methacrylate)

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**SUMMARY:** The thermal degradation of poly(methyl methacrylate) has been studied under nitrogen and air. The presence of oxygen increases the initial decomposition temperature by 70 °C. The stabilizing effect of oxygen is explained by the formation of thermally stable radical species that suppress unzipping of the polymer. This assumption is supported by the experimental fact that introduction of NO into the gaseous atmosphere increases the initial decomposition temperature by more than 100 °C.

### Introduction

The thermal degradation of poly(methyl methacrylate) (PMMA) has been extensively studied in nitrogen<sup>1–15</sup> as well as in oxygen and air<sup>1,3–5,9–11,13–20</sup>. The stabilizing effect of oxygen on the thermal degradation of PMMA was first reported by Bresler et al.<sup>17</sup> Recently Hirata et al.<sup>4</sup> reported that in the oxygen containing atmosphere, the initial temperature of degradation increases by about 50 °C as compared to that for degradation in nitrogen. Kashiwagi et al.<sup>10,13</sup> proposed mechanistic explanations to this effect.

In this study we employ thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to study the thermal degradation of PMMA in both pure nitrogen and oxygen-containing atmospheres. The present work provides further insight into the stabilizing effect of oxygen on the initial stages of PMMA degradation.

### Experimental part

The PMMA samples (Aldrich,  $\bar{M}_w \approx 996000$ ) were dried at  $\approx 120$  °C overnight. TGA experiments were performed by using a Rheometric Scientific TGA 1000M+. PMMA samples of 1–2 mg were placed in aluminium pans and heated at heating rates of 0.5–20 °C · min<sup>-1</sup> up to 600 °C. The experiments were conducted in flowing atmospheres of nitrogen, air, and in a mixture of 1.6 vol.-% nitric oxide with nitrogen at flow rates of 100 ml · min<sup>-1</sup>. The gas supply line was equipped with a valve that allowed for quick switch of gasses while an experiment was being performed. A Mettler-Toledo DSC821<sup>e</sup> was used to conduct DSC runs. PMMA samples (10–15 mg) were placed in open aluminium pans and heated at 20 °C · min<sup>-1</sup> up to 600 °C under air and nitrogen flows at a rate of 80 ml · min<sup>-1</sup>.

### Results

#### Degradation in nitrogen and air

As seen in Fig. 1, the PMMA degradation under nitrogen shows two steps at the heating rate of 18 °C · min<sup>-1</sup>. The

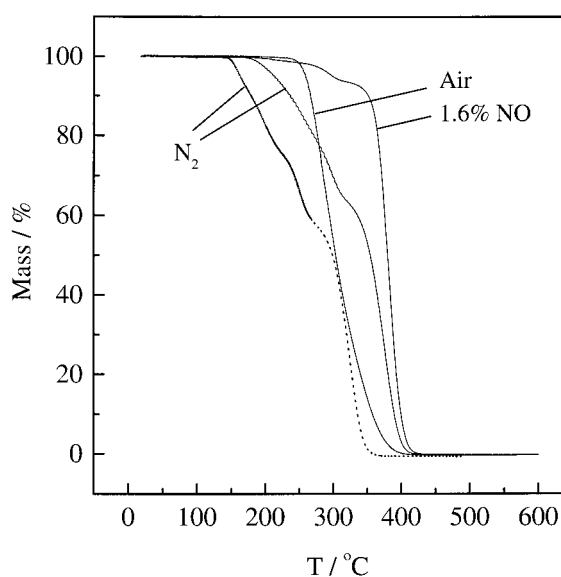


Fig. 1. TGA curves for PMMA degradation under various atmospheric conditions. 1.6% indicates the concentration of NO in its mixture with N<sub>2</sub>. Data obtained at heating rates of 0.5 (dotted line) and 18 °C · min<sup>-1</sup> (solid lines)

steps occur in the temperature ranges of 180–350 °C and 350–400 °C, respectively. At a heating rate of 0.5 °C · min<sup>-1</sup> one may observe an additional degradation step that occurs below 220 °C. Unlike the degradation under nitrogen, the process in air proceeds in one step. Additionally, we can see that the initial temperature for degradation under air is about 70 °C higher than that for the process under nitrogen.

Fig. 2 presents DSC data collected under nitrogen and air. The thermal degradation under nitrogen shows three overlapped endothermic peaks with minima at 260, 300, and 380 °C. Under air, however, DSC data shows only a single broad endothermic peak that stretches from 200–450 °C. The instability of the DSC signal in the vicinity of maximum has been reproduced in three successive runs. The integral heat consumption in the temperature

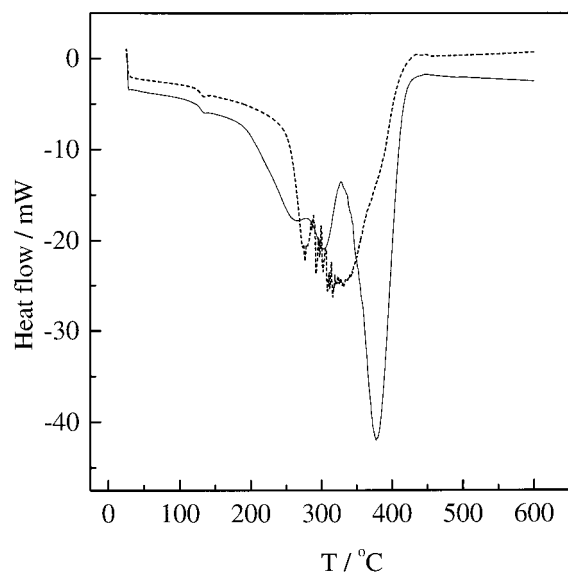


Fig. 2. Overlay of DSC scans collected under air (dashed line) and nitrogen (solid line). The masses of PMMA samples are 9.8 and 15.5 mg for scans under  $N_2$  and air, respectively. Heating rate is  $20\text{ }^\circ\text{C} \cdot \text{min}^{-1}$

region  $140\text{--}440\text{ }^\circ\text{C}$  has been evaluated as 1080 and  $550\text{ J} \cdot \text{g}^{-1}$  for respective degradations under nitrogen and air.

#### Effect of switching between air and nitrogen on degradation

Fig. 3 shows that switching of gaseous atmospheres between air and nitrogen affects the thermal degradation of PMMA. In air this process is characterized by a slow rate. Upon switching to a nitrogen atmosphere, the degradation rate increases significantly. Switching back to air

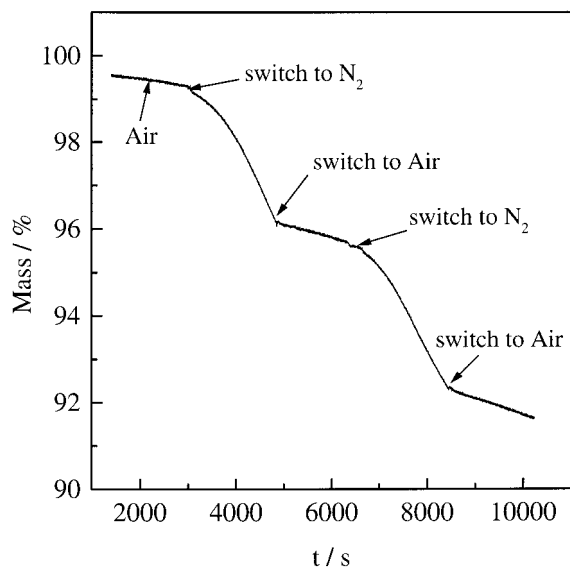


Fig. 3. TGA curve showing the effect of switching of gaseous atmospheres between air and nitrogen on the thermal degradation of PMMA at  $200\text{ }^\circ\text{C}$

causes the reaction rate to immediately slow down. This switching of reaction atmospheres was repeated at regular intervals until a 9% mass loss was achieved. The effect appears to be reversible.

#### Visual analysis of partially degraded samples

Several runs performed under various atmospheric conditions were stopped at 20% mass loss and analyzed visually. The sample decomposed in nitrogen was a white powder material similar to the original PMMA sample. The sample degraded in air was a single chunk of clear glassy material that contained a few bubbles.

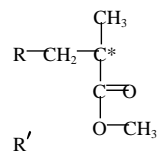
## Discussions

### Degradation in nitrogen

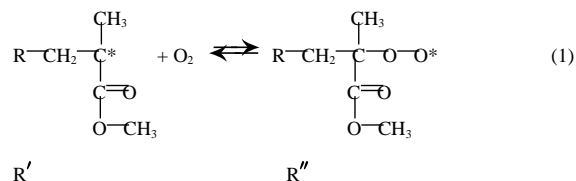
The two step degradation of PMMA was first noticed by Grassie and Melville<sup>21,22</sup> who suggested that the process is initiated at vinylidene end groups, which resulted from a bimolecular radical termination during polymerization<sup>23</sup>. Once the vinylidene terminated chains have unzipped, the further degradation is initiated by random scission that corresponds to the second mass loss step<sup>23</sup>. At slower heating rates, one may observe an additional step that precedes the two above-mentioned steps. Kashiwagi et al.<sup>10</sup> assign this step to degradation initiated at abnormal head-to-head linkages that were formed as a result of termination by combination of growing polymer chains. Our TGA and DSC data (Fig. 1 and 2) suggest that the processes of degradation initiated at the abnormal linkages and vinylidene end groups are strongly overlapped.

### Stabilizing effect of oxygen

The initiation at both vinylidene end group and the head-to-head linkage results in formation of the polymer radical,  $R'$



In an oxygen-containing atmosphere, this radical is likely to react with oxygen to form a new polymer radical ( $R''$ )



$R'$

$R''$

As compared to  $R'$ , we estimate<sup>24</sup>  $R''$  to be more thermally stable by  $\approx 100 \text{ kJ} \cdot \text{mol}^{-1}$  and, therefore, able to suppress unzipping of the polymer chain. If unzipping is suppressed, degradation follows only random scission that produces only high molecular weight species, which do not vaporize. As a result, the TGA experiments conducted under air show a noticeable delay in the mass loss as compared to the experiments performed under nitrogen (Fig. 1).

According to our data (Fig. 3), formation of the polymer radical ( $R''$ ) is reversible. In experiments performed under air, the amount of oxygen significantly exceeds the stoichiometry required by Eq. (1). This means that the reversible process is shifted toward formation of  $R''$ . Since this process is exothermic, an increase in temperature should favor the reverse reaction. Therefore, further heating should cause  $R''$  to ultimately decompose to oxygen and the original radical ( $R'$ ).

The proposed scheme also explains the initial acceleration of degradation under air as compared to degradation under nitrogen, as follows. Oxygen delays degradation by deactivating potential reaction centers ( $R'$ ) formed as a result of initiation at the vinylidene end groups or the head-to-head linkages. Hence, the potential reaction centers are accumulated in a less reactive form of the polymer radical  $R''$ . In the vicinity of  $240^\circ\text{C}$ ,  $R''$  decomposes quickly releasing the highly reactive reaction centers,  $R'$ . The release of a great number of  $R'$ -radicals over a short period of time causes a noticeable acceleration of the initial degradation of PMMA in an oxygen containing atmosphere.

The TGA curves for degradation under nitrogen and air cross at approximately 20% of mass loss (Fig. 1). At this point the PMMA samples decomposed under the corresponding conditions are at the same temperature and extent of degradation. However the appearance of the quenched samples is markedly different. Under air, the separate grains of PMMA coalesce into a single body that suggests that the decomposing polymer is a viscous liquid. This sample has a markedly lower molecular weight than the sample decomposed under nitrogen, which consists of separate grains. This conclusion agrees with measurements of viscosity<sup>11</sup> and the number average molecular weight<sup>5</sup>. The escape of gaseous products from PMMA is accompanied by the formation of bubbles, the popping of which causes the instability in the DSC signal at  $270\text{--}330^\circ\text{C}$  (Fig. 2). As a decrease in  $\bar{M}_n$  is primarily caused by random scission, we may assume that oxygen promotes this process. Beside that, oxygen causes highly exothermic oxidation that significantly diminishes the overall endothermicity of degradation (Fig. 2).

Brown and Kashiwagi<sup>13</sup> have recently proposed a mechanism to explain the stabilizing effect of oxygen. The mechanism assumes that oxygen attacks hydrogen activated by the terminal vinylidene group to form a

hydroperoxide. The latter undergoes  $\beta$ -scission forming a hydroxy-terminated polymer and a carbonyl vinyl ester compound. According to this mechanism oxygen also promotes random scission that results in acceleration of degradation at the later stage. This process is accompanied by elimination of an ester compound and water, neither of which have been experimentally observed by Song et al.<sup>18</sup>, who studied the products of PMMA degradation in the presence of oxygen. The major oxidation product (2.2 vol.-%) was 2-methyloxirane carbonic acid methyl ester that resulted from main chain scission<sup>18</sup>. The second major oxidation product was methyl pyruvate (0.37 vol.-%). Therefore, the above-mentioned mechanism does not agree with the experimental data by Song et al.<sup>18</sup>

Another mechanism was earlier proposed by Kashiwagi et al.<sup>10</sup> This mechanism includes an irreversible formation of  $R''$  (cf. Eq. (1)), which after rearrangements, traps oxygen in the polymer chain and eliminates methyl pyruvate, which has been experimentally detected by Song et al.<sup>18</sup> Note that the amount of methyl pyruvate found (0.37 vol.-%) significantly exceeds the maximum theoretical yield obtained under the assumption that methyl pyruvate is formed only in a reaction initiated at a weak link which presumably is present in each polymer chain. This indicates the existence of an alternative channel that also yields this product. Therefore the detection of methyl pyruvate does not provide an unequivocal evidence for the above mechanism. Nevertheless this does not discard this mechanism as a plausible explanation for the stabilizing effect of oxygen.

The only weakness of the mechanism proposed by Kashiwagi et al.<sup>10</sup> is that it is specifically developed for oxygen. For this reason it does not predict the stabilizing effect of other species. On the contrary, our mechanism predicts that any species of a low electron affinity should cause a stabilizing effect similar to that of oxygen.

#### *Degradation in NO-containing atmosphere*

The thermal degradation of PMMA in a NO-containing atmosphere has been conducted to provide the further evidence in support of the radical reaction (1) as being a process that delays degradation of PMMA. According to our mechanism any species of a low electron affinity should also demonstrate a stabilizing effect. Nitric oxide, which is a stable radical in its ground state, was therefore a natural choice. As seen in Fig. 1, introduction of NO in the atmosphere of decomposing PMMA has increased the onset temperature of PMMA degradation by  $\approx 100^\circ\text{C}$  as compared to that for degradation under nitrogen. The initial 5% mass loss is likely to result from formation of volatile byproducts of a reaction between NO and PMMA.

## Conclusion

A mechanism has been proposed to explain the stabilizing effect of oxygen on the thermal degradation of PMMA. This mechanism explains the initial delay of degradation as well as the subsequent acceleration of the process. The proposed mechanism predicts that other species of low electron affinity should also cause a stabilizing effect, which has been confirmed by conducting degradation in the NO-containing atmosphere.

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