

THERMAL DEGRADATION OF POLY(ETHYL METHACRYLATE) AND ITS COPOLYMER WITH POLY(ETHYL ACRYLATE)

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Abstract

The thermal degradation behaviour of poly(ethyl methacrylate) homopolymers and poly(ethyl methacrylate) and poly(ethyl acrylate) copolymers synthesized by using the benzoyl peroxide-di-methyl aniline redox pair at different temperatures (18–35°C) was investigated. Contrary to some reports in the literature, the thermal degradation of PEMA was observed to take place in multi steps. These are assigned to be loss of labile end groups, side chain scission, anhydride formation and main chain degradation steps. Dominating chemical formations at the end of these steps were characterized by FTIR spectroscopy.

The homopolymer samples synthesized at 18°C showed a greater thermal stability against degradation. Copolymerization with small amounts of ethyl acrylate was observed to impart thermal stability to PEMA by stabilizing mainly the end groups against degradations.

Keywords: poly(ethyl acrylate), poly(ethyl methacrylate), thermal degradation

Introduction

Polymethacrylates degrade to lower molecular weight compounds or to the monomers on heating or irradiation with high energy radiation. The decomposition or stability of methacrylate polymers is related to their structures such as type of ester groups molecular weight and its distribution, stereoregularity and copolymer composition. Poly(methyl methacrylate) comprises the most widely studied member of this group [1–4]. Although data have been reported on the glass transition temperature [5–7] of poly(ethyl methacrylate), its thermal degradation has not been studied in detail [8].

The only literature data available on the thermal degradation of PEMA are those of Grassie and Mc Callum [8], Smith and coworkers [9] and Malhotra and coworkers [10]. Without giving any detailed information, Grassie and Mc Callum mentioned their observation of the similarity of the thermal degradations of PEMA and

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poly(*n*-butyl methacrylate). Malhotra *et al.* however in their isothermal weight loss studies report that up to 40% weight loss values, the thermal decomposition of PEMA is closely resembling that of PMMA. Their GPC analysis also shows that the decomposition of PEMA is dominated by depolymerization. In a recent review by Hatada *et al.* [11] poly(ethyl methacrylate) has been classified under the group of polymethacrylates which undergo single-step degradation during thermal treatment in N₂. No experimental proof or comments have been reported on the thermal stability of PEMA.

In this study, the bulk polymerization of ethyl methacrylate and copolymerization of ethyl acrylate and ethyl methacrylate were performed by using different ratios of the benzoyl peroxide-*N,N*-dimethyl aniline redox pair at different temperatures. Then, the thermal degradation behaviours of homo- and copolymers were studied by thermogravimetry and FTIR spectroscopy, and the glass transition temperatures were determined by differential scanning calorimetry.

Experimental

Ethyl acrylate (EA) and ethyl methacrylate (EMA) monomers were purified by passing them three times through a column filled with alumina (adsorption type) and vacuum distilled. *N,N*-dimethyl aniline (DMA) supplied by BDH Chemical Ltd. was used as received. Benzoyl peroxide (BPO), supplied by Fisher Scientific Company, was dissolved in chloroform, precipitated by methanol and then recrystallized.

The bulk polymerization of EMA was performed by using different ratios of the redox pair (BPO and DMA) at different temperatures (18, 25, 35°C). The bulk copolymerization was carried out for 1:10 volume ratio of EA and EMA respectively, at 25°C.

A DuPont (Model 910) differential scanning calorimeter was used for the determination of glass transition temperatures, T_g .

A second DuPont instrument (Model 951), a thermogravimetric analyzer was used for the thermal degradation studies, in pure dry nitrogen atmosphere, between 30 and 600°C. The flow rate of nitrogen gas was 25 ml min⁻¹. The heating rate was 10°C min⁻¹ for studies performed both by DSC and TG.

The viscometric molecular weights of the homopolymers were calculated by using the following equation [12]:

$$[\eta] = 15.49 \cdot 10^{-5} \cdot M_v^{0.679} \quad \text{dL/g (25°C; THF)}$$

A Nicolet (Model 520) FTIR instrument was used to record the IR spectra of the original and thermally degraded polymers using KBr disks.

Results and discussion

The thermal degradation of poly(ethyl methacrylate) and its copolymer with poly(ethyl acrylate) was studied by taking the typical weight loss curves. In the fol-

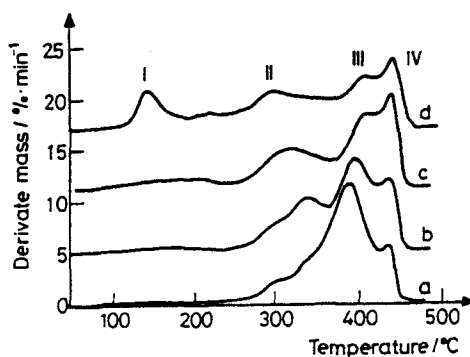


Fig. 1 DTG curves of homopolymers synthesized at 18°C. [BPO]/[DMA] ratios for the curves a, b, c, and d are 0.44, 1.16, 4.00 and 6.50, respectively

lowing figures, however, to avoid overcrowding of curves, only the derivative thermogravimetric (DTG) traces are given. In Fig. 1 DTG curves of PEMA obtained at 18°C with different ratios of the redox pair are given. Qualitatively and quantitatively very similar curves were obtained for PEMA prepared at 25 and 35°C.

Homopolymers were subjected to multi-step thermal degradation. This is evidenced by the appearance of distinct peaks in the DTG curves. The first peak in the DTG curves is considered to be due to the loss of labile groups most probably from the chain ends (Peak I on curve 'd', Fig. 1). Peaks II, III and IV are related to consecutive processes of formation of polymethacrylic acid, anhydride structure and the degradation of the polymer itself by the decomposition of the partially degraded backbone carrying anhydride groups. A similar explanation has been proposed for the thermal degradation of PEMA by Grassie and Mc Callum but without giving any experimental evidence [8]. The assignment of these peaks to various thermal decomposition processes is supported by FTIR studies as will be shown below.

The rate and the extent of loss of labile groups increase with increasing BPO concentration for the homopolymer samples produced at every temperature. This behaviour can be considered as an indication of end group effect.

The molecular weights (M_v) of homopolymers synthesized at 18°C changed between 430 000 and 70 000 corresponding to [BPO]/[DMA] ratios of 0.44 and 6.50, respectively. For $M_v = 430\,000$, the first peak could not be recorded due to the limited availability of labile end groups. The polymerization temperatures used in this study are rather low as compared to thermally-initiated polymerization. Benzoyl peroxide used as one component of the redox pair, does not decompose appreciably at the low polymerization temperatures of 18–35°C. Its presence in increased concentrations, however, can lead to its inductive decomposition by the growing chains. This will cause the formation of lower molecular weight polymers with peroxy end groups. The presence of such thermally labile end groups will further decrease the thermal stability of the polymer. As M_v decreased and the quantity of labile groups increased, it became possible to notice this first peak.

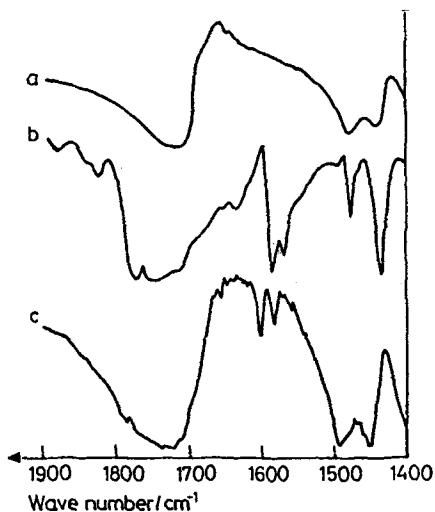


Fig. 2 C=C stretching region of the IR spectra of PEMA polymerized by γ radiation (curve a), BPO (curve b), homopolymer sample synthesized at 18°C with a [BPO]/[DMA] ratio of 6.50 (curve c)

The above approach has also been confirmed by the observation of the peak at 1602 cm^{-1} corresponding to the C=C stretching of the aromatic ring originating from BPO in the FTIR spectrum of a PEMA sample obtained with [BPO]/[DMA]=6.50 (the sample used in Fig. 1d) given in Fig. 2. For comparison, the IR spectrum of a PEMA sample obtained by gamma irradiation of its monomer is also included in this figure, together with the spectrum of BPO in the $1400\text{--}2000\text{ cm}^{-1}$ region.

The effect of polymerization temperature on the thermal degradation behaviour of PEMA is comparatively shown in Fig. 3. The [BPO]/[DMA] ratio is kept at 0.44 for the synthesis of these samples. As the temperature is raised, peak I, i.e. the loss of labile groups, becomes more significant. The maximum degradation temperature

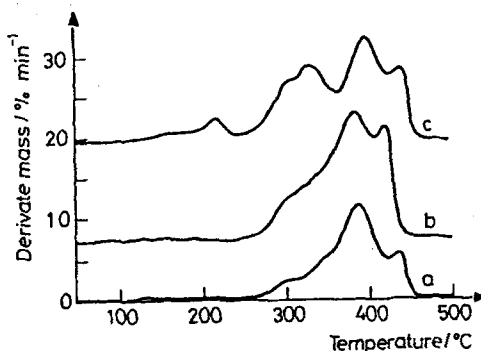


Fig. 3 The effect of polymerization temperature. [BPO]/[DMA] ratio is 0.44. The temperatures for the curves a, b and c are 18.25 and 35°C

remains nearly constant for the PEMA samples produced at these temperatures. Peak II i.e. the side chain scission effect, becomes more significant with increasing temperature. The relative thermal instability of PEMA synthesized at higher temperature is a generally observed phenomenon. It is very well known that polymerizations carried out at relatively high temperatures yield lower molecular weight products with wider molecular weight distributions.

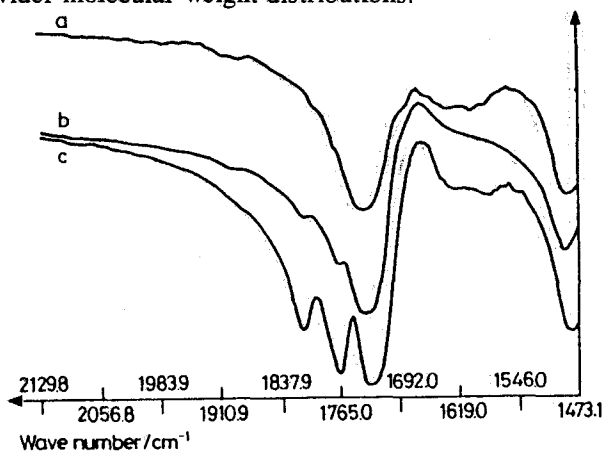


Fig. 4 C=O region of the IR spectra of PEMA, synthesized at 35°C at a [BPO]/[DMA] ratio of 4.00 (curve a), after thermal treatment of the sample for 50 min at 300°C (curve b), after thermal treatment for 8 min at 370°C

The experimental evidence for the explanation related to peaks II and III is also based on IR spectra. The C=O stretching region of the IR spectra taken before and after thermal treatment are shown in Fig. 4. The C=O stretching band of PEMA was originally observed at 1736 cm^{-1} . When PEMA was kept at 300°C for 50 min, new shoulders on the lower wavelength side of the original carbonyl peak started to appear (Fig. 4b). These peaks became more distinct and their intensities increased upon heating the same sample to 370°C for 8 min (Fig. 4c). The new peaks split from the parent carbonyl peak are observed at 1767 and 1811 cm^{-1} . Matsuzaki and coworkers [13] in their analysis of the IR spectra of thermally treated poly(*t*-butyl methacrylate) observed the appearance of strong absorptions at 1760 and 1810 cm^{-1} . These bands were assigned as due to absorptions of anhydride carbonyls. Our spectroscopic results are in very good agreement with these assignments.

Almost simultaneously with the formation of anhydride structures, methacrylic acid type formations have also been observed. This has been evidenced by peaks appearing at 3670 cm^{-1} , which are due to OH bands. Spectra subtraction of the IR spectrum of PEMA heated to 270°C for 30 min from that of unheated PEMA yielded a broad peak centred at 3670 cm^{-1} .

It is therefore clear from these findings that during the thermal degradation of PEMA the major reaction prior to backbone degradation is side-chain decomposition with the formation of anhydride structures.

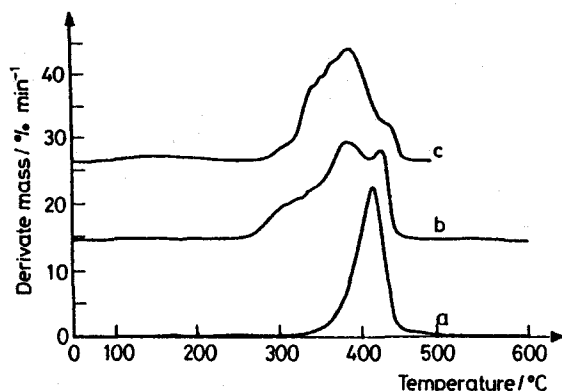


Fig. 5 DTG curves for PEA (a), PEMA (b) and copolymer (c)

Because of the considerable overlap of the peaks, it is not possible to use the current methods of TG analysis (Freeman-Carroll, etc.).

The DTG curves of homopolymers of poly(ethyl acrylate), PEA, poly(ethyl methacrylate) and their copolymers with a 1:10 composition are given in Fig. 5. PEA degrades in a single step with maximum weight loss taking place at 416°C. The degradation of the copolymer resembles that of PEMA, major component of the copolymeric structure (90%), i.e. degradation takes place in multi stages overlapping each other. The formation of a copolymer of EA and EMA has been confirmed by the DSC traces taken for homo- and copolymers, Fig 6. The T_g values were found to be 53, -8 and 34°C for PEMA, PEA and their copolymer, respectively. The existence of both monomers on the polymeric backbone has also been proved by spectroscopic techniques.

The incorporation of ethyl acrylate even in small amounts seems to impart some thermal stability to PEMA mainly by suppressing the degradations that would be initiated from the end groups. 50% weight losses were observed to take place at 357, 410, 391°C for PEMA, PEA and their copolymers, respectively. This can be considered as an additional thermal stabilization provided by the EA moieties in the copolymer.

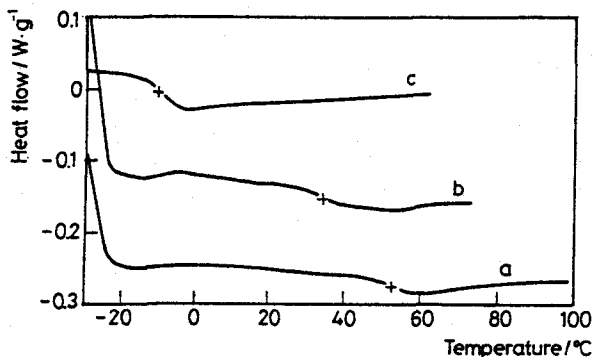


Fig. 6 DSC curves for PEMA (a), copolymer (b) and PEA (c)

In conclusion, contrary to the results of some works in the literature, this study has shown that poly(ethyl methacrylate) undergoes a multi-step thermal degradation. The thermal stability of this polymer is found to be greatly affected by the chemical structure of its chain-ends. Random copolymerization of ethyl methacrylate proved to be an effective way of thermal stabilization of this polymer.

References

- 1 T. Kashiwagi, A. Inaba, J. E. Brown, K. Hatada, T. Kitayama and E. Masuda, *Macromol.*, 19 (1986) 2160.
- 2 A. Inaba, T. Kashiwagi and J. E. Brown, *Polym. Deg. and Stability*, 221 (1988) 1.
- 3 L. E. Manring, *Macromol.*, 21 (1988) 528.
- 4 J. Rhchly and J. Pavlinec, *Polym. Deg. and Stability*, 28 (1990) 1.
- 5 J. A. Shetter, *J. Polym. Sci.*, B, 1 (1963) 209.
- 6 T. Hata and T. Nose, *J. Polym. Sci.*, C, 16 (1967) 2019.
- 7 Z. G. Gardlund and J. J. Laverty, *J. Polym. Sci.*, B, 7 (1969) 719.
- 8 N. Grassie and J. R. Mc Callum, *J. Polym. Sci.*, A, 2 (1964) 983.
- 9 S. D. Smith, T. E. Long and J. E. Mc Grath, *J. Polym. Sci.-Chem. A*, 32 (1994) 1747.
- 10 S. L. Malhotra, L. Minh, L. P. Blanchard, *J. Macromol. Sci.-Chem.*, A, 19 (4), (1983) 559.
- 11 K. Hatada, T. Kitayama, N. Fujimoto and T. Nishiura, *J. Macromol. Sci.-Pure and Appl. Chem.*, A, 30 (1993) 645.
- 12 G. Samay, M. Kubin, J. Podesva, *Angew. Makromol. Chem.*, 72 (1978) 185.
- 13 K. Matsuzaki, T. Okamoto, A. Ishida and H. Sobue, *J. Polym. Sci.*, A, 2 (1984) 1105.