# Thermal properties of ethyl α-hydroxymethylacrylate–methyl methacrylate copolymers

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The degradation and glass transition temperatures of a series of methyl methacrylate (MMA)–ethyl α-hydroxymethylacrylate (EHMA) copolymers have been studied by t.g.a./i.r. and d.s.c. Thermal degradation yielded intramolecular lactone and intermolecular crosslinking formation, with concurrent loss of ethanol and/or methanol involving adjacent or near-neighbour EHMA or MMA units. Glass transitions of copolymers have been analysed as a function of sequence distribution and their values compared to the theoretical ones derived using Johnston's equation. The partially degraded copolymers increased their glass transition temperatures as a consequence of the above mentioned lactone and crosslinking formation.

**(Keywords: thermal properties; degradation; glass transition temperature)**

## *Introduction*

Ethyl α-hydroxymethylacrylate (EHMA) is a monomer which contains three different functionalities including an alcohol, an ester and a polymerizable double bond. The hydroxyl group was expected to increase both the hydrophilicity and the hydrogen bonding capability of the monomer. In this way, Mathias and Wright[1] have utilized EHMA alone or copolymerized with other monomers[2] to improve the mechanical properties of wood. Other possible applications as a new acrylate crosslinking agent have also been explored[3]. A comprehensive review of the chemistry of EHMA has been published elsewhere[4].

The thermal properties of 2-vinyl-4,4′-dimethylazolactone–EHMA copolymers have been studied to evaluate the stability and crosslinking activity of various functional groups in polymers[5]. Our group has published the copolymerization behaviour of EHMA with methyl methacrylate (MMA)[6] and the present paper focuses on the thermal properties of these copolymers.

## *Experimental*

*Homopolymerization and copolymerization.* The synthesis of EHMA and purification of MMA, tetrahydrofuran (THF) and 2,2′-azobisisobutyronitrile (AIBN) have been described previously[6]. Homopolymerization and copolymerization were carried out at 50°C in a THF solution (3 mol dm$^{-3}$) using AIBN ($1.5 \times 10^{-2}$ mol dm$^{-3}$) as initiator. Copolymer samples were obtained at conversions of $<10\%$. Other experimental details have been given elsewhere[6].

*T.g.a.* All the experiments were carried out using a thermogravimetric analyser (Perkin–Elmer TGS2/System 4) coupled to a data logger (Perkin–Elmer TADS 3700). The instrument was calibrated both for temperature and weight by the usual methods. Samples ($\sim$10–15 mg) were heated from 30 to 500°C at a rate of 10°C min$^{-1}$ under dry nitrogen flow (20 cm$^3$ min$^{-1}$), and weight loss was continuously recorded.

*D.s.c.* Glass transition temperatures ($T_g$s) were measured using a differential scanning calorimeter (Perkin–Elmer DSC/TAC7DX, PC series) with a water circulating system. The temperature scale was calibrated from the melting points of high purity chemicals (lauric and stearic acids and indium). Samples ($\sim$10 mg), weighed to $\pm 0.002$ mg with an electronic autobalance (Perkin–Elmer AD4), were scanned at 10.0 K min$^{-1}$ under dry nitrogen (20 cm$^3$ min$^{-1}$).

*I.r. analysis.* I.r. spectra were recorded in KBr pellets on a spectrometer (Perkin–Elmer 781) at room temperature.

## *Results and discussion*

*T.g.a. studies.* Homopolymerization of both MMA and EHMA as well as copolymerization of different monomer mixtures of MMA and EHMA were carried out at 50°C in THF using AIBN as initiator[6]. The reactivity ratios were determined through the non-linear least-squares analytical procedure suggested by Tidwell and Mortimer[7] giving $r_{\mathrm{MMA}} = 1.265$ and $r_{\mathrm{EHMA}} = 1.285$.

As is well known, the mode of termination in addition polymerization may lead to the incorporation of a defect at the polymer chain ends which has long been thought to contribute to polymer instability[8]. In this way, thermal degradation of samples of poly(methyl methacrylate) (PMMA) is principally end-initiated at temperatures below 350°C, while random scission becomes the important initiation process at higher temperatures[9,10]. The

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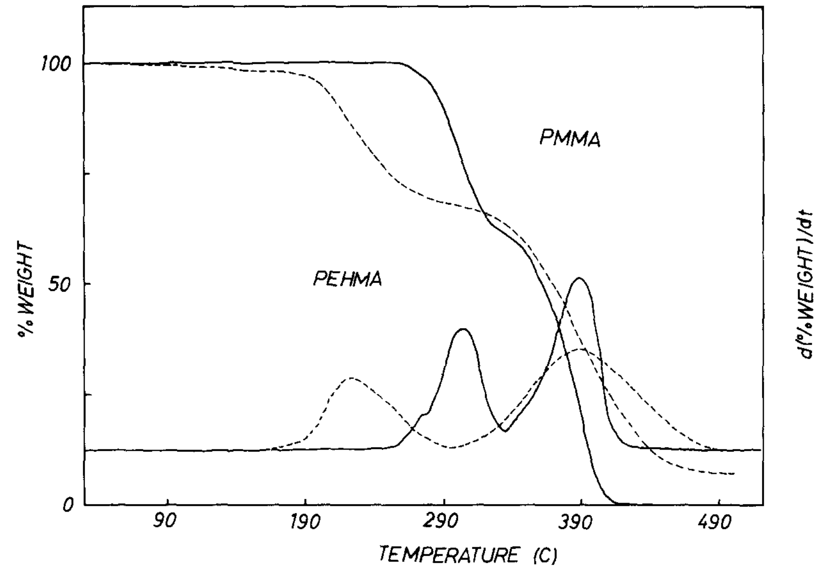

**Figure 1** T.g.a. thermograms for PMMA and PEHMA

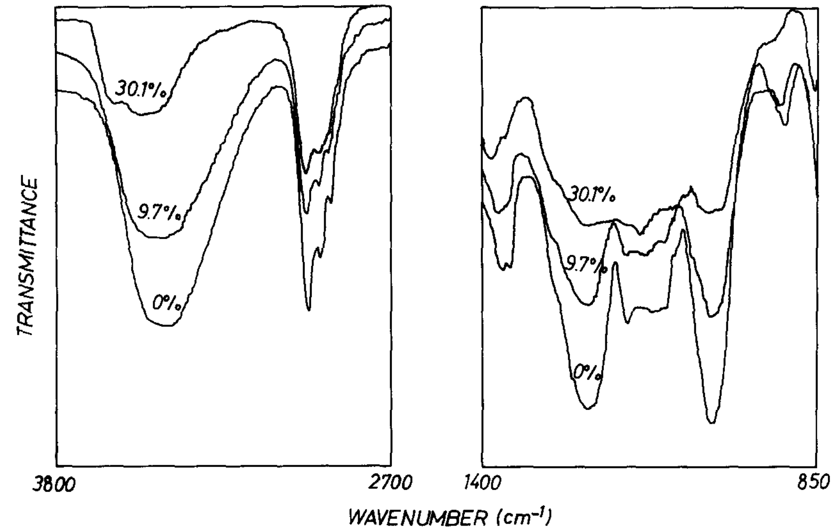

**Figure 2** I.r. spectra of PEHMA before thermal treatment (bottom) and after 45 min at 160°C (middle) and 205°C (top)

thermogravimetric curve observed for PMMA in this study (*Figure 1*), compared well with those of Kashiwagi *et al.*[10].

Poly(ethyl $\alpha$-hydroxymethylacrylate) (PEHMA) shows a two-stage degradation (*Figure 1*) with two distinct peaks in the thermogravimetric curve with maxima around 225 and 390°C. PEHMA begins to degrade to $\sim$170°C in agreement with the results of Ueda *et al.*[11]. After an initial first stage breakdown, the polymer residue remains practically stable to $\sim$303°C, at which point extensive breakdown occurs leaving a carbonaceous residue (2.7%). In the first stage of breakdown the total weight loss (30%) is in good agreement with the calculated value (35%) for the weight loss corresponding to the random inter-intramolecular transesterification process between the pendent OH groups and ester moieties resulting in the loss of ethanol.

The first stage degradation behaviour of PEHMA has also been studied under isothermal conditions over the range of 130–205°C for up to 45 min. In all cases, the polymer residue was insoluble in most common organic solvents which indicates a crosslinking process as a consequence of the intermolecular transesterification reaction. The polymer residues were also analysed by i.r. spectroscopy. *Figure 2* shows the i.r. spectra of samples thermally degraded to several percent weight loss. The most obvious features are the decrease in intensity of the OH band at $\sim 3500\,\mathrm{cm}^{-1}$ and the peaks at 1240 and $1035\,\mathrm{cm}^{-1}$ corresponding to the stretching C–O absorption. Reduction of peaks at 2900, 2930 and 2980 $\mathrm{cm}^{-1}$ are also observed. These facts confirm the intermolecular transesterification process mentioned above. Similar results have been obtained by Muthiah and Mathias[5] in the thermolysis of PEHMA at 250°C for different degradation times.

As can be seen in *Figure 3*, where t.g.a. curves of copolymers with different MMA molar fraction composition ($F_{\mathrm{MMA}}$) are shown, the introduction of small amounts of EHMA into the PMMA chain considerably alters the degradation pattern. The onset of the weight

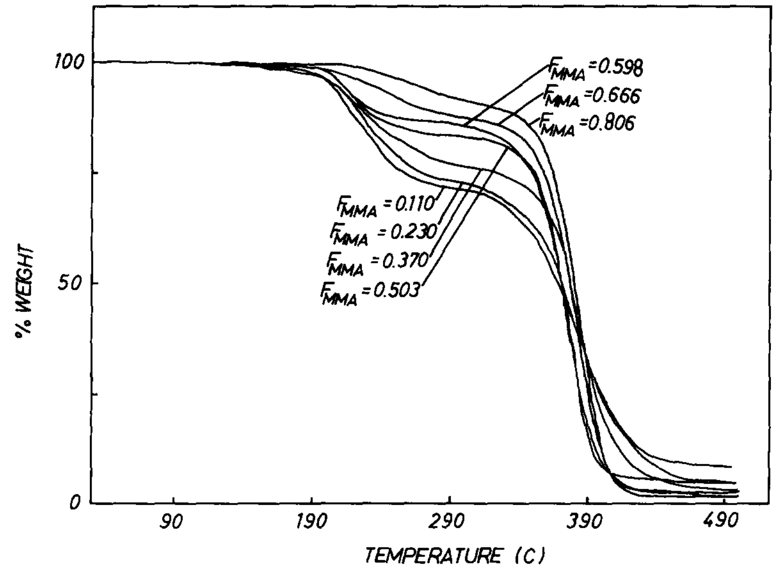

**Figure 3** T.g.a. thermograms for a series of MMA–EHMA copolymers obtained at low conversion. $F_{MMA}$ is the methyl methacrylate molar fraction in the copolymer chain

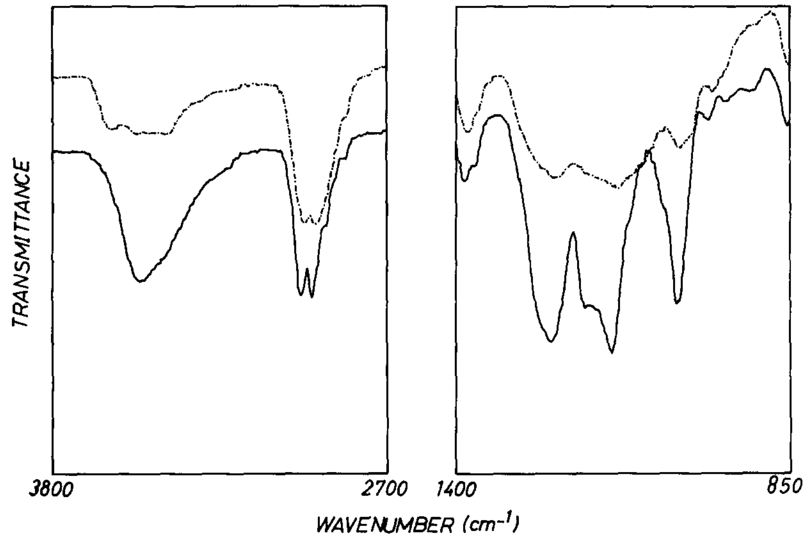

**Figure 4** I.r. spectra of a MMA–EHMA copolymer ($F_{MMA}$=0.503) before thermal treatment (bottom) and after 45 min at 205°C (top)

loss is lowered with respect to that of PMMA, but after the first stage of breakdown, the remaining polymer has a considerably higher stability than PMMA.

On the other hand, the onset of weight loss, attributable to EHMA units, shifts to higher temperatures with increasing MMA molar fraction level in the copolymers. This fact would indicate that an EHMA unit flanked by two MMA units is stabilized relative to an EHMA triad. A similar trend is observed in MMA–2-sulfoethyl methacrylate copolymers[12].

The initial weight loss ranged from 7 to 27%, each case corresponding, almost quantitatively, to the theoretical yield of methanol and ethanol in the random inter-intramolecular transesterification reaction produced between the OH pendent group with an adjacent EHMA unit (to release ethanol) or an adjacent MMA unit (to release methanol).

The copolymer samples were also degraded under isothermal conditions at 205°C until the weight loss observed in the first stage of dynamic degradation was obtained. The remaining copolymers were insoluble in common organic solvents and, as can be seen from *Figure 4*, the i.r. spectra showed similar changes to those produced by degraded PEHMA. These facts seem to indicate that the inter- intramolecular reaction produced in the first stage of degradation gives rise to the formation of lactone rings and crosslinking structures. The formation of this kind of structure produces a stabilizing effect on the depolymerization reaction of the PMMA chain. This fact could be explained by considering these structures as ‘blocking’ groups which interrupt the unzipping process, with pure PMMA having a long zip length[13]. In this way, there are a number of MMA copolymers which under programmed heating conditions show a first stage of degradation as a consequence of the intramolecular reaction between an MMA unit and an adjacent comonomer unit. Thus, a process of lactonization has been observed in MMA–vinyl acetate[14], MMA–vinyl

**Table 1** Methyl methacrylate molar fraction in the feed ($f_{MMA}$), in the copolymer ($F_{MMA}$) and values for the $T_g$, before and after the first stage of decomposition, at a heating rate of 10.0 K min$^{-1}$ for different MMA–EHMA copolymers obtained at low conversion

| Monomer feed ($f_{MMA}$) | Copolymer composition ($F_{MMA}$) | $T_g^a$ (K) | $T_g^b$ (K) |
|---|---|---|---|
| 0 | 0 | 371.4 | 457.5 |
| 0.140 | 0.110 | 372.0 | 445.5 |
| 0.260 | 0.230 | 373.4 | 420.7 |
| 0.392 | 0.370 | 375.4 | 408.1 |
| 0.486 | 0.503 | 378.8 | 404.4 |
| 0.578 | 0.598 | 383.0 | 398.0 |
| 0.664 | 0.666 | 383.8 | 393.0 |
| 0.797 | 0.806 | 389.4 | 392.5 |
| 1 | 1 | 396.6 | – |

[a] $T_g$ of copolymers before thermolysis
[b] $T_g$ of copolymers after the first stage of decomposition

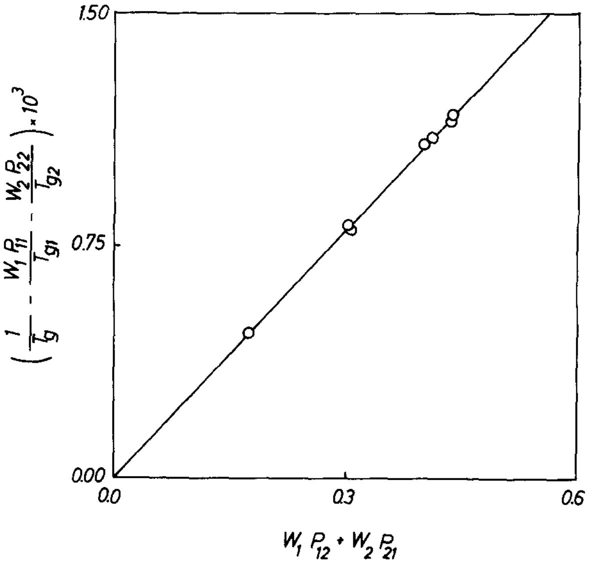

**Figure 5** Plot of the $T_g$ of a series of MMA–EHMA copolymers obtained at low conversion according to the linearized expression of Johnston

chloride[15] and MMA–vinyl bromide[16] copolymers. In all these cases, the formation of lactone rings has a stabilizing effect.

*D.s.c. studies.* One of the most important characteristics of polymers is their $T_g$. The $T_g$ value is not only important for setting the appropriate processing conditions but also for the properties that the end product will have.

The simplest relationships which describe the effect of the composition of the monomeric units of a linear copolymer on the $T_g$ are the DiMarzio–Gibbs and Fox equations[17,18]; generally these do not fit the experimental data accurately. However, there are some other equations which give very similar theoretical curves in very good agreement with the experimental results[19,20]. Among them, the Gordon–Taylor–Wood equation[21,22] includes adjustable parameters and is based on the 'free volume' concept. On the other hand, equations such as those from Johnston[23], Barton[24] and Couchman[25], which take into account the sequence distribution, have become popular and are extensively used. All these equations include a weighted contribution of an imaginary alternating copolymer and are capable of reproducing $T_g$–composition behaviour for many copolymer systems.

Johnston's[23] equation assumes that $M_1M_1$, $M_1M_2$ or $M_2M_1$ and $M_2M_2$ diads have their own $T_g$, the copolymer $T_g$ being described by:

$$\frac{1}{T_g} = \frac{W_1P_{11}}{T_{g11}} + \frac{W_2P_{22}}{T_{g22}} + \frac{W_1P_{12} + W_2P_{21}}{T_{g12}}$$

where $W_1$ and $W_2$ are the weight fraction of monomeric units in the main chain, $T_{g11}$ and $T_{g22}$ are the glass transition temperatures of the respective homopolymers and $T_{g12}$ the supposed glass transition temperature for the alternating sequence $M_1M_2$ or $M_2M_1$. The probabilities of having various linkages, $P_{11}$, $P_{12}$, $P_{21}$ and $P_{22}$, may be calculated for a given monomer feed composition from statistical considerations[26] using monomer reactivity ratios.

$T_{g12}$ is unknown for the present system, but it has been estimated from our own experimental $T_g$ data of the corresponding homopolymers and those of a series of copolymers obtained at low conversions using a linearized form of the above equation. *Table 1* gives the $T_g$s determined by d.s.c. as a function of MMA molar fraction composition in the copolymer. Values of $T_{g11}$, PMMA, and $T_{g22}$, PEHMA, are in good agreement with those reported in the literature[5,18]. As can be seen in *Figure 5*, the experimental data yield a straight line from which the value of $T_{g12} = 377.9$ K is obtained. Taking into account this $T_{g12}$ value, the curve of *Figure 6* has been drawn according to the Johnston's equation[23]. The good agreement between experimental and theoretical values indicates that Johnston's equation[23] and the terminal model through reactivity ratios may be used to describe the dependence between the experimental $T_g$ of EHMA–MMA copolymers and their sequence distribution.

However, Hirooka and Kato[27] have observed that the $T_g$ for diads, $T_{g12}$, calculated from the $T_g$ of a series of copolymers of varied compositions, does not always correspond with that of the chemically synthesized alternating copolymer[28]. These authors found that the $T_{g12}$ derived from the $T_g$ of copolymer systems is higher,

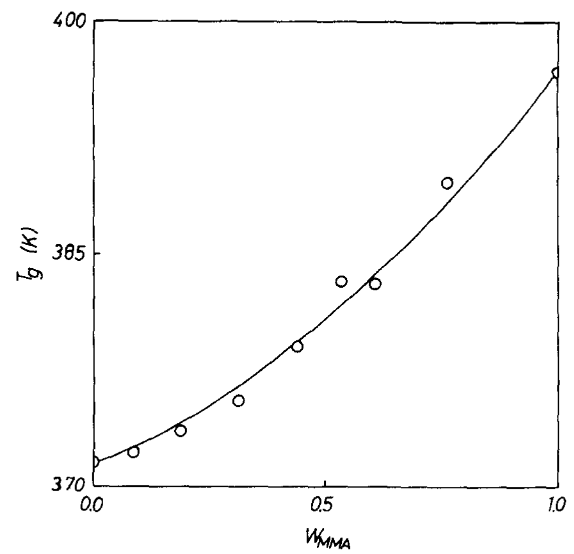

**Figure 6** Plot of the $T_g$ of a series of MMA–EHMA copolymers obtained at low conversion as a function of MMA weight fraction in the copolymer chain. The solid line is drawn using Johnston's equation

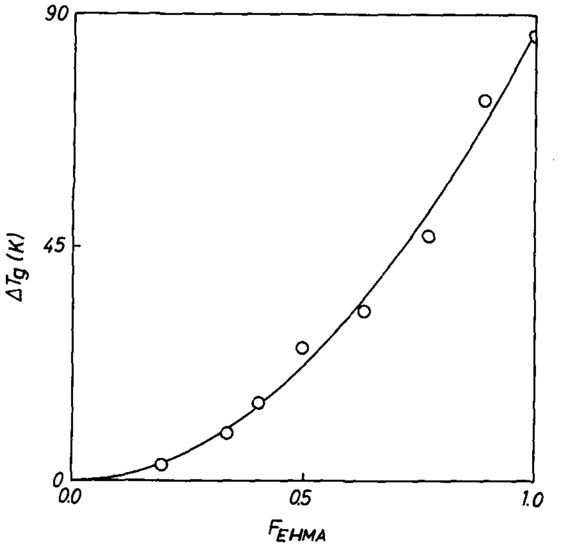

**Figure 7** Relative increments in the $T_g$ of MMA–EHMA copolymers observed after thermolysis with respect to those observed before thermolysis

lower or similar to that experimentally determined in the strictly alternating copolymer. In order to explain such deviations, Tonelli[29] has used the conformational entropy as a characterizing parameter for the polymer intramolecular chain flexibility. He pointed out that positive, negative or no deviations from bulk additive, namely, $T_{g12}$ estimated from $T_g$–sequence distribution behaviour, are produced when the conformational entropy for a given copolymer chain is lower, higher or similar, respectively, to the weighted sum of entropies calculated for the constituent homopolymer chains.

On the other hand, the $T_g$ of the polymer is related to the chain flexibility and this parameter is, to a large extent, a reflection of the rotational barrier about the bond linking two monomer units. In copolymers obtained in the free radical polymerization of EHMA and MMA, there are chains which have EHMA–EHMA, MMA–MMA, EHMA–MMA or MMA–EHMA links. Depending on that the rotational barrier of the heterolink bond being similar, higher or lower than the averaged rotational barrier of the homolink bonds, the copolymer $T_g$–composition behaviour will be linear or show positive or negative deviations from linearity[30]. Hirooka and Kato[27] have proposed that the difference between the average $T_g = (T_{g11} + T_{g22})/2$ and the supposed transition temperature of the alternating copolymer $T_{g12}$ may be regarded as a measure of the heterolink stiffness. In our case, the value of $T_{g12}$ obtained using Johnston's equation[23] is lower than that of the average $T_g$ corresponding to an equimolecular random copolymer. Therefore, a negative deviation from linearity is found for the dependence between $T_g$ and copolymer composition, which indicates a heterolink stiffness lower than the average of the homopolymer links. The cause of this effect is not clear since chain flexibility not only depends on the rotational barrier but also on the chain packing, side chain stiffness, dipole interactions, etc.

Thermal curing of these copolymers opens up the possibility of a variety of applications where increased $T_g$ and insolubility are desired. In this sense, as has been mentioned before, thermolysis of both PEHMA and EHMA–MMA copolymers under controlled conditions resulted in loss of alcohol (ethanol or methanol) with concomitant lactone formation and crosslinking. As a consequence, once the first stage of decomposition has occurred, an increase in the $T_g$ of both PEHMA and EHMA–MMA copolymers is observed (*Table 1*). As is shown in *Figure 7*, the increase in $T_g$ is larger for copolymer with high EHMA molar fraction composition. Samples with lower EHMA incorporation were little affected. In a similar way, Kress *et al.*[31] found that methyl α-hydroxymethylacrylate–styrene copolymers increase their $T_g$s when the samples analysed by d.s.c. were submitted to successive and higher heating cycles.

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