Thermal behaviour of TEGMMA copolymers obtained by photopolymerization using iron complexes

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Abstract: Copolymers of methyl methacrylate (MMA) and triethyleneglycol dimethacrylate (TEGDMA) obtained by photoinitiated polymerization using Fe(III) complexes were submitted to thermogravimetry (TGA) under dynamic air atmosphere and N_2, and differential scanning calorimetric analysis (DSC). Thermal events were observed only between 90 - 110 °C. Glass transitions were observed at *ca*. 100 °C, followed by an exothermic peak at 170 °C. The exothermic peak was assigned to a thermal curing process due to the presence of unreacted vinyl groups of the monomers. DSC revealed to be a useful tool to evaluate the curing completeness in this kind of material, using small amounts of sample in relatively short time.

Keywords: copolymers; cross-linking; thermogravimetry (TG); differential scanning calorimetry (DSC).

Introduction

Copolymers of bifunctional and monofunctional vinyl monomers with high cross-linked structures or networks are becoming increasingly important materials in many areas such as coatings, films, packaging industries and biomaterials [1,2]. These different applications require specific material properties, which are determined amongst others, by the microstructure of the polymer chain, the interactions between chains and the types of additive. Typically, during the copolymerization of multifunctional monomers with monofunctional monomers, the development of a 3-D network restricts the mobility of polymer segments, so that the subsequent decrease in free volume causes reduction in the mobility by several orders of magnitude [3,4]. Consequently, a series of phenomena occur, such as self-acceleration, self-deceleration, reaction-diffusion-controlled termination [5], trapping of radicals, and limiting of the ultimate double-bond conversion. Since the kinetics and network formation of cross-linked systems are quite complex, a thorough understanding of polymer network structure and mechanical property evolution is still being pursued.

When a polymer is heated at temperatures below that of decomposition several events will happen, such as the cure of the unreacted vinyl groups, or rearrangements of the chains that might modify the glass-transition temperature (T_g). The T_g temperatures are strongly affected by the degree of crosslinking of the material. The relationship between cure temperature (T_{cure}) and glass transition temperature (T_g) of the polymer is especially important since there is significant debate about whether high-T_g materials can be obtained from monomers cured at low temperature (e.g., room temperature). The investigation of this

problem is also important for practical applications.

In the present work, methyl methacrylate (MMA) - triethyleneglycol dimethacrylate (TEGDMA) copolymers obtained using Fe(III) complexes as photoinitiators were analyzed by thermoanalytical methods, including thermogravimetry (TG) and differential scanning calorimetry (DSC), order to evaluate the thermal decomposition pathways, the completeness of curing and the determination of the glass transition temperatures.

Material and Methods

Materials

The photoinitiator, hexaaquo iron (III) chloride, $FeCl_3.6 H_2O$ (Across Organics, 99%) was used as received. The monomers methyl methacrylate (MMA) (Aldrich, 99%) and triethyleneglycol dimethacrylate (TEGDMA) were washed twice with 5% NaOH in water and dried over $CaCl_2$ in order to eliminate the inhibitors. Structures of the monomers are shown below.
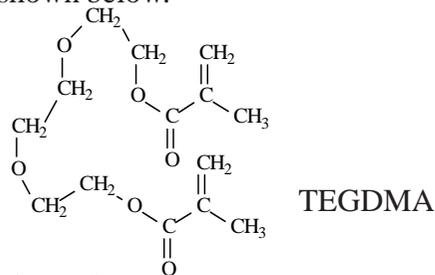

Figure 1. Photopolymerization rates (R_p) for different MMA concentration in methanol.
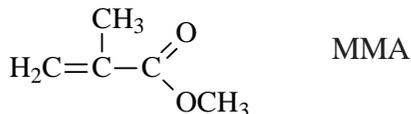

Figure 2. Typical TG/DTG curves for TEGMMA6 under (a) N_2 atmosphere and (b) air atmosphere.

Photopolymerization procedure

The copolymers were synthesized by light-induced polymerization of methyl methacrylate (MMA) and triethyleneglycol dimethacrylate (TEGDMA) in presence of $FeCl_3.6 H_2O$ in methanol. The process was conducted in a photodilatometer cell [6-9], so that polymerization kinetics could be followed. The concentrations of the photoinitiator and TEGDMA monomer were fixed at $2.5.10^{-4}$ and 0.2 mol L^{-1}, respectively, while the concentration of MMA was varied from 3.0 to 9.0 mol L^{-1} (The notation TEGMMA3 to 9, corresponds to copolymers obtained using MMA concentration between 3 and 9 mol L^{-1}). The solutions were thoroughly deoxygenated by bubbling oxygen-free nitrogen for 20 minutes.

The photodilatometer consisted of two capillaries attached to a cylindrical vessel (8.5 mL), which was placed in a constant temperature bath (25.00 ± 0.01) °C in front of the irradiation source. Light from a 200 W Hg(Xe) lamp in an Oriel Universal Arc Lamp was filtered by a monochromator set at 360 nm placed between the lamp and the reaction vessel. The polymerization rates (Rp) were calculated from

$$R_p = \frac{\Delta v}{F.f.\Delta t}[M](molL^{-1}s^{-1}) \qquad (1)$$

where *Dv* is the contraction in volume in the capillary (calculated from the variation in a cathetometer) at time *t*; *f* the volume fraction of monomer in the solution; *F* the volume contraction related to the densities of polymer and monomer in solution [*F* = *(d*p " *d*m)/*d*p], and [M] corresponds to the monomer molar concentration.

After irradiation, copolymers were precipitated by addition of cold methanol, washed, filtered and dried in a desiccator.

Actinometry was performed using ferrioxalate/phenanthroline salt. The quantum efficiency of this actinometer is » 1.0 at wavelengths below 405 nm.

Instrumentation

The TG curves of dried samples were recorded using a TGA-950 modulus coupled to a TA-2000 thermal analyser, TA Instruments, using ca. 7 mg sample mass in a Pt sample holder. The used heating rate was 10 °C min^{-1} under nitrogen or air atmosphere (100 mL min^{-1}).

The DSC curves were recorded on a DSC 910 modulus coupled to a TA-2000 thermal analyser, TA Instruments, in covered aluminium sample holders with a central pinhole. Samples of ca. 20 mg were heated at a 40 °C min^{-1} rate, under nitrogen flow of 100 mL min^{-1}.

Results and Discussion

Photopolymerization

Table 1 shows some of the results corresponding to the photopolymerization of MMA and TEGDMA in methanol in the presence of FeCl$_3$ using a 360 nm monochromator. Although the polymerization rates increase with the MMA concentration up to 6.0 M, and decrease thereafter, the experimental reaction constant decreases steadily over all the range of MMA concentrations used (Figure 1). This increase can be ascribed to two concurrent factors: higher MMA concentrations lead to less viscous solutions so that radical recombination will become easier, lowering the overall polymerization rate. Additionally, higher concentrations of MMA will lead to the gradual replacement of the hexaaquo iron complex by a hexaMMA iron complex, in which the main absorption peak is displaced to the blue, so that the absorption at ~360 nm decreases. The monomer conversion degrees and the quantum yields showed the same behaviour observed for polymerization rate [11].

Thermal Analysis

The TG curves for the copolymers obtained were similar for all the samples. Under air, the decomposition started at 185.7 °C yielding a carbonaceous residue that burned from 28 to 400 °C. TG profile under N$_2$ showed that the polymer decomposed in a single step from 183 to 400 °C with mean residues of ca. 2.5%, in both cases. Figure 2 shows the TG/DTG curves for TEGMMA6 under N$_2$ (Figure 2.a) and air (Figure 2.b). Similar behaviour was observed for the other copolymers.

Table 1. Polymerization rates, (R$_p$), experimental rate constants, (k$_{exp}$), conversion percentages and quantum yields, (f$_p$), for the copolymerization of MMA and TEGDMA in methanol, photo-copolymerized by FeCl$_3$ 2.5.10^{-4} M

Copolymers	Conversion (%)	R$_p$/10^{-5} (M s^{-1})	k$_{exp}$ (10^{-5} s^{-1})	ϕ_p (mol einstein^{-1})
TEGMMA3	6.1	5.48	1.83	102
TEGMMA4	7.6	6.27	1.57	116
TEGMMA5	7.9	7.10	1.42	132
TEGMMA6	16.8	7.24	1.21	134
TEGMMA7	12.4	6.58	0.94	122
TEGMMA8	11.9	5.73	0.72	106
TEGMMA9	11.0	5.14	0.57	95.4

The DSC curves were determined in the -50 to +180 °C range, in order to characterize eventual second order transitions at sub-room temperature. However, the main thermal events were observed only between 90 and 110 °C. Evidences of a glass transition around 100 °C, followed by an exothermic peak at 150-170 °C, were observed depending on the sample (Figure 3).

It is well known that when copolymerizing linear monomers with dimethacrylate, up to 30% of the total amount of C=C bonds remain unreacted, as pendant groups [12]. Therefore, the exothermic peak at 150 - 170 °C can be assigned to a thermal curing process due to the presence of the unreacted groups of the dimethacrylate monomers. Evaluating the heat released during the curing, and using the reported value of ~13 kcal mol^{-1} for the polymerizing heat, it can be calculated that between 5 and 10% of the remaining vinyl groups are cured during the analysis [13,14].

This assumption is supported by experiments involving cycles of heating the copolymers up to 180 °C followed by cooling in liquid N$_2$. In this case the

exothermic peak at 150 - 170 °C almost disappears as can be observed in Figure 4b. The same behaviour, no peak due to the curing process, is also observed for a freshly pre-heated sample slowly cooled to room temperature (Figure 4c).

The baseline change is better defined when the sample is slowly cooled, suggesting a glass transition. The glass transitions were determined as the temperature at the mid-point of the second order transition between 80 – 140 °C and the results are summarized in Table 2.

The effect of composition on the T_g depends on the nature of both constituents of the copolymer and, in the present case, can be estimated from the T_g of MMA and TEGDMA homopolymers. In an ideal copolymer (not crosslinked), in which no strong interactions are present, the ideal glass transition (T_g^0) can be calculated using the Fox Equation [15,16],

$$\frac{1}{T_g^o} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (2)$$

were w_1 and w_2 are the molar fractions of each monomer in the copolymer.

Table 2 shows the glass transition temperatures T_g taken from DSC curves, compared with the T_g^0 calculated from the copolymer composition. As can be seen from Figure 5, whereas the experimental glass transition temperatures decrease steadily with the increase of the MMA concentration, the Fox equation predicts a slow increase. These difference is expected when taking into account the crosslinking induced by the diacrylate, which is not considered in that equation. It is also noteworthy to observe the coincidence of both values at the higher MMA concentrations. This behaviour results from the lower crosslinking densities obtained when the monofunctional monomer is at very high concentrations.

Table 2. Glass transition experimental, T_g, and calculated by Fox Equation, T_g^0, for TEGMMA copolymers

Copolymers	[MMA] / mol L^{-1}	T_g / °C	T_g^0 / °C
TEGMMA3	3.0	128	86.9
TEGMMA4	4.0	118	90.9
TEGMMA5	5.0	118	93.5
TEGMMA6	6.0	106	95.3
TEGMMA7	7.0	112	96.6
TEGMMA8	8.0	98.0	97.2
TEGMMA9	9.0	100	98.2

Conclusions

The non-polymerized double bonds present in the copolymer are cured during the high temperature thermal analysis, and disappear completely after the first cycle. This behaviour is confirmed by the presence of an exothermic peak around 150-170 °C.

A transition centred at around 105 °C is present in the DSC of all copolymers, and was assigned to the glass transition process. This temperature is always higher than the T_g^0 calculated by the Fox equation showing that crosslinking occurred during the photopolymerization, especially at the lower concentrations of MMA. When the proportion of the monofunctional monomer is higher (> 6 M), the experimental glass transition temperature approaches the calculated one.

DSC revealed to be a useful tool to evaluate the curing completeness in this kind of material, using small amounts of sample and performing the determinations in relatively short times.

Acknowledgements

I. C. Rigoli, C. C. Schmitt, L. A. Ramos, M. G. Neumann, E. T.G. Cavalheiro, Comportamento térmico de copolímeros TEGMMA obtidos por fotopolimerização usando complexos de ferro

Resumo: Copolímeros de metacrilato de metila (MMA) e dimetacrilato de trietilenoglicol (TEGDMA) obtidos por fotopolimerização usando complexos de Fe(III) como fotoiniciador foram submetidos a analíse térmica, TG e DSC, sob atmosfera de ar e de N_2. Eventos térmicos foram observados entre 90 -110 ^{0}C. Transições vítreas foram observadas acima de 100 ^{0}C, seguida por um pico exotérmico à 170 ^{0}C. O pico exotérmico foi atribuído ao processo de cura térmica devido a presença de grupos vinilícos dos monômeros que não se converteram. A técnica de DSC revelou ser uma ferramenta útil para avaliar o processo de cura desse tipo de material, usando pequenas quantidades de amostras e um curto tempo de analíse.

Palavras-chave: copolímeros; reticulação; termogravimetria (TG); calorimetria exploratória diferencial (DSC).

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