

Thermal Decomposition of Copolymers Used in Dental Resins Formulations Photocured by Ultra Blue IS

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ABSTRACT: Kinetics of thermal decomposition of acrylates copolymers used in dental resins formulations were studied with dynamic thermogravimetric analysis experiments. The kinetic parameters, including activation energy, pre-exponential factor, and 60 min half-life temperature, which were calculated by the Flynn and Wall method, are presented. The results indicate that thermal decomposition of the material occurred in three different stages characterized by different mechanism. These three events were separated and the kinetics parameters were determined. The loss mass was observed in the onset of the thermal decomposition for the all of copolymers studied. When the copolymers were submitted to thermal

treatment before of thermal analysis was not observed the loss mass in the beginning of the process. The analysis of intermediates by GC of the condensed material extracted after thermal treatment at TB copolymers showed the presence of the methacrylic acid and 2-hydroxyethyl methacrylate, which are products of decomposition of BisGMA and triethyleneglycol dimethacrylate monomers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3295–3300, 2007

Key words: thermogravimetric analysis (TGA); thermal decomposition; photopolymerization; TEGDMA/BisGMA; crosslinking

INTRODUCTION

BisGMA (2,2-bis[4-(2-hydroxy-3-methacryloyloxyprop-1-oxy)-phenyl]propane, bisphenol-A glycidyl ether dimethacrylate) and TEGDMA (triethyleneglycol dimethacrylate) monomers are widely used matrices in dental restorative materials, teeth bonding agents, and fissure sealing agents.¹ Polymerized light-cured composite dental resins require highly crosslinked three-dimensional network structures and photopolymerization of multifunctional monomers allows for the facile production of highly crosslinked polymers network (thermoset polymers) that are useful in a variety of applications. In addition, photoinitiated polymerization of multifunctional monomers occurs rapidly with temporal and spatial control of the reaction. These monomers exhibit many complex features including autoacceleration and autodeceleration, limiting double bond conversion and polymerization kinetics that are dependent on the rate of polymerization, and a reaction diffusion-controlled termination mechanism. Most of this polymerization behavior can be attributed to the mobility of the

reacting species in the system. Previous reports have shown that the physical and mechanical properties of TEGDMA/BisGMA are connected to the degree of conversion (degree of cure, degree of polymerization, or rate at which methacrylate C=C bonds are converted to aliphatic C—C bonds).^{2–6}

Thermal analysis techniques, using differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), or dynamical mechanical analysis (DMA), are suitable for examining the characteristics of polymers. The study of thermal degradation processes provide more specific information regarding internal structures of dental resins. Many factors affect the thermal degradation of polymers, including the molecular weight distribution, branching chains, crosslinked density, and end-groups. Copolymers exhibit more intricate thermal behavior than homo-polymers, because they are readily affected by the ratio of monomers or degree of conversion.^{7,8} However, the thermal behavior of TEGDMA/BisGMA-based dental resins has been described in only a few reports owing to the complexity of the thermal degradation of polymers. TGA is a technique in which the mass of the sample is monitored as a function of temperature or time, while the sample is subjected to a controlled temperature program.^{9,10}

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Kinetic analysis

The kinetic parameters can be determined by several methods, e.g., Kissinger,¹¹ Friedman,¹² Flynn and

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Wall,¹³ Horowitz-Metzger,¹⁴ and Ozawa.¹⁵ Among the Flynn and Wall approach represents a relatively simple method for determining activation energy directly from weight loss against temperature data obtained under dynamic temperature at several heating rates.

Traditionally, a constant heating rate as well as isothermal thermogravimetric analysis has been used to obtain kinetic information. The constant heating rate method developed by Flynn and Wall is often preferred because it requires less experimental time and overcomes the short-coming of isothermal methods.

The thermal degradation kinetics, on the basis of Flynn and Wall method, requires a minimum of three different heating profiles per material. The approach assumes the basic Arrhenius Equation and a first-order kinetics, which is generally true for most of the polymers:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \quad (1)$$

where α is the degree of decomposition, t is the time (s), A is pre-exponential factor (1/s), E_a is activation energy (J mol⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹), and n is the reaction order.

On the basis of TG/DTG curves performed at different heating rates, Flynn and Wall express eq. (1) as

$$E_a = \left(\frac{-R}{b}\right) \frac{d \ln \beta}{d(1/T)} \quad (2)$$

where b is a constant (0.457), assuming $n = 1$, β is a heating rate (K min⁻¹), and T is a temperature of weight loss (K).

From selected fraction of thermal decomposition in the TG plot as points of equivalent weight loss, which is beyond any initial weight loss due to volatiles, a plot of $\log \beta$ versus $1/T$ is constructed. The slope of this straight-line plot is then used to calculate the activation energy (E_a) for different conversion levels. The pre-exponential factor (A) is then calculated by the interactive method of Zsakò and Zsakò. The kinetic parameters do have a physical meaning and can be used to help in elucidating the solid-state reaction mechanisms.^{16,17}

EXPERIMENTAL

Materials

The dimethacrylate monomers TEGDMA and BisGMA, and they were used as received without further purification. Five copolymers were prepared

from mixtures of TEGDMA and BisGMA with the following weight ratios 30 : 70, 40 : 60, 50 : 50, 60 : 40, and 70 : 30, respectively. For light curing 0.5 wt % camphorquinone (CQ) was used as photoinitiator and 0.25 wt % of ethyl 4-dimethylaminobenzoate 99% (EDB) as coinitiator. Since BisGMA is a viscous liquid, the CQ and EDB were first dissolved in dichloromethane, then a certain amount of this solution was added to the monomers mixture, and the solvent was subsequently evaporated under vacuum. The mixtures were stored in the dark until the photocuring started.

Preparation of copolymers

Disc grooves Molds in discs with 10 mm in diameter and 1 mm in thickness were fabricated in a Teflon mold covered with polyethylene film. The desired mixture of monomers was inserted into the groove and irradiated for 40 and 60 s. The irradiation was carried out with an ultra blue IS light emitting diode (produced by DMC Instruments, Brazil). This irradiation unit emitted radiation predominantly in the 475 ± 15 nm range, where also CQ absorbed ($\lambda_{\max} = 470$ nm, $\epsilon = 3.8 \times 10^4$ cm² mol⁻¹).¹⁸ The unit was used at a distance of 3 mm from the sample. The copolymers obtained were named TB3070, TB4060, TB5050, TB6040, and TB7030. TB is associated the name of monomers TEGDMA and BisGMA and the numbers is associated with the different weight ratios of monomers in the mixture, respectively.

TG Experiments

TG/DTG experiments were performed using a TA Instruments SDT-Q600 Simultaneous Thermogravimetric Analyzer, using an alumina sample holder under nitrogen atmosphere at a flow rate of 100 mL min⁻¹ in a temperature range from 25 to 800°C. The samples mass used were about 8 mg each. TG and DTG curves were analyzed with Universal Analysis 2000 version 4.1D from TA Instruments. A series of TG measurements were performed at different heating rates of 2.5, 5, 10, and 20°C min⁻¹ from 25 to 800°C to study the kinetics of the copolymers decomposition. Conversions of 30, 35, 40, 45, 50, 55, 60, 65, 70, and 75% of sample weight loss were used for subsequent calculations. The kinetic dates were analyzed by Thermal Specialty Library version 1.4 (TA Instruments).

Characterization of thermal decomposition intermediates

Thermal decomposition intermediates of the TB copolymers were obtained at temperatures indicated

by the TG curves. A certain amount of sample was inserted in a glass tube 200×20 mm, to which a thermometer was attached. This set was then inserted into a glycerin bath and heated until 220°C . The fumes condensed at the upper part of the tube, which was out of the heating region, were collected with a mixture of ethanol : water (75 : 25 v/v) and inserted in a gas chromatograph. The chromatographic peaks were then characterized by comparison with those from standards.

Chromatograms were obtained with a by Shimadzu 14B gas chromatograph. The chromatographic column was the polar CBP20 type (Shimadzu), length: 25 m; internal diameter: 0.25 mm; temperature: 75°C and detector was flame ionization detector (set at temperature: 200°C). Helium was used as carrier gas.

Determination of kinetic parameters

A series of TG measurements were performed at different heating rates of 2.5, 5, 10, and $20^\circ\text{C min}^{-1}$ from 25 to 800°C to study the kinetics of the copolymers decomposition. The kinetic aspects for activation energy (E) and pre-exponential factor (A) determination using the isoconversional method of Flynn and Wall has widely been described and they are not presented here.^{13,19-23}

Since successive mass loss events were observed in the TG curves, the temperature ranges for each process were considered between the minimum values in the DTG curves, as an approach. Then conversions of 30, 35, 40, 45, 50, 55, 60, 65, 70, and 75% of sample weight loss were used for subsequent calculations, for each process. The kinetic data were ana-

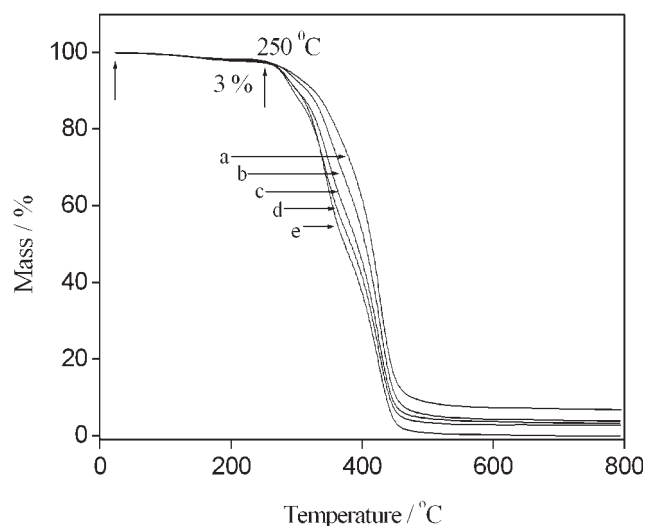


Figure 1 TG curves for the copolymers: a, TB3070; b, TB4060; c, TB5050; d, TB6040; and e, Tb7030.

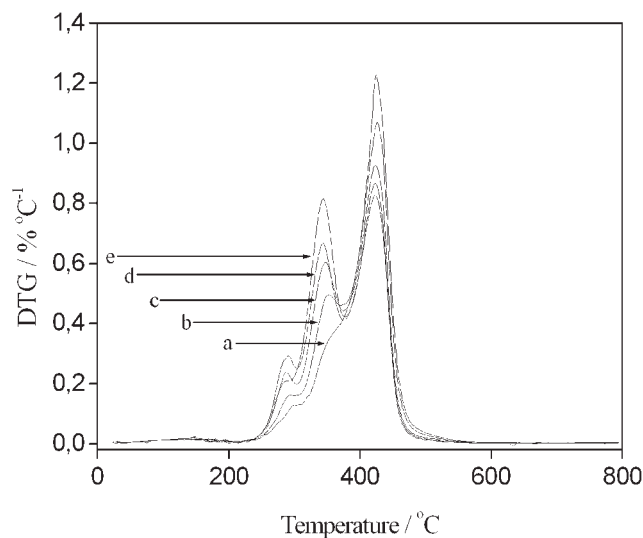


Figure 2 DTG curves for the copolymers: a, TB3070; b, TB4060; c, TB5050; d, TB6040; and e, Tb7030.

lyzed by the Thermal Specialty Library version 1.4 (TA Instruments) software.

RESULTS AND DISCUSSION

Thermal behavior

Figures 1 and 2 show the TG and DTG curves for copolymers TB in different weight ratios of monomers TEGDMA and BisGMA in the mixture, respectively.

It is observed a mass loss of about 3% until 250°C for all the copolymers studied. The thermal decomposition starts at about 250°C (T_0) and is characterized basically by three events for the copolymers with different weight ratios of monomers. Thermal decomposition revealed to be a complex, heterogeneous process, consisting of several partial reactions and several stages of decomposition as expected for a highly crosslinked polymer. These three events can be seen in the DTG curves in the Figure 2, characterized by three peaks with maximum temperature of the first (T_1), second (T_2), and third (T_3) event. The maximum of each peak corresponds to the maximum degradation rate attained in each event. Temperature of the third event was constant at 424°C while for the first and second events variations in T_1 and T_2 was observed as showed in Table I.

The loss mass observed in the onset of the thermal decomposition process can be associated the degree of conversion of the copolymers. In general the unreacted double bonds may either be present as free monomer or as pendant groups (radicals) trapped on the network. Moreover, trapped radicals present certain implications with respect to the long-

TABLE I
Temperature at Maximum of Thermal Decomposition
for Each Sample of Copolymer

Copolymers	T_1 (°C)	T_2 (°C)	T_3 (°C)
TB3070	298	360	424
TB4060	293	350	425
TB5050	287	347	424
TB6050	290	345	424
TB7030	289	343	424

term properties of the materials. For example, the unreacted monomer may leach from the polymerized material and irritate the soft tissue. TEGDMA is suspected to be propitious to bacterial growth around the restoration.^{24–26} When the copolymers were submitted to thermal treatment (isotherm of 200°C by 15 min) before of thermal analysis is not observed the loss mass in the beginning of the process (Fig. 3). Moreover, this mass loss may be assignment of the presence of free monomers or pendant groups in the copolymers structure.

Thermal treatment and decomposition of TB copolymer

The analysis of intermediates by GC of the condensed material extracted after thermal treatment at 220°C for the TB copolymers shows the presence of the methacrylic acid (MA) and 2-hydroxyethyl methacrylate (HEMA) with retention time of 10.2 and 11.7 min, respectively, (Fig. 4). MA and HEMA are decomposition products of monomers TEGDMA and BisGMA.²⁷

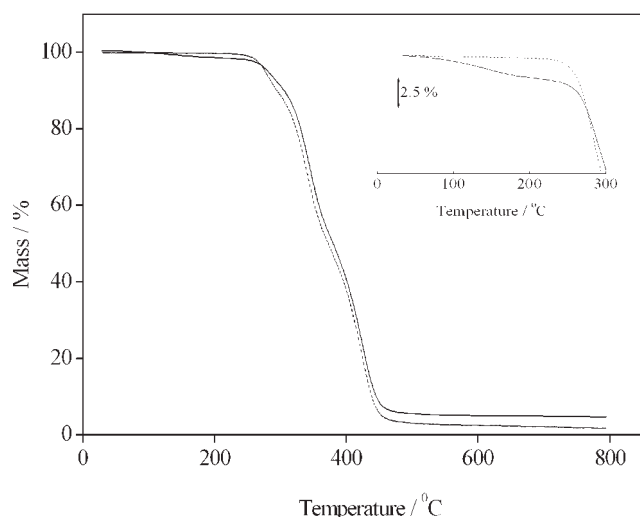


Figure 3 TG curves before (—) and after (---) the thermal treatment (isotherm at 200°C by 15 min).

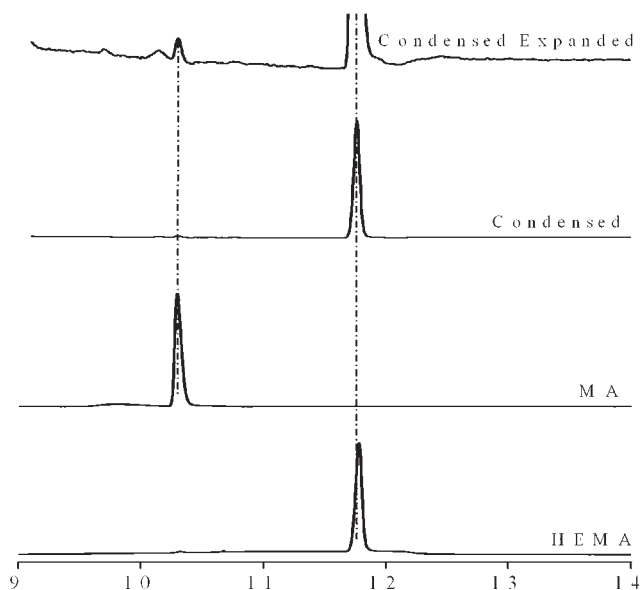


Figure 4 GC of the condensed material obtained from analyses of TB copolymer submitted to thermal treatment.

In fact the mass loss in the beginning of the thermal decomposition can be assigned to the evaporation and scission of material present in the copolymers (monomers that not converted and/or radicals trapped in the polymer structure). MA is produced by scissoring of unpolymerized monomers BisGMA and TGDMA. HEMA is also produced from TEGDMA monomers. It is not observed the presence of MA and HEMA at temperature up to 250°C suggesting that the scission of TEGDMA and BisGMA occurred in the initial phase of the thermal decomposition, and their amounts decreased with increasing degree of conversion of the copolymers.²⁸

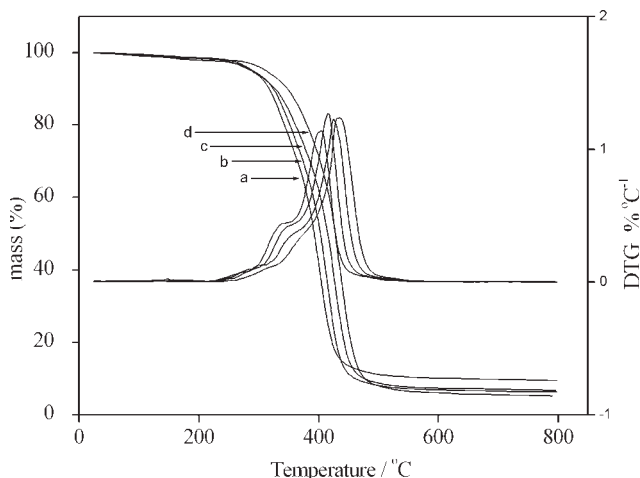


Figure 5 TG and DTG curve of TB3070 at different heating rates.

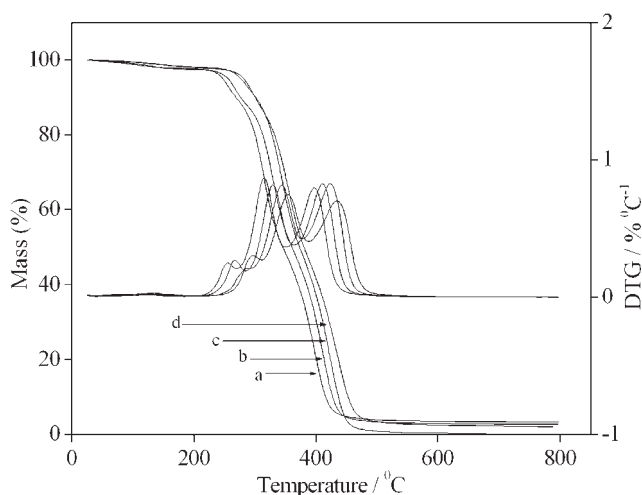


Figure 6 TG and DTG curve of TB7030 at different heating rates.

Decomposition kinetics

Figures 5 and 6 shows the overlaid mass loss and DTG curves for the TB3070 and TB7030 copolymers at several heating rates of (a) 2.5 C min^{-1} , (b) 5 C min^{-1} , (c) 10 C min^{-1} , and (d) $20^\circ\text{C min}^{-1}$.

The results show a dependence of thermal degradation behavior of the polymer on the heating rate (a, 2.5; b, 5.0; c, 10; and d, $20^\circ\text{C min}^{-1}$). The TG curves revealed that the whole curve is moved towards higher temperatures when the heating rate is increased (Figs. 5, 6). It can be observed that with higher proportion of monomer TEGDMA in the copolymer composition higher the evidence of presence the three stages on the decomposition processes (Fig. 2). The BisGMA is more viscous than TEGDMA and viscosity is a measure of the resistance of molecules to flow and high viscosity value is indicative of the presence of intermolecu-

lar interactions. These interactions can cause a decreased mobility of monomer molecules during polymerization and also a decreased flexibility of the corresponding polymeric network. With the Flynn and Wall method used to compute the TGA data, a plot of $\log \beta$ versus $1/T$ at different conversions was obtained to give a series of straight lines. If a particular specimen decomposition mechanism was the same at all conversion levels, the lines present the same slope but this is not our case with the presence of three events for the all compositions of polymers studied. Therefore, these three events were separated using different temperatures intervals once the mechanism of the thermal decomposition of copolymers TB is a complex mechanism consisting of several partial reactions. For each event activation energy (E_a) was determined from the slope, which is the value of derivate term $(d \log \beta)/[d(1/T)]$ using the Flynn and Wall method.

The values of E_a and pre-exponential factor A and 60 min half-life temperature at different conversion levels from 30 to 75% for the copolymer TB7030 are given in Table II. The other compositions of copolymers presented the same behavior and the same treatment was made.

E_a shows dependency on the degree of conversion [Table II, Figure 7]. Variations of E_a values or the thermal decomposition processes for the copolymers confirm a multi-step reaction mechanism of decomposition. Basically three stages of decomposition of TB copolymers can be expected. In the first stage it can be assigned to the decomposition of the free monomers in the beginning of the processes (between 200 and 250°C) and the thermal curing of these monomers. The second stage may be attributed to the scission the decomposition products highly linked in the copolymers chain and the third stage can be associated with decomposition reactions that

TABLE II
Kinetics Parameters at Different Conversion Levels for Each Event of Process the Thermal Decomposition to TB7030 Copolymer

Conversion %	Activation energy (kJ mol^{-1})			Log [pre-exp factor $1/\text{min}^{-1}$]			60-min Half-life temp ($^\circ\text{C}$)			
	TB7030	1°	2°	3°	1°	2°	3°	1°	2°	3°
30		118.0	166.3	218.4	10.62	13.71	16.13	217.9	282.1	358.3
35		117.7	166.5	220.8	10.62	13.73	16.30	216.7	281.9	359.0
40		117.4	166.3	222.2	10.61	13.71	16.41	215.6	281.7	359.6
45		117.2	166.0	222.9	10.62	13.69	16.44	214.6	281.5	360.2
50		117.2	165.7	221.2	10.63	13.67	16.30	213.7	281.4	360.3
55		116.9	165.5	219.4	10.63	13.65	16.16	212.8	281.4	360.4
60		116.4	165.3	217.2	10.63	13.63	15.97	211.8	281.5	360.4
65		115.8	165.4	215.3	10.60	13.63	15.81	210.6	281.7	360.4
70		115.2	165.6	213.3	10.56	13.64	15.65	209.5	282.0	360.4
75		114.7	166.1	211.6	10.50	13.64	15.50	208.4	282.51	360.5

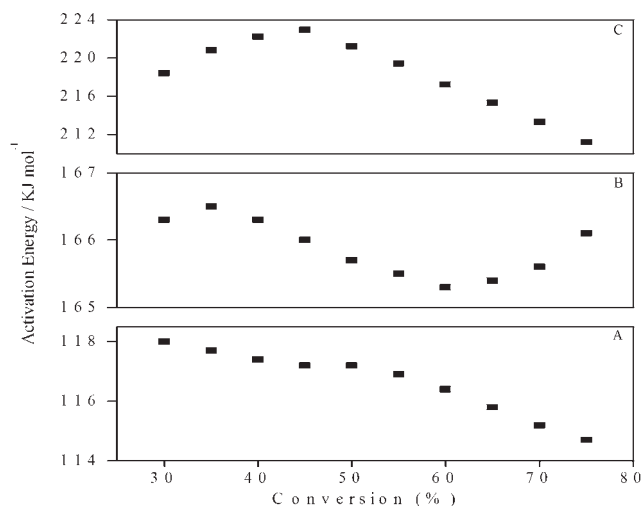


Figure 7 Activation Energy versus different conversion levels [(A) first event, (B) second event, and (C) third event] to the TB7030 copolymer.

lead to the formation of low molecular weight products.

CONCLUSIONS

Thermal decomposition of TB copolymers is a complex, heterogeneous process, consisting of several partial reactions characterized by basically three events during the processes. The presence of three events is more evidence when the proportion of the TEGDMA monomer is higher than BisGMA in the copolymer mixture and this behavior can be assigned to a difference of viscosity of the monomers. The beginning of the process was attributed to a mass loss until about 220°C due to the presence of the free monomers and/or radicals trapped in the polymer structure. The intermediates in this phase MA (methacrylic acid) and HEMA (2-hydroxyethyl methacrylate) were characterized by gas chromatography as products of degradation of monomers BisGMA and TEGDMA. When the polymer was submitted to thermal treatment the mass loss was not observed. Moreover, with the thermal treatment occurred, an increase of degree of conversion of the copolymers

suggest that MA and HEMA were generated from the residual monomers.

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