

Thermal degradation behavior of polymethacrylates containing amine side groups

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ARTICLE INFO

Article history:

Received 2 October 2007

Received in revised form 1 July 2008

Accepted 7 July 2008

Available online 16 July 2008

Keywords:

Thermal degradation

TGA/FTIR

Poly(aminomethacrylates)

PDEAEM

PMEET

ABSTRACT

The thermal degradation behavior of polymethacrylates containing amine groups such as poly(*N,N*-diethyl aminoethyl methacrylate), PDEAEM, and poly(*N*-ethyl-*m*-tolyl-aminoethyl methacrylate), PMEET, has been studied using thermogravimetry coupled with infrared spectroscopy (TGA/FTIR). PDEAEM showed two degradation stages whereas PMEET displayed only one. The thermal degradation of PDEAEM initially takes place through ester cleavage of the polymethacrylate, generating volatile tertiary amines and alcohols and polymethacrylic anhydride in the remaining solid material. This is followed by further fragmentation of the modified polymeric chain formed. It was also observed that storage of the original polymer affected the thermal decomposition behavior of PDEAEM. The main thermal degradation pathway for PMEET is an immediate backbone chain scission to yield oligomers.

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1. Introduction

Polymers based on aminomethacrylates as poly(diethylaminoethyl methacrylate) and poly(dimethylaminoethyl methacrylate) have attracted much attention in recent years because the tertiary amine function allows to fix active substances onto their surfaces [1]. Thus, these types of polymers and their copolymers have been used in various fields such as waste water purification and paper production [2], elaboration of membranes for nanofiltration and ion-exchange resins [3] and biomedical applications where absorption or desorption of proteins is controlled by temperature changes [1] as well as drug delivery systems and sensors [4] among others. Furthermore, polyelectrolytes based on polyaminomethacrylates exhibit a high flocculating activity when added to different dispersion systems, including synthetic latex. In the latter case, the flocculation mechanism is primarily determined by the interaction of the polyelectrolyte with anionic surfactant-latex stabilizers [5,6]. Moreover, like all tertiary amines, polymers containing amine groups can be easily transformed into quaternary ones to create cationic centers (ammonium salts) [1].

Despite the applications mentioned above, there are very few papers related to the thermal decomposition of polymethacrylates

containing amine groups. In this context, Zulfiqar et al. [7] reported the thermal decomposition of poly(*N*-methyl-*N*-tertbutyl-aminoethyl methacrylate), PMTBAEM while Lin et al. [8] studied the thermal degradation of the Eudragit E-100 polymer, which is a terpolymer of butyl methacrylate, 2-dimethylaminoethyl methacrylate and methyl methacrylate, in a composition of 1:2:1, respectively.

In general, it has been observed that the thermal degradation behavior of polymethacrylates depends on the type of alkyl side chain constituting the ester. Thus, it has been observed that some polymethacrylates degrade relatively easily to monomers on heating, whereas some others undergo ester decomposition without giving the corresponding monomer. Furthermore, many polymethacrylates, including those that degrade to monomers, suffer ester decomposition at relatively high temperatures followed by elimination of small molecules and formation of cyclic anhydride structures [9].

The aim of this work was to gain some fundamental knowledge on the thermal degradation pathways of two polymethacrylates containing an amine group in the side chain. Poly(*N,N*-diethyl aminoethyl methacrylate) and poly(*N*-ethyl-*m*-tolyl-aminoethyl methacrylate) were studied by Thermogravimetry coupled with Fourier Transform Infrared Spectroscopy (TGA-FTIR) analyzing the evolved gases during their thermal degradation. In addition, the partially degraded polyaminomethacrylates were also studied by both IR spectroscopy and Differential Scanning Calorimetry (DSC).

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2. Experimental

2.1. Materials

Poly(*N,N*-diethyl aminoethyl methacrylate), PDEAEM, and poly(*N*-ethyl-*m*-tolyl-aminoethyl methacrylate), PMEET, were prepared from their corresponding monomers using AIBN as initiator. DEAEM monomer was purchased from Aldrich Co. whereas MEET monomer was synthesized as reported in a previous work [10] by the reaction of methacrylic anhydride and 2-(*N*-ethyl *m*-toluidine) ethanol (Aldrich) using a triethylamine/dimethylamino pyridine system as a catalyst.

PDEAEM was prepared by bulk polymerization while PMEET was obtained by solution polymerization using toluene as solvent. Monomer and initiator were placed in glass Pyrex ampoules, which were closed and kept in an oven at 70 °C for 48 h (solutions were previously degassed with oxygen-free nitrogen for 5 min). Polymers were purified by dissolution in acetone and precipitation in water (at least three times) and finally dried under vacuum. PDEAEM was a transparent gummy solid, whereas PMEET was a yellowish brittle solid. The chemical structures of these polymers are shown in Fig. 1.

2.2. Thermal degradation study

Conventional TGA was performed using 10 mg of polymers with a Perkin Elmer TGA-7 from 50 to 600 °C and a heating rate of 10 °C/min under a nitrogen atmosphere.

The degradation of the polyaminomethacrylates was also followed from the analysis of the evolved volatile products. These experiments were performed using a Perkin Elmer TGA/FTIR system consisting of a TGA Pyris 1 coupled to a Spectrum GX FTIR. For these experiments, 20–25 mg samples were heated from 50 to 600 °C at a rate of 10 °C/min under nitrogen atmosphere. The flow rate of nitrogen into the cell for TGA/IR experiments was approximately 80 mL/min. The line that transfers the evolved gases from the TGA to the FTIR and the IR cell was maintained at 250 °C. IR spectra were recorded in the spectral range from 4000 to 650 cm⁻¹ with a resolution of 4 cm⁻¹. For each polymer, 38 spectra were obtained, each one as a result of averaging eight scans.

As thermogravimetry coupled with infrared spectroscopy studies only provides information regarding the released gases from the degraded polymer at various stages, polyaminomethacrylates were also partially degraded and examined by FTIR and DSC. For these experiments, samples were taken from the TGA pan when a significant weight loss was detected. Glass transition

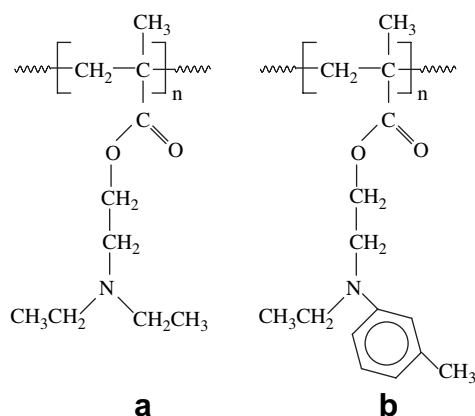


Fig. 1. Chemical structures of (a) PDEAEM and (b) PMEET.

temperatures (T_g) were measured with a Perkin Elmer Differential Scanning Calorimeter, DSC-7 by using ca. 10 mg of the sample. The polymers were encapsulated in aluminum pans and for PDEAEM, a temperature range of 0–180 °C was used, whereas for PMEET a temperature range of 40–180 °C was used, at a heating rate of 10 °C/min. T_g was taken as the midpoint of the transition.

3. Results and discussion

3.1. Degradation of poly(*N,N*-diethyl aminoethyl methacrylate), PDEAEM

Weight loss thermograms and the corresponding derivative obtained by conventional TGA are shown in Fig. 2a. As can be seen, this polymer presented two well-defined degradation stages at 356 and 426 °C. Similarly, the corresponding Gram–Schmidt plot showed the occurrence of two steps of evolved gases (Fig. 2b) located at 365 and 440 °C, which are related to the peaks of the DTGA curve. Fig. 3 shows the stack plot of IR spectra of evolved gases from thermal degradation as a function of temperature while Fig. 4 shows the IR spectrum of the evolved gases at the maximum evolution rate for each decomposition step. Finally, Fig. 5 shows the FTIR spectra of the partially degraded samples just after heating at 385 and 472 °C (these temperatures were chosen as it was considered that the partial degradation was completed) and compares these to the spectrum of the non-degraded polymer.

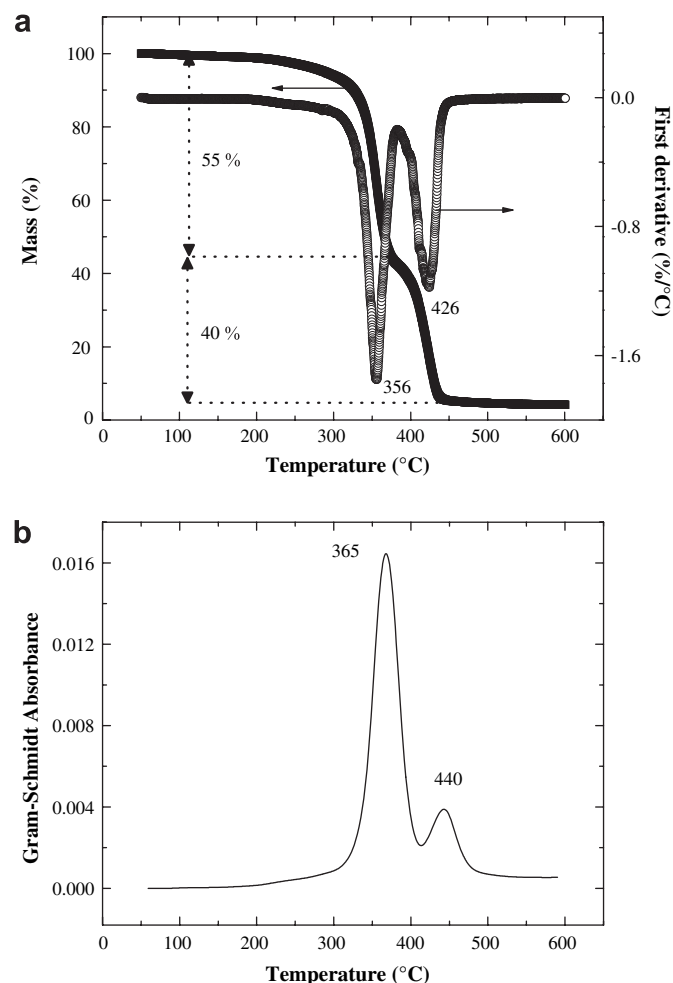


Fig. 2. TGA and DTGA curves (a) and Gram–Schmidt plot (b) for PDEAEM.

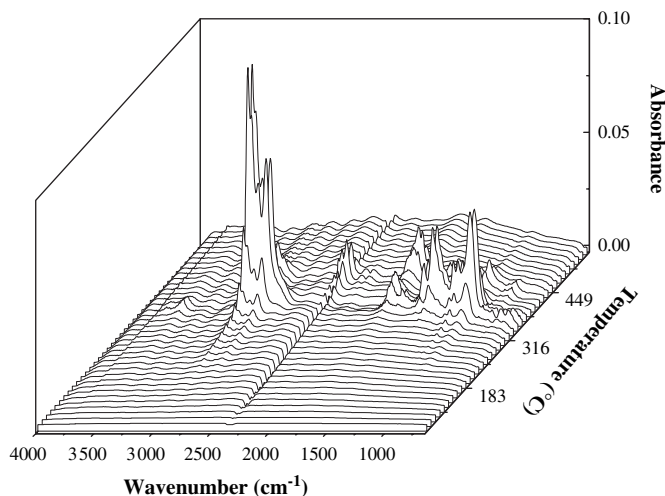


Fig. 3. Stacked plot diagram of the evolved gases for PDEAEM.

3.1.1. First stage

The FTIR spectrum of the evolved gases during the first weight loss (Fig. 4a) showed bands at 2974, 2941, 2885 and 2817 cm^{-1} , related to C–H stretching vibrations from aliphatic groups. The presence of these compounds was confirmed by the appearance of bands at 1455 and 1385 cm^{-1} , which were associated to C–H bending from methyl and methylene groups, respectively. Bands at 3510 and 1067 cm^{-1} , were also observed and were explained by the presence of alcohols. It is important to mention that the intensity of the band at 1067 cm^{-1} may be due to the presence of both O–H bending and C–O and C–N stretching vibrations from alcohols and aliphatic amines, respectively. In addition, the weight loss associated with the first degradation stage was *ca.* 55 wt% which is approximately the same as the total loss of the diethyl aminoethyl groups from PDEAEM, released at this stage.

In addition, the FTIR spectrum of the evolved gases during the first weight loss exhibited a small band at 1742 cm^{-1} , which can be attributed to C=O stretching vibration of ester group in DEAEM monomer or oligomers. The appearance of an absorption peak at 1645 cm^{-1} , attributed to C=C stretching, would validate the presence of DEAEM monomer although the double bonds may also be

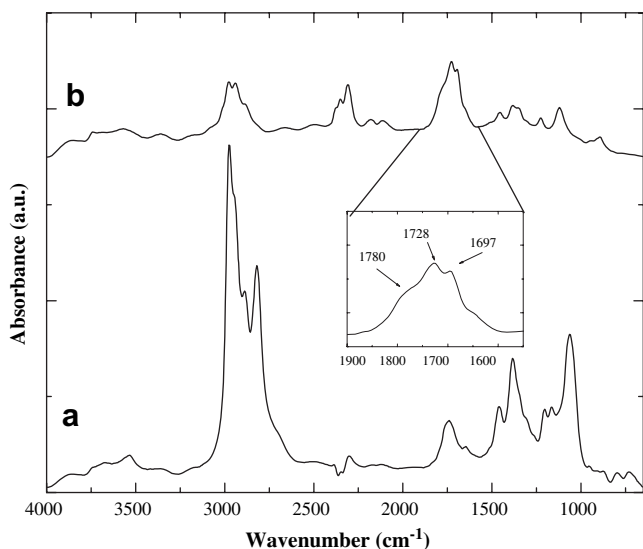


Fig. 4. FTIR spectra obtained at the maximum evolution rate for each decomposition step of the PDEAEM; (a) at 365 °C and (b) 440 °C.

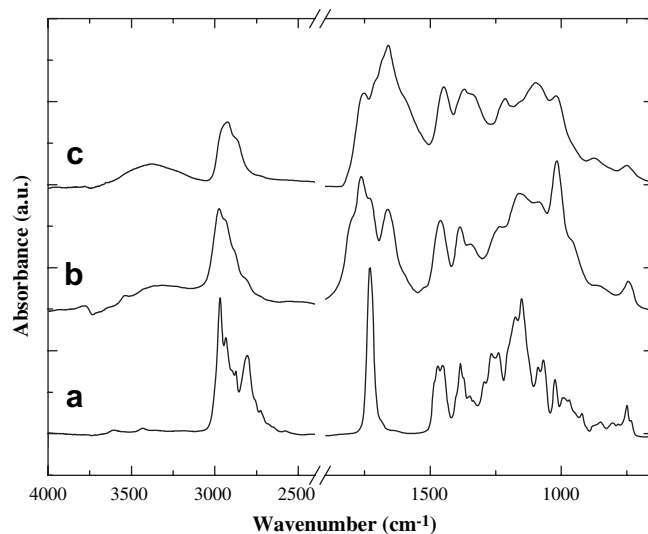


Fig. 5. FTIR spectra of PDEAEM; (a) non-degraded, (b) heated at 385 °C, and (c) heated at 472 °C.

present in the amines that are produced by the cleavage of the ester group of polymethacrylates. The presence of monomer and/or oligomers during thermal degradation of PDEAEM must be considered as secondary reaction as the amount produced was small.

Fig. 5b shows the IR spectrum of the PDEAEM heated at 385 °C, i.e. after the first gases emission region. It can be noted that the spectrum has bands that are similar to the non-degraded polymer (Fig. 5a) along with new bands at 1806 and 1762 cm^{-1} , which are typical of six-membered anhydrides obtained by intramolecular cyclization. The formation of these structures has been reported for other polymethacrylates and has been explained to be a result of the cleavage of ester linkage on the polymer [9,11–15]. Lin et al. [8] also reported the formation of six-membered cyclic anhydrides by thermally induced intramolecular ester condensation in samples of Eudragit E, a terpolymer containing 2-dimethylaminoethyl methacrylate. The DSC thermogram of PDEAEM heated at 385 °C (not displayed here) showed a glass transition temperature at 165 °C, which is 145 °C higher than that obtained for the non-degraded PDEAEM. The value of 165 °C falls within the range for the T_g of polymethacrylic anhydride as reported by Bajaj et al. [16], confirming that during the first degradation stage, this product is formed.

3.1.2. Second stage

The spectrum of the gases evolved during the second stage (Fig. 4b) showed bands attributed to aliphatic compounds (2978–2883 cm^{-1}) as well as bands related to CO_2 (2360, 2308 cm^{-1}) and CO (2182, 2112 cm^{-1}). In the carbonyl region, a broad band was observed around 1728 cm^{-1} which, after deconvolution, was clearly composed of at least three absorption bands (see inset in Fig. 4). The bands at 1780, 1728 and 1697 cm^{-1} were attributed to carboxylic acids in gaseous state, ester groups and ketone functionalities, respectively. The presence of carboxylic acid groups has been explained by hydrogen abstraction from the carbon atom in the beta-position of the ester from methacrylate groups remaining in degraded sample. This behavior has been reported previously by Bertini et al. [17] who studied the thermal degradation of several poly-*n*-alkyl methacrylates and detected 7.5–15.2 wt% of methacrylic acid in the evolved products during their decomposition. Similar results have been reported by Zulfiqar et al. [7] and Demirelli et al. [15].

The spectra also revealed the presence of ester groups in the released gases at this stage, which is in agreement with the observation that in some polymer ester groups are still present during thermal decomposition at high temperatures (*ca.* 440 °C) [8]. The presence of the ketones in the evolved gases could be due to decomposition of the polymethacrylic anhydride, formed in the previous stage, generating also CO₂ and CO as shown in Scheme 1. In this regard, several authors have reported the presence of ketone functionality, during the thermal degradation of some polymethacrylates, not only in the evolved gases [11,12] but also in the materials that remain post-decomposition [11,19].

The FTIR spectrum of the degraded polymer at 472 °C (i.e. after the second region of evolved gases) corresponded to that of a char (see Fig. 5c). It showed a band at 3375 cm⁻¹, attributed to O–H stretching, bands in the 2963–2867 cm⁻¹ range that are due to aliphatic content and a band at 1705 cm⁻¹ that could be related to ketone or carboxylic acid functionalities. Finally, the bands in the 1600–1450 cm⁻¹ range can be assigned to aromatic structures. This is supported by the findings of Fyfe and McKinnon [19] who reported that the thermal degradation of polymethacrylic anhydride at high temperatures produces phenolic compounds. This was concluded from the studies of high resolution ¹³C solid state NMR spectroscopy. Thus, the results from the present study seem to indicate that the degradation of PDEAEM follows a similar mechanism to be reported by these authors. It is also noted that although the polyanhydrides formed in previous stage have begun to decompose, the bands related to them (1800 and 1760 cm⁻¹) were still present (see Fig. 5c).

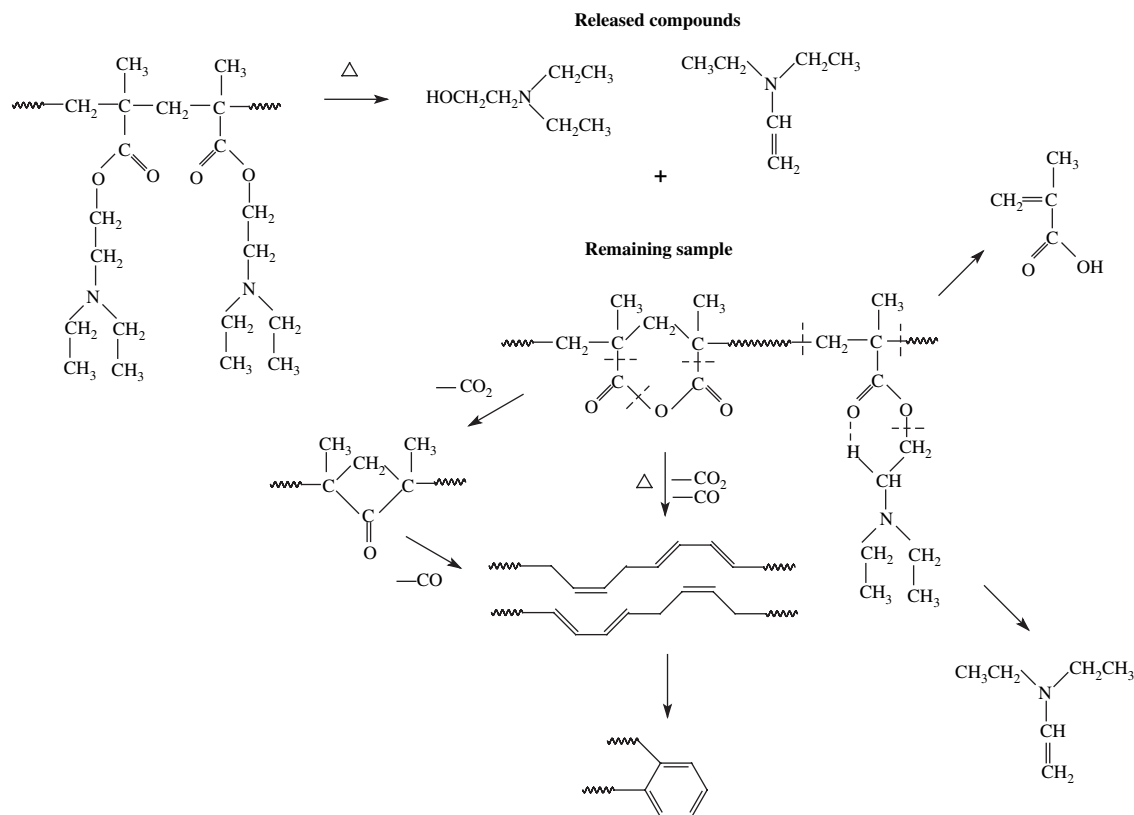
Thus, taking into account these results a mechanism for degradation of PDEAEM can be proposed. During the first stage, the cleavage of ester linkage yields tertiary amines and alcohols (in the released gases) and anhydride type structures (in the residual mass) At the second stage, the previously formed polyanhydride is

degraded to release mainly aliphatic compounds, CO₂ and CO, carboxylic acid and ketone functionalities all of which lead to aromatic structures. However, the formation of monomer and/or oligomers was also observed. Scheme 1 summarizes the suggested mechanism for thermal degradation of PDEAEM in line with the previous literature [18,19].

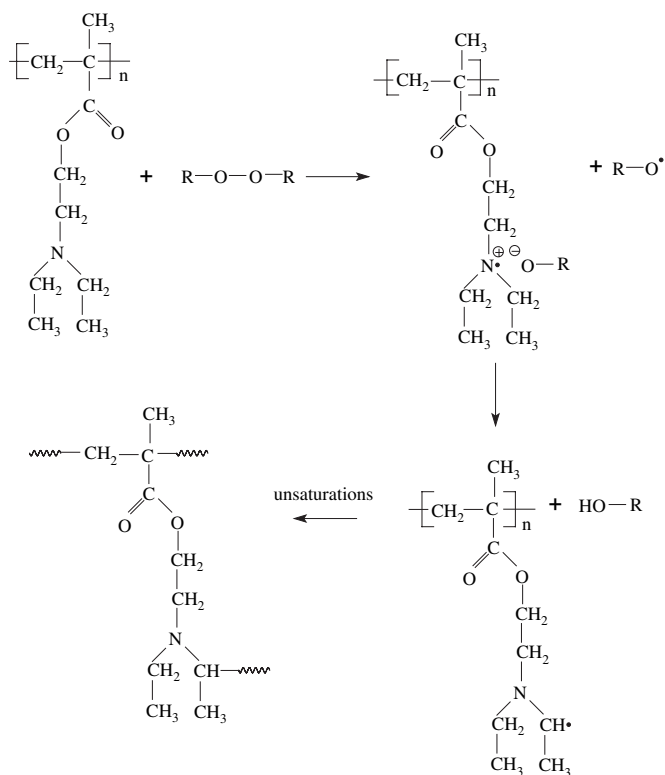
3.2. Effect of the storage on thermal degradation of the PDEAEM

It has been reported that crosslinking reactions can take place in several polyaminomethacrylates during storing [10,20,21]. The main explanations are (i) the formation of free radicals which are generated when the amine functionality (in this case from polymer) interacts with a free-radical initiator or (ii) the reaction of peroxidic impurities with tertiary amino groups of polymers.

In the present study, crosslinking of PDEAEM samples after 6 months storage was confirmed by the presence of an insoluble fraction (5–20%) in tetrahydrofuran (THF) solutions. Scheme 2 shows the suggested mechanism for additional crosslinking reactions in PDEAEM. This mechanism is based on the formation of free radicals by the redox system between tertiary amino groups from the polymer (reducing agent) and any peroxidic compounds present (oxidizing agent). Therefore, the amino radical generated is believed to attack unsaturation existing as end groups on the polymeric chain to yield a crosslinked polymer. In support of this mechanism, the presence of protons from double bonds in the polymer was confirmed by signals at 5–6 ppm in the ¹H NMR spectrum of PDEAEM (see Fig. 6). These signals are not related to residual monomer as the DEAEM exhibited signals at 6.15 and 5.67 ppm. Considering these observations, the thermal degradation behavior of crosslinked PDEAEM was studied. Fig. 7a shows the TGA weight loss and DTGA curves obtained for stored PDEAEM while Fig. 7b shows the corresponding Gram–Schmidt plot. Figs. 8 and 9



Scheme 1. Suggested mechanism for thermal degradation of fresh PDEAEM.



Scheme 2. Suggested mechanism for crosslinking reactions of PDEAEM.

show the stack plot of IR spectra of evolved gases as a function of temperature for thermal degradation of stored PDEAEM and FTIR spectra of the evolved gases at the maximum evolution rate for each decomposition step, respectively. Fig. 10 shows the FTIR spectra of the partially degraded PDEAEM after heating at 330, 400 and 478 °C.

As noted in Fig. 7a, the stored PDEAEM presents three well-defined degradation stages at 294, 375 and 440 °C which correspond to the three regions of evolved gases located at 300, 375 and 434 °C in the Gram-Schmidt plot. There was a clear difference in the thermal decomposition behavior of the stored PDEAEM with

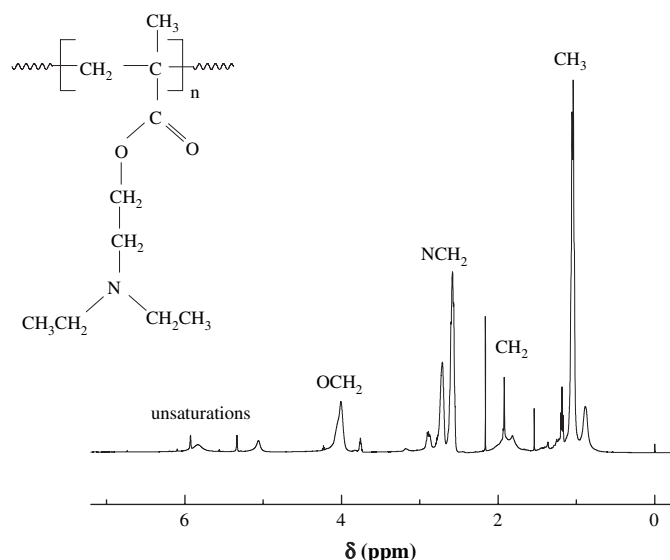


Fig. 6. ¹H NMR spectrum of PDEAEM.

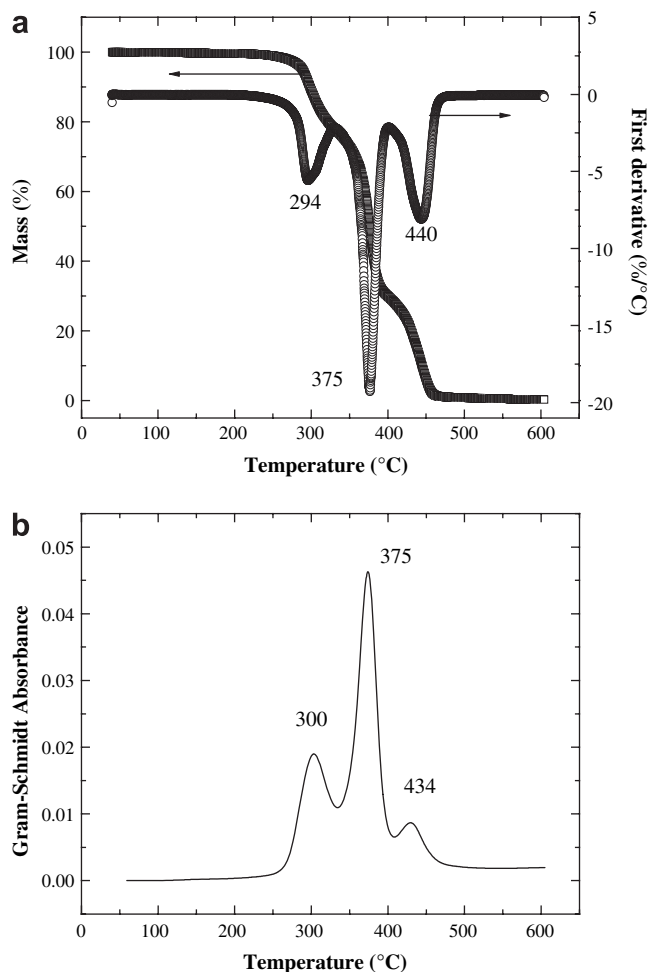


Fig. 7. TGA and DTGA curves (a) and Gram-Schmidt plot (b) for stored PDEAEM.

the as-prepared polymer which exhibited only two decomposition steps. Similar results were reported by Levchik et al. [22] where it was shown that a crosslinked polymer undergoes degradation in two steps while the original polymer (without crosslinking) degrades in a single step. The three stages of degradation are discussed in the next section.

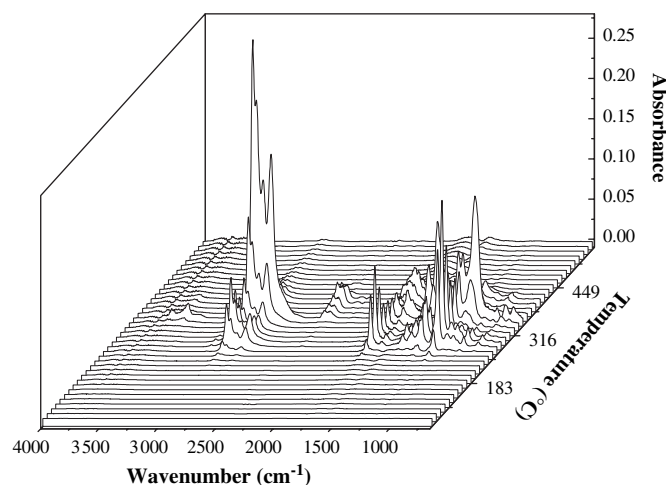


Fig. 8. Stacked plot diagram of the evolved gases for stored PDEAEM.

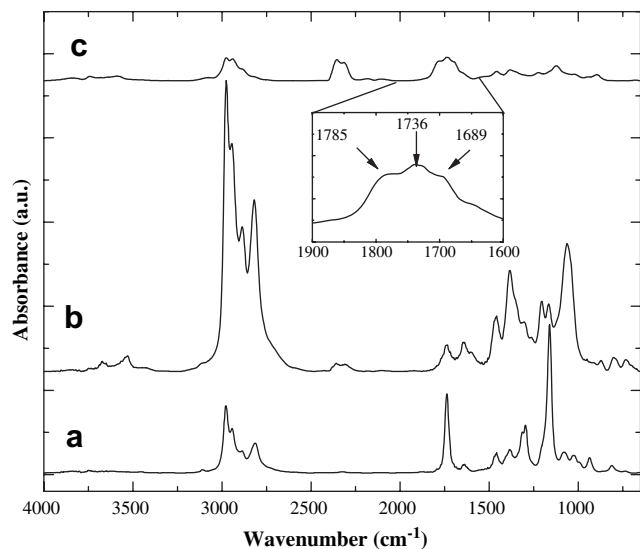


Fig. 9. FTIR spectra obtained at the maximum evolution rate for each decomposition step of the stored PDEAEM; (a) at 300 °C, (b) at 375 °C, and (c) 434 °C.

3.2.1. First stage

The FTIR spectrum obtained of the evolved gases during the first weight loss (Fig. 9a) showed bands at 2997, 2943, 2885 and 2811 cm^{-1} , related to C–H stretching from aliphatic groups. Bands at 1737 cm^{-1} , owing to the C=O stretching of ester group were also observed while the absorption at 1638 and 1160 cm^{-1} was attributed to C=C stretching and C–O stretching vibrations, respectively. This spectrum agrees well with that obtained for DEAEM monomer as seen in Fig. 11. Based on these results, it seems likely that monomer is produced during the thermal degradation of stored PDEAEM, although the presence of oligomers in the evolved gases cannot be discarded as their spectra are similar. Bertini et al. [17] carried out a study on the thermal degradation of poly-*n*-alkyl acrylates and poly-*n*-alkyl methacrylates and found that the poly-methacrylates yield monomer as the predominant degradation product under different pyrolysis conditions. In contrast, Zulfiqar et al. [7] reported that the main degradation products from thermally degrading poly-*N*-methyl-*N*-tertbutyl-aminoethyl methacrylate

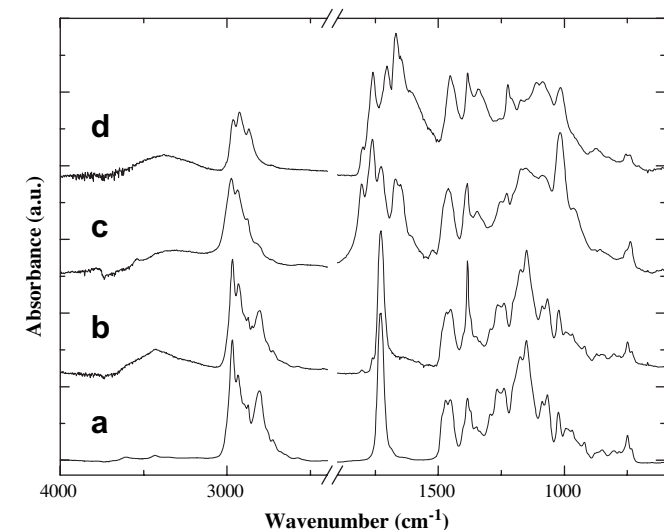


Fig. 10. FTIR spectra of stored PDEAEM; (a) non-degraded, (b) heated at 330 °C, (c) heated at 400 °C and (d) heated at 478 °C.

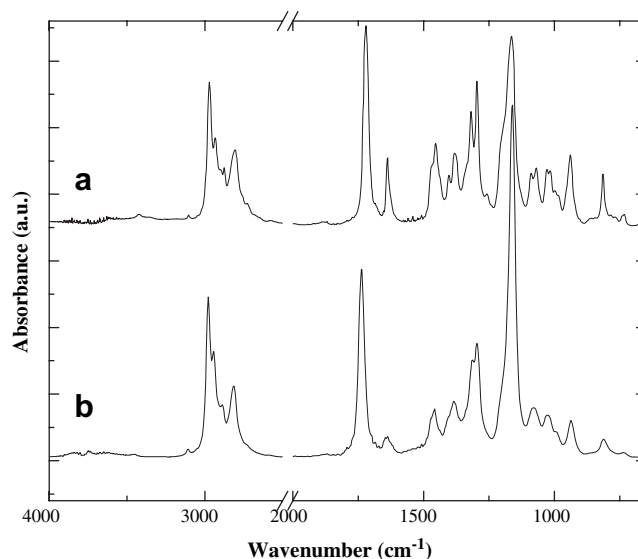


Fig. 11. FTIR spectra of (a) DEAEM monomer and (b) evolved gases at 300 °C.

(PMTBAEM), whose chemical structure is similar to PDEAEM, were oligomers although traces of its monomer were also identified.

If one considers that the first degradation stage of the stored PDEAEM can be attributed to the thermal decomposition products produced from the soluble fraction of stored PDEAEM, then it would be interesting to identify the composition of this fraction. Therefore, matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was applied using an Applied Biosystem Voyager System 6241. Spectra were recorded in reflector or linear delayed extraction mode at an acceleration voltage of 25 kV. The spectra represent averages of 200 consecutive laser shots. The extraction delay time was optimized to 500 ns. Samples were prepared by mixing a solution of matrix (2,5-dihydroxybenzoic acid: DHB) in dichloromethane/acetonitrile, and a solution of soluble fraction of stored PDEAEM in dichloromethane/acetonitrile mixture.

The MALDI-TOF mass spectrum for soluble fraction of stored PDEAEM is shown in Fig. 12. Clearly, the spectrum exhibits two series of peaks which were attributed to protonized molecular ions of the repeating DEAEM unit initiated with AIBN (*) and their corresponding sodium-cationized molecular ions (**). Average molecular mass of the species was calculated, and it was found that $M_n \approx 4380\text{--}4530$ Da; $M_w \approx 5670\text{--}6700$ Da and $PI \approx 1.25\text{--}1.53$. Thus, these results indicate that the soluble fraction of stored PDEAEM is formed by oligomers with a polymerization degree of ca. 24.

Fig. 10b shows the IR spectrum of partially degraded polymer at 330 °C, i.e. just after the first evolved gases had been detected. This spectrum is very similar to that obtained for non-degraded PDEAEM (Fig. 10a) as both spectra exhibited bands in the 2967–2804 cm^{-1} range, attributed to C–H stretching for methyl and methylene groups, a band at 1730 cm^{-1} attributed to C=O stretching of ester group and peaks in the 1475–1450 cm^{-1} range, corresponding to C–H bending vibration for methyl and methylene groups. Absorptions in the 1267–1149 cm^{-1} range could be assigned to C–O and C–N stretching vibrations of the ester and aliphatic amine groups. Finally, a band at 1020 cm^{-1} which is related to C–O–C vibration was also detected. Further bands at 3429 and 1630 cm^{-1} (attributed to O–H) vibration were also detected in the degraded polymer which were not present in the non-degraded stored polymer. This could be indicative that a few ester groups

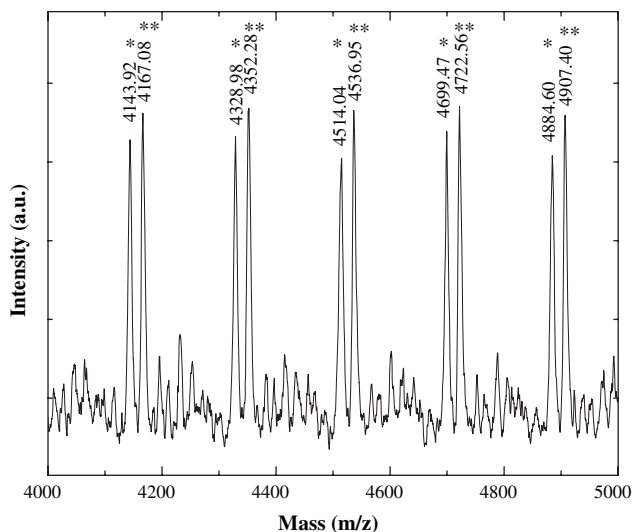


Fig. 12. MALDI-TOF spectrum of soluble fraction for stored PDEAEM.

underwent cleavage of ester linkage to yield hydroxyl compounds, probably of a carboxylic type. In addition, it was observed by DSC that the T_g was the same for both the degraded samples (at 330 °C) and the non-degraded sample.

Based on these results it can be implied that the first weight loss in the thermal degradation of stored PDEAEM is due to a depolymerization process to yield monomer, which generally starts at unsaturated chain-ends of the polymer. It is here where termination occurred by disproportionation during its synthesis [11], and the rupture of main chain occurred to yield oligomers. A similar behavior has been reported by several authors for other polymethacrylates [9,11,12,17,23]. However, the amount of monomer produced for this polymer (crosslinked PDEAEM), ca. 20 wt%, is lower than that reported by Bertini et al. [17] who obtained values ranging from 59 to 83% for other poly-*n*-alkyl-methacrylates.

3.2.2. Second stage

Fig. 9b shows the IR spectrum obtained of the evolved gases during the second stage of degradation of the stored PDEAEM. Clearly, bands associated with aliphatic compounds (2976–2818 cm^{-1}), carbon dioxide (2359 and 2310 cm^{-1}), ester groups (1737 cm^{-1}) and double bonds (1637 cm^{-1}) were observed. It should be noted that, at this stage, there is an increase on aliphatic to ester ratio (I_a/I_e), i.e. the ester band tends to disappear, in comparison to the first degradation stage. This could be explained by an additional release of compounds such as tertiary amines (produced by the cleavage of the ester groups of polymethacrylates) and a significant reduction in the emission of monomer and/or oligomers.

It is also possible that the additional compounds released were unsaturated tertiary amines as the intensity of ester group (1737 cm^{-1}) and double bonds (1637 cm^{-1}) were quite similar (see Fig. 9b). This reaction has also been suggested by Zulfiqar et al. [7] for thermal the degradation of PMTBAEM. In fact, Zulfiqar et al. [7] suggested that the H-abstraction from the carbon in the beta-position in the ester alkyl groups is the reason of the formation of the double bond. Therefore, the weight loss occurred at this stage could be attributed mostly to the loss of the diethylamino ethyl groups from polyaminomethacrylate.

FTIR spectrum of the evolved gases at this stage also exhibited bands at 1460 and 1388 cm^{-1} , which are associated to C–H bending from methyl and methylene groups, respectively, and peaks at 3510 and 1062 cm^{-1} , which could be related to the presence of alcohols. The intensity of the band at 1062 cm^{-1} is not only due to the

presence of O–H bending and C–O stretching vibration from alcohols but also due to C–N stretching vibration of aliphatic amines.

Fig. 10c shows the IR spectrum of the stored PDEAEM heated at 400 °C, i.e. after the second gases emission region. Once again, the spectrum exhibited bands related to the non-degraded polymer, although bands related to six-membered anhydrides were also observed. Therefore, the presence of slight amounts of carbon dioxide in the evolved gases was due to the decarboxylation of the anhydride structures as reported by other authors [19,24]. In agreement with this observation, this sample exhibited a T_g close to that reported for polymethacrylic anhydride.

Therefore, for the second degradation stage, it is suggested that the main thermal degradation pathway is the cleavage of ester linkage of the polymethacrylate structure which generates tertiary amines (in the evolved gases) and polymethacrylic anhydride (in the remaining sample).

3.2.3. Third stage

Typically, the results obtained at this stage were similar to those attained in the second stage of thermal degradation of pristine PDEAEM. Spectrum of the evolved gases during the third stage (Fig. 9c) showed bands attributed to aliphatic compounds, and bands related to CO_2 and CO. Similarly, a broad band around 1740 cm^{-1} was observed, which clearly arises from overlapping of three absorption bands (see inset in Fig. 9). The FTIR spectrum of the polymer degraded at 478 °C, i.e. after third evolved gases region, corresponded to that of a char and showed a band attributed to O–H stretching, bands due to aliphatic moieties and a band

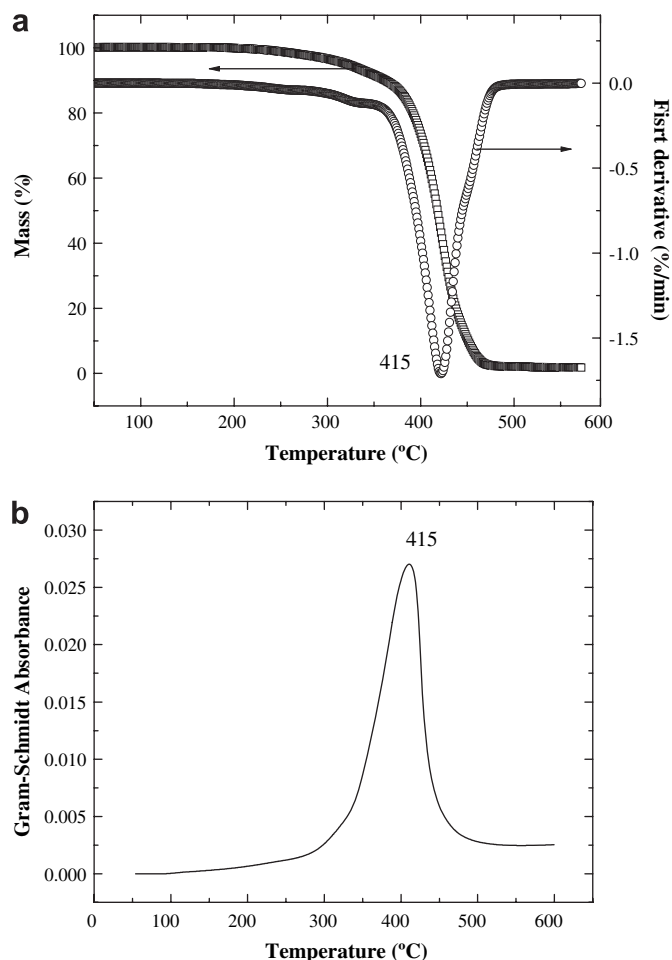


Fig. 13. TGA and DTGA curves (a) and Gram-Schmidt plot (b) for PMEET.

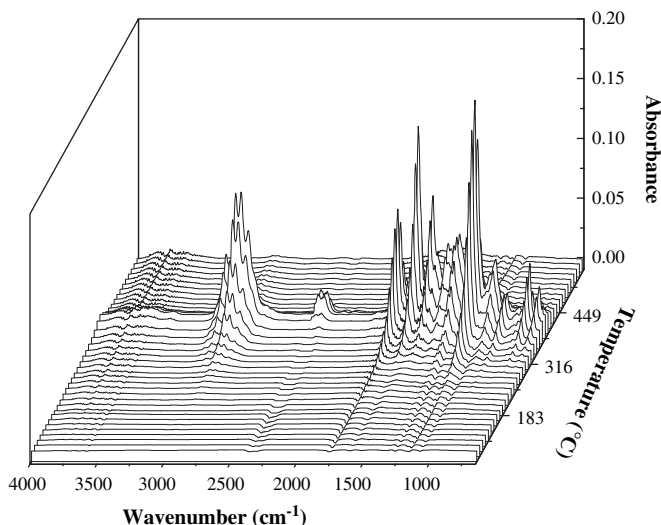


Fig. 14. Stacked plot diagram of the evolved gases for PMEET.

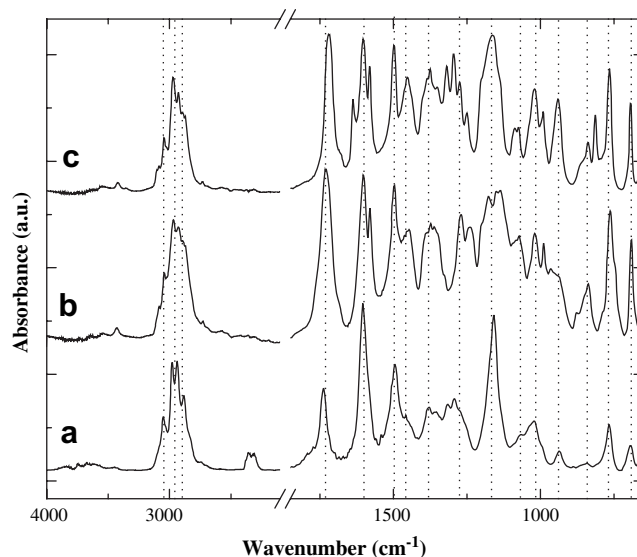


Fig. 15. FTIR spectra of (a) evolved gases at the maximum evolution rate and (b) PMEET and (c) MEET monomer.

at 1705 cm^{-1} , related to ketone or carboxylic acid functionalities. Finally, the bands in the $1600\text{--}1450\text{ cm}^{-1}$ range, were assigned to aromatic structures.

In contrast to the finding for freshly prepared PDEAEM, the decomposition mechanism for stored PDEAEM exhibited three stages. During the first stage of degradation, depolymerization yielded monomer and the rupture of main chain to yield oligomers; at the second stage, cleavage of ester linkage yielded tertiary amines and anhydrides; finally, at the third region, the previously formed polyanhydride underwent a degradation to release mainly aliphatic compounds, carboxylic acid and ketone functionalities.

3.3. Degradation of poly(*N*-ethyl-*m*-tolyl-aminoethyl methacrylate), PMEET

TGA weight loss curve and the corresponding derivate curve (DTGA) obtained for PMEET are shown in Fig. 13a. It is evident that

this polymer exhibited only one weight loss which started *ca.* $200\text{ }^{\circ}\text{C}$ and its maximum rate decomposition temperature was located at $415\text{ }^{\circ}\text{C}$. As expected, the Gram–Schmidt plot showed the existence of only one region of evolved gases (see Fig. 13b), clearly related to the peak of the DTGA curve.

Fig. 14 shows the stack plot of IR spectra of evolved gases from thermal degradation of PMEET as a function of temperature. Fig. 15a shows the IR spectrum of the evolved gases, at the maximum evolution rate. The spectrum presents bands at 3058 cm^{-1} , associated to $=\text{C-H}$ stretching, bands at 2980 , 2938 and 2886 cm^{-1} , related to C–H stretching for aliphatic compounds and a band at 1736 cm^{-1} due to carbonyl stretching of ester group. Bands related to C=C stretching of aromatic compounds were observed at 1604 and 1494 cm^{-1} while a band attributed to C–O stretching was located at 1158 cm^{-1} . As noted, this spectrum shows a good match to that reported for pristine (non-degraded) PMEET (Fig. 15b). This



Scheme 3. Schematic representation of the suggested mechanism for main degradation pathway of PMEET.

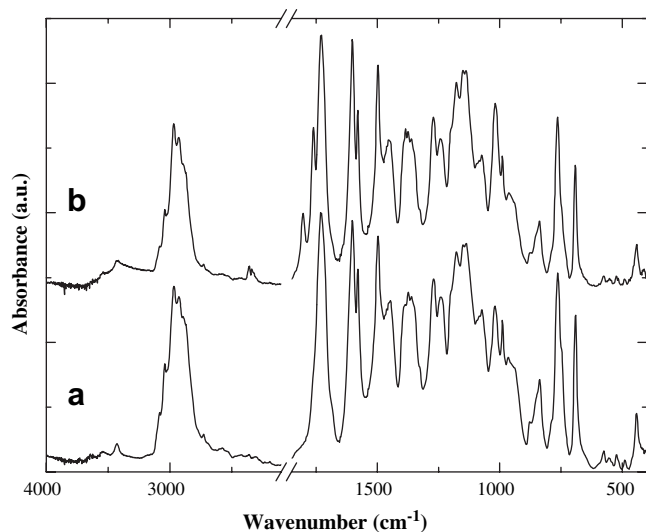


Fig. 16. FTIR spectra of PMEET; (a) non-degraded and (b) heated at 415 °C.

would imply that the predominant mechanism during thermal degradation of this polymer is the scission of the polymeric main chain to yield oligomers (see Scheme 3). Depolymerization to monomer, as exhibited by other methacrylates [7,17] was discarded due to the absence of a band at 1636 cm^{-1} in the FTIR spectrum of the evolved gases (this band was exhibited by the IR spectrum of the MEET and was related with the stretching vibration of $\text{C}=\text{C}$ from monomer).

Although these results support that the predominant degradation mechanism is the fragmentation of polymeric chain, the presence of bands at 2360 and 2310 cm^{-1} in the IR spectrum of the evolved gases indicates that other secondary reactions such as decarboxylation (release of CO_2) are also taking place during thermal decomposition of this polymer.

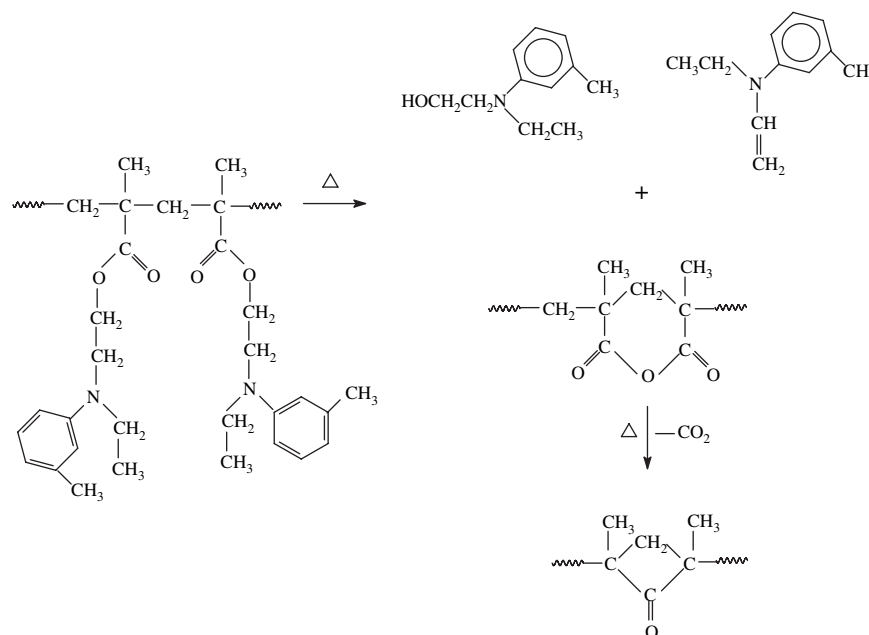
Despite the changes in chemical structure of polymers can be followed by FTIR after each significant weight loss, in the case of PMEET, the above procedure was not performed as this polymer

exhibited only one weight loss and the residual mass after this transition was very small (ca. 2 %wt). Therefore, the changes in the PMEET structure were studied by FTIR in the remaining mass at 415 °C , i.e. at the maximum rate of decomposition.

Fig. 16 shows the FTIR spectra of the non-degraded PMEET and the PMEET heated at 415 °C . Although the spectra are very similar (which confirms that the main pathway of thermal decomposition of this polymer is the fragmentation of the polymeric chain), PMEET heated at 415 °C shows two bands at 1803 and 1760 cm^{-1} , which were not displayed by the non-degraded PMEET. These bands are typical of a six-membered anhydrides obtained by intramolecular cyclization and their presence has been explained for other methacrylates by the cleavage of ester linkage of the polymer structure [9,11–15]. Taking into account these findings, the presence of small amounts of carbon dioxide in the evolved gases could be explained by decarboxylation of the anhydride structures as reported by other authors [19,24]. The cleavage of ester linkage yielded anhydride structures and 2-(*N*-ethyl *m*-toluidine) ethanol which was confirmed by the presence of an OH absorption band at 3410 cm^{-1} (see Scheme 4).

DSC thermograms of PMEET preheated at 415 °C showed a T_g of 56 °C which was lower than the 84 °C obtained for non-degraded PMEET. This fact could be attributed to the presence of PMEET oligomers in the remaining mass as it is well known that the T_g value increases with an increase in the molar mass of the polymers. Thus, if we assume that the residual mass at 415 °C contains PMEET oligomers, the expected T_g should be lower than that reported for the pristine polymer.

This molecular weight reduction was determined by GPC using an Agilent HPSEC 1100 chromatographer. This analysis was performed using a 10^4 – 10^6 ZORBAX PSM 1000S column, THF as solvent and 1 mL/min flow rate. The molecular weight was determined from the retention time using a calibration curve derived from monodisperse standard polystyrene (PS) and, the values of molecular weights of polymers were calculated as PS equivalents as the Mark–Houwink parameters were not available for PMEET. Unfortunately, the retention times obtained in this way for both undegraded PMEET and degraded PMEET were very similar to that of the solvent, i.e. the molecular weights were very low. Therefore,



Scheme 4. Suggested mechanism for the secondary reactions generated during thermal degradation of PMEET.

the hypothesis of molecular weight reduction needs to be proven by other techniques.

Taking into account the present results for this polymer, it can be suggested that the thermal degradation behavior of PMEET is similar to that obtained by Zulfiqar and co-workers [7] for PMTBAEM, who reported that the major proportion of cold ring fraction products obtained for this polymer consisted of modified MTBAEM oligomers, including some anhydride structures.

However, it is important to mention that TGA, TGA/FTIR and DSC are not enough to propose an unequivocal mechanism for the thermal degradation of polymers containing amine groups. Hence, TGA coupled to Mass spectrometry (TGA-MS) tests are currently being conducted and will be presented in a later communication.

Finally, it should be noted that an alternative explanation for the obtained results is that the thermal degradation behavior of polymethacrylates containing amine groups depends to some degree on temperature. Thus, for PDEAEM, because of the presence of aliphatic amines, side group elimination reactions may occur at a slightly lower temperature than its backbone scission, hence resulting in two TGA peaks. In the case of PMEET, because of the presence of aromatic amines, side group elimination may be delayed and may be identified at a slightly higher temperature. As only one degradation peak was detected, this process occurs simultaneously with the main-chain scission degradation.

4. Conclusions

PDEAEM samples as polymerized underwent thermal decomposition under nitrogen atmosphere in two stages. However, after 6 months storage, PDEAEM degradation occurred in three stages. The main products for the fresh polymer after cleavage of ester linkages were alcohols and both saturated and unsaturated tertiary amines in the released gases. In the remaining material, polymethacrylic anhydrides were formed and then further fragmented to ketones and aromatics with phenolic moieties. In addition, depolymerization was observed at the early stages of degradation of stored PDEAEM. In contrast, the main thermal degradation pathway for PMEET was an immediate backbone chain scission, although anhydride structures were also found to form through secondary reactions.

Acknowledgements

This work was supported by CONACYT (Mexico). A.M.F. thanks CSIC and CONACYT for partial financial support (project CSIC-CONACYT 2005MX0027). We also thank referee's comments and suggestions to improve this paper.

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