

Characterization of Methacrylic Polymers by Calorimetry and Infrared Analyses

CLAUDIA R. E. MANSUR, ELISABETH E. C. MONTEIRO

Instituto de Macromoléculas Professora Eloisa Mano/Universidade Federal do Rio de Janeiro (IMA/UFRJ),
P.O. Box 68525, 21945-970, Rio de Janeiro, RJ, Brazil

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ABSTRACT: Methyl methacrylate–methacrylic acid (MMA–MAA) copolymers, prepared by the action of concentrated nitric acid (65% HNO₃) on methyl methacrylate in absence of other reagents, were characterized using calorimetry (DSC) and infrared (FTIR) analyses. DSC curves of ester/acid copolymers suggested the anhydride formation at ~ 200°C, which was corroborated by thermogravimetry (TG). This structure was assigned by FTIR spectra. The results obtained by DSC data are in good agreement with the hydrolysis degree of the MMA–MAA copolymers obtained from chemical titration. The molecular weight of the copolymers were estimated by viscometry. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 345–354, 1998

Key words: methacrylic copolymers; calorimetry; infrared analysis; polyanhydride; hydrolysis degree

INTRODUCTION

The action of nitric acid on acrylic monomers has been investigated in this laboratory.^{1,2} It is an unusual reaction that occurs when methyl methacrylate (MMA) is mixed with concentrated nitric acid: A polymer of high molecular weight is formed. The results already obtained demonstrated the capacity of the concentrated nitric acid (HNO₃, 65%) to start the polymerization reaction when it is kept in contact with acrylic and methacrylic esters/acids, at room temperature and in the absence of the other components in the reaction mixtures. These reactions produced polymers of high molecular weight when the monomer is an acid, and ester–acid copolymers of high molecular weight when the monomer is an ester. The studies showed that the nature of the product depends on the temperature, the molar ratio monomer : HNO₃, and the reaction time.^{1–5}

The MMA–MAA copolymers studied were ob-

tained by the reaction of the MMA monomer and concentrated HNO₃. This acid in the liquid phase is in equilibrium with water and nitrogen oxide species, including the paramagnetic NO and NO₂, which act as initiator of the polymerization by the free radical mechanism. The MMA monomer does not polymerize with NO and NO₂, but the MMA molecules are slowly hydrolyzed by the HNO₃. The MAA molecules react quickly in the presence of NO or NO₂, generating a free radical species that attacks the MMA and forms high molecular weight chains.^{1,2}

The purpose of the present work is to study the MMA–MAA copolymers, prepared through this reaction, by calorimetry and infrared analyses to obtain detailed information on the molecular changes that can take place on heating of these copolymers.

Differential scanning calorimetry (DSC) is a suitable method for the polymer characterization. There is a long list of applications of this technique related to the thermal properties of materials such as the phase behavior of polymer systems, crystallization, heats and rate of polymerization, curing and decomposition.^{6–8} It is widely

Correspondence to: C. R. E. Mansur.

Table I Parameters Used for Viscometric Analyses¹⁴

Polymer	Solvent	Temperature (°C)	$K \times 10^5$ (dL/g)	α
PMMA	THF	25	7.5	0.72
MMA–MAA	THF	25	7.5	0.72
PMAA	Methanol	26	242	0.51

used as a method for determining the glass transition temperature (T_g) of polymers as well as compatibility studies.⁹

The poly(methacrylic acid) (PMAA), obtained through polymerization reaction of the monomer (MAA) with the concentrated nitric acid, was analyzed by DSC and the results showed that the reaction conditions have little influence on the glass transition temperature ($T_g \sim 161$ – 164°C).¹ The T_g values of poly(methyl methacrylate) (PMMA) can change with the tacticity of the polymer. The predominant syndiotactic PMMA presents the glass transition temperature at $\sim 115^\circ\text{C}$, while the isotactic configuration has a T_g at $\sim 45^\circ\text{C}$.¹⁰

EXPERIMENTAL

Materials

Commercial methyl methacrylate and methacrylic acid were distilled under vacuum to remove the inhibitor and kept in a refrigerator until use. Concentrated nitric acid (65% HNO_3 , sp. gr. 1.41) was obtained from REAGEN S.A. and used as received.

Preparation of Polymers

Poly(methyl methacrylate) (PMMA) was prepared by suspension polymerization technique,^{11,12} at 72°C , reaction time of 3 h, and with 2,2'-azobisisobutyronitrile as an initiator.

The polymerization reactions of the methyl methacrylate–methacrylic acid (MMA–MAA) copolymers were carried out at 30°C , volume ratio of monomer (methyl methacrylate) : HNO_3 1 : 5, and the samples were collected after 12, 24, 48, 120, and 196 h. The polymers obtained were purified using the same methodology described previously.^{1,2}

Poly(methacrylic acid) (PMAA) was obtained at 30°C , volume ratio of monomer (methacrylic acid) : HNO_3 1 : 1 and reaction time of 18 h.

Blanks for nitric acid and pure monomer were run and all reactions were carried out with at least two independent samples.

The MMA–MAA copolymers samples were

named according to the time reaction. Then, the MMA–MAA copolymers abbreviation are CRA-12, CRA-24, CRA-48, CRA-120, and CRA-196.

Characterization of Polymers

The molecular weight was evaluated by viscometry using a Mettler Toledo Low Shear 40 reometer operating with coaxial cylinders. The absolute viscosities of samples were measured between $\dot{\gamma} = 2.5 \text{ s}^{-1}$ and $\dot{\gamma} = 10 \text{ s}^{-1}$, where the solutions present Newtonian behavior. The reduced viscosities, η_{red} , were obtained by the expression¹³:

$$\eta_{\text{red}} = \frac{\eta_{\text{rel}} - 1}{c}$$

where c is the concentration of the solution in g/dL and η_{rel} is relative viscosity. Reduced viscosity data were plotted as a function of concentration and extrapolated to infinite dilution to obtain the intrinsic viscosity, $[\eta]$. The viscosity-average molecular weight was calculated using the Mark-Houwink-Sakurada equation¹⁴:

$$[\eta] = K\bar{M}_v^\alpha$$

where K and α are constants taken from the literature¹⁴ and are shown in Table I.

The MAA carboxyl group content of the copolymers was determined by dissolving the samples in tetrahydrofuran (THF) and adding 0.05 N ethanolic solution of NaOH and backtitrating the ex-

Table II Characterization of the Polymers

Polymer	Reaction Time (Hours)	\bar{M}_v (10^{-6})	COOH Content (%)
PMMA	—	0.69	—
CRA-12	12	1.60	24
CRA-24	24	1.81	29
CRA-48	48	2.02	32
CRA-120	120	2.02	43
CRA-196	196	2.23	51
PMAA	—	0.14	—

Table III Operating Conditions of DSC Analyses

Operation Condition	PMMA	PMAA	MMA-MAA Copolymers
Temperature range (°C)	30-150	—	30-200
	30-230	—	30-230
	100-300	100-300	100-300
Heating rate (°C/min)	10	10	10
Cooling rate (°C/min)	200	200	200
Atmosphere	nitrogen	nitrogen	nitrogen

cess with 0.05 *N* HCl using phenolphthalein as indicator.

Polymers characterization data are summarized in Table II.

Calorimetry

DSC scans were run using a Perkin-Elmer DSC-7 instrument equipped with TAS-7 software and a Perkin-Elmer PE-7700 professional computer. The equipment was calibrated with indium ($T_m = 156.6^\circ\text{C}$ and $\Delta H_f = 6.8 \text{ cal/g}$) as standard. The operation conditions are shown in Table III.

Samples of $\sim 10 \text{ mg}$ were sealed in aluminum pans and were submitted to repeated heating/cooling cycles in all temperatures intervals. After the first heating, the samples were cooled down at a cooling rate of $200^\circ\text{C}/\text{min}$.

The glass transition temperature was measured at the half-height of the heat capacity (ΔC_p) jump in the glass transition zone¹⁵ recorded during the second scan. The first-order transition temperatures were obtained at the maximum of the peak.¹⁶

Infrared Analyses

The FTIR analyses were carried out using a Perkin-Elmer FTIR 1720x spectrometer, equipped with diffuse reflectance accessory (DRIFT). The spectra were obtained at a 2 cm^{-1} resolution, 100 scans, and processed by a Perkin-Elmer IR data manager (IRDM). The recorded spectra, in absorbance units, were converted first to %Y and then to KM (Kubelka-Munk) units. The data processor presents the results in KM units using the Kubelka-Munk relationship between concentration and reflectance given by¹⁷:

$$F(R) = K/S = (1 - R)^2/2R$$

where: $F(R)$ is the Kubelka-Munk function, R is

the diffuse reflectance of an infinitely deep sample, relative to a transparent matrix, S is the scattering coefficient, and K is the absorption coefficient (proportional to concentration).

Thermogravimetry

The thermogravimetry was carried out using a Perkin-Elmer, model TGA-7 thermobalance. The thermobalance accuracy was within 0.1% and chromel-alumel thermocouple precision of $\pm 2^\circ\text{C}$. The thermocouple calibration was performed with alumel ($T_c = 163^\circ\text{C}$), nickel ($T_c = 354^\circ\text{C}$), and perkalloy ($T_c = 596^\circ\text{C}$) standards. The samples weighing $\sim 3.0 \text{ mg}$ were heated from 30 to 600°C with a heating rate of $10^\circ\text{C}/\text{min}$. The analyses were run with nitrogen atmosphere at a flow rate of $33 \text{ mm}^3/\text{min}$ for the sample and $60 \text{ mm}^3/\text{min}$ for the furnace.

RESULTS AND DISCUSSION

Polymers Characterization by DSC and FTIR Analyses

Figure 1 shows the DSC curves recorded from the second scan. It can be seen that the T_g shifts

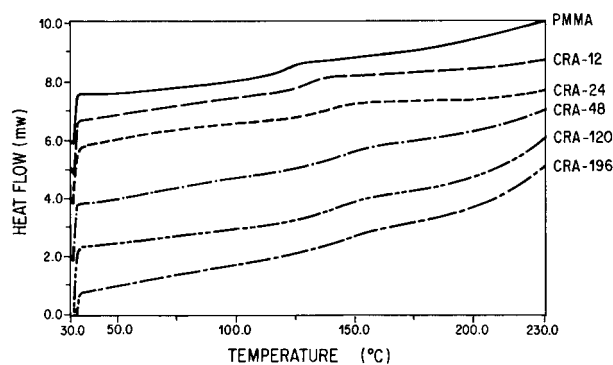


Figure 1 DSC curves of PMMA and MMA-MAA copolymers recorded between 30-230°C; second scan.

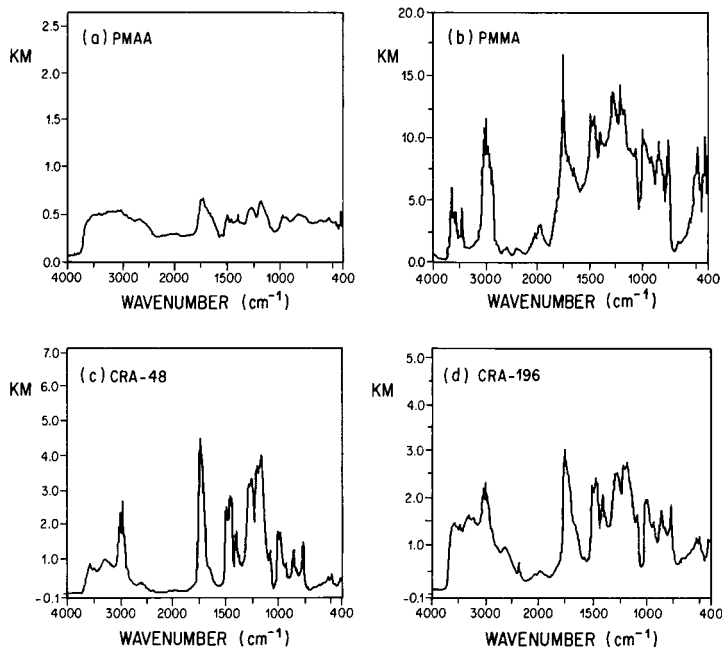


Figure 2 FTIR spectra (DRIFT) of PMAA, PMMA, and MMA-MAA copolymers analyzed before the calorimetric measurement recorded between 30–230°C.

towards high values with the increase of the polymerization reaction time, using nitric acid. This indicates the increase of the hydrolysis degree, as was discussed in previous works.^{1,2} The value of T_g obtained for the PMMA (115°C) sample suggests that this polymer is predominantly syndiotactic, as reported in the literature.¹⁰

It is also observed in Figure 1 that the width of the transition zone changes with the reaction time. This suggests the presence of different molecular environment among the polymer chains as proposed by Prud'Homme et al.,^{18,19} and is under investigation in our laboratory.

The calorimetric measurements were followed by infrared spectrometry. The pans were removed from the calorimeter, carefully opened, and the

remaining samples were analyzed in FTIR spectrometer using the diffuse reflectance accessory (DRIFT). Figure 2 shows the spectra of the PMAA, PMMA, and two MMA-MAA copolymers registered before the thermal analyses. The spectrum of the PMAA [Fig. 2(a)] presents the broad "bonded" O-H absorption (3500–2600 cm^{-1}), typical of carboxylic groups and the presence of C=O absorption at 1700 cm^{-1} . Figure 2(b) shows the spectrum of the PMMA that presents the C=O absorption at 1733 cm^{-1} and the typical C-O-C absorptions at 1192–1150 cm^{-1} . The spectra of the MMA-MAA copolymers [Fig. 2(c) and (d)] show the presence of the characteristic absorptions of the PMAA and PMMA; the broad "bonded" O-H absorption, C=O absorption, in-

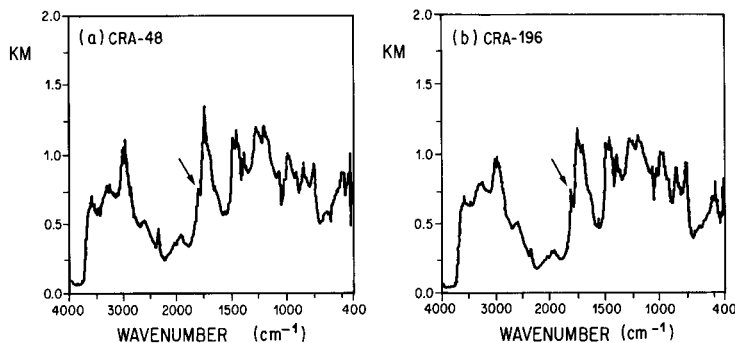
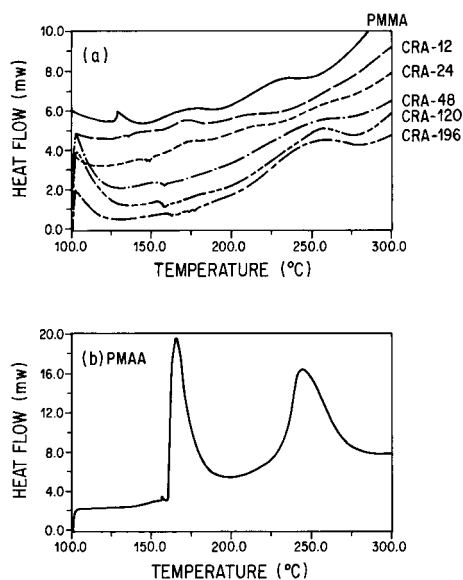


Figure 3 FTIR spectra (DRIFT) of PMAA, PMMA, and MMA-MAA copolymers analyzed after the calorimetric measurement recorded between 30–230°C.

Table IV Glass Transition Temperature for PMMA, PMAA, and MMA-MAA Copolymers

Polymer	Transition Recorded at First Scan (°C)	T_g (°C)		ΔC_p (J/g°C)	
		Range 30–230°C	Range 100–300°C	Range 30–230°C	Range 100–300°C
PMMA	230	115	121	0.307	0.337
CRA-12	210	129	129	0.248	0.245
CRA-24	211/257	137	134	0.203	0.243
CRA-48	251	144	135	0.215	0.215
CRA-120	254	145	135	0.180	0.194
CRA-196	246	146	136	0.173	0.258
PMAA	243	—	166	—	0.154

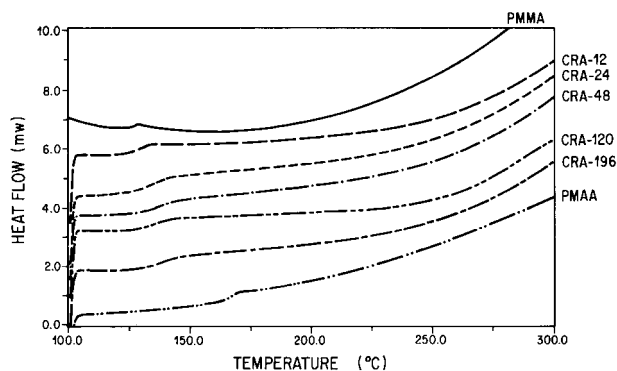
cluding the carbonyl peaks at 1700 and 1733 cm^{-1} , and the C—O—C absorptions. Figure 3 presents the spectra of these MMA-MAA copolymers registered after the thermal analyses. It can be observed that the absorptions shown in Figure 2, and an additional absorption at 1802 cm^{-1} , are characteristic of the anhydride carbonyl stretching vibration. This suggests the formation of polyanhydrides structures that may be partial and irregular. Grant and Grassie²⁰ investigated the thermal decomposition of PMAA and reported that when poly(methacrylic acid) is heated around 200°C, the main reaction is the anhydride formation. For this reason new measurements were carried out at a different temperature range (100–300°C).

**Figure 4** DSC curves of PMAA, PMMA, and MMA-MAA copolymers recorded between 100–300°C; first scan.

Polyanhydride Structure Determination

The glass transition temperature (T_g) and ΔC_p of PMMA, PMAA, and MMA-MAA copolymers, as well as the transition recorded on the first scan are listed in Table IV for the two temperature ranges. Figures 4 (first scan) and 5 (second scan) present the DSC curves recorded from 100 to 300°C. The curves from the first scan are quite different from the second; they suggest that the first-order transition corresponds to the formation of polyanhydride through the methanol elimination, as shown by Jamieson and McNeill.²¹ The second scan indicates that the polyanhydride production may be completed and that the T_g values can be obtained.

From Table IV it can be seen that the T_g values obtained in the second temperature range (100–300°C) are lower than that observed in the first range (30–230°C). The behavior of this transition observed in the second temperature range can be due to the polyanhydride formation. The high values measured in the first range can be attributed

**Figure 5** DSC curves of PMAA, PMMA, and MMA-MAA copolymers recorded between 100–300°C; second scan.

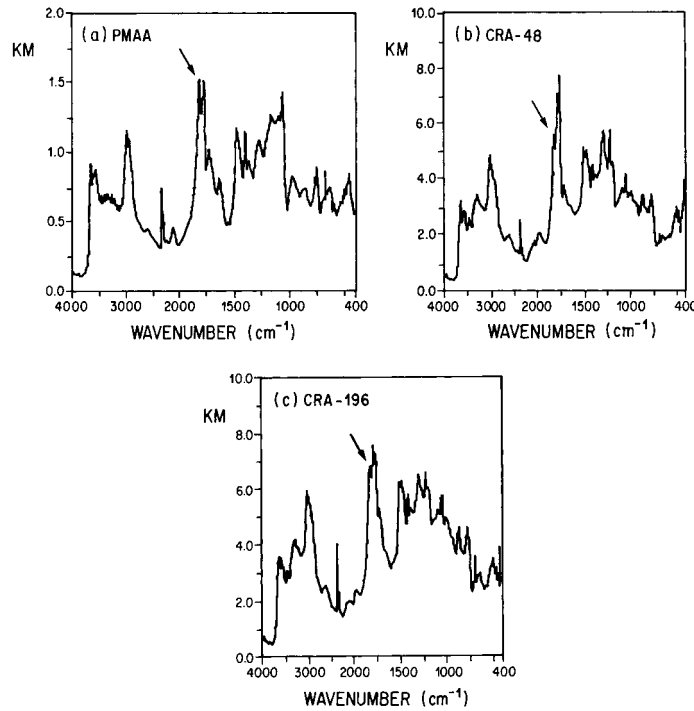


Figure 6 FTIR spectra (DRIFT) of PMAA and MMA-MAA copolymers analyzed after the calorimetric measurement recorded between 100–300°C.

to the presence of inter- and intramolecular hydrogen bonding promoted by the carboxylic groups of the polymer chain. Figure 6 shows the FTIR spectra.

Figure 4 also shows that the CRA-12 and CRA-24 copolymers present the anhydride formation in more than one step. When the COOH groups content becomes higher in the copolymer chain

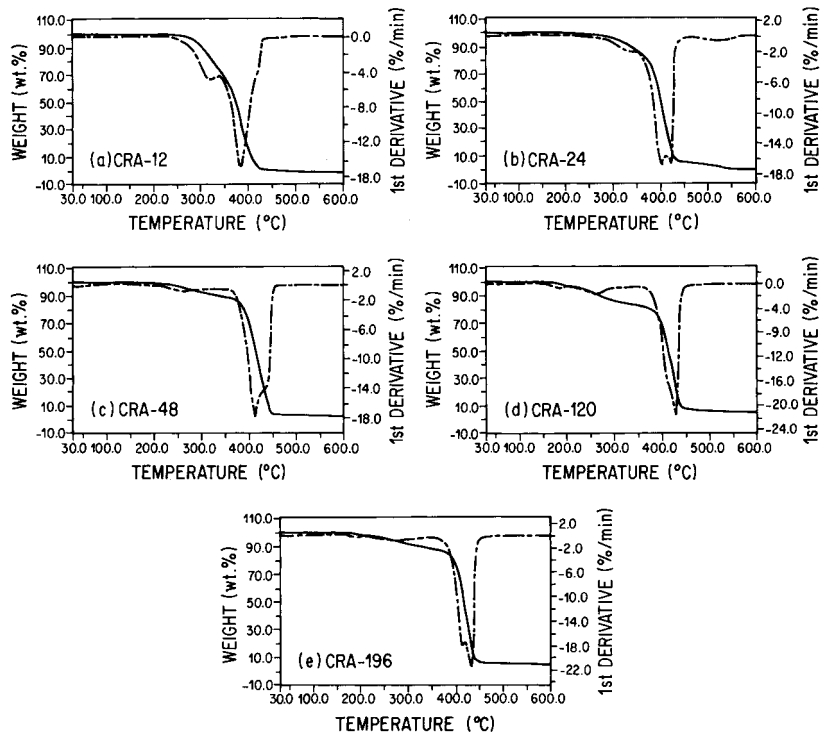


Figure 7 Thermogravimetric curves of MMA-MAA copolymers.

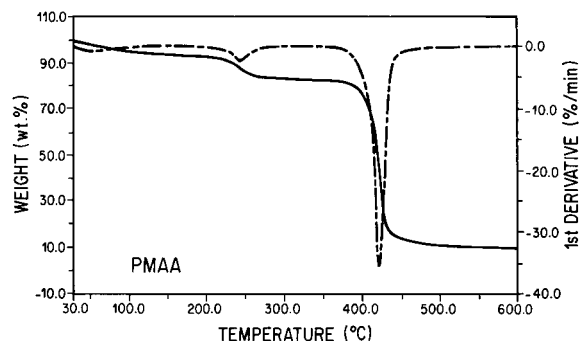


Figure 8 Thermogravimetric curve of PMAA.

(CRA-48, CRA-120, and CRA-196), the anhydride conversion occurs in one step within a large temperature range. Hamoudi and McNeill^{22–25} reported that at these temperatures the polymer chain eliminates water and methanol. This was corroborated by the thermal decomposition curves of these copolymers, which showed a small weight loss in the same range of temperature (Fig. 7). Figure 8 presents the TG curve of the PMAA, and the results also show that the elimination of water occurs at 246°C. These data allowed supposition that the transitions observed between 150–180°C in Figure 4 for CRA-12 and CRA-24 samples can be ascribed to the elimination of methanol. The CRA-48, CRA-120, and CRA-196 copolymers showed these losses and the formation of polyanhydride structure as one single and large transition.

The same procedure was applied after the DSC measurements. The remaining samples were removed from aluminum pans and then these samples were analyzed by an FTIR spectrometer. Figure 6 presents the spectra. The spectrum of PMAA after heating until 300°C [Fig. 6(a)] shows absorption bands at 1816 and 1776 cm^{-1} , characteristic of the anhydride carbonyl group. The structure of the anhydride was discussed in the literature²⁰ by correlating the most probable chain backbone with the possible cyclic anhydrides, such as glutaric and succinic. They were supposed to arise respectively, from head-to-tail and head-to-head/tail-to-tail structures. It was also considered possible the interaction between nonadjacent acid groups or acid groups attached to different chains, which can result in an isobutyric anhydride type structure. However, the frequencies attributed to the succinic anhydride structure are 1865 and 1782 cm^{-1} , typical of strained ring anhydrides, are higher than the observed peaks. The comparison with the published data²⁰ allowed us

to conclude that the glutaric anhydride is the predominant structure that is obtained on heating PMAA.

Figures 6(b) and (c) show the spectra recorded from MMA–MAA copolymers. The absorptions attributed to anhydride structure are evident, but the intensities of the absorptions are different. In addition, the spectra exhibit the typical absorptions of PMMA and PMAA.

Hydrolysis Degree Obtained by DSC Data

The first DSC scan showed important features in the 100–300°C range (Fig. 4) such as the anhydride formation. Turning back to the first temperature range studied (30–230°C) some new information may be introduced. Figure 9 presents the DSC curves of the first scan registered in this temperature range for PMMA and MMA–MAA copolymers. First-order transitions are observed and are not reproduced in any curve of the second scan, as showed in Figure 1. This means that irreversible processes, such as a decomposition, are taking place. In agreement with the procedure used in this work, the capsules were opened and the residues were analyzed by the FTIR spectrometer. It is noted in the spectra depicted in Figure 10 absorptions at 1749, 1715, and 1690 cm^{-1} , which are detached in the broad carbonyl band. These absorptions were attributed by Manring²⁶ to PMMA, and its decomposition products: allyl acetate (1743.4 cm^{-1}), dimethyl itaconate (1743 cm^{-1}), methyl isobutyrate (1740.8 cm^{-1}), methyl acrylate (1731 cm^{-1}), dimethyl oxalate (1749 cm^{-1}), dimethyl malonate (1732 cm^{-1}), etc., and can be observed in all spectra shown in Figure 10. Manring²⁶ reported that at 160, 270, and above 300°C, head-to-head structures breaking, depolymerization of unsat-

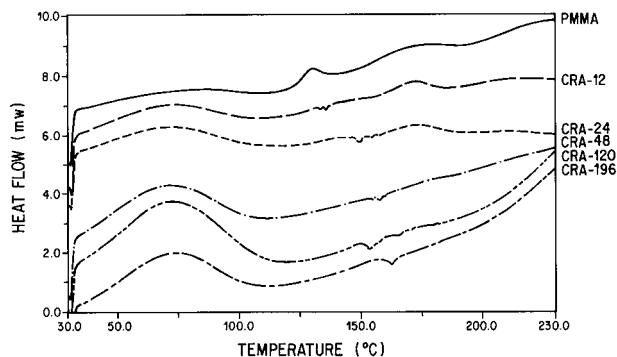


Figure 9 DSC curves of PMMA and MMA–MAA copolymers recorded between 30–230°C; first scan.

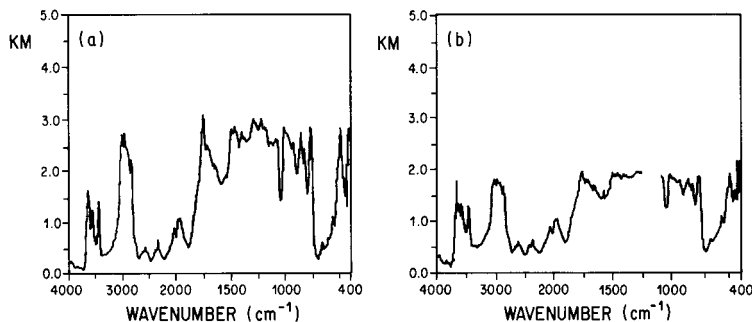


Figure 10 FTIR spectra (DRIFT) of PMMA: (a) after the calorimetric measurement recorded between 30–230°C; (b) after the calorimetric measurement recorded between 100–300°C.

urated end groups, random C—C scission, and pure monomer evolution are some of the decomposition possibilities proposed. The results obtained suggest that even below 300°C the occurrence of decomposition, it will be possible which, when evaluated by thermogravimetry gave a loss of weight around 10% (Fig. 11). This experience was followed by a test with the clear purpose of avoiding the decomposition of PMMA during the measurement of T_g . The runs were recorded between 30–150°C and are depicted in Figure 12. The curve correspondent to the first scan is similar to the recorded in the second scan. The FTIR spectrum recorded after the DSC scan was similar to the presented before [Fig. 2(b)].

These informations suggested a correlation between the first-order thermal transitions, recorded and depicted in Figure 9, and the hydrolysis degree of the copolymers. Tables V and VI exhibit the results.

The relationship between the first-order transition and the decomposition of PMMA in the range 118–160°C (Table V) showed a good agreement with the hydrolysis degree obtained using chemical titration data (Table II), except for the CRA-

48 copolymer. The available amount of this copolymer was small, and the curve recorded presented poor resolution when compared with the another ones.

From Table VI it can be noted that a good relationship cannot be observed in the second temperature range. Perhaps at these temperatures the polyanhydride formation and PMMA decomposition are occurring, and the results become difficult to correlate.

CONCLUSIONS

The viscometric analysis showed that the molecular weight of the MMA–MAA copolymers increases with the reaction time until 48 h. After this time, the molecular weight remained constant. The chemical titration revealed that the hydrolysis degree increases with the increasing of the reaction time.

DSC curves showed that the temperature range is important for the determination of T_g due

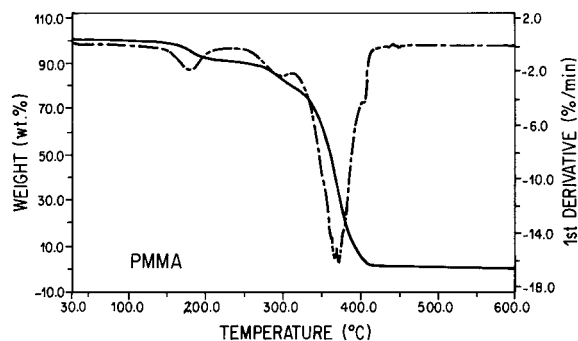


Figure 11 Thermogravimetric curve of PMMA.

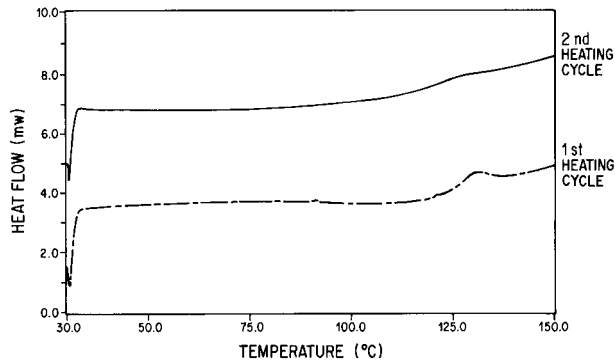


Figure 12 DSC curves of PMMA recorded between 30–150°C.

Table V Correlation between the First-Order Transition Temperature Measured between 118–160°C, and the Hydrolysis Degree of PMMA and MMA–MAA Copolymers

Sample	T (°C)	ΔH (J/g)	Hydrolysis Degree (%)
PMMA	130	2.505	0
CRA-12	136	2.084	21
CRA-24	136	1.692	32
CRA-48	153	1.063	58
CRA-120	149	1.391	44
CRA-196	155	1.099	56

to the anhydride formation that occurs around 200°C and the FTIR spectra characterized their structures. This formation was confirmed by the thermogravimetry curves recorded from MMA–MAA copolymers and PMAA.

The T_g values obtained in the temperature range of 100–300°C were lower than that observed in the temperature range of 30–230°C. This behavior can be attributed to the presence of inter- and intramolecular hydrogen bonding promoted by the carboxylic groups of the polymer chain, which was observed before the anhydride formation.

DSC and FTIR data indicated the decomposition of the PMMA and MMA–MAA copolymers when these polymers were heated in the temperature range of 30–230°C. The TG curves showed this decomposition. The first-order transition recorded in DSC curves of the MMA–MAA copolymers and the decomposition of PMMA in the temperature range of 118–160°C allowed us to establish a relationship that showed a good agreement with the hydrolysis degree obtained by chemical titration. This relationship cannot be obtained in

Table VI Correlation between the First-Order Transition Temperature Measured between 160–195°C, and the Hydrolysis Degree of PMMA and MMA–MAA Copolymers

Sample	T (°C)	ΔH (J/g)	Hydrolysis Degree (%)
PMMA	170	6.490	0
CRA-12	171	5.437	16
CRA-24	172	4.786	26
CRA-48	174	2.191	66
CRA-120	161	2.163	67
CRA-196	166	1.045	84

the temperature range of 160–195°C due to the polyanhydride formation.

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