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Characterisation of lithium and sodium salts of poly(methacrylic acid) by FTIR and thermal analyses

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Abstract

Lithium and sodium salts of methacrylic acid were prepared and polymerised by free radical initiation. Monomers and polymers were characterised using infrared (FTIR) analyses and the glass transition temperatures of the polymers were determined by differential scanning calorimetry (DSC). The thermal degradation behaviour was studied using thermogravimetry (TG) and showed high thermal stability of the salts. The solid degradation products have been investigated by FTIR and the results suggest that methacrylic salts polymerise under heating prior to degradation. The spectra of the residues obtained from the degradation of the monomers and polymers showed that they are composed of metal carbonate/bicarbonate. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(methacrylic acid) salts; Structural characterisation; Thermal characterisation

1. Introduction

The properties of polymers and copolymer salts of acrylic and methacrylic acid have been studied in the literature. The ionic group attached to the polymer chain has a dramatic influence on the polymer properties that is not observed in conventional homopolymers or in copolymers based in non-ionic species [1,2].

Polymer properties and applications are extremely dependent on the kind of interactions existing in polymer chains. Ionic interactions are among the strongest known types of forces that may exist between molecules. The presence of ionic groups in the polymer as a pendant group promotes the formation of ion-rich aggregates in the non-polar polymer matrix. These ion-rich aggregates lead to a variety of ionic interactions that change the polymer properties with each modification applied. These interactions depend on the type of polymer backbone (elastomer or plastic), type of pendant group (anionic/cationic), degree of neutralisation and the type of substitute (cation/anion) in the pendant group (multivalent, monovalent, metal, amine). This has made the study of these non-homogeneous polymer systems a rich area for research and development of materials [2].

McNeill and co-workers [3–8] studied the thermal degradation behaviour of ammonium, alkaline, and alkaline earth metal polymethacrylates using thermal volatilisation analyses (TVA) and discussed the degradation mechanism of these materials. They concluded that the principal degradation products are monomer, the corresponding isobutyrate, carbonate, oxide, carbon dioxide and a fraction of liquid volatile that is complex and contains a variety of aldehydes and ketones. They also concluded that the ionic radii of the metal can affect the microstructure of the polymer chain and that syndiotacticity is enhanced with larger ionic radii metals [3–5]. The thermal degradation of zinc, lead, copper, cobalt and nickel polymethacrylates were also studied [6–8].

In the present work, the thermal degradation behaviour of lithium and sodium salts of poly(methacrylic acid) has been studied. The degradation behaviour of the monomers has been also investigated and the results compared with those obtained from the respective polymers. The studies were carried out using calorimetry, infrared analyses and thermogravimetry.

2. Experimental

2.1. Preparation of monomers and polymers

Commercial methacrylic acid was distilled at reduced pressure prior to use to remove the inhibitor. The monomer salts were prepared by neutralisation of methacrylic acid

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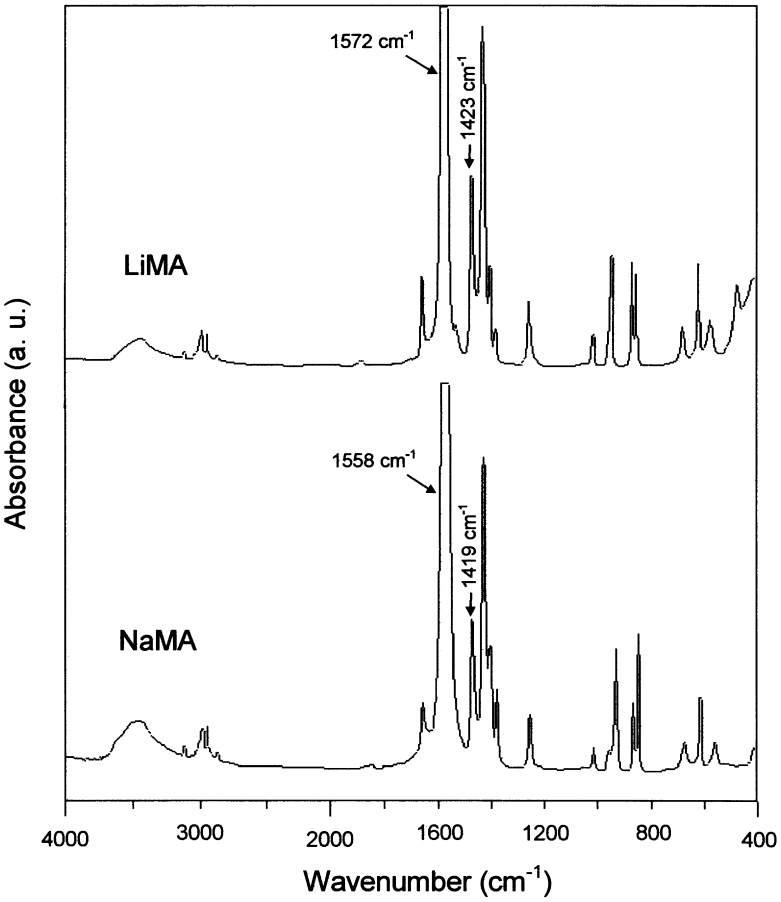

Fig. 1. FTIR spectra of LiMA and NaMA.

with sodium hydroxide and lithium carbonate, using methanol as solvent and a temperature of 15°C, with vigorous stirring. The monomers were purified twice by dissolution in methanol and precipitation with diethyl ether.

The polymers were prepared by free radical polymerisation in methanol solution at 60°C using 0.1% (w/v) of 2,2′-azoisobutyronitrile (AIBN) as initiator. The polymers were filtered, washed with methanol several times and dried under vacuum at room temperature [4].

2.2. Characterisation of monomers and polymers

2.2.1. Infrared analyses

Infrared spectra of polymers and monomers were recorded on a Perkin–Elmer FTIR spectrometer (Model 1720x). The spectra were obtained at a 2 cm^{-1} resolution, 20 scans and processed by a Perkin–Elmer IR data manager (IRDM). The samples were examined as KBr discs.

The residues from thermogravimetry (TG) were subjected to FTIR analyses using the same spectrometer equipped with diffuse reflectance accessory (DRIFT). The spectra were obtained at a 2 cm^{-1} resolution and 80 scans under nitrogen atmosphere. 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 by Ref. [9]:

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

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). The spectral data obtained from infrared analyses of the decomposition residues were improved applying a Savitski–Golay function to the data using the Smooth and Derivative preprocessing routine from the Perkin–Elmer QUANT+ system [10] in the range 2000–1000 cm^{-1}. Second-order derivatives over six window widths (37 data points) were used as derivative parameters.

2.2.2. Calorimetry

The calorimetric measurements were carried out using a Perkin–Elmer DSC-7 instrument equipped with a Perkin–Elmer PE 7700 professional computer and TAS-7 software. The equipment was calibrated with indium ($T_m = 156.6$°C and $\Delta H_f = 6.8$ cal/g) as standard. The samples weighing 4–8 mg were sealed in aluminium pans and heated under

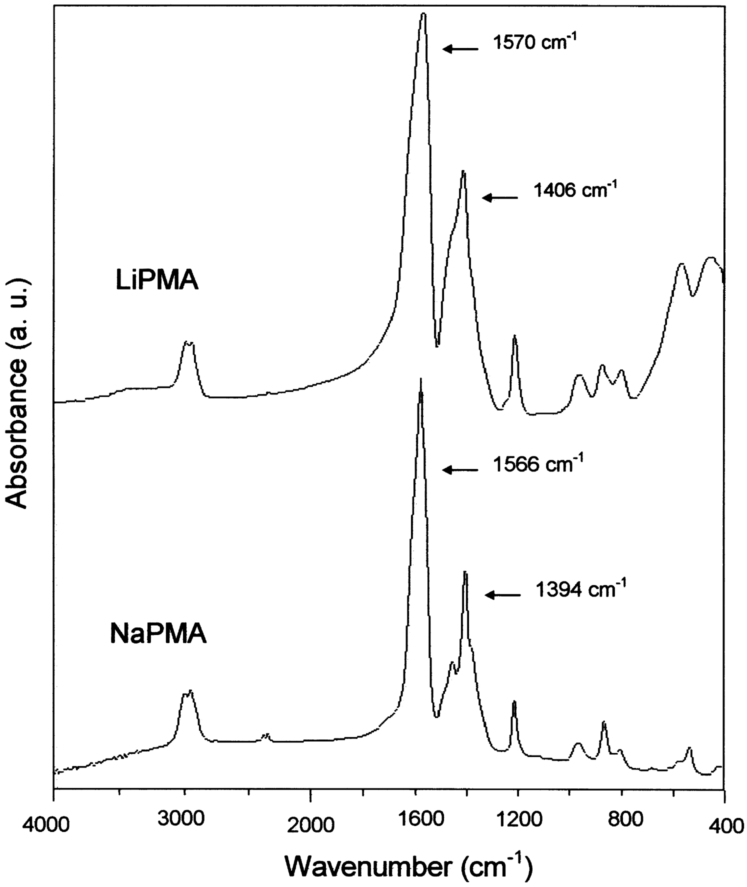

Fig. 2. FTIR spectra of LiPMA and NaPMA.

nitrogen atmosphere from 300 to 400°C, at a heating rate of 10°C/min.

The glass transition temperature of each polymer was determined as the temperature at the midpoint of the transition ($\frac{1}{2}\Delta C_p$), as described by Wunderlich et al. [11], recorded during the first scan.

2.2.3. Thermogravimetry

The thermal degradation of the monomers and polymers was conducted from 30 to 650°C with a heating rate of 10°C/min, under dynamic nitrogen at a flow rate of 33 mm^3/min for the sample and 60 mm^3/min for the furnace. Samples weights were 3–7 mg. The experiments were registered using a Perkin–Elmer, model TGA-7 thermobalance calibrated with alumel ($T_c = 163$°C), nickel ($T_c = 354$°C) and perkalloy ($T_c = 596$°C) standards.

Table 1

Stretching vibration modes of the carboxylate anion. $\Delta\nu = \nu_{\text{monomer}} - \nu_{\text{polymer}}$ (cm^{-1}). Crystal ionic radii [16]: Na$^+$, 0.095 nm; Li$^+$, 0.060 nm

Monomers and polymers	Stretching vibration (cm^{-1})			
	Asymmetric	$\Delta\nu$	Symmetric	$\Delta\nu$
LiMA	1572		1423	
		2		17
LiPMA	1570		1406	
NaMA	1558		1419	
		−8		25
NaPMA	1566		1394	

3. Results and discussion

3.1. Infrared analyses

The FTIR spectra of lithium and sodium methacrylic acid salts are depicted in Fig. 1 and no remarkable differences are observed between them as reported by Hamoudi and McNeill [12]. The spectra show the characteristic infrared absorptions of the metal methacrylates due to a strong asymmetric, and a weak symmetric stretching mode of the carboxylate ion, close to 1550 and 1420 cm^{-1}, respectively, and the absence of the C=O stretching vibration band at 1698 cm^{-1}.

The polymerisation of methacrylic salts was confirmed from the spectra shown in Fig. 2, by the band-broadening, absence of the C=C group stretching bands at ~1640 cm^{-1} and the decrease of intensity of the CH_2 wagging vibrations at ~890 cm^{-1}, characteristic of the vinylidine group from the monomer salts [13,14].

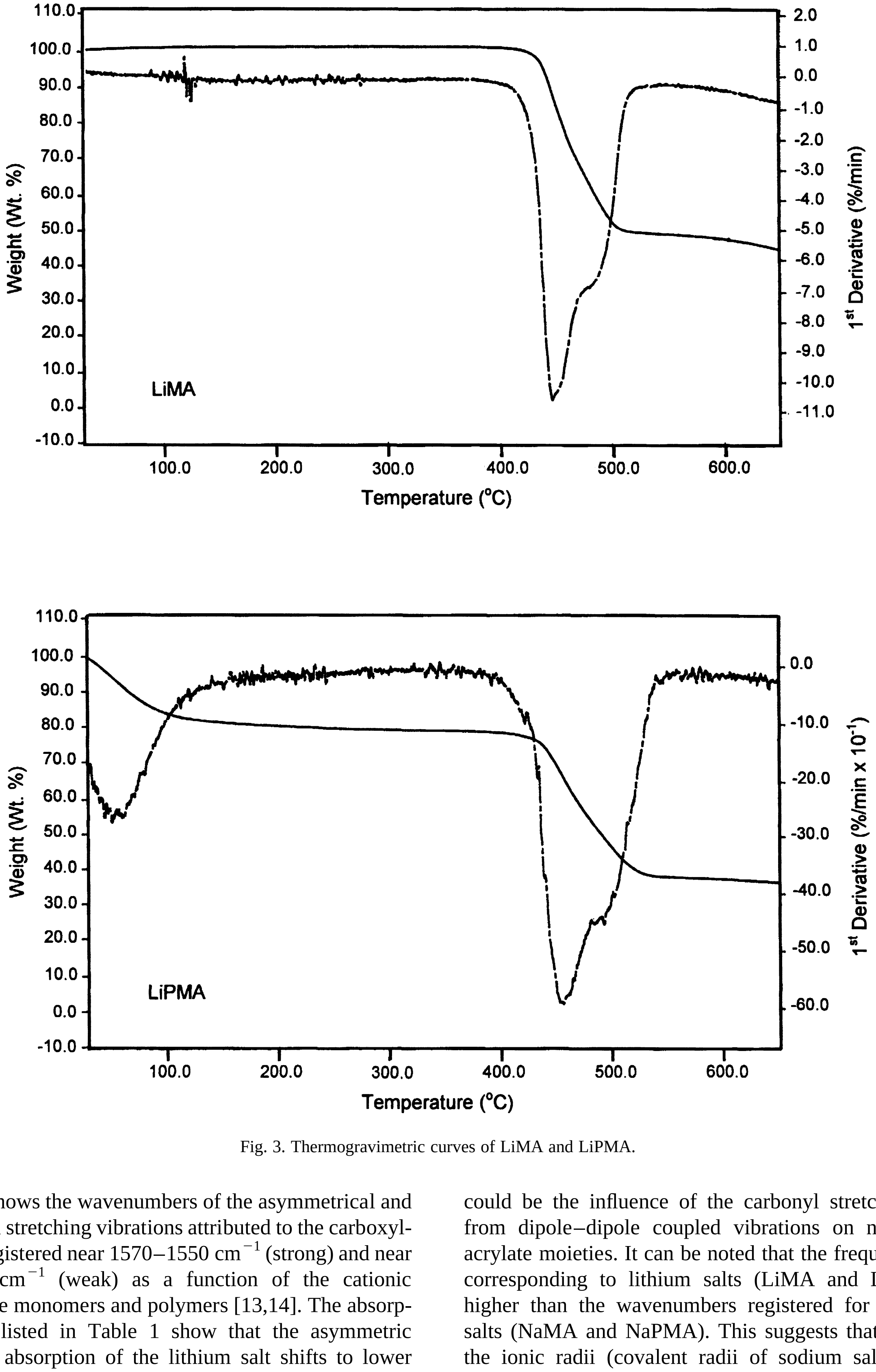

Fig. 3. Thermogravimetric curves of LiMA and LiPMA.

Table 1 shows the wavenumbers of the asymmetrical and symmetrical stretching vibrations attributed to the carboxylate anion registered near 1570–1550 cm^{-1} (strong) and near 1420–1400 cm^{-1} (weak) as a function of the cationic groups of the monomers and polymers [13,14]. The absorption bands listed in Table 1 show that the asymmetric carboxylate absorption of the lithium salt shifts to lower frequencies on polymerisation and the opposite is observed for the sodium salts. On the other hand, the symmetric vibrations shift to lower frequencies. The explanation could be the influence of the carbonyl stretching modes from dipole–dipole coupled vibrations on neighbouring acrylate moieties. It can be noted that the frequency values corresponding to lithium salts (LiMA and LiPMA) are higher than the wavenumbers registered for the sodium salts (NaMA and NaPMA). This suggests that the size of the ionic radii (covalent radii of sodium salts $>$ lithium salts) would introduce differences on the oscillators' coupling. McNeill and co-workers pointed out a number of features that are influenced by the size of the metal ion

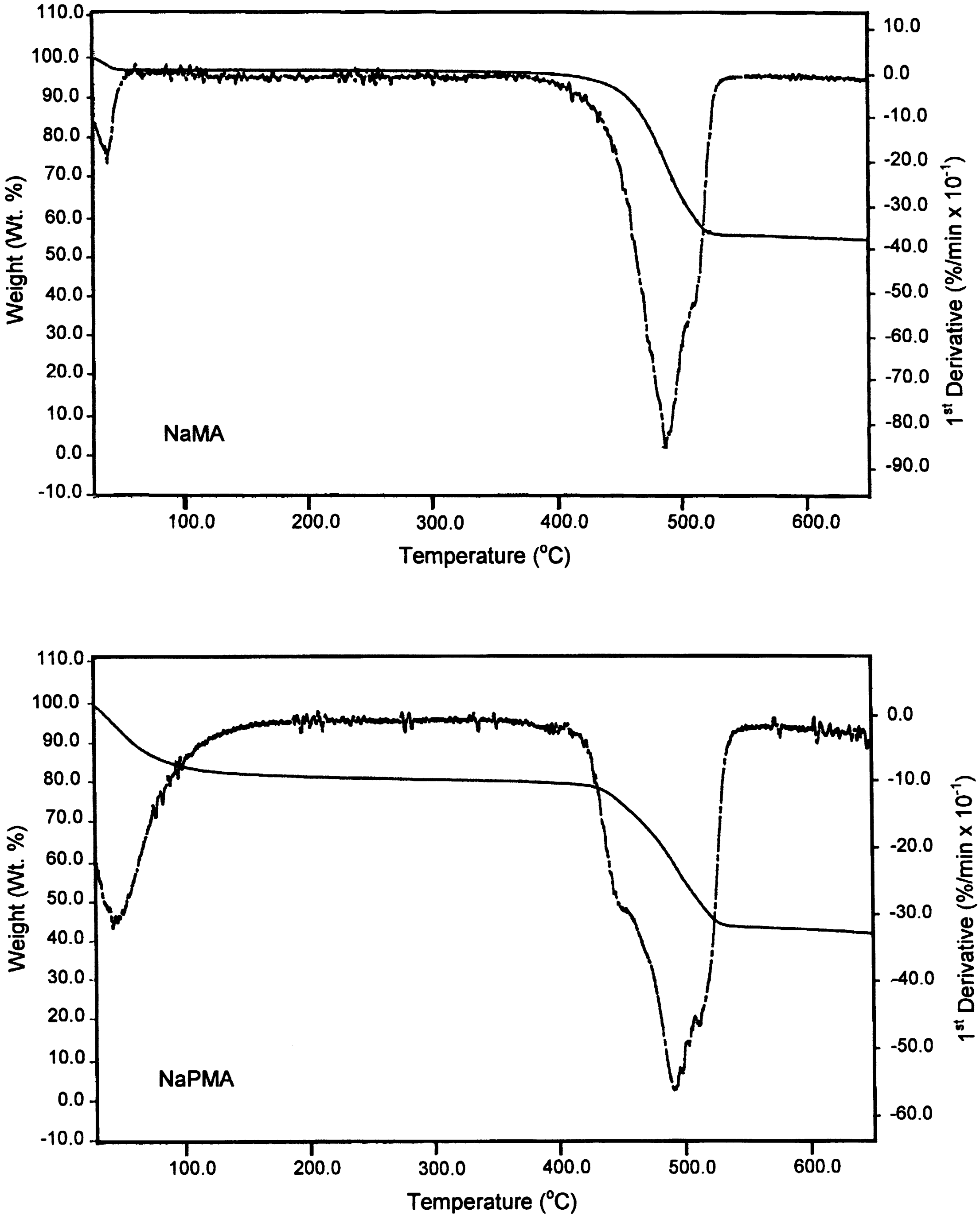

Fig. 4. Thermogravimetric curves of NaMA and NaPMA.

[4,5,12]. However, the available infrared data did not allow any conclusion on this subject.

3.2. Calorimetry

The DSC curves were recorded in the range of 300–400°C and the glass transition temperatures (T_g) of the polymers were obtained from the first scan. The observation of this transition becomes very difficult from the second scan. It may be probably due to the reorganisation of the macromolecules upon a heating/cooling cycle, which increases the stiffness of the chain.

The measured glass transition temperature of NaPMA was 363°C and the transition width (ΔT_g) was 24°C. The result obtained for T_g is higher than that reported by Otocka and Kwei [15] (310°C). The reported value was obtained by extrapolating the T_g shift as a function of sodium methacrylate content in a styrene–sodium methacrylate copolymer.

The value of the glass transition obtained for LiPMA was 359°C and ΔT_g was 9°C. This lower value obtained for T_g

Table 2
Onset temperature (T^0), temperature of maximum decomposition rate ($T_{d,max}$) and percentage of residue at 650°C from thermogravimetric analyses

	Sample	T^0 (°C)	$T_{d,max}$ (°C)	Residue (%)
Monomer	LiMA	435	446	45
	NaMA	452	482	57
Polymer	LiPMA	433	455/492	49
	NaPMA	433	453/491	55

suggests that the metal linked to the macromolecule chain can promote a shift of T_g with increasing metal size. Cations are generally classified as Lewis acids, and act as acceptors towards the donor atoms of the carboxylate anion [16]. The measured ΔT_g of the studied polymer salts showed that $(\Delta T_g)_{NaPMA}$ is larger than $(\Delta T_g)_{LiPMA}$. This indicates that local composition and temperature fluctuations are more probable in NaPMA and allow to propose that broadening of T_g width is also being influenced by the bond distance between metal and oxygen in these polymers, increasing with the increase of the bond distance.

3.3. Thermogravimetry

The thermal degradation behaviour of the monomers (LiMA and NaMA) and polymers (LiPMA and NaPMA) were studied in the range 30–650°C, using nitrogen atmosphere. The results showed that both metal polymethacrylates exhibit high temperature resistance and produce much residue.

The thermogravimetry curves obtained for the monomer and the respective polymer are presented in Fig. 3 for lithium salts and in Fig. 4 for sodium salts. The results from these curves are listed in Table 2. The first weight loss indicates evaporation of water/methanol and shows that both polymers are hygroscopic as pointed out by McNeill and Zulfiqar [4]; this suggests that the moisture content may be found by TG.

The DTG curves show the high thermal stability of the salts and corroborate the hypothesis presented by McNeill and Zulfiqar that the decomposition of these polymers is more complex than the monomer salts [4].

The temperature of maximum decomposition rate obtained for the monomer salts of lithium and sodium was 446 and 482°C, respectively. The normalised percentage of residue at 650°C from the original sample was 45% for LiMA and 57% for NaMA. The thermogravimetric curves of polymers are wider and show that the weight loss occurs in more than two steps. The first one (30–150°C) probably is loss of water and residual solvent. The second step occurs above 400°C with a maximum decomposition rate at 457°C

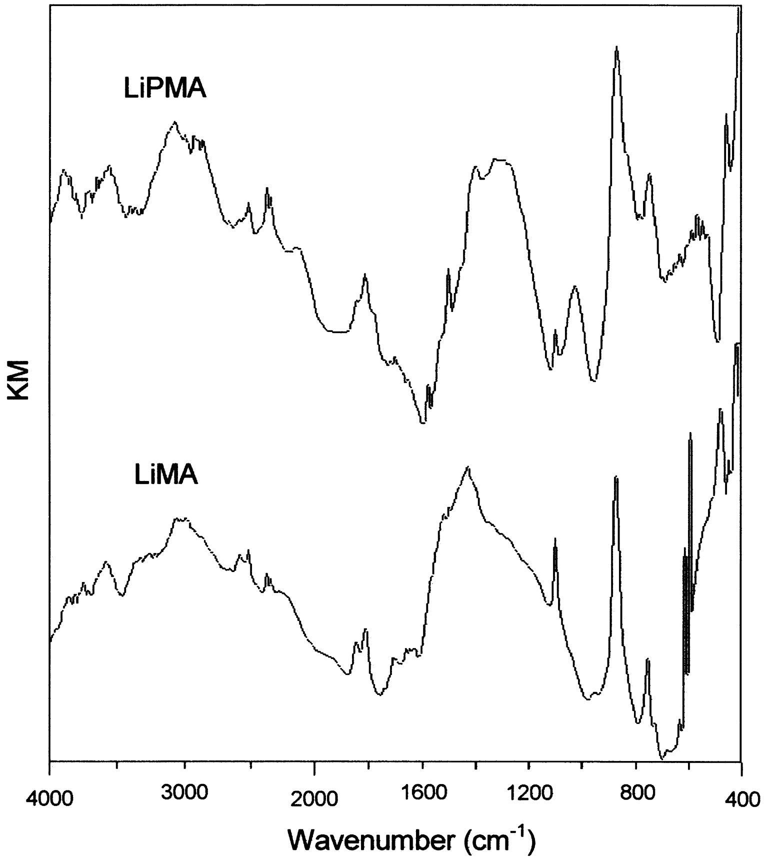

Fig. 5. FTIR spectra (DRIFT) of residues from degradation of LiMA and LiPMA after heating at 650°C.

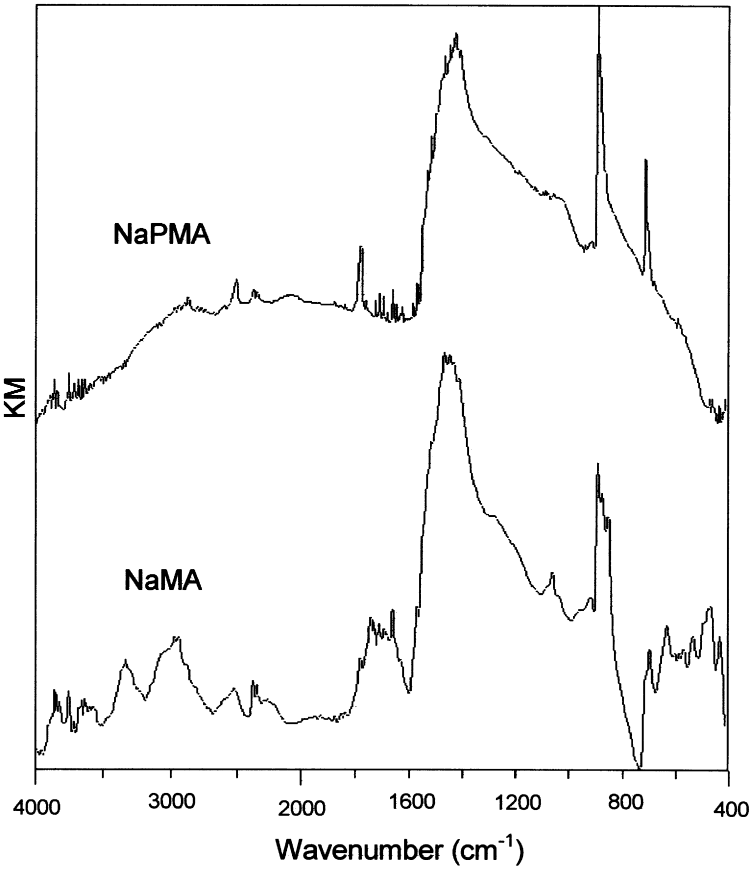

Fig. 6. FTIR spectra (DRIFT) of residues from degradation of NaMA and NaPMA after heating at 650°C.

for LiPMA and 491°C for NaPMA. The content of residue at 650°C was 49% for LiPMA and 55% for NaPMA.

The DTG curves show that both polymers present more than one peak at the principal degradation stage. The products obtained at this degradation step and the mechanisms involved have been discussed in the literature by McNeill and Zulfiqar [4]. Thermal parameters such as onset temperature (T^{o}), temperature of maximum decomposition rate ($T_{d,max}$) and percentage of residue shown in Table 2, and the shape of DTG curves can be considered coherent to those obtained by thermal volatilisation analyses.

These results corroborate the scheme proposed by McNeill and Zulfiqar [5], where thermal polymerisation is a more favourable process during heating and can occur before decomposition. However, the complete elucidation of the decomposition process needs complementary studies.

3.4. Residue analysis

The thermogravimetric analyses were followed by infrared spectrometry. The residues of monomer and polymer salts were characterised by FTIR (DRIFT) and the spectra are showed in Fig. 5 (LiMA and LiPMA) and Fig. 6 (NaMA and NaPMA). The spectra obtained from lithium and sodium salts present remarkable similarities indicating the presence of various products. The presence of the broad absorption in the region of 1600/1200 cm^{-1}, may be related to the stretching band from the carboxylate anion [13,14]. This broad absorption is also assigned to the sodium carbonate asymmetric stretching vibrations [13]. The presence of the out-of-plane deformation at 875 cm^{-1} and the absorption assigned to the in-plane deformation of the carbonate group [13,14,17] at 712 cm^{-1} indicate that the residues from decomposition of methacrylic salts after heating at 650°C, are composed of metal carbonate. The same kind of residue arises from the polymers.

McNeill and Zulfiqar [4] showed a relationship between the carbon dioxide evolution and the ionic radius of the corresponding cation of the polymer salt. They demonstrated that carbon dioxide production increases as the ionic radius increases. The analyses of the degradation products carried out in the present work corroborate the McNeill and Zulfiqar data [4].

The poor resolution of the lithium and sodium salts spectra depicted in Figs. 5 and 6, respectively, allows some assumptions supported by spectrum handling. The formation of anhydride structures in the lithium salts could be suggested taking into account that the small peaks registered at 1839 and 1804 cm^{-1} in the LiMA spectrum are typical of anhydride carbonyl stretching modes [13] (Fig. 5). This suggests the occurrence of intramolecular elimination of metal oxide or carbonate. However, the spectrum of

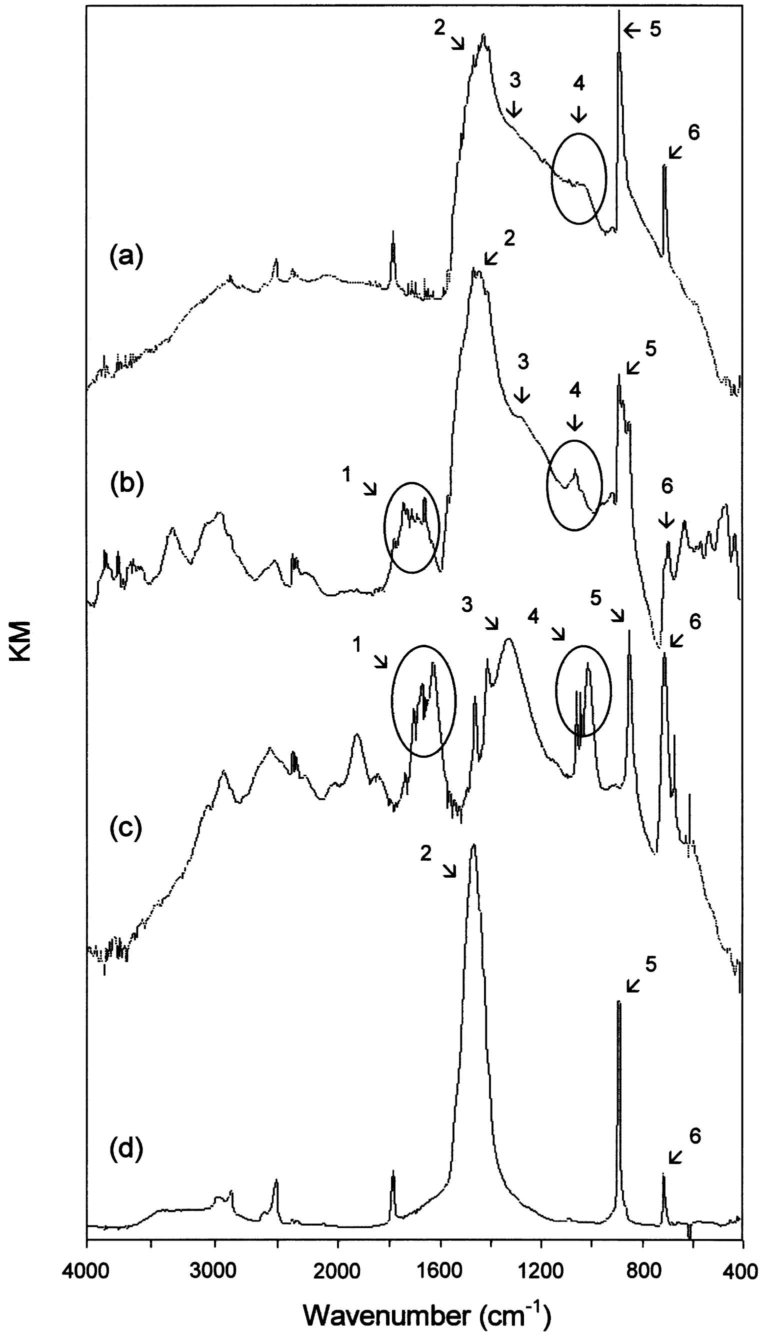

Fig. 7. FTIR spectra (DRIFT) of residues from: (a) NaPMA; (b) NaMA; (c) sodium bicarbonate; and (d) sodium carbonate.

LiPMA shows a different pattern in this region, which compromises this assumption. McNeill and Zulfiqar [4] ruled out this hypothesis in their work using thermal volatilisation analysis. They postulated a mechanism supported by the great variety of liquid volatile products detected from the degradation of poly(methacrylic acid) salts. The spectra of sodium containing products of degradation (Fig. 6) are more complex between 1800 and 1600 cm^{-1}. This led to inconclusive interpretation. The results presented here were obtained from the degradation residues and corroborate the data shown by McNeill and Zulfiqar [4], which pointed out the complexity of the problem. McNeill and Zulfiqar [4,5] suggested that at high temperatures, when side group scissions occur, a more favourable environment promotes the formation of carbonate and oxide in the degradation residue.

It is known that sodium bicarbonate is obtained/decomposed from a reversible thermal reaction of sodium carbonate, carbon dioxide and moisture and these ingredients may be included in the decomposition product. Then, it is reasonable to investigate the presence of bicarbonate in the cooled residue. The spectra of sodium bicarbonate and sodium

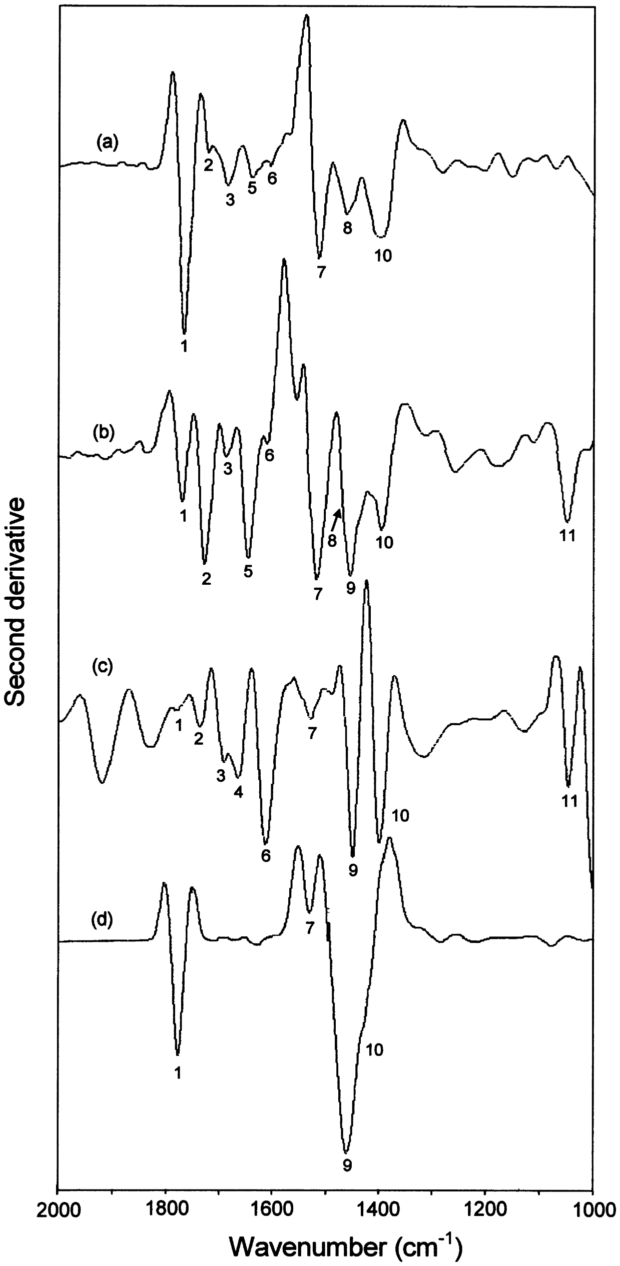

Fig. 8. Second-order derivative spectra of residues from: (a) NaPMA; (b) NaMA; (c) sodium bicarbonate; and (d) sodium carbonate.

carbonate were run under the same conditions used to obtain the spectra of NaMA and NaPMA decomposition residues, and are depicted in Fig. 7, where the intensities are in Kubelka–Munk units. Fig. 7 shows the spectrum of NaPMA (spectrum *a*), NaMA (spectrum *b*), $NaHCO_3$ (spectrum *c*) and Na_2CO_3 (spectrum *d*). The comparison of the spectra shows that at least six regions, assigned in the spectra, allow the following comments supported by the literature [13,14,17]:

- *region 1* between 1770 and 1624 cm^{-1} is a set of absorptions that are more evident in the spectrum of NaMA and $NaHCO_3$;
- *region 2* can be considered as the broad absorption, with a peak at 1458 cm^{-1}, that is remarkable in the spectra of the monomer and polymer residues as well as in the sodium carbonate spectrum—this absorption can be attributed to the asymmetrical stretching of the CO_3^{-2} group;
- *region 3* was considered as the broad absorption at 1321 cm^{-1} in the spectrum of bicarbonate—this absorption can be observed as a shoulder in spectrum *a* and spectrum *b*; this absorption is observed in the sodium bicarbonate spectrum used as reference [17];
- *region 4* was assigned as another set of absorptions registered between 1091 and 950 cm^{-1} that is more evident only in the spectrum of $NaHCO_3$—the profile of this absorption is also observed in the sodium bicarbonate spectrum [17];
- *region 5* can be interpreted with caution—spectrum *a* and spectrum *d* show this region as a peak, at 882–878 cm^{-1}, spectrum *b* shows a set of absorptions between 879 and 840 cm^{-1}, and spectrum *c* shows this absorption at 838 cm^{-1}—this absorption is related to the carbonate out-of-plane bending;
- *region 6* can be observed in all spectra as a peak at 700 cm^{-1}, that is attributed to the carbonate in-plane bending.

The bands observed between 1600 and 800 cm^{-1} in the decomposition residues could be related to some features characteristic of carbonate. However, the spectrum of the residue obtained from the monomer salt presents some regions shown in the spectrum of bicarbonate. Then, the interpretation outlined from these results does not allow definite conclusions.

Interference in spectral data can be removed by a derivative pre-processing routine [10] and may be useful in improving spectra interpretation. The second derivative procedure was applied in the spectral range between 2000 and 1000 cm^{-1} to the polymer and monomer residue spectra as well as sodium bicarbonate and sodium carbonate. This region presents the typical pattern of bicarbonate/carbonate absorptions [17]. The result is depicted in Fig. 8. The second derivative of the spectrum registered from the NaPMA residue corresponds to the profile (a). The line (b) is the second derivative obtained from the spectrum of NaMA residue. The third pattern (c) corresponds to the second derivative of $NaHCO_3$, and line (d) shows the result obtained for the spectral processing applied to the spectrum of Na_2CO_3.

The more intense peaks of Fig. 8 were assigned and their relative intensities were listed in Table 3. Peaks 1–6 can be ascribed to *region 1* (1770–1624 cm^{-1}) of Fig. 7. The profile registered in Fig. 7, combined with the information obtained from Table 3 suggests that the presence of sodium carbonate is more probable than sodium bicarbonate in the residue obtained from NaPMA. Peak 9 is also remarkable in Fig. 8. It corresponds to the absorption assigned as *region 2* (peak at 1458 cm^{-1}) in Fig. 7 (asymmetrical stretching of

Table 3
Evaluation of the relative intensity of peaks from the second derivative DRIFT spectra of TG decomposition residues. Intensity grade: + + + + high; + + + medium; + + low; + fair; − not remarkable

Peak number	Absorption (cm^{-1})	Relative intensity of DRIFT second-derivative peaks			
		NaPMA	NaMA	$NaHCO_3$	Na_2CO_3
1	1779–1777	+ + + +	+ +	+	+ + +
2	1736–1735	+	+ + +	+ +	−
3	1700–1695	+ +	+	+ +	−
4	1670	−	−	+ + +	−
5	1655–1653	+ +	+ + +	−	−
6	1618	+	+	+ + +	−
7	1529–1521	+ + +	+ + + +	+ +	+ +
8	1474	+ +	+ +	−	−
9	1458–1452	+ +	+ + +	+ + + +	+ + + +
10	1411–1399	+ +	+ +	+ + + +	+ +
11	1051–1047	−	+ +	+ +	−

the carbonate group). This peak may be overlapped in the register (a), but it is observed in the registers (b), (c) and (d). Peak 10 was observed at the frequency of an absorption registered in the bicarbonate spectrum taken as reference [17]. This absorption was assigned in all spectra. Peak 11 is the last absorption and can be considered as one of the peaks that compose *region 4* (1091–950 cm^{-1}) in Fig. 7. This absorption was observed in the spectrum of bicarbonate. The results suggest that the high number of absorptions registered in the profile of sodium bicarbonate are observed also in the second derivative of the spectrum registered for NaMA. This may give some support to the hypothesis where the decomposition monomer residue of sodium salt has a tendency to produce sodium carbonate/bicarbonate.

4. Conclusions

FTIR, DSC and TG were used in the study of polymers prepared from lithium and sodium methacrylic salts. The T_g values obtained in the temperature range of 300–400°C suggest increasing of the macromolecule organisation during heating, which can introduce changes in the polymer structure. The T_g width indicates that the size of the metal involved in the macromolecule and the bond distance between metal and oxygen would play a role in the local composition of the system. These results are coherent with infrared data.

The thermogravimetry (TG) showed that the monomers and polymers are stable up to high temperatures and the DTG curves showed more than one peak at the principal stage of thermal breakdown. The percentage of residue at 650°C from the original sample was high in all cases. All data corroborate the scheme proposed by McNeill and Zulfiqar [5]

FTIR (DRIFT) spectra of the decomposition residues gave some support to the idea that the presence of sodium carbonate is more probable than sodium bicarbonate in the residue obtained from NaPMA. On the other hand, absorptions assigned to sodium bicarbonate were observed in data obtained from NaMA residues. Research in this field proceeds in this laboratory.

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