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Infrared study on methyl methacrylate–methacrylic acid copolymers and their sodium salts

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Abstract

Near, mid and far infrared spectra have been recorded for methyl methacrylate–methacrylic acid copolymers and their sodium salts. Methyl methacrylate–methacrylic acid copolymers, with various methacrylic acid contents were prepared by free radical polymerization. The sodium salts of (methyl methacrylate–methacrylic acid) copolymers were prepared by reaction of methacrylic acid units with sodium hydroxide. The acid content in copolymers was estimated by calorimetry and by reactivity ratios of monomers. The results showed that sodium MMA–MAA copolymers prepared by neutralization form ionic clusters and retain in its backbone non-neutralized acid groups. The results showed the effect of composition on spectroscopic data. The absorption/retention of water was observed in the examined samples.

Keywords: Methacrylic copolymer sodium salts; Infrared analyses; Infrared characterization

1. Introduction

Poly(methacrylic acid) and copolymers salts represent a class of materials that are known as ionic polymers and generally are water-soluble. These polymers present pendant ionic groups that can form ionic aggregates that usually provides strong influence on physical properties [1]. Investigations in various types of ionic polymers have been done still now in order to correlate the structure of ionic aggregates with the polymer property [1–4]. Fourier transform infrared spectroscopy (FTIR) was used in various studies of methacrylic acid polymers neutralized with alkaline, alkaline earth and transition metals [5–8]. Han and Williams [5,6] used FTIR spectra of different ionomers based on ethylene–methacrylic acid copolymers, and different ions to propose mechanisms and models for ionomers formation based on existence of multiplets and clusters. Gotoh and co-workers [7] studied ionomers of poly(methyl methacrylate-*co*-methacrylic acid) crosslinked by titanium (IV) and zirconium (IV) ions using FTIR spectra and based on the splitting of the carboxylate absorptions suggested the possible coordination structures of P(MMA/MAA)-Ti.

Near-infrared (NIR) spectra has been used in polymer characterization and is considered a convenient analytical method because is rapid and accurate. It is a very useful technique that includes a large number of applications such as crystallinity, structural conformation, interactions, copolymer composition, etc. [9–11]. However, the available information on polymers is spread and limited to the most representative types of commercial products.

Research on far infrared spectroscopy of polymers is limited to few examples and the focus of the reported data is related to ionomers [12–16]. This spectroscopic method may be more sensitive in detecting the existence of ionic clusters than other methods such as rheological measurements and small-angle X-ray scattering [14]. The application of this technique is important on correlating the cation local environment involved or not in aggregates, registered in this region of infrared (700 to 200 cm^{-1}) and can contribute to a best understanding of intermolecular interactions [14,15].

The purpose of this work, was obtain spectroscopic data of poly(methyl methacrylate–methacrylic acid) polymers (MMA–MAA copolymers) and the corresponding sodium salts using infrared spectroscopy, in the regions of near, mid

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and far infrared, and investigate the influence of copolymer composition on the typical absorption bands.

2. Experimental

2.1. Preparation of polymers

MMA–MAA copolymers were prepared by free radical polymerization in methanol solution at 80 °C using 2% (w/v) benzoyl peroxide as initiator with a reaction time of 3 h. The methyl methacrylate:methacrylic acid volume ratios were 1:4, 2:3, 3:2 and 4:1. The MMA–MAA copolymer abbreviations are CoMAA80, CoMAA60, CoMAA40 and CoMAA20, respectively. The copolymers were precipitated with water, filtered, washed with water several times and dried under a vacuum at room temperature. PMMA, PMAA and poly(methyl acrylate) (PMA) were prepared as previously described [8].

The sodium salts of MMA–MAA copolymers were obtained by neutralization of MMA–MAA copolymers dissolved in methanol at a concentration of 1% (w/v) with 0.5 M NaOH methanol solution, at 40 °C, with vigorous stirring for 3 h. The sodium copolymers were precipitated with diethyl ether, filtered, washed with diethyl ether several times and dried under a vacuum at room temperature. The sodium copolymers abbreviations for salts prepared from CoMAA80, CoMAA60, CoMAA40 and CoMAA20 are Na[PCo80], Na[PCo60], Na[PCo40] and Na[PCo20], respectively.

2.2. Characterization of MMA–MAA copolymers

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 aluminum pans and heated under nitrogen atmosphere from 100 to 300 °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 (1/2 ΔC_p) as described by Wunderlich et al. [17] recorded during the second scan.

2.3. Infrared analyses

FTIR spectra (4000–400 cm^{-1}) were acquired on a Perkin–Elmer FTIR 1720x spectrometer at a 2 cm^{-1} resolution, and 20 scans. The samples were examined as KBr disks and as cast films from 2% (w/v) methanol solution at room temperature.

Near-infrared spectra of PMMA, PMAA, and sodium copolymers were recorded using cast films from 2% methanol solution at room temperature. NaPMA and PMMA–PMAA copolymers were examined as powder. The measurements were carried out using the same spectrometer from 10,000–3000 cm^{-1} (1000–3333 nm) at 8 cm^{-1} resolution, and 100 scans. The spectra of powders were recorded using the diffuse reflectance accessory (DRIFT). The spectra were processed by a Perkin–Elmer IR data manager (IRDM) and presented in the Kubelka–Munk (KM) format [8]. The spectral data obtained from infrared analyses were improved applying a normalizing function given by the data manager program.

Far-infrared spectra (600–150 cm^{-1}) were measured with a NICOLET Magna 760 spectrometer at a 4 cm^{-1} resolution and 128 scans. The samples of PMMA, PMAA and their copolymers were examined as films cast from methanol solution. The spectra of the sodium salts were run as CsI disks.

3. Results and discussion

3.1. Copolymer composition

MAA carboxyl group content (wt%) of the copolymers were estimated by calorimetry (DSC), using the glass transition temperature of the MMA–MAA copolymers using the Braun–Kovacs approach [18,19], and by the reactivity ratios of monomers MAA and MMA [20].

Braun and Kovacs [18] proposed a free-volume theory that predicts the existence of a singular point (cusp) on plotting the dependence of T_g upon the concentration of systems composed by two components such as blends and copolymers. At this point, the free-volume of polymer 2 becomes zero at a critical temperature, T_{crit}. The corresponding volume fraction, ϕ_{crit}, can be calculated and the theoretical curve can be compared with the experimental results. This theory is useful for systems composed by two polymers or copolymers where $T_{g2} - T_{g1}$ is larger than about 50° and in the absence of strong interactions. This theory was applied to the MMA–MAA system and presented reasonable fitting despite the strength of the system interactions. The adequate relationships proposed by Lu and Weiss [21] to calculate T_g using composition data cannot be applied now because the composition is the unknown term and the reverse pathway will be drawn.

Using the equations proposed by Braun and Kovacs for

$$T_{g2} > T_{g1} \Rightarrow T_{crit} = T_{g2} - (f_{g2}/\Delta\alpha_2) \quad (1)$$

and

$$\phi_{crit} = f_{g2}/[\Delta\alpha_1(T_{g2} - T_{g1}) + f_{g2}(1 - \Delta\alpha_1/\Delta\alpha_2)] \quad (2)$$

where f_{g2} is the free-volume fraction of polymer 2 (PMAA) at T_{g2} and is equal to 0.025.

Above T_{crit}, the glass transition temperature is given by

$$T_{g2} - T_g = (\phi_1/\phi_2)(\Delta\alpha_1/\Delta\alpha_2)(T_g - T_{g1}) \quad (3)$$

and below T_{crit} by

$$T_g = T_{g1} + (f_{g2}/\Delta\alpha_1)(\phi_2/\phi_1) \quad (4)$$

to calculate the volume fraction ϕ_1 and ϕ_2.

If $T_{crit} = 414$ K and $\phi_{crit} = 0.327$, the value of $\Delta\alpha_1$ is assumed to be 0.00058 K^{-1} and $\Delta\alpha_2 = 0.001$ K^{-1}.

The values of T_g measured by DSC were used on estimating the values of ϕ_1 and ϕ_2 from Eqs. (3) and (4).

The composition of copolymers can be estimated by the reactivity ratio given by the classic equation [20]

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (5)$$

where F_1 is the mole fraction of monomer 1, f_1 and f_2 represent mole fractions in the monomer feed and r_1 and r_2 the monomer reactivity ratios.

Using values of $r_{PMAA} = 1.4$ and $r_{PMMA} = 0.58$ from the literature [22] the values of ϕ_1 and ϕ_2 were estimated. The data obtained using the two methods are presented in Table 1 as COOH content. The differences among the values found using these methods can be ascribed to the uncertainties of the experimental and theoretical considerations used in the calculations. These results were plotted using T_g as a function of volume fraction as depicted in Fig. 1.

The experimental curve presents a good fitting with the curve outlined by the Braun and Kovacs theory. The same occurs with the data obtained by the application of the copolymer equation. The cusp is slightly suggested between 0.4 and 0.6 PMAA. Despite the good fitting, these results must be regarded with caution taking into account the restrictions inherent to the method used to estimate the amount of methacrylic acid units incorporated to the copolymer backbone.

3.2. FTIR analyses

Fig. 2 shows the FTIR spectra for MMA–MAA copolymers. Spectral changes due to copolymer composition are evident. The spectra present the broad 'bonded' O–H stretching vibration typical of carboxylic groups (3700–3100 cm^{-1}) that changes with the MAA content in

Table 1
Probable COOH content in MMA–MAA copolymers estimated by calorimetry (DSC) and by monomers MAA and MMA reactivity ratios

Copolymer	Obtained by DSC		Obtained by r_1, r_2	
	COOH (%)	T_g (K)[a]	COOH (%)	T_g (K)[b]
CoMAA80	82	431	85	432
CoMAA60	73	428	67	425
CoMAA40	54	420	46	416
CoMAA20	31	404	23	398

[a] Experimental value.
[b] Calculated from Braun–Kovacs equation.

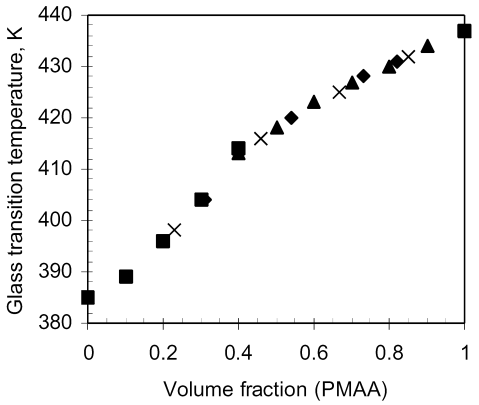

Fig. 1. T_g as a function of volume fraction estimated from (◆) experimental data; (■) Braun–Kovacs equation below T_{crit}; (▲) Braun–Kovacs equation above T_{crit} and (×) T_g estimated from ϕ_1, ϕ_2 from r_1, r_2 calculation.

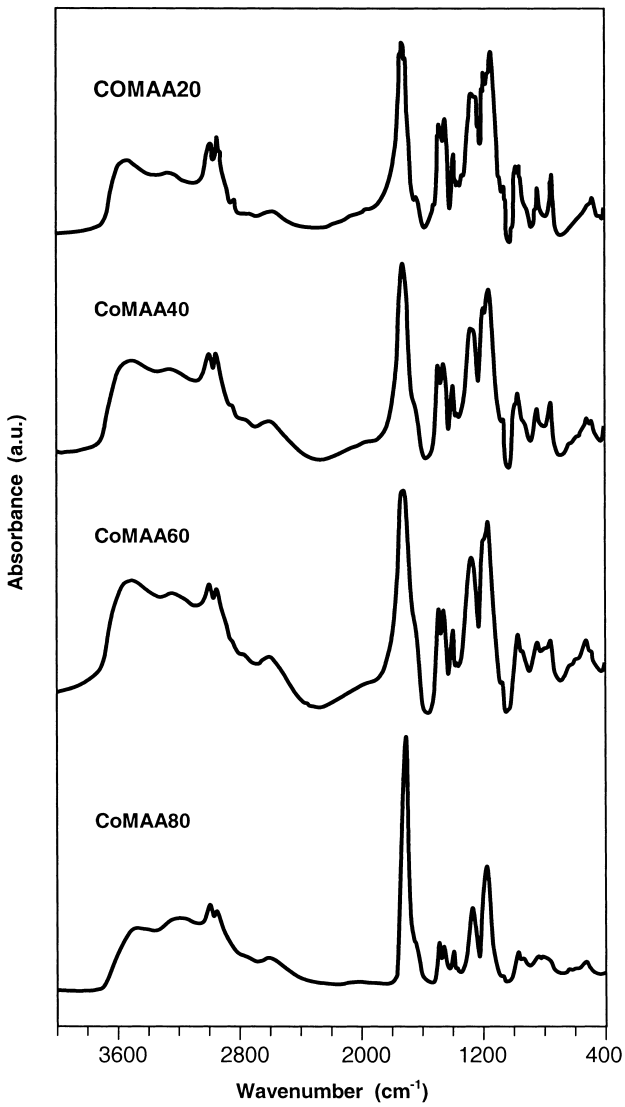

Fig. 2. FTIR spectra of MMA–MAA copolymers CoMAA20, CoMAA40, CoMAA60 and CoMAA80.

the copolymer. The C=O stretching vibration is typical of the ester/acid carbonyl groups at ~1732/1710 cm^{-1}, and the region below 1600 cm^{-1} presents some differences in the profile pattern of the absorptions. The CH_3, CH_2 deformation vibrations are clearly observed at 1487, 1452 and 1389 cm^{-1}, in all spectra [23]. The region between 1000 and 600 cm^{-1} is more sensitive to copolymer composition. However, this region shows peaks that are typical of PMMA and PMAA and the interpretation of the spectra becomes very difficult.

The FTIR spectra of sodium salts of MMA–MAA copolymers are depicted in Fig. 3. The carbonyl absorption region presents the ester/acid absorptions at ~1720 cm^{-1} and the asymmetric carboxylate stretching band near 1560 cm^{-1}. The intensities of these bands change with copolymer composition. The neutralization of the acid units decreases the intensity of the ν(C=O) while it increases the bands from $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$. Table 2 shows the wavenumber of the C=O stretching vibrations in the region of 1900–1400 cm^{-1} as a function of copolymer composition. The peak wavenumber of the ν(C=O) absorption also shifted to lower frequencies. Han and Williams [5,6] pointed out that the increase of the degree of neutralization promotes the formation of clusters and multiplets. These clusters and multiplets involve metal cations (Na^+) that act as electron acceptors (Lewis acid) and acid carbonyl groups non-neutralized as electron donors [2,3]. This absorption is absent in pure sodium salt of PMAA as reported before [8].

Fig. 3 also shows the presence of the broad O–H

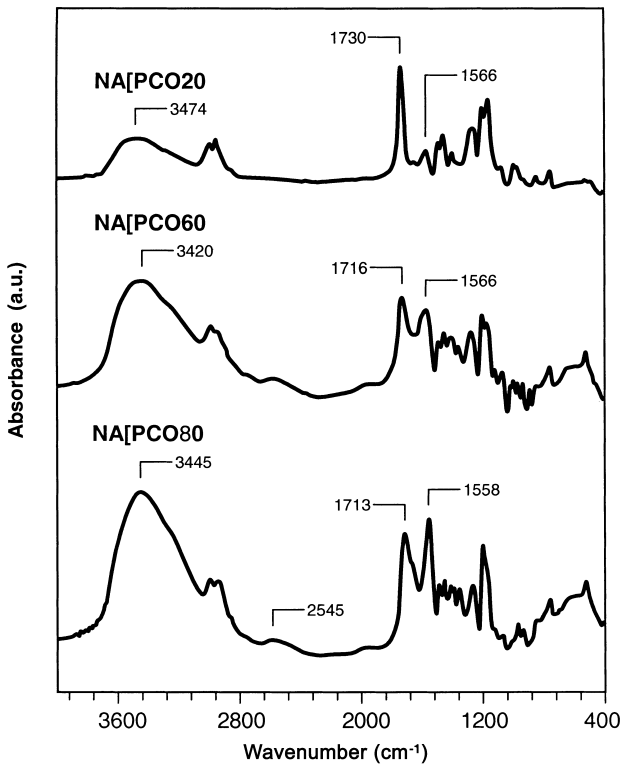

Fig. 3. FTIR spectra of sodium salts of MMA–MAA copolymers Na[PCo20], Na[PCo60] and Na[PCo80].

Table 2
FTIR C=O stretching vibrations in 1900–1400 cm^{-1} region

Assignments	Absorption bands (cm^{-1})			
	Na[PCo20]	Na[PCo60]	Na[PCo80]	NaPMA [8]
νC=O ($COOCH_3$)	1730	1716	1713	–
ν_{asym}C=O (COONa)	1566	1566	1558	1566
ν_{sym}C=O (COONa)	$1395^{(sh)}$	1401	1410	1394

(sh)-Shoulder observed using scale expansion.

stretching vibration characteristic of the carboxylic groups near 3440 cm^{-1}. These spectra indicate that the acid/base neutralization is not complete and the sodium copolymer still have non-neutralized acid groups as reported by Kutsumizu and co-workers [24]. This absorption can be attributed to the OH stretching vibration from groups with weaker bonding. The spectra of copolymers depicted in Fig. 2 show clearly a different profile in this region. FTIR of systems composed by ethylene–methacrylic acid copolymers [EMAA] with high MAA content (18, 32, 44, and 55 wt% MAA) were studied by Lee and co-workers [25]. The MAA content of the copolymers CoMAA20 and CoMAA40 are in this range and this reference can give some help in the present work. The broad O–H stretching band observed in the spectra shown in Fig. 2 results from various structures containing different hydrogen bond strengths, which are sensitive to the environment of the carboxylic acid group associated with the absorption. The band shows two maxima above 3000 cm^{-1}. The maximum around 3500 cm^{-1} is usually ascribed to the 'free' hydroxyl stretch and near 3200 cm^{-1} the absorption is attributed to the self-associated carboxylic groups. The overtone and combinations bands [23,25] are also observed in all spectra as a broad band centered at approximately 2600 cm^{-1}. The mentioned work discusses the complexity of the system, now increased by the presence of the ester groups from MMA.

Lee and co-workers [25] pointed out that at room temperature the large majority of the carboxylic acid groups exist as intermolecular dimers. The spectra of the sodium copolymers presented in Fig. 3 show the broad 'bonded-OH' stretching vibration, near to 3440 cm^{-1}, that can be attributed to the OH stretching vibration from groups with weaker bonding. This suggests that the ion pairs and those non-neutralized COOH groups can form associative structures, which gradually changed from ion pairs to triplets, to quartets, etc. until multiplets are formed. This assumption is based on the theory proposed by Eisenberg [26] once the copolymers studied in this work is composed by ester and acid sequences randomly distributed in the backbone. This happens probably due to the incomplete neutralization and fast precipitation of sodium copolymer. Han and Williams [5] reported that the concentration of the poly(ethylene-*co*-methacrylic acid) influenced the rate of neutralization. Then, high concentrations of copolymer decrease the rate of

neutralization. On the other hand, the presence of small amounts of water is helpful in increasing the rate of neutralization. However, these authors assigned that the influence of water on the rate of neutralization is dependant on the ionization of the carboxyl group [5]. The copolymers Na[PCo20], Na[PCo60] and Na[PCo80] present a broad absorption in this region indicating different aggregation forms. However, it is convenient to remind that the presence of water residues in the samples is also possible.

Water molecules remain as residues even in freeze-dried samples and promote the formation of aggregation forms, which involve different numbers of ion pairs [5]. Han and Williams [6] showed that the process of cluster formation is a chemical equilibrium process and is water sensitive. The absorption attributed to the OH stretching vibration around 3400 cm^{-1} may be associated with the OH groups of sorbed water molecules that form hydrogen bonds [24]. The information can be also used to explain the pattern observed in the 3600–2500 cm^{-1} region of the sodium copolymers spectra. The profile of the absorption near 3440 cm^{-1} is similar to the OH absorption from the EMAA associated with the OH groups of sorbed water as reported by Kutsumizu and co-workers [24]. Thus, the absorptions presented in Table 2 suggest that according to the interpretation given by these authors the examined samples can present different degrees of water sorption. The C=O asymmetric and symmetric stretching vibrations at ~1560 and ~1400 cm^{-1} typical of metal carboxylate (COONa) are exhibited at frequencies that were ascribed to the COONa ion pair from hydrated EMAA-based ionomer. On the other hand, Andreeva et al. [13] assigned the carboxylate absorption at 1565 cm^{-1} to the asymmetric vibration of the carboxylate ion in ionic clusters and the same vibration at 1550 cm^{-1} in ionic multiplets. Na[PCo20] and Na[PCo60] present this absorption at 1566 cm^{-1} and Na[PCo80] at 1558 cm^{-1} (Table 2). These results indicate the possible existence of clusters in Na[PCo20] and Na[PCo60] and multiplets in Na[PCo80]. The complete interpretation of the results became very difficult because the studied copolymers have different carboxyl content randomly distributed in the backbone and can present various association species as well as moisture absorption.

3.3. NIR analyses

NIR spectra can give complementary information on the constitution of copolymers. Fig. 4 shows NIR spectra of PMMA, PMAA and MMA–MAA copolymers. The spectra allow some remarks on the typical absorptions and Table 3 presents their assignments [10,23,27–32]. The spectra show more evident changes in the absorption bands in the region 1800–2600 nm. The band at 1920/1932 nm can be attributed to the second overtone of the carbonyl stretching vibration of PMAA as assigned by the literature [23,28, 30–32] for carboxylic acids. This absorption increases with the methacrylic acid content in the copolymer and is

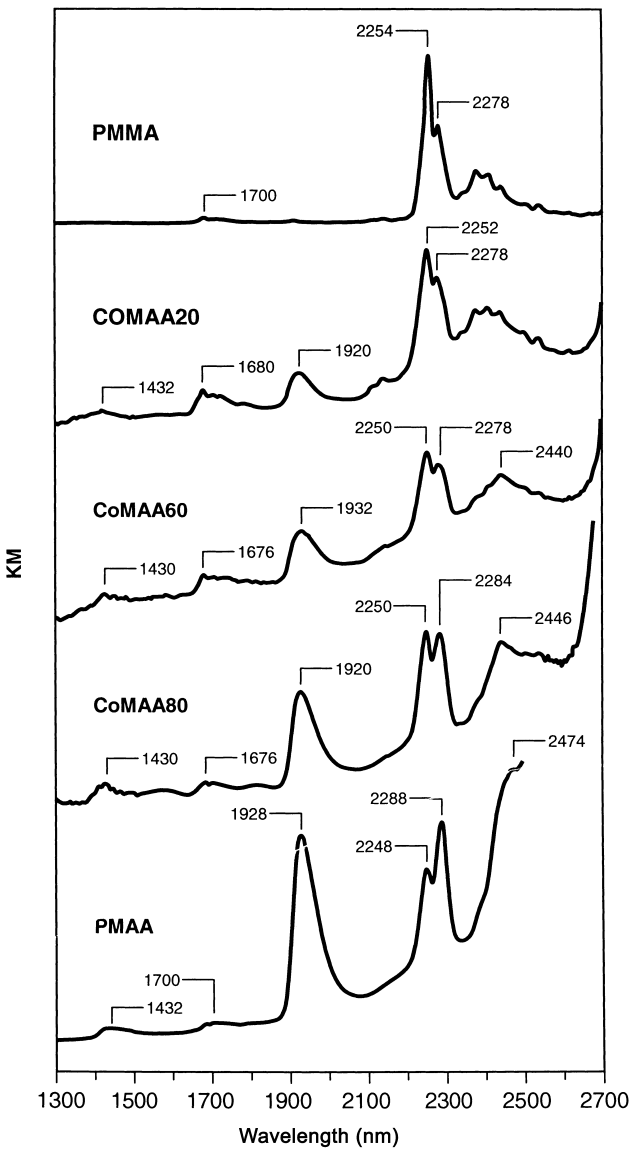

Fig. 4. NIR spectra of PMMA, PMAA and MMA–MAA copolymers CoMAA20, CoMAA60 and CoMAA80.

practically absent in the spectrum of PMMA. The spectra depicted in Fig. 4 show expressive changes of the bands registered above 2100 nm. The intensity of the absorption at 2250 nm (4444.4 cm^{-1}) apparently diminishes with the increase of the copolymer acid content. At the same time an apparent increase of the nearest absorption at 2278 nm (4389.8 cm^{-1}) is observed. PMAA and CoMAA80 present also a shift to higher wavelength. The absorptions were registered at 2288 and 2284 nm, respectively. Roy and Kradjel [31] assigned the absorption at 2250 nm to OH/C=O stretch combination. CH_3, CH_2 and $COOCH_3$ groups compose PMMA chain. Then, a contribution of the ester group to the absorption is suggested. This idea received support with the spectrum of poly(methyl acrylate) (PMA) presented in Fig. 5. The spectrum exhibits these two absorptions at 2252 and 2276 nm with a profile similar to

Table 3
NIR typical absorption bands of PMMA, PMAA and MMA–MAA copolymers

Assignment [23,27–29,31]	Wavelength (nm)				
	PMMA	CoMAA20	CoMAA60	CoMAA80	PMAA
CH_3 combination	2278	2278	2278	2284	2288
CH_3 combination	2254	2252	2250	2250	2248
C=O (acid carbonyl stretch) second overtone[a]	–	1920	1932	1920	1928
C–H/CH_2, CH_3 stretch, first overtone	1700	1680	1676	1676	1700
O–H/acid carboxyl stretch, first overtone[a]	–	1432	1430	1430	1432

[a] OH from water is also observed at ~1400 nm and near 1900 nm.

the spectrum of PMMA. The difference between the two polymers is the methyl groups attached to the main chain absent in poly(methyl acrylate). This indicates that the absorption near 2250 nm can arise from different combination bands. Whetsel [29], Goddu [30] and Crandall [32] suggested that the absorption probably result from combinations involving the C–H stretching bands and the C–H deformation bands. The methacrylate unit presents CH_3 and CH_2 groups and the corresponding stretching absorptions are registered at 2998 and 2954 cm^{-1} respectively, in the mid-infrared region. The deformation bands of these groups were observed at 1487 and 1452 cm^{-1}. Furthermore, the absorption at ~2960 cm^{-1} was assigned to the C–H stretching of the O–CH_3 group and the asymmetric deformation band occurs at 1455 cm^{-1} [23]. This indicates the complexity of the band assignment. The NIR spectra showed that the relative intensity of the absorption diminishes when COOH group substitutes the ester group. The absorption is still observed in the spectrum of PMAA and NaPMA. The region above 2300 nm is typical of each sample. Goddu [30] reported that bands at 2278 and 2440 nm were correlated with the methyl content of the polymers. These bands are due to combination of the C–H stretching bands and the C–H deformation bands [29,30]. However, as the acid content increases, these CH_3 absorptions are overlapped by the strong absorption in the 2700–3000 nm region, attributed to the O–H stretching vibration of the carboxylic group. Further work in the 2200–2400 nm region will give some contribution to

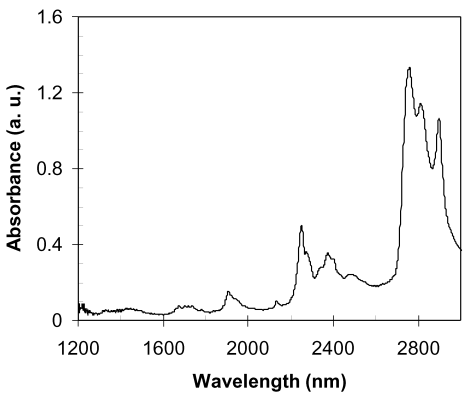

Fig. 5. NIR spectrum of poly(methyl acrylate) (PMA).

spectra-structure relationships. The absorption bands attributed to first overtone of the CH stretching mode at ~1700 nm suggest that the increase of the carboxyl group content in the MMA–MAA copolymer promotes a decrease in the relative intensity of 1676 nm absorption. However, the absorptions at this region are weak as compared to the bands observed above 1800 nm. Fig. 4 also presents weak absorptions near 1430 nm. This absorption is attributed to weak C–H combination bands [30], to the first overtone of the monomer hydroxyl stretching vibration of the COOH group [28,29,31] and is one of the four absorptions of water in the near-infrared region. The NIR spectrum of water has absorptions at about 2760, 2700, 1900 and 1390 nm that may be shifted to longer wavelengths because of various types of hydrogen bonding [28–30]. The determination of water is usually carried out directly by measuring the absorption at 1450 or 1920 nm [29,30]. The low intensity of the band at 1430/1432 nm in Fig. 4 can suggest the presence of water. However, it is very difficult to determine its amount in the copolymers because the absorptions of water are very close to the hydroxyl bands of the COOH group. This indicates that copolymers with different MAA content that are proportional to the MMA: MAA (wt%) used in polymerization were obtained as indicated by DSC. However, the spectra suggest the presence of residual water in the examined samples. This corroborates the interpretation of the FTIR spectra.

NIR spectra of sodium salts of MMA–MAA copolymers are shown in Fig. 6 and Table 4 shows the characteristic absorptions. The absorption band broadening is observed in all spectra. The broad absorption centered near 2470 nm indicates an increase of the OH carboxylic vibration and some moisture absorbed in the films used as samples. The increase is suggested by the relative intensity of the broad band as compared to the absorptions near 2250/2280 nm. These two absorptions maintained their profiles. The increase of the COOH units in the polymer chain decreased the apparent intensity of the absorption at 2252 nm that was not affected by the neutralization with NaOH. The absorption at ~1930 nm due to C=O (acid carbonyl stretch) second overtone is also more intense and a frequency shift to higher wavelength is observed. This suggests incomplete neutralization of acid groups in copolymers and this

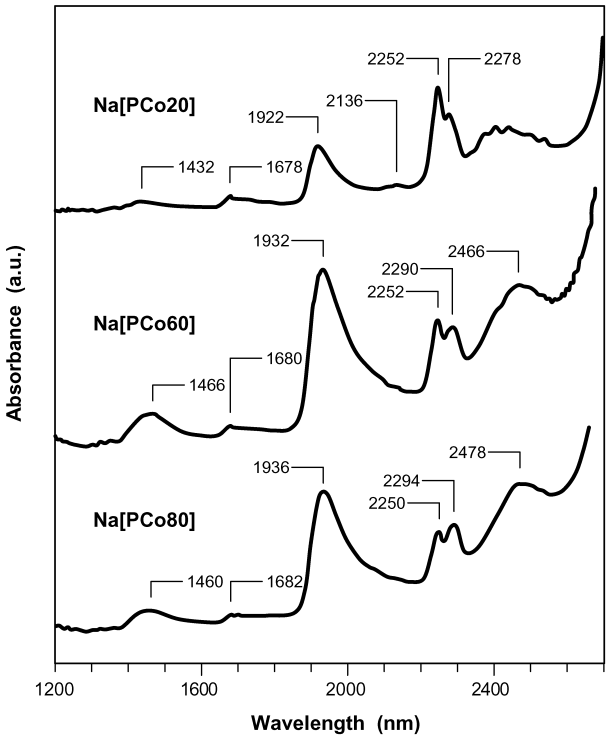

Fig. 6. NIR spectra of sodium salts of MMA–MAA copolymers Na[PCo20], Na[PCo60] and Na[PCo80].

hypothesis is coherent with FTIR results. The broadening of absorptions indicates that after neutralization the samples undergo changes on their chemical environment. It can be also ascribed to the high solubility in water of the sodium salts of MMA–MAA copolymers. Water can be retained in polymeric matrix even after drying process. Fukuda et al. [33] demonstrated the influence of the relative humidity in the near-infrared spectrum of moisture sensitive polymers. The region around 1450 nm presents a shift to high wavelength that is more evident for the samples with high COOH content.

Fig. 7 exhibits the NIR spectrum of NaPMA. It can be noted that this spectrum shows absorptions better resolved in the examined range. Table 4 shows the absorptions near

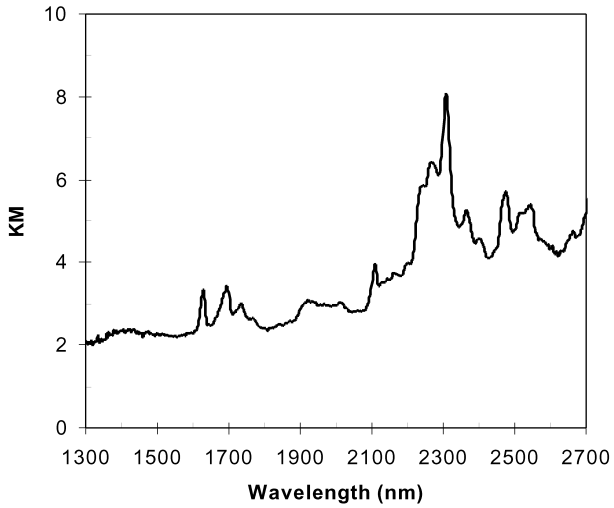

Fig. 7. NIR spectrum of NaPMA.

2250/2280 nm that gives support to the interpretation given for Figs. 4–6. The spectrum also shows a small peak at 2112 nm that was attributed to the third overtone of the carboxylate ion of NaPMA (at 1557 cm^{-1} in mid-IR). This absorption is buried by the absorption at ~1900 nm in Na[PCo60] and Na[PCo80] copolymers but can be observed in the spectrum of Na[PCo20]. The relative humidity, water sorption, etc. influenced these results, but the information given by the spectra encouraged complementary studies.

3.4. Far infrared analyses

Far infrared spectra in the region of 600–150 cm^{-1} were obtained for PMMA, PMAA and MMA–MAA copolymers. The spectra showed broad absorptions. Fig. 8 exhibits the spectra. Table 5 summarizes the frequencies of the more typical absorption bands and their assignments [14,16].

The absorption bands above 500 cm^{-1} and between 483 and 491 cm^{-1} may be also observed in the copolymers spectra recorded in the mid-infrared region as a weak absorption [34,35]. The assignment of these absorptions is not completely clear, but it was attributed to the

Table 4
NIR typical absorptions of NaPMA and sodium salts of MMA–MAA copolymers

Assignment [23,29,31]	Wavelength (nm)			
	Na[PCo20]	Na[Pco60]	Na[PCo80]	NaPMA
C–H combination	–	2466	2478	2478
CH_2 combination	–	–	–	2312
CH_3 combination	2278	2290	2294	2274
CH/C=O stretch combination	2252	2252	2250	2246
COO^- third overtone[a]	2136	–	–	2112
C=O (acid carbonyl stretch) second overtone[b]	1922	1932	1936	1944
C–H/CH_2, CH_3 stretch, first overtone	1678	1680	1682	1700
O–H/acid carboxyl stretch, first overtone[a]	1432	1466	1460	–

[a] NaPMA COO^- fundamental absorption was observed at 1557 cm^{-1}.
[b] OH from water is also observed at ~1400 nm and near 1900 nm.

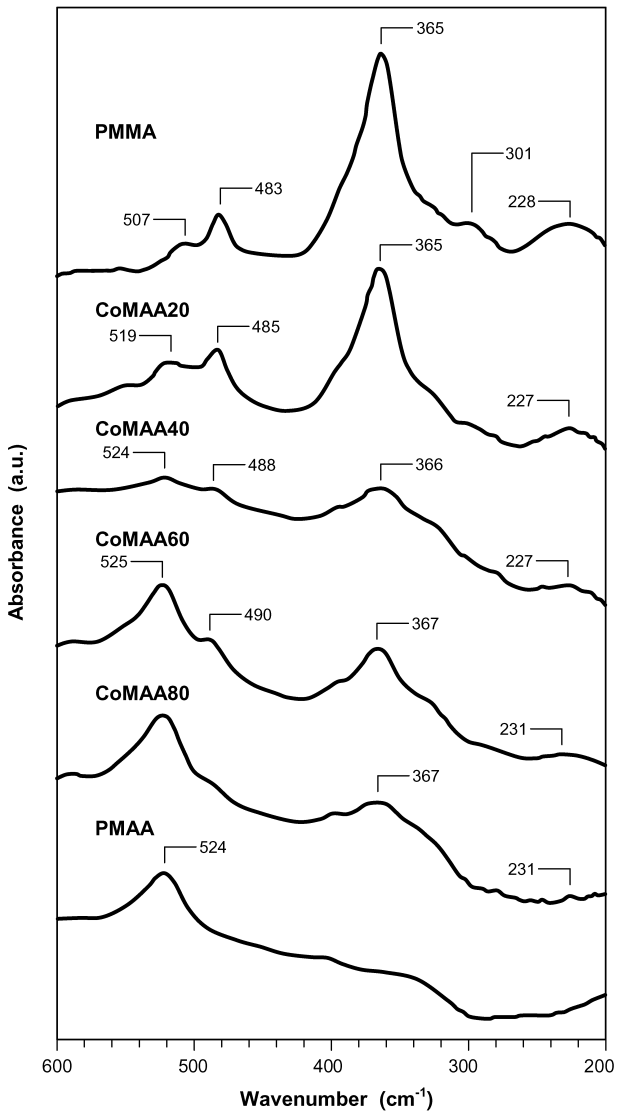

Fig. 8. Far-IR spectra of PMMA, PMAA, CoMAA20, CoMAA40, CoMAA60, and CoMAA80.

out-of-plane bending (or wagging) of the C–C–C groups from the polymer backbone by Tsunashima et al. [16]. The authors suggested another explanation for this absorption based on hydrogen bonding effects where the dimers of the pendant COOH group act as crosslinks. Fig. 8 shows that the absorption is observed at 507 cm^{-1} in PMMA increases with the carboxylic content in the copolymers and is the most meaningful absorption in PMAA at 524 cm^{-1}. This absorption increase suggests the influence of the carbonyl group on the chain vibrational modes. The opposite effect is observed in the absorption near 483–491 cm^{-1} that shows a progressive decrease of the absorption with the increase of the acid content in the polymer chain. The absorption is a peak at 483 cm^{-1} in PMMA became a shoulder at ~491 cm^{-1} in CoMAA80 and may be overlapped by the absorption at 524 cm^{-1} in PMAA. The same behavior is showed in the spectrum of PMMA. It presents an intense absorption band at 365 cm^{-1} that decreases in the spectra of the copolymers and in the spectrum of PMAA seems a shoulder at ~358 cm^{-1}. This absorption was attributed to the C–C–C bending [14,16]. The influence of the carboxyl group in this absorption is evident. This effect can be also observed in the absorption at 228 cm^{-1}. This band was attributed to a weak internal mode of the polymer by Rouse et al. [14]. The absorption at ~410 cm^{-1} that was assigned at 405 cm^{-1} by Rouse et al. [14] can be due to a vibration along the polymer backbone. The spectrum of PMAA depicted in Fig. 9 shows the mentioned absorptions and the absorption typical of the hydrogen bonded dimer at 165 cm^{-1} according to the assignment of Moller and Rothschild for carboxylic acids [36].

The data listed in Table 5 show small frequency shifts in the absorption band registered at ~365 cm^{-1}. The same occurs in the absorption registered at 483 cm^{-1} for PMMA. According to Tsunashima et al. [16] and Kutsumizu and co-workers [24], these frequency displacements indicate that the polymer backbone become more rigid. This may be promoted by the occurrence of clustering to form more ordered aggregates or by crosslinks from dimers of the pendant COOH groups as suggested by Tsunashima and Moller [16,36]. These results are coherent with the DSC and mid-FTIR data.

It is known that water presents strong absorptions in this region of spectra [15]. The band broadening exhibited in Fig. 8 indicated that there is some water retained in the polymer and copolymer samples as showed by the near-infrared spectra.

Table 5
FAR-IR frequencies of MMA–MAA copolymers

Assignment [14,16,23]	Wavenumber (cm^{-1})					
	PMMA	CoMAA20	CoMAA40	CoMAA60	CoMAA80	PMAA
C–C–C skeleton vib. (?)	507	519	524	525	524	524
C–C–C skeleton vib. (?)	483	485	488	490	491	–
C–C–C bending	–	–	–	–	401	414
C–C–C bending/twisting	365	365	366	367	368	358 (sh)
Polymer weak internal mode	228	227	227	231	–	–
Vibrations of aggregates	–	–	–	–	–	165

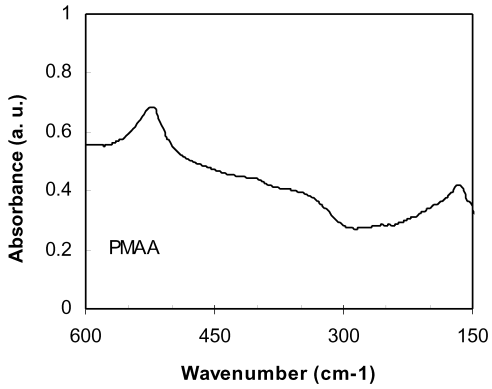

Fig. 9. Far-IR spectra of PMAA.

The far-IR results from the sodium salts of MMA–MAA copolymers are listed in Table 6 and Fig. 10 shows the spectra of sodium salts of MMA–MAA copolymers. The spectra show the absorption at 528 cm^{-1} in all samples. The second absorption in this region is observed at 492/495 cm^{-1} in the spectrum of Na[PCo20], Na[PCo40] and Na[PCo60]. It may be submerged by the absorption at 528 cm^{-1} in the spectrum of Na[PCo80]. The spectra also show weak absorptions at 420, 406 and 419 cm^{-1}, for Na[PCo40], Na[PCo60] and Na[PCo80], respectively. Rouse et al. [14] assigned this absorption as the C–C–C bending along the polymer chain that can be observed in the 350–450 cm^{-1} frequency range in straight-chain alkanes.

The results in Table 6 and Fig. 10 showed that changes occurred on the wavenumber and in the intensity of the absorptions. The mentioned work [14] pointed out in the spectrum of Na^+ ionomer the absorption at 386 cm^{-1}. They suggested that the vibration that gives rise to this band is associated with the anion site. They proposed that the band is a perturbed carboxylate ion mode that is result of two coupled vibrational modes (C–C–O and O–C–O bending motions). The absorption occurs near 370 cm^{-1} in this work. However, the spectra of MMA–MAA copolymers showed this absorption at 365 cm^{-1}. This band is absent in the acid form. Then it is possible that this absorption arises from vibrations of the carboxylic group and can be observed either in esters (at lower frequencies) or in carboxylate ions. The primary cation-motion band is observed at about

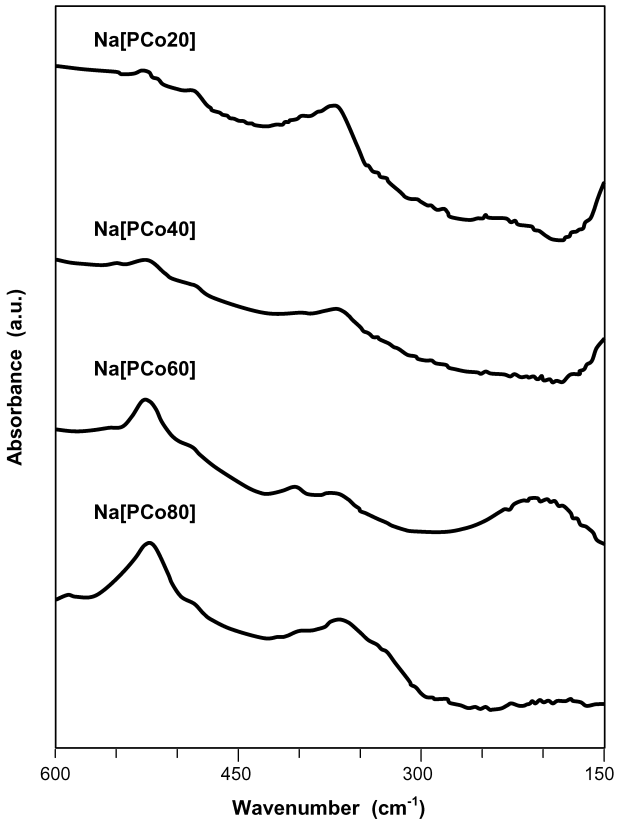

Fig. 10. Far-IR spectra of Na[PCo20], Na[PCo40], Na[PCo60] and Na[PCo80].

250 cm^{-1} and is fairly suggested in the Na[PCo20] spectrum. This band was assigned to the vibration of an aggregate involving few ions [14]. This absorption is also observed as a shoulder in the NaPMA spectrum depicted in Fig. 11. The spectrum of NaPMA shows an intense absorption at 195 cm^{-1} assigned to the vibration of aggregates involving many cations and anionic sites close together.

Effects of the formation of ionic clusters also appear in the COO^- vibrational and C–C–C skeletal deformation modes. The neutralization of the carboxylic groups indicated the occurrence of these effects. The spectra recorded for the non-neutralized copolymers exhibited

Table 6
FAR-IR frequencies of sodium salts of MMA–MAA copolymers

Assignment [14,16]	Wavenumber (cm^{-1})				
	Na[PCo20]	Na[PCo40]	Na[PCo60]	Na[PCo80]	NaPMA
C–C–C skeleton vib. (?), COO^-	528	528	526	528	545
C–C–C skeleton vib.	492	492	495	–	–
Internal mode	–	420	406	419	464
Perturbed COO^- mode	374	371	371	378(sh)	401
Na–O in multiplets	249	–	–	280	245(sh)
Internal mode	–	–	205	214	–
Na^+ (cluster mode)	–	–	–	–	195

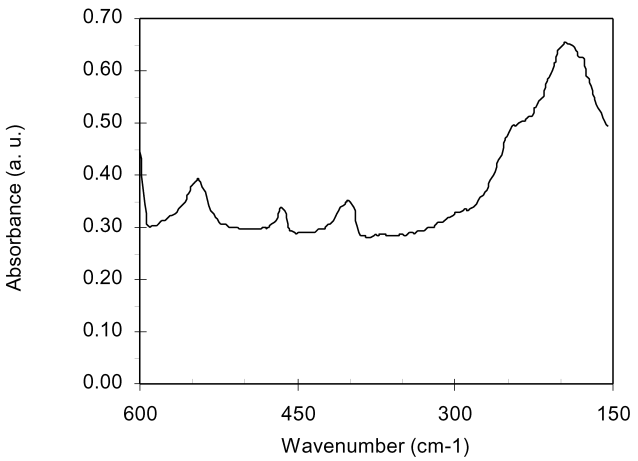

Fig. 11. Far-IR spectrum of NaPMA.

small frequency shifts in the absorption observed at $\sim 370\ cm^{-1}$ in the sodium copolymers. These higher energy shifts seem to be related to the aggregate formation and other interaction effects remembering that the neutralization of the samples examined was incomplete. Following the interpretation given by Rouse et al. [14] and Tsunashima et al. [16] these vibrations may indicate the presence of many Na–O modes corresponding to the aggregates of COO^- groups such as ionic multiplets or clusters.

4. Conclusion

The study of MMA–MAA copolymers in near, mid and far infrared showed that the acid groups are not completely neutralized on preparing the sodium salts of these copolymers. The spectra indicated that the COOH content in the copolymer influenced the relative intensity of absorptions associated to this group in all examined ranges. The NIR results suggest the influence of the ester group in the absorption at 2250 nm and the effect caused by the presence of water residues seems to be small in this range. The neutralization of the carboxylic groups promoted the rise of different clusters and other aggregates (clusters, dimers, triplets, multiplets, etc.). The results also indicate that the increase of sodium carboxylate groups in copolymers promotes an absorption/retention of water in the polymer matrix even after drying.

The spectroscopic data showed that the presence of different types of aggregates could explain the results obtained in the estimation of the COOH content by DSC.

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