

Thermal Analysis and NMR Studies of Methyl Methacrylate (MMA)–Methacrylic Acid Copolymers Synthesized by an Unusual Polymerization of MMA

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Received 9 September 1999; accepted 7 June 1999

ABSTRACT: Methyl methacrylate–methacrylic acid (MMA–MAA) copolymers were prepared from the polymerization reaction of the methyl methacrylate (MMA) monomer with concentrated nitric acid (65% HNO₃) at different reaction times in the absence of other reagents in the reaction mixture. The hydrolysis degrees of the MMA–MAA (sodium salts) copolymers estimated by thermogravimetry (TG) corroborated the data obtained by chemical titration. By calorimetry (DSC), a relationship between the glass transition temperature (T_g) and the hydrolysis degree was obtained. The results presented a deviation from linear behavior and it was related to the strength of the interactions involved in the copolymer chains. The equation that relates the glass transition temperature to the interaction parameter, χ , for miscible binary polymer blends was applied for the MMA–MAA copolymers and demonstrated the composition dependence of χ . The molecular mobility was determined by nuclear magnetic resonance (NMR) in the solid state and through the proton spin-lattice relaxation time in the rotating frame. The NMR data were in a good agreement with the results obtained by calorimetry. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 495–507, 2000

Key words: methacrylic copolymers; glass transition temperature; calorimetry; molecular mobility; nuclear magnetic resonance

INTRODUCTION

The polymerization of methyl methacrylate using concentrated nitric acid as an initiating agent in the absence of other reagents was reported previously.^{1–3} High molecular weight ester–acid copolymers were produced from this reaction, and the studies showed that the nature of the product depends on the temperature, the monomer:HNO₃ molar ratio, and the reaction time.^{1,2} In this work, methyl methacrylate–methacrylic acid (MMA–MAA) copolymers, obtained through this reaction,

were studied using thermogravimetry (TG), differential scanning calorimetry (DSC), and nuclear magnetic resonance in the solid state (NMR).

The decomposition curves of poly(methyl methacrylate) (PMMA) and poly(methacrylic acid) (PMAA) are quite similar. The polymers decompose in two steps at the same temperature range and the quantitative evaluation of methacrylic copolymers by thermogravimetry becomes very difficult.^{4–8} On the other hand, the degradation curves of the MMA and alkali metal methacrylate copolymers present three steps.^{9–12} The complexity of the problem showed that many questions remain unclear. These features encouraged this study and allowed presenting the characterization and the determination of the hydro-

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Contract grant sponsors: CNPq; CAPES; FINEP.

Journal of Applied Polymer Science, Vol. 75, 495–507 (2000)

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CCC 0021-8995/00/040495-13

lysis degree that occurred in the ester units during the polymerization step.

DSC is very useful in the investigation of the thermal properties of a single polymer and systems composed of two components such as blends and copolymers.^{13–15} Random copolymers and compatible blends exhibit a single glass transition temperature (T_g), usually lying intermediate between the T_g of the corresponding pure homopolymers. It can be predicted by a number of relationships originally applied to relate the glass transition temperature of random copolymers and compatible polymer blends to their composition.^{15–20} Examples are the well-known rule of mixtures and the equations proposed by Fox and by Gordon–Taylor.¹⁸ The equation of Gordon–Taylor introduces a parameter, k , defined as the ratio of the difference in thermal expansion coefficients ($\Delta\alpha_2/\Delta\alpha_1$) between the rubbery and glassy states for homopolymers 1 and 2. The parameter k was also defined by various authors^{19–23} as the ratio of the increment of the heat capacity of the two components, ΔC_{p_i} , at the glass transition temperature when T_{g2}/T_{g1} is close to unity. The constant k increases with increasing strength of the polymer interactions and can be used as a measurement of miscibility.^{18,19} However, the predictions of those equations show deviation from linearity in systems with strong intermolecular interactions.

These equations predict a monotonous dependence of the T_g upon the concentration and do not allow for the presence of a break (cusp) in the curve that may often be observed experimentally.²⁰ The literature indicates that several systems exhibit this singular point as a function of composition^{20,21} and Braun and Kovacs¹⁶ (free-volume theory) predicted it. According to this theory, when $T_{g2} - T_{g1}$ is larger than about 50°, the free volume of polymer 2 becomes zero at a critical temperature, T_{crit} . This critical temperature and the corresponding volume fraction, ϕ_{crit} (relative to polymer 1), can be calculated and the theoretical curve can be compared with the experimental data.^{16,20,21}

The model of the copolymers considered as binary blends of the two constituent mers would predict a monotonic variation of the T_g with the composition and include the mer–mer interactions.^{16,22} Lu and Weiss²³ extended the theoretical considerations proposed by Couchman²⁴ and proposed a relation, which includes a term involving the Flory–Huggins interaction parameter, χ , on correlating the T_g with the composition.

The majority of polymers exhibit a multiplicity of relaxation processes that can be detected by static and dynamic methods. NMR allows the study of molecular movements in polymers over a wide frequency range, offering information on the size domain of polymer systems.¹⁴ This powerful technique is another method of determining T_g .¹⁵

Combined solid-state NMR techniques such as magic angle spinning (MAS) and cross-polarization magic angle spinning (CP/MAS)²⁵ are useful routines to give detailed responses on the molecular structure. MAS can give information on the flexible region, if the delay between the pulses is short enough for that. CP/MAS shows all types of carbon-13 and the heterogeneity in the structure can be detected. An important response on the sample molecular structure is a comparison of MAS and CP/MAS spectra that permits evaluating the structural heterogeneity.

The molecular mobility in polymers can be investigated by a series of ¹³C-CP/MAS spectra, varying the contact time during the cross-polarization mode. One of the advantages of CP/MAS experiments is that the resolution allows relaxation data to be obtained on each resolved carbon type of the molecule in the solid state. NMR in the solid state offers a variety of relaxation times. However, direct information on the dynamic molecular mobility can be obtained through the proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}$). In these experiments, the proton $T_{1\rho}$'s were obtained from a series of identical matched cross-polarization transfers from protons to carbons started at variable times after the protons are spin-locked. In this way, these transfers track the decay of the protons after being placed in the rotating frame. The proton $T_{1\rho}$'s are sensitive to spatially dependent proton–proton spin diffusion. Thus, in a blend of two protonated compounds, they are sensitive to the short-range proximity of protonated chains to another one.^{26–29} The main purpose of this work was the study of the behavior of MMA–MAA copolymers by thermal analysis and solid-state NMR.

EXPERIMENTAL

Materials

Commercial MMA and MAA were distilled under a vacuum ($\approx 100^\circ\text{C}$) to remove the inhibitor and kept in a refrigerator until use. Concentrated nitric acid (65% HNO_3 , sp. gr. 1.41) and NaOH were

Table I Characterization of the Polymers³

Polymer	Reaction Time (h)	$[\eta]$ (dL/g)	$[\bar{M}_v]_{\text{PMMA}}$ (10^{-6}) ^a	$[\bar{M}_v]_{\text{COP}}$ (10^{-6}) ^b	COOH Content ^c (%)
PMMA	—	1.2	0.69	0.69	0
CRA-12	12	2.2	1.60	1.55	24
CRA-24	24	2.4	1.81	1.74	29
CRA-48	48	2.6	2.02	1.93	32
CRA-120	120	2.6	2.02	1.90	43
CRA-196	196	2.8	2.23	2.07	51
PMAA	—	1.0	0.14	0.14	100

^a Determined as PMMA using THF as the solvent, $K = 7.5 \times 10^{-5}$ dL/g, $a = 0.72$, at 25°C, and PMAA was determined using methanol as solvent $K = 242 \times 10^{-5}$ dL/g, $a = 0.51$, at 26°C.

^b Corrected according to Bugni et al.¹

^c Determined by chemical titration.

obtained from REAGEN S.A. (Rio de Janeiro, Brazil) and used as received.

Preparation of Polymers

PMMA was prepared by a suspension polymerization technique³⁰ at 72°C with a reaction time of 3 h and with 2,2'-azobisisobutyronitrile as an initiator. PMAA was obtained at 30°C, with a monomer (MAA):HNO₃ 1:1 volume ratio and a reaction time of 18 h.

The polymerization reactions of the MMA-MAA copolymers were conducted in 200-mL cylindrical glass-stoppered jars, protected from light, and fixed in a thermostatic shaking bath kept at $\pm 0.5^\circ\text{C}$ of the established temperature. Blanks for nitric acid and the pure monomer were run and all reactions were carried out with at least two independent samples. The reaction temperature was 30°C, the volume ratio of the monomer (MMA):HNO₃ was 1:5, and the samples were collected after 12, 24, 48, 120, and 196 h of the reaction.¹⁻³

Pouring the reaction mixture in 10 times the volume of water and filtering in a sintered glass filter purified the copolymers. The product was washed with water until complete removal of the nitric acid, dissolved in acetone, and precipitated by pouring in 5 vol of distilled water. The white precipitate was filtered under a vacuum and dried in a vacuum at room temperature for 1 or more days to a constant weight.¹⁻³

The sodium salts of PMAA and the MMA-MAA copolymers were obtained by adding adequate quantities of NaOH methanol solutions. The MMA-MAA copolymer samples were named according to the time reaction. The MMA-MAA co-

polymer abbreviations are CRA-12, CRA-24, CRA-48, CRA-120, and CRA-196; the MMA-sodium methacrylate (MMA-NaMA) copolymer abbreviations are CRS-12, CRS-24, CRS-48, CRS-120, and CRS-196.

Characterization of Polymers

Polymer characterization data are summarized in Table I. Viscosity measurements were described previously³ and the viscometric molecular weights of the products, \bar{M}_v , were obtained using the approximation outlined by Bugni et al.,¹ where samples of these copolymers were submitted to total esterification using diazomethane according to a conventional technique.

TG

TG was carried out on a Perkin-Elmer Model TGA-7 thermobalance. The thermobalance accuracy was within 0.1%, and the chromel-alumel thermocouple precision, $\pm 2^\circ\text{C}$. 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 ≈ 3.0 mg were heated from 30 to 600°C with a heating rate of 10°C/min. The analyses were run with a nitrogen atmosphere at a flow rate of 33 mm³/min for the sample and 60 mm³/min for the furnace.

A calibration curve was constructed for the quantitative analysis. PMMA and NaPMA were mixed on a micromill, Perkin-Elmer, resulting in mixtures of known concentrations (5, 15, 30, 45, and 60 wt % NaPMA). The thermogravimetric analyses (TGAs) of these mixtures were run and the results were plotted using the normalized

Table II Probable Composition of the Copolymers According to Bugni et al.¹

Copolymer	COOH (%)	DP _{COOMe}	DP _{COOH}	<i>m/n</i>	Proportion MMA : MAA
CRA-12	24	12,160	3840	3.17	3 : 1
CRA-24	29	12,850	5250	2.45	5 : 2
CRA-48	32	13,740	6460	2.13	2 : 1
CRA-120	43	11,510	8690	1.32	4 : 3
CRA-196	51	10,930	11,370	0.96	1 : 1

mass residue (%) of the degradation curves as a function of the NaPMA content.

DSC

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 $\Delta H_f = 6.8$ cal/g) as the standard.

Samples of ≈ 10 mg were sealed in aluminum pans and were submitted to a repeated heating/cooling cycle. The heating rates were $10^\circ\text{C}/\text{min}$, and after the first heating, the samples were cooled at a cooling rate of $320^\circ\text{C}/\text{min}$. The reference and sample cells were kept under a nitrogen purge during the measurements. The DSC curves were recorded from 30 to 200°C . The glass transition temperature was measured at the half-height of the heat capacity (ΔC_p) jump in the glass transition zone³¹ recorded during the second scan.

NMR in the Solid State

All NMR spectra were obtained on a VARIAN VXR 300 spectrometer operating at 299.9 and 75.4 MHz for ^1H and ^{13}C , respectively. All experiments were done at the ambient probe temperature and performed using gated high-power decoupling. Zirconium oxide rotors of 7-mm diameter with Kel-F caps were used to acquire the NMR spectra at rates of 6 kHz. Carbon-13 spectra were referred to the chemical shift of the methyl group carbons of hexamethyl benzene (17.3 ppm). The ^{13}C measurements of PMMA, PMAA, and the copolymers MMA–MAA were carried out in the cross-polarization mode with magic-angle spinning (CP/MAS) with a 90° pulse (5 μs), spectral width of 50,000 Hz, and 2 s of delay. The variable contact time experiment was also performed and a range of contact time was established as 200–8,000 μs . Proton $T_{1\rho}^{\text{H}}$ was determined from the

intensity decay of carbon-13 peaks with increasing contact times, using a computer program.

RESULTS AND DISCUSSION

Viscometry

From Table I, it can be seen that copolymers obtained from that unusual reaction present high molecular weight ($>10^6$), and the hydrolysis degree increases with the reaction time. However, the effect on the molecular weight can be considered small. The molecular weights were estimated using the method proposed by Bugni et al.¹ which uses the expressions

$$\text{DP}_{\text{COOMe}} = \text{DP}_{\text{PMMA}}w_1 \quad (1)$$

$$\text{DP}_{\text{COOH}} = \text{DP}_{\text{PMMA}}w_2 \quad (2)$$

$$[\bar{M}_v]_{\text{cop}} = \text{DP}_{\text{COOMe}}M_1 + \text{DP}_{\text{COOH}}M_2 \quad (3)$$

where DP_{COOMe} , M_1 , and w_1 are the polymerization degree, the molecular weight, and the weight fraction of MMA, respectively; DP_{COOH} , M_2 , and w_2 refer to the MAA units; and DP_{PMMA} is the polymerization degree of PMMA. Table II shows the probable composition of the copolymers obtained from these calculations.

Bugni et al.¹ suggested that the formation of the copolymer is at least a two-step process. The first step is the hydrolysis of the monomer MMA to MAA promoted by the nitric acid medium. At the same time, the concentrated nitric acid furnishes the paramagnetic species of NO and NO_2 starting the polymerization. The free radicals produced attacks the monomer MMA and the reaction propagates. Meanwhile, the hydrolysis reaction occurs until the equilibrium is reached and the MAA units increase with time in the copoly-

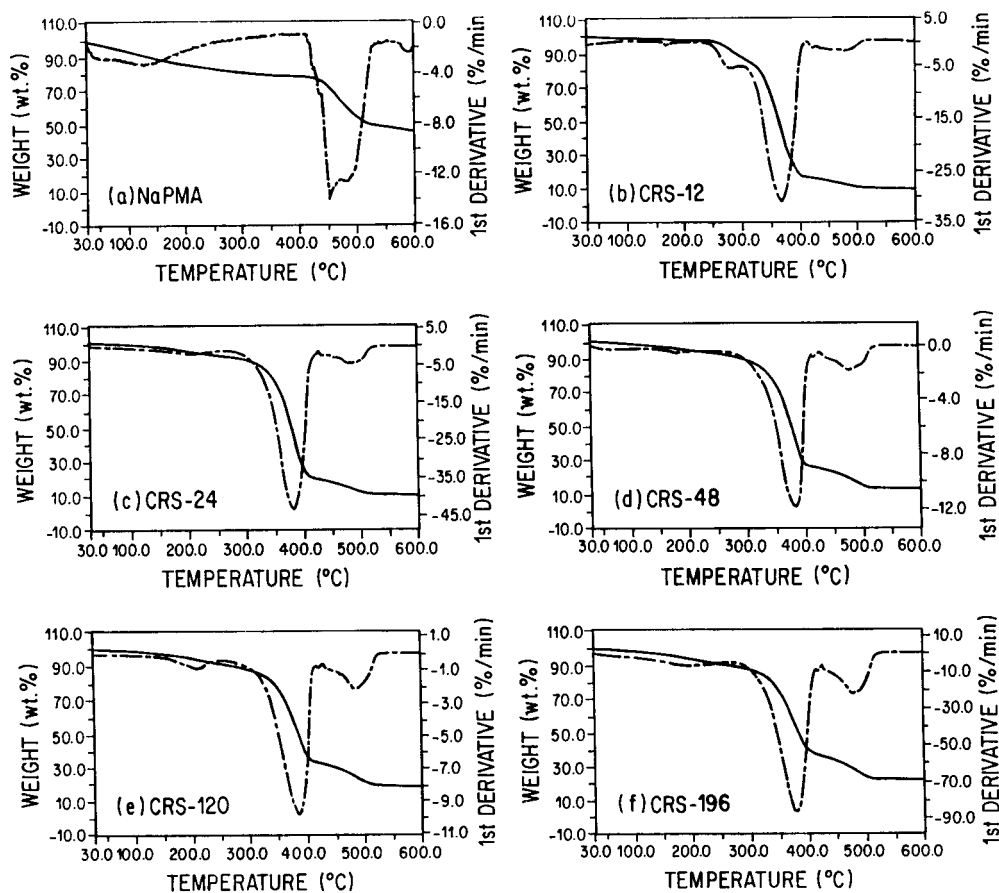


Figure 1 TG curves of NaPMA and the neutralized copolymers.

mer chain. The distribution of COOH groups in the macromolecular chain is still the subject of study, because the reaction presents many unexplained features. It is known that the COOH groups in the long chain are formed by hydrolysis of the monomer MMA and by hydrolysis of the ester units of the polymer as the reaction time increases ($\approx 10\%$), increasing the MAA content.¹

TG

The TG curves of the MMA-MAA copolymers were discussed in a previous work.³ It was shown that at approximately 200°C the MMA-MAA copolymers lose water and methanol through an intermolecular reaction of adjacent MMA and MAA monomer units, producing anhydrides. This first stage which corresponds to a mass loss of $\approx 12\%$ for pure PMMA is not clear for the samples obtained from copolymers prepared from 12, 24, and 48 h of reaction, indicating that the mass loss is small. Samples with higher COOH group content show this stage.

The curve profiles were coherent with the suggestion that three processes occur above 300°C: chain scission and depolymerization of sequences of MMA units, terminating as anhydrides rings; fragmentation of MMA units to give methanol; and fragmentation of anhydride ring structures.^{3,8}

To determine the hydrolysis degree of the MMA-MAA copolymers by the TG curves, the acid groups of the copolymer chains were neutralized. The TG curves of NaPMA and the neutralized copolymers are shown in Figure 1.

It can be seen that the TGA of NaPMA showed that the temperature of the maximum conversion (percentage mass loss) rate was about 450°C. The degradation curves of the MMA-NaMA copolymers presented the degradation peak corresponding to the decomposition of the copolymer salt. The temperature of the maximum conversion rate was about 483°C. All curves showed three degradation steps and higher thermal stability as compared with MMA-MAA copolymers.³

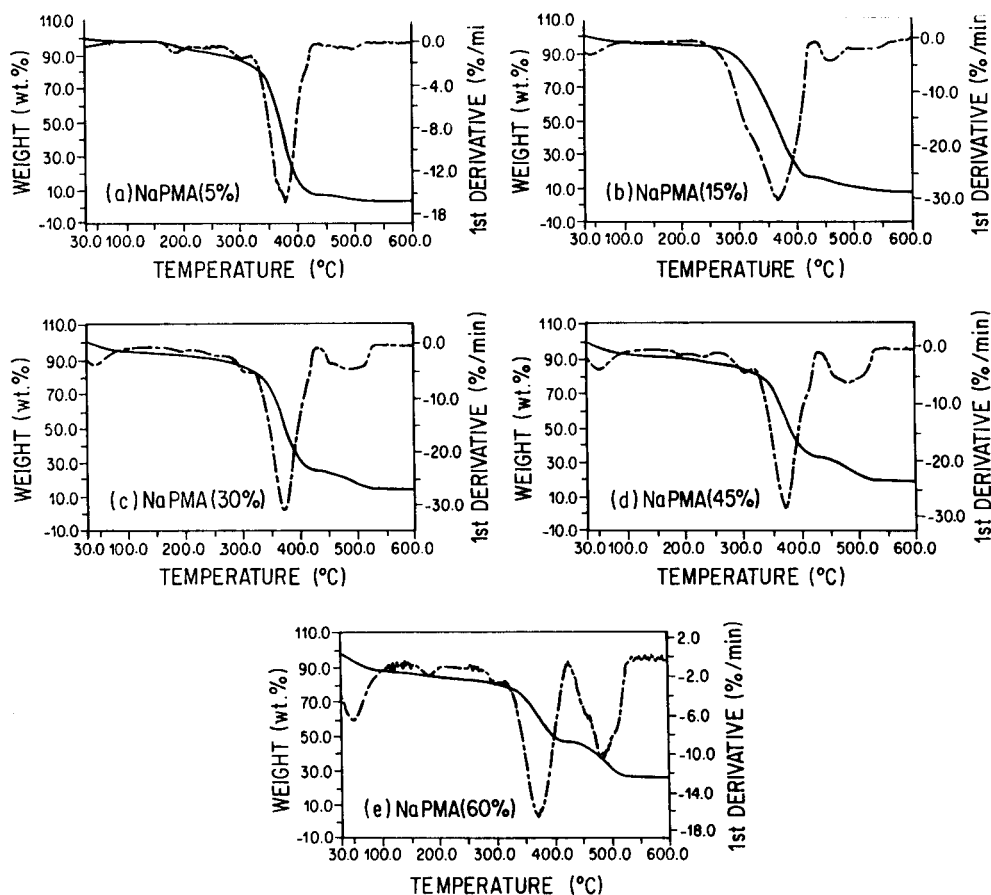


Figure 2 TG curves of PMMA/NaPMA homopolymers blends.

The first stage was attributed to the methanol and MMA monomer formation as pointed out by Hamoudi and McNeill^{9,10} and the mass loss was very subtle as pointed out by Mansur and Monteiro³ for the corresponding copolymers. This step presented the maximum degradation temperature at about 190°C for the copolymers CRS-12, CRS-24, and CRS-48 and around 220°C for the copolymers CRS-120 and CRS-196. The temperature shifts and the broadening of the peaks were attributed to increase of the hydrolysis degree of the copolymers. The second stage could be due to the degradation of MMA units in the copolymer and the maximum degradation temperature was registered at 380°C. Degradation of unsaturated chain ends of PMMA could be the origin of the peak at 290°C presented by the copolymer CRS-12. The NaPMA degradation occurred in the third step.

The literature¹¹ shows that the residues from MMA-NaMA copolymer degradation can be ascribed to NaPMA and the metal carbonate and carbon compose this residue. The quantitative

analysis assumes the existence of these degradation residues. A calibration curve was then constructed using a known proportion of a PMMA/

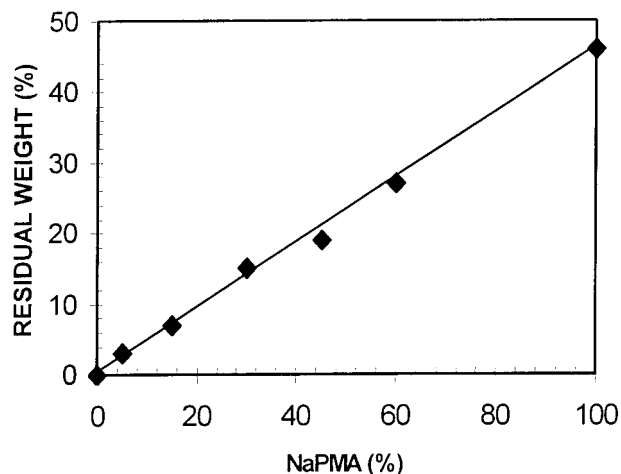


Figure 3 Calibration curve constructed using the TG residue as a function of the NaPMA content in the blend.

Table III Determination of COOH Content of PMMA-PMAA Copolymers from TG Using the Calibration Curve

Copolymer	Residue (wt %)	Hydrolysis Degree (wt %)	
		TG ^a	Titration
CRS-12	10	22	24
CRS-24	12	26	29
CRS-48	15	33	32
CRS-120	19	42	43
CRS-196	21	46	51

^a Determined as NaPMA.

NaPMA homopolymer blend and the degradation residue was plotted as a function of NaPMA wt % in the mixture. The NaPMA degradation residue was also used, and this value was about 46 wt %, as shown in Figure 1. Figure 2 presents the TGA of the mixtures. The curves show a progressive increase of residue with increase of the NaPMA content. The calibration curve constructed using the TG residue as a function of the NaPMA content in the blend is depicted in Figure 3. The results of the NaPMA wt % (hydrolysis degree) in the copolymers obtained from the calibration curve are presented in Table III and were considered satisfactory when compared with the titration results.

Calorimetry

The TG curves showed the anhydride formation above 200°C. The previous work³ showed through

Table IV Thermal Properties of PMMA, PMAA, and MMA-MAA Copolymers Measured Between 30 and 200°C Using DSC

Sample	T_g (K)	ΔC_p (J/g °C)
PMMA	388	0.307
CRA-12	402	0.247
CRA-24	408	0.224
CRA-48	414	0.196
CRA-120	417	0.190
CRA-196	418	0.181
PMAA	439	0.154

Data were collected from the second scan.

DSC and infrared analyses that, in the 30–230°C temperature range, the anhydride formation is too small to influence the T_g and ΔC_p values of the copolymers. Therefore, the correlation between the T_g with the hydrolysis degree was carried out in the 30–200°C temperature range. The second DSC scans are depicted in Figure 4.

Table IV presents the values of the T_g and ΔC_p obtained from these analyses. The data showed that the T_g increases with the reaction time. The value of ΔC_p diminishes and there is a clear tendency to achieve the value obtained for PMAA, indicating an increase in MAA units. The value obtained for PMMA agrees with that reported by Lu and Jiang.³²

Wang et al.³³ pointed out that the specific heat, C_p , is a second-order thermodynamic property, which is associated with molecular motion. It can be used as an indicator of the difference in segment motion or chain packing between a polymer

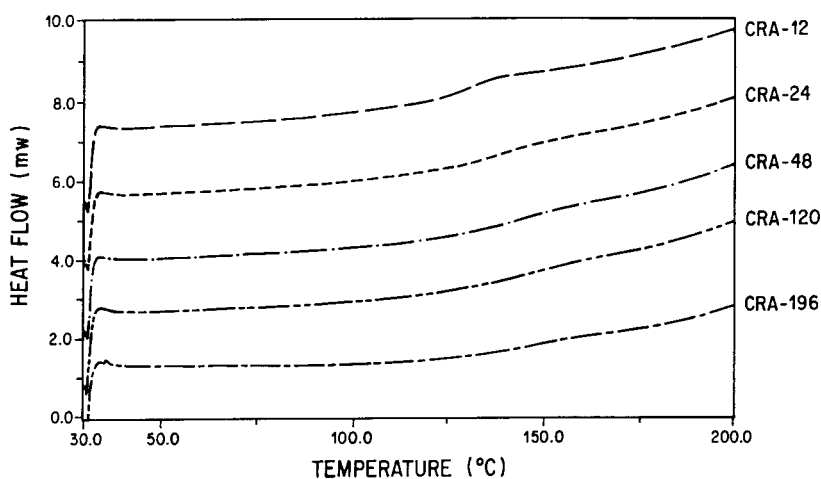


Figure 4 Second DSC scans of PMMA-PMAA copolymers recorded between 30 and 200°C.

blend and a complex of the same composition. When the ΔC_p values were correlated with the molar fraction of MAA of the copolymers, the relationship obtained and depicted in Figure 5 showed that the ΔC_p 's of the copolymers were slightly less than the weight-averaged values expected for a theoretical PMMA–PMAA blend. This result is consistent with the assumption that the formation and dissociation of hydrogen bonds are reversible with the temperature for both small molecules and polymers in the solid state. The T_g measurement involves cycling and, therefore, this process may introduce changes in the segment motion or chain packing. Wang et al.³³ described this process in detail for hydrogen-bonded polymer complexes and some of the assumptions presented at that time may be applied to the PMMA–PMAA copolymers. Hydrogen bonding between the heterochains decreases the mobility of the polymer chains. However, dissociation occurs with increasing temperature so that the net result of the balance between association–dissociation can affect the ΔC_p and negative excess heat capacities were obtained.

The equation of Gordon–Taylor was applied to this system. The result is depicted in Figure 6, where T_g is a function of the MAA content (hydrolysis degree) determined by thermogravimetry (Table III). The value of k was given by the ratio $\Delta C_{p2}/\Delta C_{p1}$ once the T_{g2}/T_{g1} is not very far from unity ($T_{g2}/T_{g1} = 1.13$). Figure 6 shows that the T_g values increase with the PMAA content, as expected. A deviation of the linear behavior (rule of mixtures) is observed when the carboxylic content in the copolymer is higher than 20%.

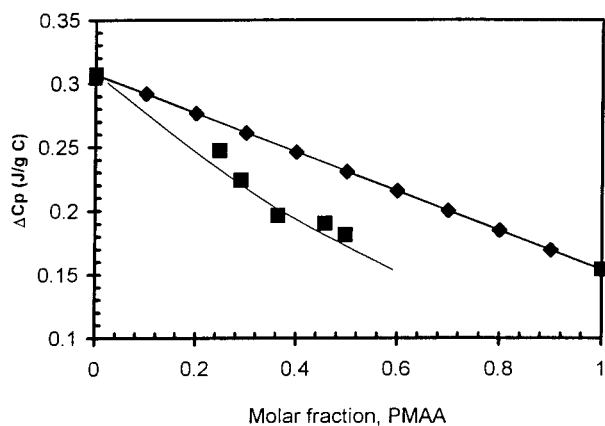


Figure 5 ΔC_p as a function of the composition of PMMA–PMAA copolymers obtained by plotting the data given from (■) experimental measurements and (◆) the mixture rule.

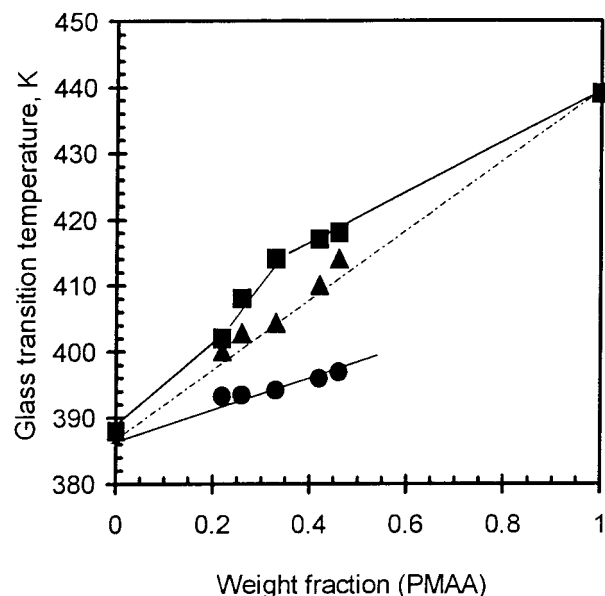


Figure 6 T_g as a function of the composition of PMMA–PMAA copolymers obtained by plotting the data given from (■) experimental measurements, (▲) the mixture rule, and (●) the Gordon–Taylor equation using $k = \Delta C_{p2}/\Delta C_{p1}$.

This unusual pattern (cusp) has been discussed in the literature^{20,21,34,35} and can be related to the increase of the interactions between the copolymer chains promoted by the increase of hydrogen bonding. Lu and Weiss²³ pointed out that the value of the parameter k given by $\Delta C_{p2}/\Delta C_{p1}$ ($k = 0.502$) is adequate for systems where the interactions are very weak. The opposite occurs in the system studied here, which has carboxyl groups arising from the hydrolysis of the MMA ester groups. This suggested that the value of k could be determined from eq. (4) by plotting T_g versus $[(T_{g2} - T_g) w_2/w_1]$ as an initial approach:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (4)$$

where T_g is the glass transition temperature of the copolymer; T_{g1} and T_{g2} , those of components 1 and 2; and w_1 and w_2 refer to the corresponding weight fractions. Figure 7 shows the straight line obtained (correlation coefficient = 0.9676) and the new value of k is 1.773. When this value was substituted in the Gordon–Taylor equation, a good fit with the experimental data was obtained.

The theoretical approach proposed by Braun and Kovacs¹⁶ to describe the role of interaction in miscible systems uses eqs. (5)–(8) to determine

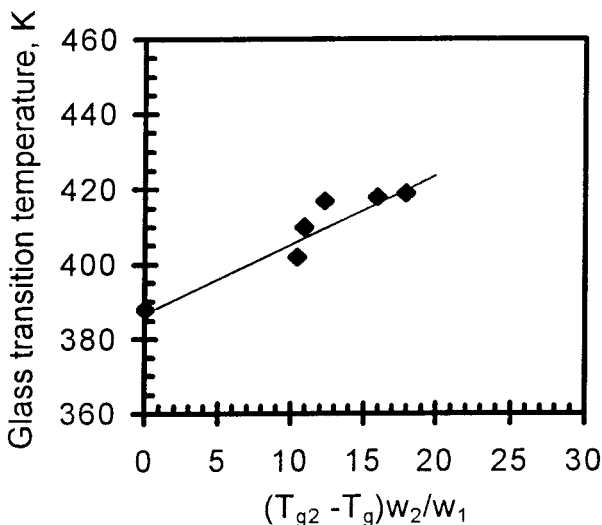


Figure 7 T_g data for PMMA-PMAA copolymers plotted according to the Gordon-Taylor equation.

$\Delta\alpha_1$ and $\Delta\alpha_2$. This concept can be applied to copolymers, taking into account that copolymers can be considered as an ideal mixture^{16,17,22,36}:

$$T_{\text{crit}} = T_{g2} - (f_{g2}/\Delta\alpha_2) \quad \text{if} \quad T_{g2} > T_{g1} \quad (5)$$

$$\phi_{\text{crit}} = f_{g2}/[\Delta\alpha_1(T_{g2} - T_{g1}) + f_{g2}(1 - \Delta\alpha_1/\Delta\alpha_2)] \quad (6)$$

where f_{g2} is the free-volume fraction of polymer 2 at T_{g2} and it is equal to 0.025. Above T_{crit} , Braun and Kovacs¹⁶ showed that T_g is given by

$$T_{g2} - T_g = (\phi_1/\phi_2)(\Delta\alpha_1/\Delta\alpha_2)(T_g - T_{g1}) \quad (7)$$

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

$$T_g = T_{g1} + (f_{g2}/\Delta\alpha_1)(\phi_2/\phi_1) \quad (8)$$

The system studied here has the value of $T_{g2} - T_{g1} = 51$ K, which is closer to the limit established by Braun and Kovacs.¹⁶ Then, if the classic value of 0.00048 K⁻¹ is assumed for $\Delta\alpha_2$ and a value of 0.00058 K⁻¹ for $\Delta\alpha_1$ is taken from literature³⁷ on calculating the T_g predicted by eq. (7), the experimental values could be considered above T_{crit} once $T_{\text{crit}} = T_{g2} - 52$. The curve generated with these results is shown in Figure 8, where T_g is a function of the PMAA volume fraction (curve 1). It does not exhibit a good fit with the experimental data (curve 2). However, the experimental T_g -composition curve shows a cusp

when the value of ϕ_2 is 0.327 and the corresponding value of T_g is 414 K. If this value is considered as T_{crit} to calculate $\Delta\alpha_2$ using eq. (5), the result obtained was equal to 0.001 K⁻¹. Curve 3 was obtained using eqs. (7) and (8) to describe the T_g -composition behavior and the values of $\Delta\alpha_1 = 0.00058$ K⁻¹ and $\Delta\alpha_2 = 0.001$ K⁻¹. The data points show a best fit with the experimental data. However, the cusp is not outlined. This result suggests that the effective volume of a statistical segment can be affected by the strength of the system interactions.

If the values of $\Delta\alpha_1 = 0.00058$ K⁻¹ and $\Delta\alpha_2 = 0.001$ K⁻¹ will be used to calculate the parameter k as the ratio $\Delta\alpha_2/\Delta\alpha_1$, the result is 1.724, which is closer to the value given by the slope (1.773) of the line shown in Figure 7. When the strength of the interactions is strong such as in hydrogen bonding, electron donor-acceptor complexes, ionic interaction, and transition metal complexes, another expression will be more adequate to describe the T_g -composition behavior²³:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + \frac{A w_1 w_2}{(w_1 + k w_2)(w_1 + b w_2)(w_1 + c w_2)^2} \quad (9)$$

where $b = M_2/M_1$ is the molar mass ratio of the chain segments, $c = \rho_1/\rho_2$ is the component density ratio, A and k are given by

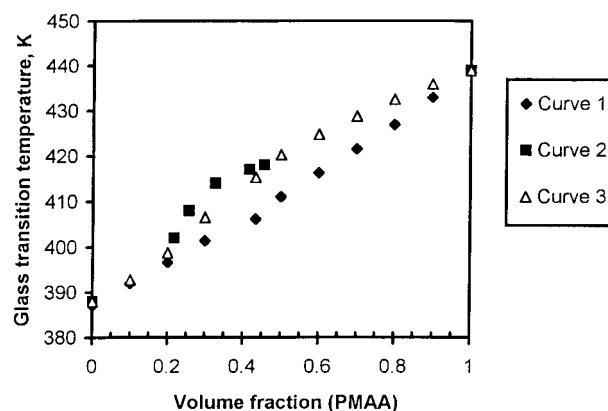


Figure 8 T_g as a function of PMAA volume fraction using the Braun-Kovacs approach. (Curve 1) Data given by eq. (7) with the value of $\Delta\alpha_1 = 0.00058$ K⁻¹ and the value of $\Delta\alpha_2 = 0.00048$ K⁻¹. (Curve 2) Experimental measurements. (Curve 3) Data given by eqs. (7) and (8) with the value of $\Delta\alpha_1 = 0.00058$ K⁻¹ and the value of $\Delta\alpha_2 = 0.001$ K⁻¹.

Table V Glass Transition Temperature and Interaction Parameter (χ) of MMA–MAA Copolymers

Polymer	w_2 (%)	T_g (K)	χ	χ_{app}	$(\Delta\chi/\chi) \times 100$ (%)
CRA-12	22	402	-2.82	-2.93	3.9
CRA-24	26	408	-3.93	-4.11	4.6
CRA-48	33	414	-4.17	-4.42	5.9
CRA-120	42	417	-3.42	-3.68	7.5
CRA-196	46	418	-3.10	-3.36	8.4

Values of A were obtained using $\rho_1 = 1.17 \text{ g cm}^{-3}$ for PMMA (from ref. 38) and $\rho_2 = 1.1872 \text{ g cm}^{-3}$ (experimental) for PMAA.

$$A = \frac{\chi R(T_{g1} - T_{g2})c}{M_1 \Delta C_{p1}} \quad (10)$$

and

$$k = (\Delta C_{p2} - w_1 \delta C_p^l) / (\Delta C_{p1} - w_2 \delta C_p^g) \quad (11)$$

where χ is the Flory–Huggins interaction parameter, and δC_p^l and δC_p^g are the specific heat changes due to mixing in the liquid and solid phases.²³ In eq. (11), δC_p^j is usually small compared with ΔC_{pi} , and k can be approximated by $k = \Delta C_{p2} / \Delta C_{p1}$.

The positive deviation of the experimental values from additivity shown in Figures 5, 6, and 8 indicated the presence of strong interactions in this system and promoted the application of eqs. (9) and (10) to calculate the variation of the interaction parameter χ with the copolymer composition. Table V shows the data. All the parameters can be determined by experiment. However, an

analysis of the second term of eq. (9) allowed some interesting comments. The product $w_1 w_2$ yields values between zero and 0.25 ($w_1 = w_2 = 0.5$); the term $(w_1 + k w_2)$ changes from 1 to the value of k and showed the most significant dependence on composition. The values obtained for the copolymers changed between 0.77 and 0.89. The parameters b and c are closer to unity and their influence on the values of A can be considered negligible.

When the influence of the parameters k , b , and c in the second term of eq. (9) is small, the equation becomes similar to the Kwei's equation:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \quad (12)$$

A new set of χ values was obtained, neglecting the dependence of parameters b and c and are also shown in Table V. The value of χ is minimum at the weight fraction of 33% PMAA (CRA-48). This value corresponds to the singular point obtained above using the T_g –composition relationships. Table V also shows that the approximations promoted a change of χ values, which varied in a range between 3.9 and 8.4%.

The positive deviation of T_g and the negative χ values with composition are indications of very strong interchain interactions, which decrease the mobility of the polymer chains. This system can be considered as thermodynamically miscible and presents a lower critical solution temperature (LCST). This critical temperature is characteristic of systems presenting hydrogen-bonding interactions. The curves obtained for T_g and χ shown in Figures 8 and 9 are similar to the results presented by Lu and Weiss²³ for donor–acceptor blends and corroborate the ΔC_p data. The increase of COOH groups increases hydrogen bonding, stiffening the polymer chain, and an in-

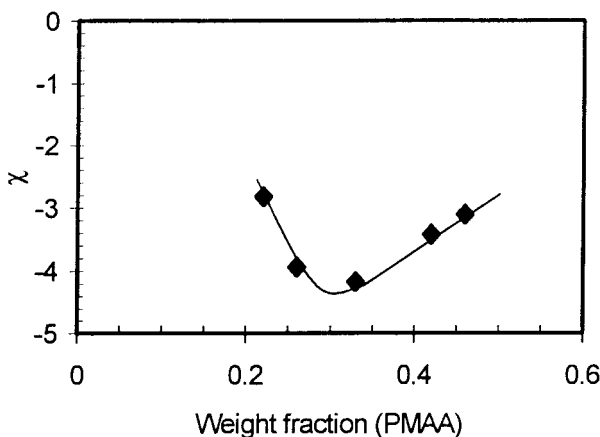


Figure 9 Flory–Huggins interaction parameter, χ , as a function of PMAA weight fraction in the PMMA–PMAA copolymers.

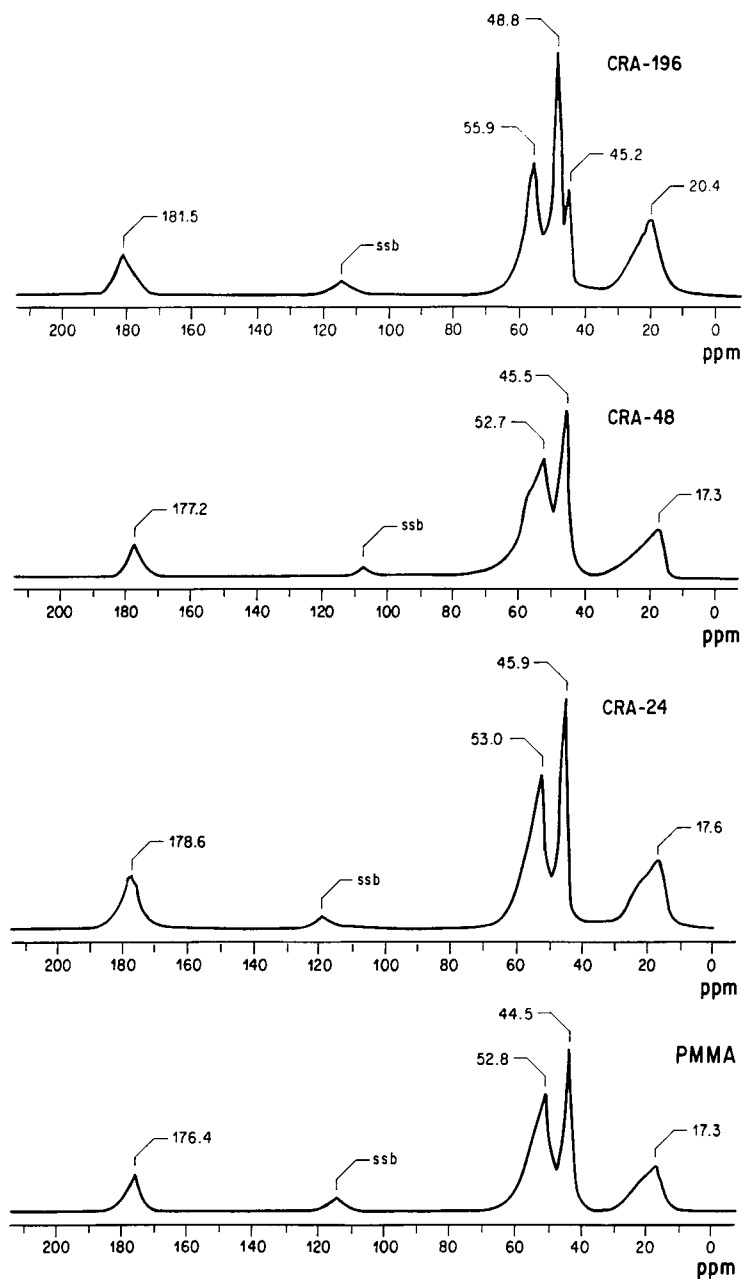


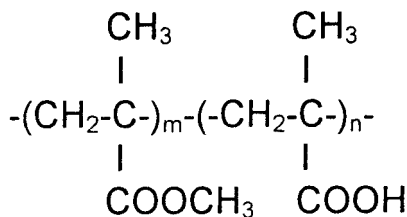
Figure 10 ^{13}C -CP/MAS spectra of PMMA and MMA-MAA copolymers.

crease of T_g is observed. However, on heating, these bonds are broken, decreasing the interactions and the negative χ value becomes smaller. This is a restriction of the method suggested for determining χ in hydrogen-bonded systems. The method involves heating which disrupts the strong interactions and probably the values of χ calculated using DSC data were less negative (absolute value decreases) than those obtained from other methods. However, as pointed out by Lu

and Weiss,²³ this is a convenient method of qualitative evaluation of χ .

NMR

The NMR ^{13}C -CP/MAS spectra of some copolymers (CRA-24, CRA-48, CRA-196) and pure PMMA are shown in the Figure 10. The NMR peaks of the copolymers were assigned based on Structure A:



Structure A

The ^{13}C -CP/MAS chemical shifts of pure PMMA were assigned at 17.3 ppm ($\alpha\text{-CH}_3$), 44.5 ppm (quaternary carbon), 52.8 ppm ($\text{—CH}_2\text{—}$), and 176.4 ppm (ester carbonyl). The PMAA ^{13}C -CP/MAS spectrum showed similar chemical shifts except for the carboxyl group which was located at 187 ppm. Figure 10 shows that the carbonyl shifts to higher frequencies with increase of the hydrolysis degree. It is also shown that the spectrum of the sample CRA-196 presents a different pattern of the aliphatic carbon region with the resolution enhanced. The spectra suggested that the predominant microstructure was syndiotactic according to the literature.^{2,39-41}

The same behavior was observed for the copolymers when a series of ^{13}C -CP/MAS NMR spectra was obtained using the variable contact time experiment. This indicated that all copolymers examined presented the same molecular domain and that PMMA dominates the relaxation process.

The dynamics at the molecular level of PMMA and MMA-MAA copolymers was investigated due to the ability of the CP/MAS/high-power hydrogen decoupling (HPHD) to generate high-resolution ^{13}C spectra.^{29,30} The values of the hydrogen spin-lattice relaxation time in the rotating frame, $T_{1\rho}^{\text{H}}$, extracted from the relaxation decay curve were obtained by this experiment.³⁰ The results are presented in Table VI. The changes observed in the $T_{1\rho}^{\text{H}}$ parameters indicated that the reaction time, the hydrolysis degree, and the molecular weight could influence the communication of the spins. The spin diffusion indicated that the chain stiffness increased with the hydrolysis degree. It could be promoted by the increase of hydrogen bonding. That response corroborated the data obtained from DSC measurements.

CONCLUSIONS

The results obtained by using TGA demonstrated that this technique is a suitable method in deter-

Table VI Proton Spin-Lattice Relaxation Time in the Rotating Frame Values for PMMA and MMA-MAA Copolymers

Sample	PMMA Chemical Shift, δ (ppm) ^a			
	176.4	52.8	44.5	17.3
	$T_{1\rho}^{\text{H}}$ (ms)			
PMMA	3.9	1.4	2.7	1.9
CRA-12	4.1	1.6	2.6	2.3
CRA-24	3.6	2.1	2.4	2.2
CRA-48	3.8	—	3.0	2.7
CRA-120	3.7	2.2	2.4	2.1
CRA-196	3.1	3.8	2.3	1.1

^a Used as reference.

mining the hydrolysis degree of MMA units in the polymerization reaction initiated by concentrated nitric acid. The data obtained from the DSC measurements showed that the T_g -composition dependence of the MMA-MAA copolymers can be described by the well-known relationships proposed by Braun and Kovacs regarding the effect of the interactions on the free volume. The results obtained for T_g showed a cusp that was not predicted by the theories proposed for miscible polymer blends and copolymers. When the effect of strong interactions was introduced, it was possible to estimate the dependence of the interaction parameter on the copolymer composition. Despite the reported results, some features remain unclear and a better description of the behavior described here is needed once the NMR data are in good agreement with DSC results.

The authors would like to thank PETROBRAS/CENPES/DIQUIM for the NMR analyses and the Brazilian agencies CNPq, CAPES, and FINEP for financial support.

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