



Study of glass transition in functionalized poly(itaconate)s by differential scanning calorimetry, Raman spectroscopy and thermogravimetric analysis



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ABSTRACT

The control of the glass transition temperature (T_g) in functionalized polymers is crucial for materials engineering and pharmaceutical applications. Tailoring must overcome experimental and theoretical issues regarding the thermodynamical phenomena involved. In this work, we study the glass transition of poly(monoitaconate)s and poly(diitaconate)s systems functionalized by internal plasticization. Differential scanning calorimetry (DSC) and Raman spectroscopy are used to determine T_g , whereas thermal degradation analysis (TGA) is used to determinate the temperature limit where conformers relax independently, defined as T^* in the Adams–Gibbs model. Our results show that the values of T_g obtained through DSC and Raman are consistent and that TGA can be used to estimate a lower bound limit for T^* . We mainly conclude that a larger steric hindrance between the carboxylic group in the side chain and the backbone increases T_g and decreases the variation of specific heat and configurational entropy at different domain regions. Similar behavior is observed when chlorine atoms are substituted in the phenethyl groups.

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1. Introduction

The control of the glass transition temperature (T_g) in polymers is crucial for materials engineering. However, the glass transition is a complex phenomenon due to the random variation of thermodynamic parameters, which must be measured and simulated using different approaches [1–3]. One method to modify T_g is the internal plasticization of the polymer [4–10]. The main advantage of this method is that the pendant groups are covalently bonded to the lateral chains as opposed to additives, which can be lost by evaporation or leaching. Indeed, the presence of flexible pendant groups in the main polymer backbone induces a change in T_g , as observed esters of poly(methacrylic acid) [8] and poly(acrylic acid) [9].

Despite scientific debates in the polymers community, the Adam–Gibbs (AG) model [11–14] is one of the most accepted theories that explain glass transition phenomena. It gives the theoretical basis of the widely used Vogel–Fulcher–Tammann (VFT) equation [11–13] used for different cooperatively rearranging regions [14]. The theory claims that when increasing the temperature of a polymer up to T_g the chains relax and global thermodynamic variables, such as specific heat, exhibit smooth and continuous changes. Above T_g , the polymer volume continuously begins to expand allowing conformers to finally relax independently. The

frequency and the magnitude of the molecular oscillations are such that a change to a new bond angle can be reversed in negligible time. This corresponds to the temperature limit defined as T^* in the AG theory, which is above the thermal degradation temperature [15].

In this work, we study the effect of internal plasticization on the glass transition and degradation of functionalized poly(itaconate)s. The glass transition was analyzed by combining differential scanning calorimetry (DSC) and Raman spectroscopy, whereas the degradation process was studied using dynamic thermal degradation analysis (TGA).

2. Materials and methods

2.1. Synthesis of poly(itaconate)s

The samples were prepared from diesterification and monoesterification in itaconic acid using the appropriate compounds: benzyl alcohol, phenethyl alcohol, alcohol-4-chlorophenethyl and alcohol-2-chloro-phenethyl. The mass polymerization was carried from the initiator α, α' -azobis-isobutyronitrile (AIBN) in nitrogen atmosphere in a temperature range from 60 °C to 70 °C. The polymers were solubilized in tetrahydrofuran and precipitated in methanol and then were dried under vacuum at 37 °C for two weeks [16,17]. The characterization of alcohol, monomer and polymer was made by nuclear magnetic resonance (^1H NMR). The obtained polymers were: poly(phenethyl

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monoitaconate) (PMPHl); poly (2chlorophenethyl monoitaconate) (PM-2Cl-Phl); poly(phenethyl diitaconate) (PDPHl) and poly (4chloro phenethyl diitaconate) (PD-4Cl-Phl). Fig. 1 resumes the polymer systems produced by internal plastification.

2.2. DSC and Raman spectroscopy

Prior to the measurement of T_g by DSC, the samples were heated to 110 °C and then cooled down to -10 °C. Next, the T_g was determined using a Mettler Toledo DSC 821 system. The samples were dried under vacuum before each measurement. DSC thermograms were carried out between 35 °C and 110 °C at a heating rate of 20 °C/min in nitrogen atmosphere. Raman spectroscopy was performed with a LabRam 010 instrument from ISA using a 5.5 mW HeNe laser beam (633 nm) without filtering. We used a Linkam TMS 94 controller and THMS 600 stage to vary the sample temperature in the same range as DSC measurements with a precision of 0.1 °C. The temperature was varied with a heating rate of 10 °C/min, and before taking a spectrum the temperature was stabilized for 1 min to assure that the sample was in equilibrium with the stage. After measuring, the Raman spectra were deconvoluted using Gaussian profiles. Finally, the calorimetric flow (DSC) and the peak area (Raman) were plotted as a function the temperature for all the polymer systems.

2.3. Thermogravimetry

The dynamic thermal degradation analysis (TGA) of the polymers was performed by a Mettler Toledo TGA thermobalance at a heating rate of 20 °C/min under nitrogen atmosphere at 25 °C to 950 °C. All the polymer systems were weighed in the same thermobalance with an accuracy of 0.001 g.

3. Results

3.1. Glass transition analysis

The glass transition is usually detected by measuring the inflection of the calorimetric flow (DSC) above a certain temperature T_i being T_g the midpoint of the total inflection range. In this work, it was also performed by Raman spectroscopy. The area of Raman peaks represents the amount of molecular vibrations or phonons with specific energies, thus represents a key parameter to study thermodynamic transitions. In particular, the glass transition is caused by changes in the microscopic dynamics showing small momentum transfer that correspond to correlations larger than the short-range order in the system [15]. When the sample is heated, thermal motions might produce changes in the Raman peak area that are associated with the movements of twisting angles of different molecular groups. Therefore, the peak area may suffer changes around T_g due to both bulk and surface transitions [18–20].

The raw Raman spectra measured at room temperature and the adjusted Gaussian peaks of all the polymer systems are shown in Fig. 2. The overall vibrational interpretation is plausible for polymers of similar families. Vibrations in the [1500–2800] cm^{-1} range were not observed due to the high intensity of the fluorescence signal. Vibrations in the [2850–3000] cm^{-1} range correspond to symmetric (ν_s) and asymmetric (ν_a) stretching of methylene groups ($-\text{CH}_2-$), while in the [3020–3100] cm^{-1} range, correspond to the ν_s and ν_a ($-\text{CH}-$) stretching, belonging to the phenyl groups [18–21] In particular, the peak with the highest intensity around 3060 cm^{-1} was studied as a function of the temperature.

In order to complement DSC and Raman analyses around T_g , Fig. 3 shows the thermal evolution of the DSC flow and area of the peak Raman showed in the spectra of Fig. 2 around 3060 cm^{-1} . As a standard criterion, T_g was assigned to the middle point of the decreasing Arrhenius range in the DSC curve. Whereas two inflections are observed in the area of the peaks, which corresponds to surface (low temperature) and

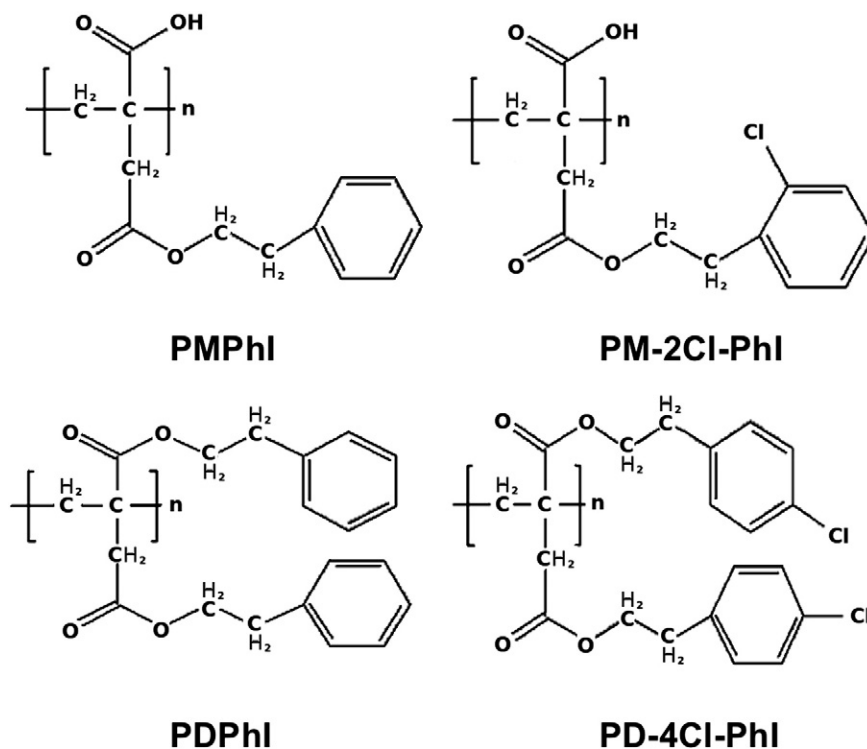
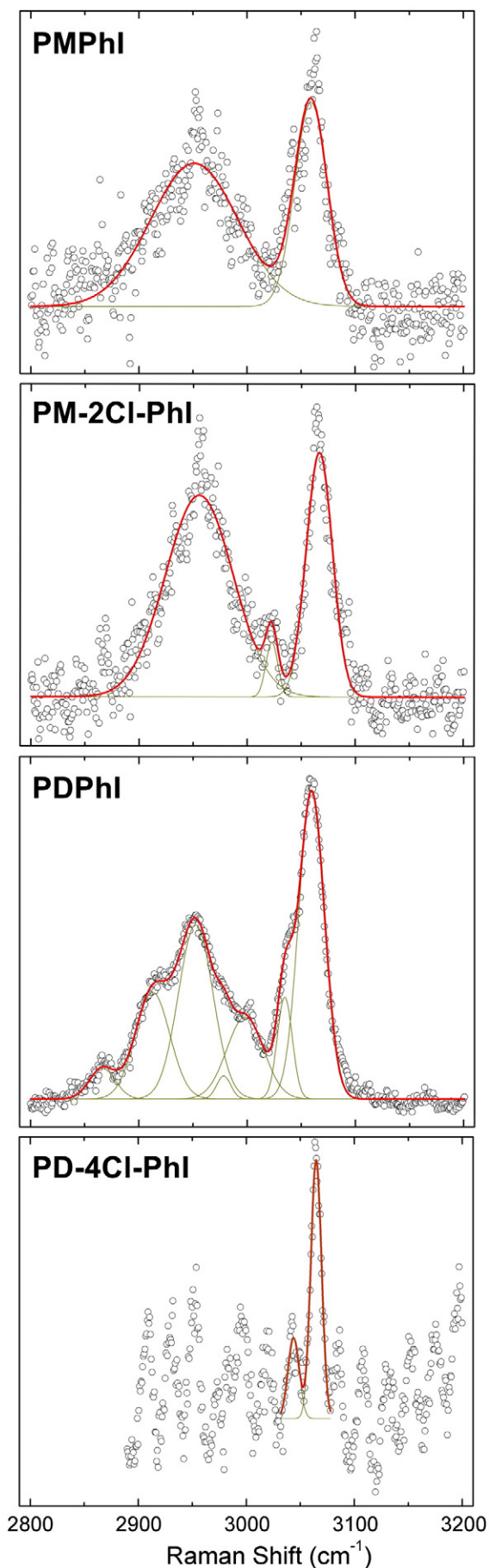


Fig. 1. Sch. of the functionalized polymer systems produced by internal plastification: poly(phenethyl monoitaconate) (PMPHl); poly (2chlorophenethyl monoitaconate) (PM-2Cl-Phl); poly(phenethyl diitaconate) (PDPHl) and poly (4chloro phenethyl diitaconate) (PD-4Cl-Phl).



bulk (high temperature) glass transitions [22]. All the T_g values estimated by DSC and Raman are resumed in Table 1. We note that the DSC values of T_g for PD-4Cl-Phl and PM-2Cl-Phl fall between surface and bulk transition temperatures determined by Raman, suggesting that in this case, T_g obtained by DSC represents an average between both transitions. We disown why the samples containing Cl behave in this manner. The values of the differential heat capacities at constant pressure (ΔC_p) were calculated from the slope of the DSC curves shown in Fig. 3 and are resumed in Table 1.

3.2. Degradation analysis

Thermogravimetric analysis was used as a technique to understand the degradation mechanisms underlying in vitreous temperatures needed to achieve the flexibility change of each member of this family of polymers [4]. As shown in the thermal degradation analysis of Fig. 4A, several mass/temperature rate minima were observed in the monoesterificated systems (PMPHl and PM-2Cl-Phl), whereas Fig. 4B shows only one in the monoesterificated systems (PDPHl and PD-4Cl-Phl). In general the presence of several mass loss minima in the case of monoesterificated systems is correlated with the formation of anhydride rings, which are then oxidized and degraded at higher temperatures [23,24]. The thermal degradation temperature (T_D) for these systems was chosen in the deepest temperature minima (Table 1).

Taking into account that T^* is considered as a critical point in the modeling of the thermal evolution of the polymer systems, we propose an experimental method to estimate a lower bound limit for T^* (T_L) from the thermal degradation data. As discussed by Matsuoka [15], above the degradation temperature the polymer volume is expanded to finally allow most conformers to relax individually at an extrapolated temperature T^* of around 500 °C, after analyzing data for more than a hundred polymers. Moreover, as mentioned by Rault [25], at this temperature the intermolecular coupling has any thermodynamic effect and the molecules execute independent and uncoupled motion. We claim that T^* is always higher than the temperature where the mass/temperature rate measured by TGA saturates. Below this temperature the molecules have indeed thermodynamic inter- and intra-molecular interactions since they are responsible for the dynamics of the mass loss of the polymers. The value of T_L is therefore determined by the intersection of the fitted linear behaviors at the high temperature region of the thermal degradation curve, as shown in Fig. 4.

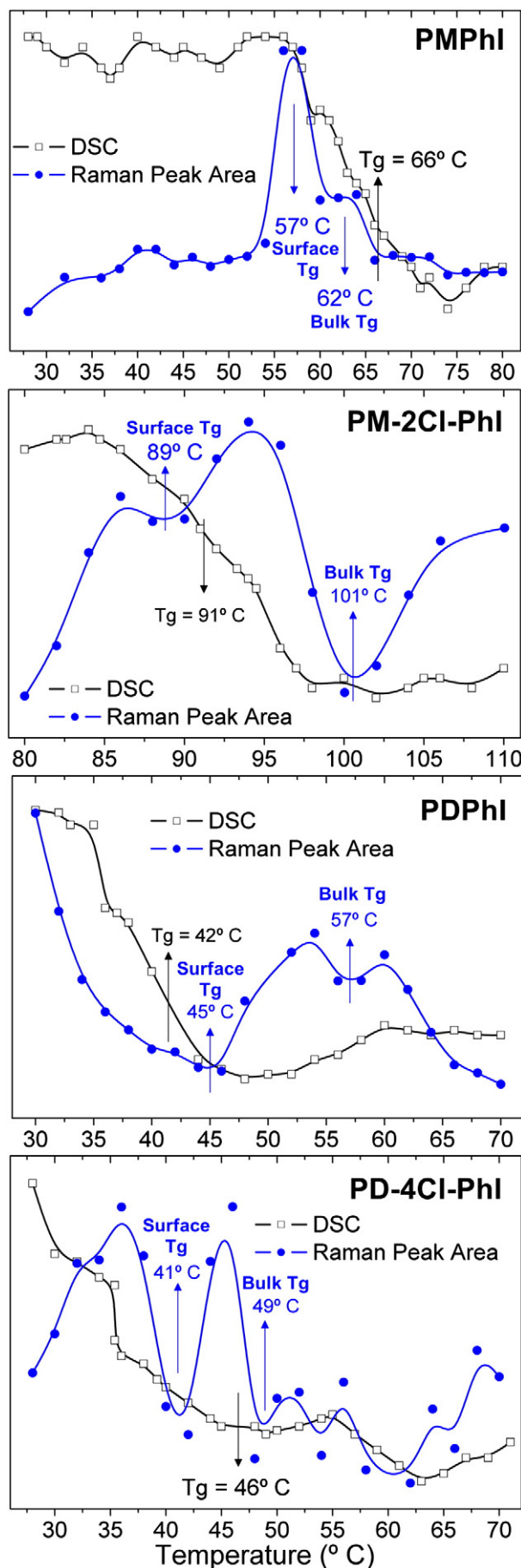
4. Discussion

The ordering of the glass transition temperatures measured by DSC is PDPHl < PD-4Cl-Phl < PMPHl < PM-2Cl-Phl, as shown in Table 1. This order is related with different capacities to absorb and release heat, plus the differences in the entropy between the liquid and glass phases in the Arrhenius range [T_i , T_g]. Therefore, depends on the configurational heat capacity (ΔC_p) and the configurational entropy (S_c), whose relation is presented in Eq. (1) [14,26].

$$S_c \sim \int_{T_i}^{T_g} \frac{\Delta C_p(T)}{T} dT \quad (1)$$

Both ΔC_p and S_c are modified by the degree of interaction between the side chains and the backbone. A stronger interaction implies less configurational states and therefore a decrease of ΔC_p and S_c . Fig. 5A shows ΔC_p values measured by DSC in the Arrhenius [T_i , T_g] range as a function of $1/T_g$, for all the polymer systems. It is worth to note that

Fig. 2. Raw Raman spectra (dots) measured at room temperature and adjusted Gaussian profiles (dark yellow) of the polymers systems. The peak with the highest intensity around 3060 cm^{-1} was studied as a function of the temperature.

**Table 1**

Summary of thermodynamic data obtained by DSC (T_g , T_i and ΔC_p), Raman spectroscopy (T_{gs} and T_{gb}) and TGA (T_D and T_L). Errors in the temperature are in the order of 0.5 °C, whereas in ΔC_p , in the order of $10^{-5} \text{Jg}^{-1} \text{K}^{-1}$.

	DSC			Raman		TGA	
	T_g (°C)	T_i (°C)	ΔC_p ($10^{-4} \text{Jg}^{-1} \text{K}^{-1}$)	T_{gs} (°C)	T_{gb} (°C)	T_D (°C)	T_L (°C)
PMPHl	66	59	0.4	57	62	386	545
PM-2Cl-Phl	91	86	0.1	89	101	405	546
PDPHl	42	38	2.8	45	57	394	450
PD-4Cl-Phl	46	37	2.0	41	49	376	420

the PM-based polymers have higher T_g and lower ΔC_p than PD-based polymers due to a larger steric hindrance between the carboxylic group in the side chain and the backbone. This effect is even more intense when chlorine atoms are substituted in the phenethyl groups allowing retaining the mobility of the backbone [27–29].

In order to correlate the DSC and Raman data, different cooperatively rearranging regions must be identified according to the VFT equation within the AG framework model [13,14]. In particular, the parameter z is defined as the domain size at the short-range intramolecular arrangements, as described in Eq. (2). The term T_0 is defined as the Vogel temperature, which is a divergence-limit for the Arrhenius behavior of the relaxation time with the temperature [2]. In analogy this value was chosen as T_i for DSC and T_{gs} for Raman (Table 1). The parameter z^* is defined as the domain size at the long-range intermolecular arrangements, as described by Eq. (3), where the lower limit of T^* is considered, i.e., $T^* \approx T_L$. It is worth to note that z^* diverges for $T_g \approx T_0$, where the domain size has grown so large that all conformers are locked together.

$$z = \frac{T_g}{T_g - T_0} \quad (2)$$

$$z^* = \frac{T_g}{T_g - T_0} \frac{T^* - T_0}{T^*} \quad (3)$$

From the definition of the domain arrangements z and z^* , intramolecular and intermolecular cooperatively entropies can be defined as $S_z = S_c/z$ and $S_{z^*} = S_c/z^*$, respectively. These terms can be understood as the configurational entropy S_c in a domain that consists of z intramolecular (z^* intermolecular) conformers due to cooperative restrictions around the glass transition. Nevertheless, both S_z and S_{z^*} decrease towards zero when T_g is close to T_0 , whereas S_c tends towards zero only close to -273 °C [15].

The plots of Fig. 5B correspond to S_{z^*} versus S_z estimated by DSC and Raman spectroscopy around the glass transition. All the experimental points fall within a straight line whose slope corresponds to 1.814 ± 0.008 for DSC and 1.820 ± 0.021 for Raman. This value corresponds to the ratio between the intramolecular and intermolecular cooperatively entropies [15]. Since the smaller fitting error (0.008) is slightly larger than the slopes difference (0.007), we claim that both DSC and Raman show the same intermolecular/intramolecular configurational probability, which is indeed an evidence that any thermodynamic extensive quantity can be scaled by this ratio.

Fig. 3. Thermal evolution of the DSC calorimetric flow power (mW) and area of the Raman peaks ($\text{Cts} \cdot \text{cm}^{-1}$) showed in the spectra of Fig. 2 around 3060 cm^{-1} . The DSC curve decreases above T_i and the midpoint of the falling range corresponds to T_g . The Raman peak area changes around T_g due to the surface glass transition temperature (T_{gs}) (low temperature) and bulk glass transitions temperature (T_{gb}) (high temperature).

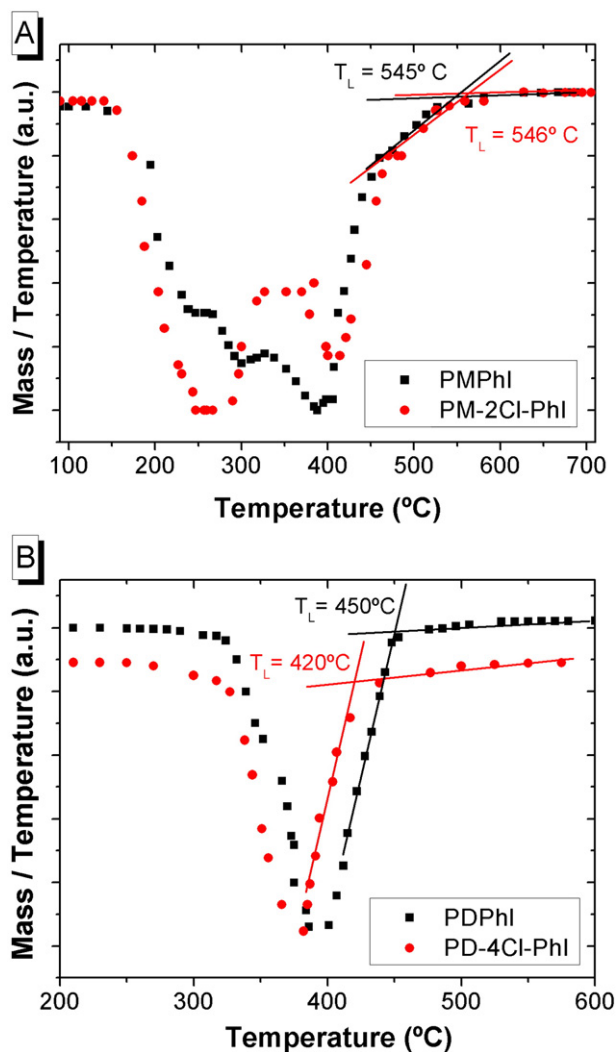


Fig. 4. Mass/temperature rate of the thermal degradation analysis of the polymer systems: A) PMPhI and PM-2Cl-PhI, B) PDPHl, PD-4Cl-PhI. The value of T_D was chosen in the deepest temperature minima, whereas T_L was determined by the intersection of the fitted linear behaviors at the high temperature region of the thermal degradation curve.

5. Conclusions

The glass transition of functionalized poly(itaconate)s by internal plasticization was studied by differential scanning calorimetry, dynamic thermal degradation and Raman spectroscopy. The results show that the value of T_g was consistent within the different techniques. As a standard criterion, T_g was assigned to the middle point of the decreasing Arrhenius range in the DSC curve, whereas two transition points were observed in the area of Raman peaks. These correspond to surface (low temperature) and bulk (high temperature) glass transitions. Thermogravimetric analysis was used as a technique to understand the effect of plastification on the degradation mechanisms and moreover to estimate a lower bound limit for the conformer relaxation temperature T^* .

Considering the experimental data analyzed in the context of the AG theory, we conclude that the PM-based polymers have higher T_g and lower ΔC_p than PD-based polymers due to a larger steric hindrance between the carboxylic group in the side chain and the backbone. This effect is also evidenced when chlorine atoms are substituted in the phenethyl groups. Therefore, the configurational entropy is reduced due to the number of arrangements in domains (z and z^*) that grow in a cooperative manner. Moreover, intramolecular and intermolecular cooperatively entropies show a constant configurational probability ratio

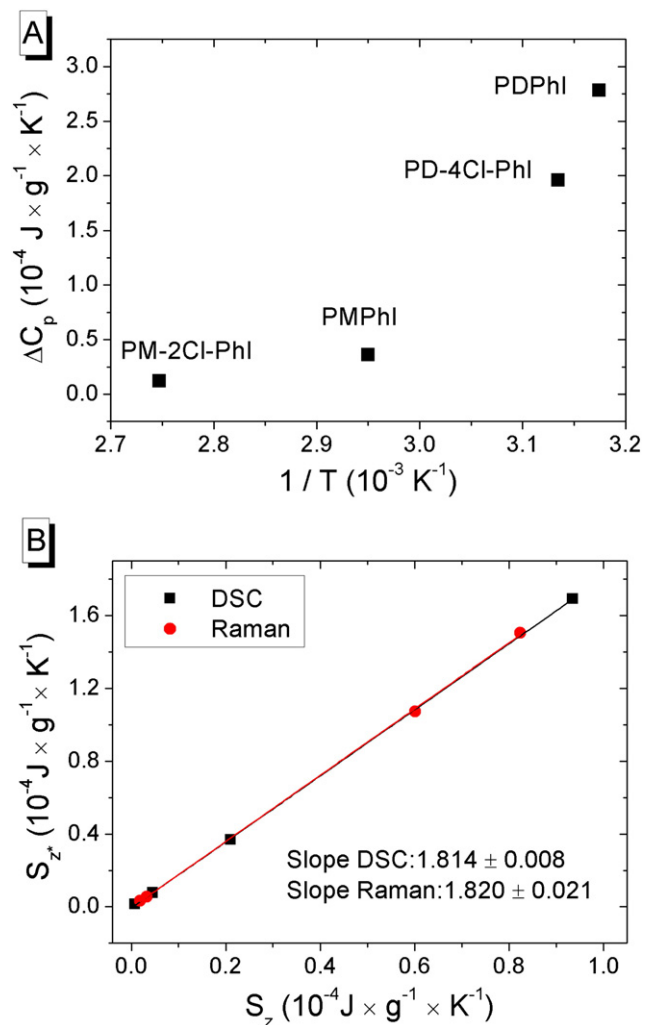


Fig. 5. A) ΔC_p measured by DSC in the Arrhenius [T_i, T_g] range, as a function of $1/T_g$ for all the polymer systems. B) Intramolecular ($S_z = S_c/z$) versus intermolecular ($S_{z^*} = S_c/z^*$) cooperatively impediment entropy estimated by DSC and Raman spectroscopy around the transition temperatures.

$S_{z^*}/S_z = 1.8$, which suggests that any thermodynamic extensive quantity can be scaled by this ratio.

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