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Subglass and Glass Transitions of Poly(di-*n*-alkylitaconate)s with Various Side-Chain Lengths: Dielectric Relaxation Investigation

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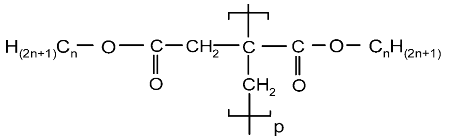
ABSTRACT: Dielectric relaxation measurements were performed on a series of poly(di-*n*-alkylitaconate)s with various side-chain lengths. The experimental data were analyzed by adjustment with one or the sum of several Havriliak−Negami functions. They demonstrated the existence of several relaxation processes with significant dielectric relaxation strengths. The comparison of the results obtained by increasing the length of the side groups permitted an assignment of the γ, β_{fast}, and β_{slow} secondary relaxations to motions of the alkyl side chains, ester group located after the CH_2 unit, and ester group directly attached to the main chain, respectively. In poly(di-*n*-alkylitaconate)s with six carbon atoms at least in the alkyl part, the existence of an additional low-temperature glass transition α^{L} was clearly established. The α^{L}-process replaces the β_{fast}-process observed in the lower derivatives. It is located in quite the same temperature and frequency ranges and exhibits a non-Arrhenius behavior. It is likely related to cooperative motions of the alkyl side chains and ester group next to the CH_2 spacer unit.

1. Introduction

Secondary relaxations in solid polymers are due to local motions involving either pendant groups or main-chain units.[1] Therefore, a deeper knowledge of the local motions that occur in the glassy state is a necessary step to understand the relationships that may exist between the chemical structure of polymers and some of their macroscopic properties. Identification of the mobile units and cooperativity of the processes as well as the nature of the interactions that take place between atoms and chain packing are some of the main questions to be addressed. To obtain such information, we have used an approach based on (i) the study of materials as a function of progressive changes introduced in their chemical structure and (ii) the comparison of results obtained from different techniques. The polymers used in the present work are the poly(di-*n*-alkylitaconate)s (PDAI). These polymers are well-known to exhibit a complex relaxational behavior which strongly depends of the alkyl side-chain length. Their chemical formula is



$$\left[H_{(2n+1)}C_n-O-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{CH_2}{|}}{\overset{|}{C}}-\underset{\underset{O}{\|}}{C}-O-C_nH_{(2n+1)} \right]_p$$

where n is the number of carbons in the alkyl side chains.

The different subglass and glass relaxation processes in PDAI's have been studied for a long time mainly by differential scanning calorimetry (DSC),[2,3] dynamic mechanical analysis (DMA)[4−7] and dielectric spectroscopy.[8] It first appears that PDAI samples exhibit several secondary relaxations. For PDAI's with less than four carbons in the alkyl side chains, Cowie et al.[2−7] reported the existence of a β-relaxation close to the α-relaxation associated with the glass transition phenomenon. This process exhibits some common features with the corresponding β-relaxation reported in poly(alkyl methacrylate)s, although the mechanical spectra of PDAI's are somewhat broader.[4] According to Cowie et al. such a behavior could be due to the presence of two different ester groups in PDAI's. In addition, Diaz Calleja et al.[8] observed the existence of a second weak relaxation between −100 and −120 °C at 1 Hz which is absent in the corresponding poly(alkyl methacrylate)s. Last, both groups[4,6,8] reported the existence of a low-temperature γ-process in all samples with $n \geq 3$. For PDAI's with longer side chains a change in the physical behavior occurs when the derivative with $n = 7$ is reached. Indeed, for PDAI's with $n = 7$ to $n = 11$, the DSC thermograms exhibit two major relaxations indicative of two distinct glass−rubber transitions.[6] For these polymers, data obtained from DMA[6] show two damping peaks in addition to the γ-process previously observed. They might correspond to the two transitions observed in DSC, a fact which is supported by both their apparent activation energy, higher than that normally expected for secondary relaxations[6] and the study of copolymer samples.[5] For PDAI's with side chains of seven carbons at least, Cowie et al.[5−7] postulated that the lower glass-transition temperature, $T_g{}^{L}$, which corresponds to the calorimetrically more pronounced transition, is due to cooperative motions of the alkyl side chains which do not involve the polymer main-chain, whereas the upper glass-transition temperature, $T_g{}^{U}$, can be associated with cooperative motions of all the polymer units, including the backbone carbons. Both glass-transition temperatures increase with increasing the number of carbons in the side chains between 7 and 11. This behavior reflects the increasing tendency for the side chains to order. For side chains containing more than 11 carbons, crystallization may indeed occur.[9]

More recently, a dielectric relaxation study was performed by Arrighi et al.[10] β- and γ-relaxation processes were not detected in this work. The authors

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Table 1. Characterization of the Samples[a]

code	n	name	$10^{-4}M_n$ (g mol^{-1})	N	I_p	T_g^L(DSC) (°C)	T_g^U(DSC) (°C)
PDMI	1	poly(dimethylitaconate)	7.4	467	1.3		92
PDPI	3	poly(di-*n*-propylitaconate)	18.6	869	2.6		20
PDHI	6	poly(di-*n*-hexylitaconate)	8.7	292	2.2	indic	−38
PDOI	8	poly(di-*n*-octylitaconate)	15	424	1.9	−87	−37
PDDI	10	poly(di-*n*-decylitaconate)	2.4	60	4.1	−75	indic

[a] indic means that there are only indications.

showed the presence of a high-frequency process in addition to the conventional glass transition in PDAI's with long side chains. This process was associated with the lower glass transition and assigned to the alkyl part relaxing independently of the main chain. However, the molecular mechanism of this second glass transition was not fully understood as this process was not supposed to be dielectrically active. Furthermore, the temperature range covered in that study was somewhat too narrow to obtain all the information required to fully characterize this unusual process. As in PDAI's, it is of interest to note that an additional relaxation process connected with the alkyl part of the side chain was observed in the higher poly(*n*-alkyl methacrylate)s. It was reported by Floudas et al.[11,12] as the β_{fast}-process and by Beiner et al.[13−17] as the α_{PE}-process because of its similarities to the glass transition of amorphous polyethylene. Both processes occur in the same region and are associated with motions of the alkyl side-chain, in agreement with the poor dielectric activity reported for this process[12,13] which means that the ester group is not involved in the corresponding motion. This hypothesis was recently supported by a solid-state NMR study.[15] It should be noted that, on the basis of heat capacity spectroscopy data,[17] the α_{PE}-process is considered by Beiner as an independent glass relaxation within the alkyl nanodomains in addition to the conventional glass transition.

In this context, it was decided that a reinvestigation of the dielectric relaxations in PDAI's was fully justified in order to produce a detailed characterization of the subglass relaxations and gain additional information on the effect of the side-chain structure of the polymer. We will first report results obtained by using dielectric relaxation experiments over a wide range of temperatures and frequencies. It may be noted that dielectric properties in PDAI's are largely due to the strong electric dipole in each side ester group. The investigation of these polymers by using high-resolution solid-state ^{13}C NMR, ^{13}C NMR in solution, and molecular modeling will be published in the forthcoming papers of this series. As a first step, the present study aims to highlight the different relaxations that take place in PDAI's and to determine their frequency−temperature dependence. Of course, we will not omit a reference to Arrighi et al.[10] considering their work as a precedent to this one. Besides, it will be interesting to compare the PDAI behavior with results reported in the literature for poly(*n*-alkyl methacrylate)s.

2. Experimental Section

Dialkyl itaconic esters with side-chain lengths with $n = 1$ to $n = 10$ were polymerized by using free radical initiators.[4] PDAI samples were characterized by size exclusion chromatography in THF using a mini-Dawn light scattering instrument. The code names, number-average molecular weight M_n, number of monomer units N, and polydispersity index I_p are reported in Table 1. Heat capacity measurements were performed by using a TA instrument differential scanning calorimeter 2010 operating at 20 K min^{-1}. Two separate inflections on the C_p-T curves were seen for the higher derivatives in agreement with results reported by Cowie et al.[2]. The two glass-transition temperatures, T_g^L and T_g^U, are collected in Table 1. Both are defined by extrapolated onsets of the respective inflections.

Measurements of the complex dielectric permittivity, $\epsilon^* = \epsilon' - i\epsilon''$, vs frequency, ν, were performed in the range $10^{-2}-10^6$ Hz, using a Solartron SI 1260 impedance/gain-phase analyzer supplemented by a Novocontrol broadband dielectric converter (BDC). The measurements were carried out decreasing the temperature stepwise in 5° intervals from +150 down to −130 °C. Experiments were performed under nitrogen atmosphere to prevent adsorption of moisture. Samples were vacuum-dried for one night at 40 °C before use.

3. Results and Discussion

A detailed discussion about the dielectric behavior of PDAI's over a broad temperature range will be given in the following sections. We will first present results obtained on the lower derivatives: PDMI and PDPI.

3.1. The Lower Itaconates. With dielectric spectroscopy, we found three and four dielectrically active processes for PDMI and PDPI, respectively. Figure 1shows the dielectric loss, ϵ'', recorded isothermally near and above the calorimetric glass-transition temperature, T_g, for the derivatives with $n = 1$ and $n = 3$. The spectra show a prominent relaxation peak which moves to higher frequencies as temperature increases. This relaxation is related to the glass transition and labeled as α-relaxation. Since the loss curves are broad and asymmetric, the empirical Havriliak−Negami (HN)[18] function was used to fit the data

$$\epsilon^*(\omega) = \epsilon_U + \frac{\epsilon_R \epsilon_U}{(1 + (i\omega\tau_{HN})^a)^b}$$

ϵ_R and ϵ_U are the relaxed and unrelaxed limits of the real part of the dielectric constant, respectively. These values define the relaxation strength, $\Delta\epsilon = \epsilon_R - \epsilon_U$. The shape parameters a and b describe the symmetric and asymmetric broadening of the complex dielectric function ($0 < a, ab \leq 1$). τ_{HN} is the characteristic relaxation time with $\tau_{HN} = (2\pi\nu)^{-1}$. The HN function is a generalization of the well-known Cole−Cole and Cole−Davidson expressions.[19] As expected in these polymers,[8] dielectric α-relaxations are overlapped by strong conductivity contribution in the low frequency side. This contribution has been successfully described by a $\epsilon''(\omega) \propto 1/\omega$ law. The slight rise at high frequency is caused by an additional impedance of the measurement circuit which causes a contribution to ϵ'' of the form $\epsilon''(\omega) = K\epsilon'\omega$, where K is a fitting parameter. This contribution was included in the data analysis without any assumption. However, we have observed that the coefficient K was nearly constant for all isotherms as well as for the different samples.

At high temperature, each ϵ'' function can be fitted by a HN function without deviations. However, data

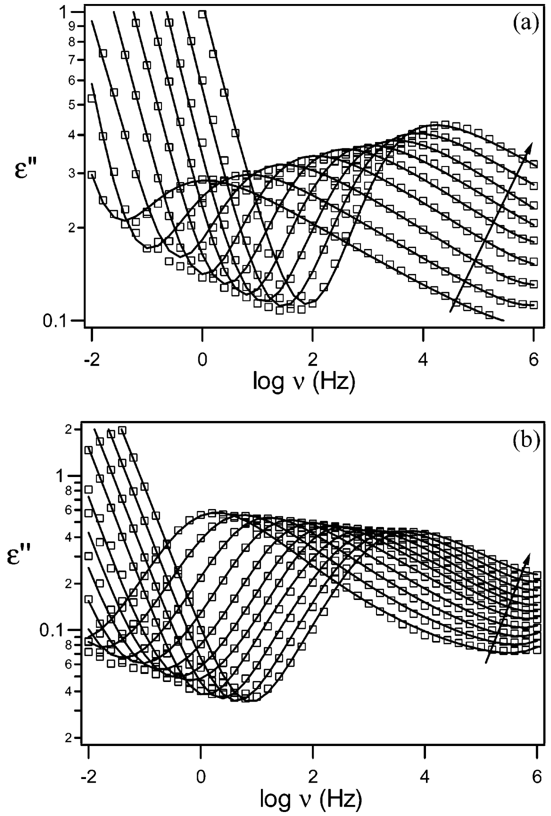

Figure 1. Frequency dependence of the imaginary part of the dielectric response ϵ^* for (a) PDMI from 95 to 135 °C and (b) PDPI from 55 to 105 °C at 5° intervals in the direction indicated by the arrow. The solid lines correspond to fits by HN functions, plus ionic conductivity and impedance effect.

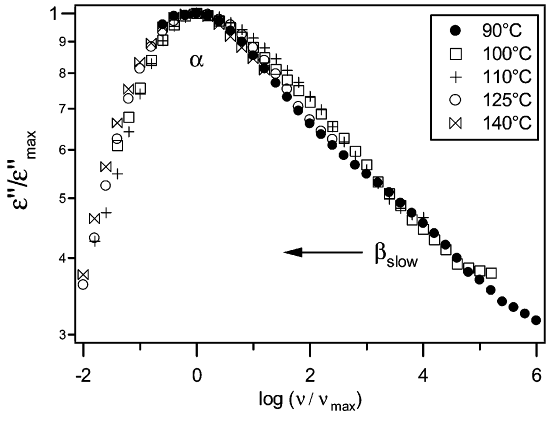

Figure 2. Normalized dielectric loss data for PDMI at various temperatures which highlight the merging of the α- and β_{slow}-relaxations.

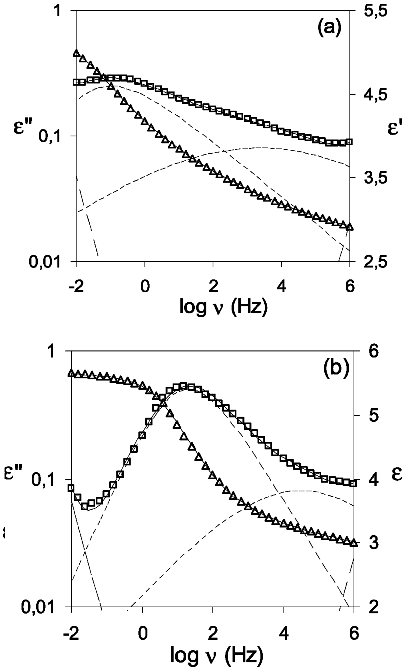

Figure 3. Frequency dependence of the real part ϵ' (Δ) and the imaginary part ϵ'' (□) of the dielectric response. The solid lines correspond to fits by HN functions for (a) PDMI at 90 °C and (b) PDPI at 65 °C. The sum of two HN functions (- -) has to be used in conjunction with the ionic conductivity (— —) and the impedance effects (— —).

obtained at temperatures equal to or below 100 °C for PDMI and 85 °C for PDPI suggest that two contributions have to be considered. To demonstrate the appearance of a second relaxation process, we used the representation of the normalized curve $\epsilon''/\epsilon''_{\max} = f(\nu/\nu_{\max})$ which is illustrated for PDMI in Figure 2. At 90 °C, a careful inspection of the curve shows a shoulder, on the high-frequency flank of the peak, related to the β_{slow}-process (this distinction is made in order to differentiate the usual β-relaxation from a faster β-process). At higher temperature, the shift of the α-peak to higher frequencies, which is much faster than that of the secondary relaxation, causes both peaks to become closer to each other. Above 100 °C, the curve seems to show a single peak which can be attributed to the fully merged α- and β_{slow}-relaxations. As a consequence, we choose a simple addition of two HN functions, which is a standard way to treat data in the merging region.[20,21] As can be seen in Figure 3, a low-frequency HN function (HN1) describes the cooperative α-process, whereas a high-frequency HN function (HN2) describes the β_{slow}-process. It should be noted that the β_{slow}-relaxation was represented by a special version of HN2 with $b_2 = 1$ as, for secondary relaxations, the dielectric response of many polymers is well described by a symmetric distribution of relaxation times.[22] It is interesting to note that the resolution of the β_{slow}-peak is better in PDMI than in PDPI. Nevertheless, in both cases, it appears that this process cannot be positioned without a large uncertainty in the frequency window; i.e., different start parameters do not yield identical final parameters. To get more information about the location of the β_{slow}-process, data obtained with realistic error bars were reported in Figure 4 for PDMI and PDPI. We can see that the temperature position of the loss peak for the β_{slow}-relaxation is only slightly affected by the side-chain length, as expected from the local character of secondary relaxations.[23] A comparison between our data and data related to the β-relaxation in PMMA[24] indicates that both processes occur in the same region. The β-relaxation in poly(n-alkyl methacrylate)s has been extensively studied by multidimensional solid-state NMR[25,26] and was described by a flip of lateral esters, conjugated to a reorientation around the local chain axis with a 20° root-mean-square amplitude.

At temperatures ranging from −15 to −75 °C, there is evidence of another relaxation, which will be labeled as β_{fast}. Figure 5 depicts some representative data of the real and imaginary parts of the dielectric constant for the studied polymers at −65 °C. The upturn in the high-frequency side is related to the impedance effects. At

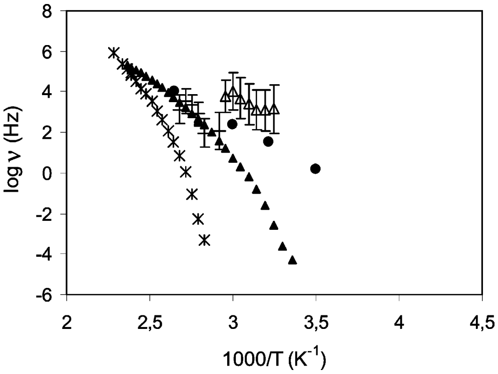

Figure 4. Arrhenius plot containing α (full symbols) and β_{slow} data (open symbols) for PDMI (*, +) and PDPI (▲, △). β_{slow} results are compared with data reported for the β-relaxation of PMMA[24] (●).

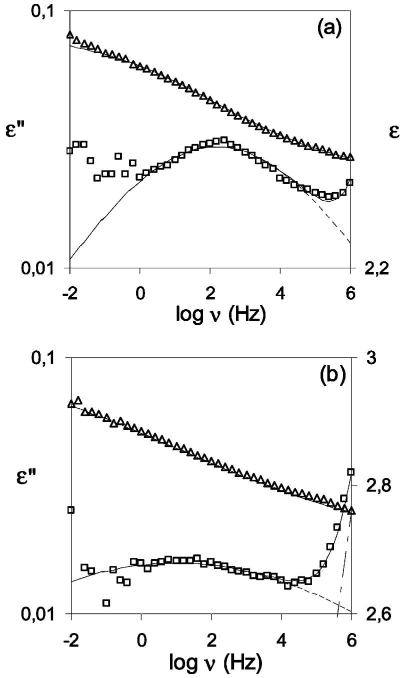

Figure 5. Frequency dependence of the real part ϵ' (△) and the imaginary part ϵ'' (□) of the dielectric response ϵ^*. The solid lines correspond to fits by HN function (- -) with the impedance effects (— —) between 1 and 106 Hz at −65 °C for (a) PDMI and (b) PDPI.

low frequency, inaccuracies resulted from the decreasing stability of the sample temperature over the duration of the measurement cycle. In the frequency range from 1 Hz to 10^6 Hz, the experimental spectra were reasonably well described by using both a single HN equation with $b = 1$ and the impedance contribution. The presence of such a relaxation peak was first reported by Diaz Calleja et al.[8] By comparing results obtained for PDMI with those of poly(methyl methacrylate) and poly(monomethylitaconate), the authors concluded that the so-called β_{fast}-process could be attributed to motions of the ester group separated from the main chain by a CH_2 unit.

It can be interesting to consider the polymer response over the full temperature range using an isochronous representation of the data. In this part, we considered the loss modulus formalism following previous works[8,27] which have shown that it can lead to a better resolution of the relaxation peaks. The dielectric loss modulus is defined as $M'' = \text{Im}[(\epsilon^*)]^{-1}$. Isochrones obtained at two different frequencies are reported in Figure 6 for PDMI and PDPI. In this figure, the three relaxation processes α, β_{slow}, and β_{fast} described above are observed. In addition, at 25 kHz and on the low-temperature side, PDPI shows a clear peak separated from the β_{fast}-process. This peak is associated with the γ-relaxation. Its apparent activation energy E_{app} is 24 kJ mol^{-1}, which is slightly lower than that reported in reference.[8] However, this result is in good agreement with the γ-relaxation observed by Cowie et al.[4,6] and for which we calculated $E_{\text{app}} = 25$ kJ mol^{-1} from the well-known formula[1] $E_{\text{app}} = (0.252-0.019 \log \nu)\, T_{\max}(\nu)$, where $T_{\max}$ is the maximum of the damping curve. It should be noted that there was some indication of this process on the low-temperature isotherms, but with a poor resolution. The γ-process was ascribed to relaxation mechanisms within the alkyl side chains, independent of the oxycarbonyl group and main chain.[4] This relaxation has also been observed in poly(n-alkyl methacrylate)s. The molecular origins of this low-temperature relaxation have been discussed by Shimizu et al.[28] and Cowie et al.[29] as a common feature for polymers which exhibit a linear four-atom sequence (C−C−C−C or O−C−C−C) in the side chain and the rotation of the central bond in this sequence is not hindered by the main chain.[28] A second possibility[4,30] was to assign this relaxation to a crankshaft-type motion[31] involving from three to five bonds. Actually, these motions should not induce a reorientation of the dipole moment of the side chain. However, other authors[32,33] have assumed that they involve small angle variations of the C=O−O−C ester bond, which are sufficient to give rise to a slight dielectric strength. Kawamura et al.[32] reported $\Delta\epsilon = 0.042$ at 117 K for a series of poly(n-alkyl methacrylate)s.

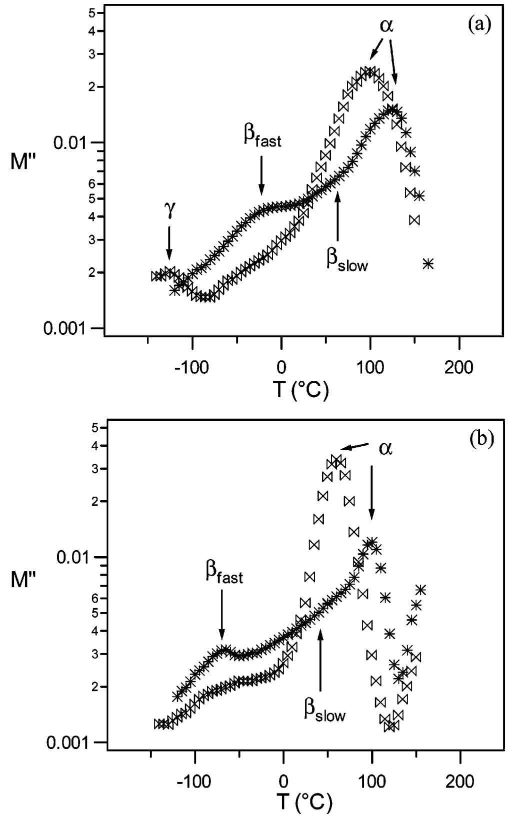

Figure 6. Dielectric loss moduli for PDMI (∗) and PDPI (⋈) as a function of temperature at (a) 25 kHz and (b) 25 Hz.

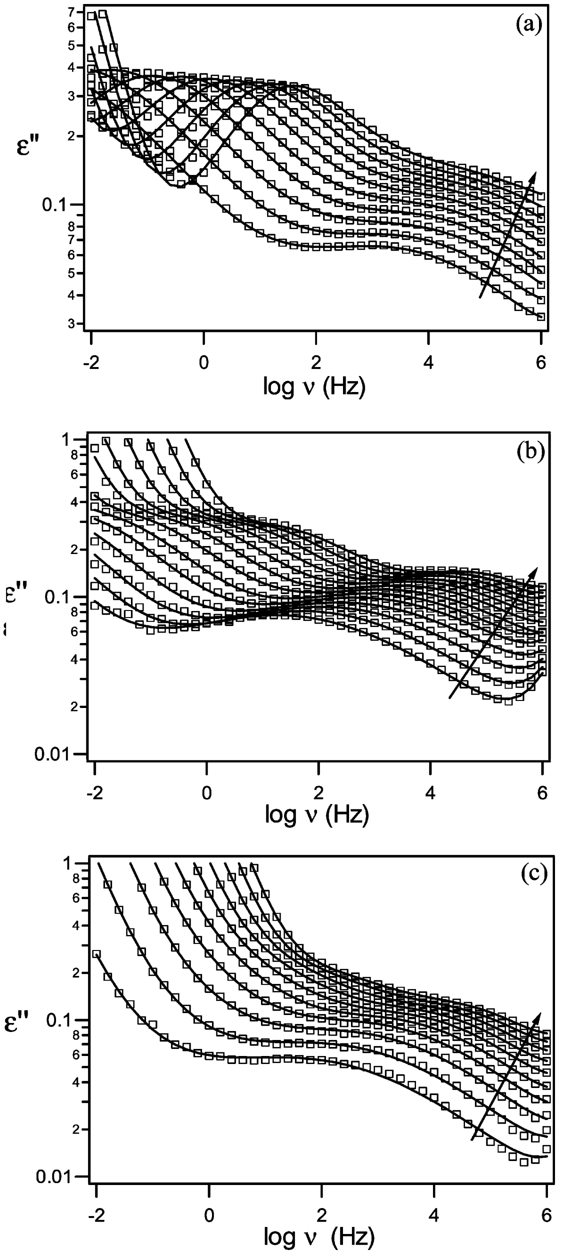

Figure 7. Frequency dependence of the imaginary part of the dielectric response ϵ^* for (a) PDHI from −20 to +25 °C, (b) PDOI from −50 to +10 °C and (c) PDDI from −45 to 0 °C at 5° intervals in the direction indicated by the arrow. The solid lines correspond to fits by HN functions, plus ionic conductivity and impedance effect.

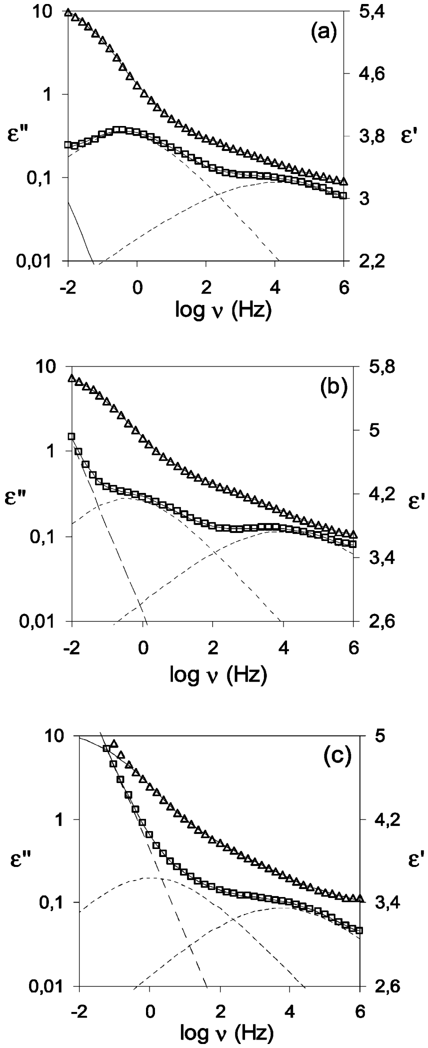

Figure 8. Frequency dependence of the real part ϵ' (△) and the imaginary part ϵ'' (□) of the dielectric response. The solid lines correspond to fits by HN functions for (a) PDHI at 0 °C, (b) PDOI at −10 °C, and (c) PDDI at −20 °C. The sum of two HN functions (- -) has to be used in conjunction with the ionic conductivity (— —).

3.2. The Higher Itaconates. Dielectric measurements were carried out in polymers containing longer side chains such as PDHI, PDOI, and PDDI. These samples exhibit three dielectric relaxation processes over the full temperature range. As previously explained for the lower derivatives, a single HN equation was adequate in representing the experimental data at high temperature. However, when the temperature decreases, two separate relaxational zones can be clearly observed for PDHI and PDOI (see Figure 7, parts a and b). In the case of PDDI, only the low-frequency process is clearly seen as the high-frequency dipolar relaxation and the conductive processes are overlapped (see Figure 7c). This fact makes the resulting fit parameters of the high-frequency peak prone to a high uncertainty. In contrast, the relaxation time can be determined with good accuracy for the low-frequency peak.

Table 2. Havriliak−Negami Fit Parameter, *a*, and Intensity Ratio between the α^U(HN1)- and α^L(HN2)-Processes, from the Curves Shown in Figure 8 for PDHI, PDOI, and PDDI

n	*T*	a_{HN1}	a_{HN2}	$\Delta\epsilon_{HN2}/\Delta\epsilon_{HN1}$
6	0°C	0.46	0.30	0.40
8	−10°C	0.46	0.34	0.55
10	−20°C	0.43	0.36	0.51

In the temperature range described in Figure 7, data were analyzed by means of the addition of two HN functions: HN1 was related to the α^U-process at low frequency and HN2 was related to the α^L-process at high frequency. In all cases, we have assumed symmetry in the relaxations peaks ($b_{HN1} = b_{HN2} = 1$), although we are aware of the asymmetric character of relaxations associated with the glass transition. This restriction was done as a first approximation, to decrease the number of fit parameters. The quality of the fit is illustrated in Figure 8 with the different contributions involved. Here, it can be interesting to consider the value of the intensity ratios $\Delta\epsilon_{HN2}$ / $\Delta\epsilon_{HN1}$ listed in Table 2. It is noteworthy that the intensity of the α^L-relaxation is approximately half of the intensity of the main process

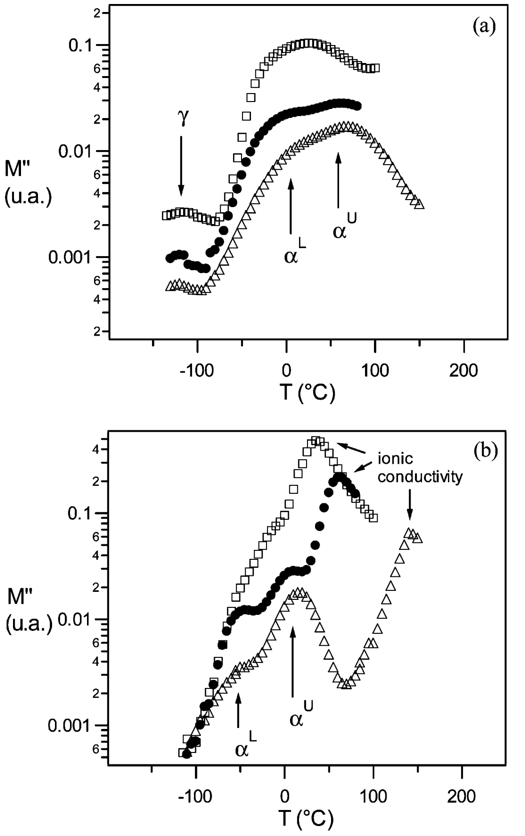

Figure 9. Dielectric loss moduli for PDHI (△), PDOI (●) and PDDI (□) as a function of temperature at (a) 25 kHz and (b) 25 Hz. PDOI and PDDI curves are shifted vertically for clarity.

due to the primary α^U-relaxation. Note that the intensity, $\Delta\epsilon$, of a given process is influenced by the peak shape parameter b and that, for both processes, b was fixed. However it was verified that different sets of b_{HN1} and b_{HN2} values in the fitting procedure give rise to intensity ratios of significant value as well.

The results treated with an isochronous presentation are shown in Figure 9. As can be observed at 25 Hz, the loss modulus exhibits an additional peak related to the conductivity contribution at higher temperatures than the α^U-process. Diaz Calleja et al.[8] observed a similar peak in PDAI's with $n = 1$ to $n = 4$. The authors suggest that this peak can be attributed to free charges coming from impurities or the remainder of solvent. Besides this peak, two large magnitude peaks associated with the two glass-transition processes are observed. The α^U- and α^L-peaks are well-separated at 25 Hz whereas both processes superimposed at high frequencies. At low temperature, the three samples investigated in this section exhibit a common γ-peak centered about −120 °C at 25 kHz. The position of this peak at a given frequency is the same as for PDPI. Thus, it is independent of the side-chain length in agreement with mechanical data.[6] For all the PDAI's investigated, peak temperatures observed for the dielectric loss modulus M'' are listed in Table 3 for the α or α^U, β_{fast} or α^L, and β_{slow}-processes at 25 Hz and for the γ-process at 25 kHz.

3.3. Further Evidence of a Slow β-Process. Results corresponding to the intensity of the main relaxation peak expressed in terms of maximum of the loss curves are shown in Figure 10 for PDMI, PDPI, and PDHI. The intensity trace for PDMI clearly indicates three different regimes. Garwe et al.[21] obtained a similar trend for poly(butyl methacrylate). Three zones were defined by the authors as follows: a high-temperature α-process (a), the merging region (b), and the low-temperature region (c) with the pronounced curved α-process detached from the local β_{slow}-process. The occurrence of an individual phenomenon in the c regime—the β_{slow}-process—is indicated by a bend in the ϵ''_{max} curve as a function of temperature for PDMI and also for PDPI. It is noteworthy that the introduction of a second HN equation related to the β_{slow}-relaxation in the fitting procedure is required at the temperature where the change of temperature dependence is observed, i.e., at 100 and 85 °C for PDMI and PDPI, respectively, as pointed out by arrows in Figure 10. It should be noted that the trace is linear for PDHI. These observations are in full agreement with Cowie et al.[4] since no definite β-relaxation could be detected by DMA for side-chain lengths longer than $n = 3$.

Table 3. Temperature of the Relaxation Peaks from the Isochronous Representation[a]

n	$T(M''_{max})$ at 25 Hz α or α^U (°C)	$T(M''_{max})$ at 25 Hz β_{slow} (°C)	$T(M''_{max})$ at 25 Hz β_{fast} or α^L (°C)	$T(M'_{max})$ at 25 kHz γ (°C)
1	100	indic	−65	
3	60	indic	indic	−125
6	15		−50	−120
8	10		−45	−120
10	indic		indic	−120

[a] indic means that there are only indications.

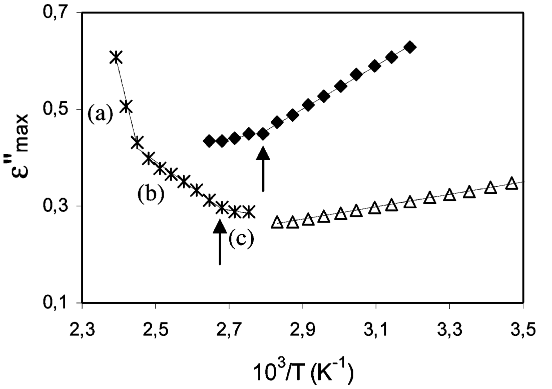

Figure 10. Maximal loss for the different ϵ'' isotherms (without fitting analysis) in the temperature range of α(α^U)- and β_{slow}-processes for PDMI (*), PDPI (◆), and PDHI (Δ).

3.4. Relaxation Map and Cooperativity Analysis. In Figure 11, we used the frequency ν at maximal loss calculated from the estimated HN parameters to plot the relaxation map for all the polymers under investigation. From PDMI to PDHI, the α(α^U)-curves shift to lower temperature when the side-chain length increases. This behavior was explained in terms of an internal plasticization of the material due to the CH_2 units in the side chains.[4,34] The α^U-curves obtained for PDHI and PDOI lie close to each other and the α^U-curves for PDDI is in a somewhat lower temperature range. This last point is somewhat surprising as an increase of the $T_g{}^U$ values is expected from $n = 7^{6,7}$ in PDAI's. We assume that the low molecular weight of PDDI ($N \ll 100$) leads to a dramatic decrease of $T_g{}^U$.

At lower temperatures, it can be observed that both β_{fast}- and α^L-processes are located in a common region on the relaxation map. Arrighi et al.[10] detected a modest strength process between 0 and 50 °C for PDAI's with $n = 5$ to $n = 8$. Its position is similar to the location of our α^L-relaxation. Similarly, the corresponding α$_{PE}$-[13−17]

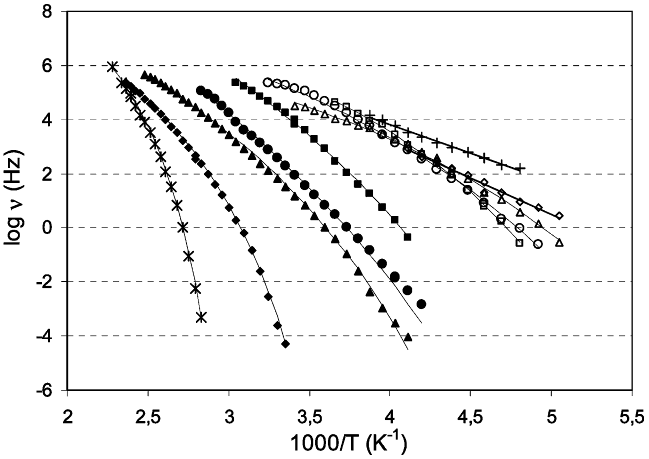

Figure 11. Dielectric relaxation for PDAI with: $n = 1$ (*, +), $n = 3$ (◆, ◇), $n = 6$ (▲, △), $n = 8$ (●, ○), and $n = 10$ (■, □). Filled symbols state for the $\alpha(\alpha^U)$-processes and empty symbols for the $\beta_{fast}(\alpha^L)$-processes. Solid lines are WLF fits.

Table 4. WLF Fit Parameters Obtained with T_g (1 Hz) as a Reference Temperature

n	T_g^U (°C)	$C_1^g(\alpha, \alpha^U)$	$C_2^g(\alpha, \alpha^U)$	T_g^L (°C)	$C_1^g(\alpha^L)$	$C_2^g(\alpha^L)$
1	95	11.5	66			
3	52	10.6	95			
6	5	10.9	118	−71	8.5	77
8	−5	13.6	145	−64	10.3	86
10	−27 ± 7	13.4 ± 1	117 ± 10	−61 ± 2	9.9 ± 1	68 ± 5

and β_{fast}-process[11,12] assigned to hindered rotations of the side chain in poly(n-alkyl methacrylate)s are located in the same region.

The temperature dependence of relaxation processes which are related to the glass transition is generally accepted to be well described by the Williams−Landel−Ferry (WLF) equation[35] within the region $T_g < T < T_g + 100$ K.[36] With $\nu = (2\pi\tau)^{-1}$, it can be written as

$$\log \frac{\nu(T)}{\nu(T_0)} = \frac{C_1^{\,0}(T - T_0)}{C_2^{\,0} + T - T_0}$$

where T_0 is a reference temperature. In this paper it was defined as the temperature at which T_g was observed at 1 Hz by dielectric relaxation.

In Figure 11, the activation curves for the $\alpha(\alpha^U)$- and α^L-processes are not linear and can be fitted properly by WLF-functions. All the results are summarized in Table 4. It is interesting to note that the T_g^L(1 Hz) values increase from PDHI to PDDI in agreement with literature[6] and DSC results. In contrast to T_g^U, the lower glass transition of PDDI does not seem to be influenced by the main-chain length. Actually, it is reasonable to think that this point is justified since the α^L-process is supposed to be decoupled from the backbone.[5,6]

As far as we are aware, it is the first time that the non-Arrhenius character of the α^L-relaxation is clearly demonstrated in PDAI's. In reference,[10] the narrow range of temperature precludes a WLF-analysis for the α^L-process in PDAI with $n \geq 6$. In contrast, the activation curves for the β_{fast}-process observed in PDMI and PDPI exhibit an Arrhenius behavior related to the local character of the underlying motion, typical for secondary relaxation processes.[29] It is interesting to note that the non-Arrhenius behavior of the α_{PE}-process has been shown[37] some time ago for poly(n-alkyl acrylate)s and poly(n-alkyl methacrylate)s. Beiner et al.[37] discussed that a strong argument for the decoupling of the low-temperature glass transition from the main chain is that this process occurs in a practically identical frequency and temperature range for several polymer series containing long alkyl side chains.

Table 5. Activation Enthalpies and Entropies of Dielectric Processes

n	$\Delta H^*(\alpha, \alpha^U)$ (kJ mol^{-1})	$\Delta H^*(\beta_{fast}, \alpha^L)$ (kJ mol^{-1})	n	$\Delta S^*(\alpha, \alpha^U)$ (J K^{-1} mol^{-1})	$\Delta S^*(\beta_{fast}, \alpha^L)$ (J K^{-1} mol^{-1})
1	573	39	1	1330	1
3	268	49	3	594	31
6	151	68	6	315	112
8	117	85	8	208	181
10	139 ± 20	103 ± 10	10	337 ± 70	260 ± 30

The cooperative character of both glass-transition processes, $\alpha(\alpha^U)$ and α^L, can be investigated by using the Starkweather[38,39] analysis. The activation entropy, ΔS^*, and enthalpy, ΔH^*, of viscoelastic relaxation may be determined from the mean relaxation time, τ, in terms of the Eyring theory of absolute reaction rates, where

$$\frac{1}{\tau} = \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right)$$

Viscoelastic relaxations are considered to be simple or complex depending on their activation entropies: low activation entropies reflect the motion of small molecular fragments without much cooperative involvement, whereas complex relaxations such as glass transitions have large activation entropies and involve cooperative motions of neighboring groups.[38,39] The plot $\ln(1/\tau T)$ vs $1/T$ gives the ΔS^* and ΔH^* values. They were calculated in the frequency ranges from 10^{-2} to 1 Hz and from 1 to 10^2 Hz for the $\alpha(\alpha^U)$- and α^L-processes, respectively. For the α^U-process in PDDI, data were extrapolated from the WLF fit. Results are reported in Table 5 for all the different samples.

The $\alpha(\alpha^U)$-relaxations have large activation entropies as expected for glass-transition processes. Note that the calculated activation entropy was 702 J K^{-1} mol^{-1} for the main relaxation of PMMA.[40] From PDMI to PDHI, we observe that increasing the alkyl side-chain length results in a strong decrease of the ΔS^* values related to the $\alpha(\alpha^U)$-process. That could be understood in the framework of a lower degree of molecular cooperativity. From PDHI to PDDI, ΔS^* values remain nearly constant showing that six methylene units are sufficient to make the backbone cooperative effects independent of the side-chain length. These conclusions are consistent with results[10] deduced from the investigation of the fragility index,[41] m, for a series of itaconate polymers. It should be noted that the fragility has been correlated to the degree of cooperativity as measured by the deviations from exponential relaxation.[42] The experimental variation of m indicates a strong change from fragile to strong liquid from PDMI to PDPI, that is with the simple addition of two CH_2 units in the side chain. Arrighi et al.[10] reported that the requirement for main-chain cooperativity decreases with side-chain length as the flexible alkyl chains induced lower dynamic constraints on each other or on another itaconate backbone. Floudas et al.[11,12] produced an analogous analysis for poly(n-alkyl methacrylate)s. In this last series, decreasing cooperativity was also discussed[14] to be a consequence of the shift of the $\alpha\beta$-crossover region to lower frequency from $n = 1$ to $n = 6$. Note that an onset of intermolecular cooperativity occurs in the crossover region and a large temperature difference ($T_{\mathrm{onset}} - T_{\mathrm{g}}$) can be associated with a significant cooperativity.[14]

The β_{fast}- and α^{L}-relaxations exhibit a completely different evolution: the entropy values increase with the number of carbons in the side chain. In PDMI, the β_{fast}-process has a near-zero entropy which reflects an isolated motion. Results obtained for PDPI indicate, as well, a rather small motional cooperativity. However, for $n \geq 6$, one can observe a strong increase in ΔS^*. The α^{L}-process has clearly a cooperative character which must be related to a much more complex relaxation in comparison to the β_{fast}-relaxation, although both processes are located in the same region on the relaxation map (see Figure 11).

About the enthalpy values, it should be noted that Arrighi et al.[10] reported $E_{\mathrm{app}} = 49$ kJ mol^{-1} and $E_{\mathrm{app}} = 55$ kJ mol^{-1} for the second high-frequency process of PDHI and PDOI, respectively. Since these values are calculated in a high-frequency window, they are underestimated in comparison with the corresponding ΔH^* values reported in Table 5 for the α^{L}-process. As a consequence, the assignment of the α^{L}-relaxation to a motion of the aliphatic side chains only,[10] which was based on the similitude between the activation energy of this process in PDAI's with long side chains and that found for polyethylene[43] by DMA, is no more entirely satisfying and will be discussed in the following section.

3.5. Discussion. In the search for the molecular origin of the α^{L}-process different observations have to be taken into account. Clearly, the comparison between the position of the α^{L}-process in PDAI's with $n \geq 6$ and the corresponding α_{PE}-[13–17] or fast β-processes[11,12] which are reported in the higher poly(n-alkyl methacrylate)s, indicates that the α^{L}-process can be related to relaxation mechanisms in the alkyl side chains. However, it seems necessary to understand the difference relative to the dielectric activity between both series of polymers for a process which was supposed to have the same origin.

The reason becomes clear when we look at the relaxation map (Figure 11) where the β_{fast}- and α^{L}-processes occur at comparable temperatures. It was established that the β_{fast}-process could be related to the ester group which is not connected to the main chain in the lower derivatives. Now, as for the β-relaxation reported in poly(n-alkyl methacrylate)s,[23,44] it is reasonable to think that the position of the local β_{fast}-process is independent of the side-chain length in PDAI's (it was already shown by comparing PDMI and PDPI results). From these observations, we proposed that the carboxyl group of the side chain next to the $\mathrm{CH_2}$ spacer unit, where one main dipole moment of the repeat unit is located, must be involved in the α^{L}-relaxation in addition to the alkyl side chain. This conclusion is consistent with the relatively high enthalpy values reported in Table 5 for the α^{L}-relaxation of PDAI's with long side chains.

4. Conclusions

In this work, we have been able to observe and characterize the low-temperature γ-relaxation, as well as two distinct secondary relaxation processes involving each of the two ester groups of the repeat unit. The ester group separated from the main chain by a spacer unit is associated with the faster β-process, the other ester group is related to the β_{slow}-process. In agreement with Arrighi et al.,[10] we reported a second high-frequency process in PDAI's with $n \geq 6$ that we called the α^{L}-process. In addition, we demonstrated the glass-transition character of this process, in terms of WLF-behavior and cooperativity, which occurs at a lower temperature than the conventional glass transition, α^{U}.

The coexistence of two cooperative relaxations, α^{L} and α^{U}, is typical for nanophase-separated block copolymers, whereas this is clearly not expected for homopolymers. It means that some nanophase separation must occur in PDAI's with long alkyl side chains in agreement with results[45] obtained from combined wide-angle and small-angle X-ray scattering measurements in PDAI's. Cowie et al.[5,6] have proposed that the polar backbone and the alkyl parts are encased in independent regions leading to a two-phase system. The frontier between the two domains is ensured by the polar barrier provided by the pendant ester linkages. Our specific contribution to this description is of a dynamic nature: it leads to the conclusion that the second ester group at the frontier between the two phases takes part in the side-chain relaxation.

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