

# Mechanical Relaxations of Poly( $\beta$ ,L-aspartate)s

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**ABSTRACT:** The dynamic mechanical thermal properties of a family of poly( $\alpha$ -alkyl  $\beta$ ,L-aspartate)s bearing various cyclic, linear, and branched alkoxy carbonyl groups in the side chain were studied. The measurements carried out by dynamic mechanical thermal analysis (DMTA) revealed the significant influence of the constitution of the side chain on mechanical relaxation phenomena. Three relaxations were observed, which are referred to as  $\gamma$ ,  $\beta$ , and  $\alpha$ , in increasing order of temperature. The first two,  $\gamma$  and  $\beta$ , are related to the local and global motions of the side chain, respectively. Relaxation  $\alpha$  is related to the motion of the main chain. Relaxation  $\beta$ , which is associated with the rotation of the side chain, is the most intense. The magnitude and temper-

ature at which this relaxation occurs depends on the volume, the length, and the degree of branching of the ester group of the side chain. A comparison between the dynamic mechanical properties of poly( $\beta$ ,L-aspartate)s and poly( $\alpha$ ,L-glutamate)s revealed that the two methylene groups spacing the ester group from the main chain provides the poly( $\alpha$ -L-glutamate)s with greater mobility, and thus, relaxations  $\alpha$  and  $\beta$  occur at lower temperatures. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 994–1003, 2006

**Key words:** poly( $\beta$ ,L-aspartate)s; mechanical relaxation; structure–property relations; poly( $\alpha$ ,L-glutamate)s

## INTRODUCTION

Poly( $\alpha$ -alkyl  $\beta$ ,L-aspartate)s are nylon 3 derivatives. The alkoxy carbonyl group is stereoregularly attached to  $\beta$ -carbon of the repeating unit. The significance of these substituted polyamides resides in the fact that their properties are intermediate between those of nylons and polypeptides. Poly( $\alpha$ -isobutyl  $\beta$ ,L-aspartate), which has been widely studied by our research group, crystallizes in helical structures with features similar to the  $\alpha$ -helix characteristic of polypeptides.<sup>1,2</sup> This polymer has been shown to have properties that are related to its helicoidal structure, such as piezoelectricity<sup>3</sup> and the formation of cholesteric liquid crystals.<sup>4</sup> Recent studies carried out on other poly( $\alpha$ -alkyl  $\beta$ ,L-aspartate)s with a great variety of side chains have shown that the formation of the helical structure is common to this family of compounds.<sup>5–8</sup> Furthermore, poly( $\alpha$ -alkyl  $\beta$ ,L-aspartate)s<sup>9</sup> and poly( $\gamma$ -alkyl  $\alpha$ ,L-glutamate)s<sup>10</sup> that have side chains of more than ten carbons have a complex biphasic structure in which the main chains form helices and the alkyl side chains are crystallized in a separated phase.

No studies on the structural relaxation phenomena of poly( $\alpha$ -alkyl  $\beta$ ,L-aspartate)s have been carried out so far. On the contrary, a pretty wealth of research has been carried out on poly( $\gamma$ -alkyl  $\alpha$ ,L-glutamate)s and poly(methacrylate)s, a couple of polymer families structurally related to polyaspartates. The formers are crystalline polypeptides with the main chain in the  $\alpha$ -helix conformation, whereas poly(methacrylate)s are amorphous polymers that resemble to poly( $\alpha$ -alkyl  $\beta$ ,L-aspartate)s, in that the alkoxy carbonyl side group is joined directly to the main chain, R being the alkyl group.

Studies by means of mechanical and dielectric relaxation in poly(methacrylates) and poly( $\gamma$ -alkyl  $\alpha$ ,L-glutamate)s show that there are typically three relaxations, referred to as  $\gamma$ ,  $\beta$  and  $\alpha$ , in increasing order of temperature.<sup>10–14</sup> In both cases, relaxation  $\gamma$  has been attributed to local motion in the alkyl end groups of the side chain. This motion usually occurs at temperatures below  $-120^\circ\text{C}$  and involves apparent activation energies of 4–11 kcal mol<sup>-1</sup>. These activation energies are similar in magnitude to the energy barrier that restricts rotation around the C—C bond in simple paraffins.

Relaxation  $\beta$  is attributed to the motions of the whole side chain, both the rotation of the ester group and cooperative motions between the side chain and groups that are adjacent to the main chain. The decrease observed by several authors in the temperature of the relaxation  $\beta$ ,  $T_\beta$ , both in terms of the dielectric<sup>12</sup>

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TABLE I  
Alkyl Side Chains, Structures, Molecular Weights, and Densities of the Studied Poly( $\alpha$ - $\beta$ ,L-aspartate)s

| Alkyl group      | —R   | $M_v(10^{-5})^a$ | $\rho$ (g mL $^{-1}$ ) <sup>b</sup> | Polymer             |
|------------------|--|------------------|-------------------------------------|---------------------|
| <i>n</i> -Propyl | —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>                   | 14.0             | 1.12                                | PAALA-3             |
| Isopropyl        | —CH(CH <sub>3</sub> ) <sub>2</sub>                                   | 3.4              | 1.16                                | PAALA- <i>i</i> 3   |
| Isobutyl         | —CH <sub>2</sub> —CH(CH <sub>3</sub> ) <sub>2</sub>                  | 2.5              | 1.18                                | PAALA- <i>i</i> 4   |
| Isoamyl          | —CH <sub>2</sub> —CH <sub>2</sub> —CH(CH <sub>3</sub> ) <sub>2</sub> | 3.7              | 1.19                                | PAALA- <i>i</i> 5   |
| Neopentyl        | —CH <sub>2</sub> —C(CH <sub>3</sub> ) <sub>3</sub>                   | 2.2              | 1.24                                | PAALA- <i>neo</i> 5 |
| Cyclopentyl      | —C <sub>5</sub> H <sub>9</sub>                                       | 2.2              | 1.09                                | PAALA- <i>c</i> 5   |
| Cyclohexyl       | —C <sub>6</sub> H <sub>11</sub>                                      | 2.8              | 1.31                                | PAALA- <i>c</i> 6   |
| Benzyl           | —CH <sub>2</sub> —C <sub>6</sub> H <sub>5</sub>                      | 4.1              | —                                   | PAALA-Bn            |

<sup>a</sup> The average molecular weights were estimated using the intrinsic viscosity measured in dichloroacetic acid at 25°C by applying the viscosimetric Mark-Houwink-Sakurada equation reported for poly( $\gamma$ -benzyl  $\alpha$ ,L-glutamate) in the same solvent.<sup>21</sup> The molecular weights of all the polymers studied are considerably greater than  $1 \times 10^4$ , which is thought to be the critical molecular weight,<sup>13</sup> below which the concentration of chain end groups is significant.

<sup>b</sup> Densities calculated according to the crystalline structures proposed in previous studies.<sup>7,8,20</sup>

and mechanical<sup>10</sup> relaxation of poly( $\gamma$ -*n*-alkyl  $\alpha$ ,L-glutamate)s is due to part of the side chain having a plasticizing effect on the cooperative motions. Other authors,<sup>15,16</sup> on the subject of poly(methacrylate)s, argue that, as the length of the side chain increases,  $T_\beta$  hardly varies and its activation energy remains constant, if it is sufficiently separate from the temperature of relaxation  $\alpha$ ,  $T_\alpha$ .

Relaxation  $\alpha$  is associated with the conformational motions of segments of the main polymer chain. This relaxation is, therefore, closely related to the glass-transition of the material. In the case of highly ordered polymers in which conformational motions are restricted, relaxation is attributed to motions in the crystalline region. Kajiyama et al.,<sup>17</sup> on the subject of poly( $\gamma$ -*n*-alkyl  $\alpha$ ,L-glutamate)s, attribute mechanical relaxation  $\alpha$  to the thermal molecular motion of helix  $\alpha$  in the crystalline phase. Watanabe et al.,<sup>10</sup> with reference to these same polymers, associate relaxation  $\alpha$  with the translation and rotation motions of the main chain's helices along the axis of the helix. Kakizaki et al.<sup>18</sup> attribute the dielectric relaxation  $\alpha$  observed in poly( $\gamma$ -*n*-alkyl  $\alpha$ ,L-glutamate)s to cooperative motions between the main chain and the side chain. Relaxation  $\alpha$  is also affected by the length and shape of the side chain, since the temperature at which it occurs decreases drastically as the length of the side chain increases, both in poly( $\gamma$ -*n*-alkyl  $\alpha$ ,L-glutamate)s<sup>10,12</sup> and poly(methacrylate)s.<sup>13,14</sup> In some cases, as the length of the side chain increases, relaxation peak  $\alpha$  is displaced to temperatures that are sufficiently low, to eventually overlap the relaxation peak  $\beta$ ; as a result, only one signal can be seen.<sup>13,14</sup> Therefore, it is concluded that relaxation  $\alpha$  depends on the degree of crystallinity of the polymer and is heavily influenced by the constitution of the side group.

In the present article, we studied, for the first time, the mechanical relaxation of a family of poly( $\alpha$ -alkyl  $\beta$ ,L-aspartate)s named PAALA-*n*, where *n* represents

the number of carbon atoms present in the alkyl side group. We observed the three types of relaxations that are typical of other families of polymers, and we also saw how relaxations  $\alpha$  and  $\beta$  influence each other, but at temperatures that are sufficiently separate from one another to be clearly attributable to the motions of the main and side chains, respectively. We related the constitution of the side chains of the PAALAs with their dynamic mechanical properties. Specifically, we studied the effect of the length, volume, and degree of branching of the side chain on the mechanical relaxation spectrum. We also compared the dynamic mechanical properties of poly( $\alpha$ -alkyl  $\beta$ ,L-aspartate)s and poly( $\gamma$ -*n*-alkyl  $\alpha$ ,L-glutamate)s.

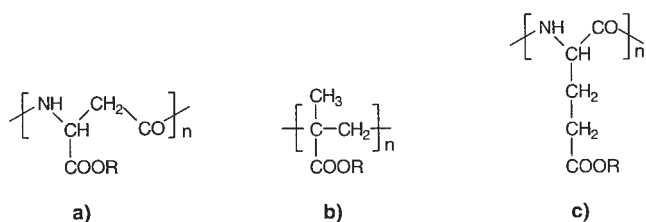
## EXPERIMENTAL

### Materials

All the PAALAs were prepared by means of unassisted anionic polymerization by ring-opening of the corresponding optically pure (*S*)-4-(alkoxycarbonyl)-2-azetidinone. Further details on polymerization, the crystalline structure of polymers, and synthesis of monomers are provided in recently published research papers.<sup>7,8,19,20</sup>

To compare the dynamic mechanical properties of poly( $\beta$ ,L-aspartate)s and poly( $\alpha$ ,L-glutamate)s, we used poly( $\gamma$ -benzyl  $\alpha$ ,L-glutamate) (PGBLG). The PGBLG (Aldrich) was used without purifying and had a viscometric molecular weight of  $4.8 \times 10^5$ .

By means of X-ray diffraction, we were able to ascertain that the samples analyzed by DMTA were largely crystalline, although there was an indeterminate proportion of amorphous material. We also checked that the degree of crystallinity of the polymers did not vary significantly, before and after the dynamic mechanical tests. Table I lists the poly( $\alpha$ -



**Figure 1** Schematic representation of the chemical formula for the constitutional repeating unit of (a) poly( $\alpha$ -alkyl  $\beta$ ,L-aspartate)s, (b) poly(methacrylate)s, and (c) poly( $\gamma$ -alkyl  $\alpha$ ,L-glutamate)s.

alkyl  $\beta$ ,L-aspartate)s studied in this work, whose repeating units are shown in Figure 1.

### DMTA measurements

The samples were prepared in a Specac P/N 15,620 Constant Thickness Film Maker Accessory, which had a spacer ring of 250  $\mu$ m. We applied a constant force of  $1 \times 10^3$  kg and heated the samples at between 130 and 200°C, depending on the polymer.

The dynamic mechanical measurements were carried out with a Rheometrics PL-DMTA MK3 analyzer within a temperature range of  $-150$  to  $+200^\circ\text{C}$  at a frequency of 10 Hz and at a heating rate of  $2^\circ\text{C}/\text{min}$ . Single cantilever bending was performed on rectangular samples ( $2 \times 12 \times 0.25$  mm<sup>3</sup>). We worked with a preset deformation of 632  $\mu$ m and in a nitrogen atmosphere.

To determine the activation energy, we carried out tests at frequencies of 0.1, 1, 10, and 100 Hz, under the same conditions, and used the Arrhenius equation

$$\ln f = \ln f_0 + \frac{E_a}{RT} \quad (1)$$

where  $E_a$  is the apparent activation energy and  $T$  and  $f$  are, respectively, the temperature and the frequency of the maximum of the loss modulus,  $E''$ , or of the loss tangent,  $\tan \delta$ .

Relaxation  $\beta$  was modeled on the semiempirical Fous-Kirkwood equation

$$E'' = \frac{E''_{\max}}{\cosh m \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{\max}} \right)} \quad (2)$$

where  $E''_{\max}$  represents the loss modulus at the temperature of the maximum,  $T_{\max}$ , and  $m$  is a shape parameter ( $0 \leq m \leq 1$ ) related to the amplitude of the relaxation. A high  $m$ -value implies a broad relaxation and an increase both in cooperativity and in the complexity of the relaxation process.

Because of the partial overlapping of relaxation  $\beta$  with relaxations  $\alpha$  and  $\gamma$ , it was necessary to deconvolute the signal using the PeakFit program (Jandel Scientific Software, San Rafael, CA) to determine the  $m$  parameter.

The magnitude of relaxation  $\beta$  was compared using the parameter

$$\Delta E' / E' = \frac{E'_U - E'_R}{E'_R} \quad (3)$$

where  $E'_U$  and  $E'_R$  are the respective storage modulus before and after relaxation.<sup>14</sup>

The contribution of each relaxation to the total relaxation of the material was evaluated as the percentage decrease in the storage modulus during the relaxation, with respect to the decrease associated with the total relaxation of the material,  $\Delta E'$  (%).

## RESULTS AND DISCUSSION

### General behavior

A representative mechanical relaxation spectrum for this family of polymers is that recorded for PAALA-*i5*, which is shown in Figures 2 and 3. Three transitions, referred to as  $\gamma$ ,  $\beta$  and  $\alpha$ , in increasing order of temperature, can clearly be seen. These transitions are shown as maximum on the loss tangent curve,  $\tan \delta$ , with temperature,  $T$ , and on the storage modulus curve,  $E'$ , with  $T$ , as changes in the slope of the curve (Fig. 2). In the loss modulus curve,  $E''$ , with  $T$ , the relaxations are also shown as maximum (Fig. 3). The same figure also shows the deconvolution of the experimental signal  $E''-T$ , which was performed to determine the Fous-Kirkwood parameter  $m$  associated with relaxation  $\beta$ . The dynamic mechanical results of the polymers studied are summarized in Table II. For PAALA-*i5*, relaxation  $\gamma$ , which can be attributed to local motions in the side chain, occurs at  $-143^\circ\text{C}$ . Relaxation  $\beta$ , associated with motions of the whole side chain (rotation), occurs at  $-13^\circ\text{C}$ , whereas relaxation  $\alpha$ , which is due to motions of the entire main chain, is near  $130^\circ\text{C}$ . The apparent activation energies estimated for relaxations  $\alpha$ ,  $\beta$ , and  $\gamma$  are 66, 24, and 7 kcal mol<sup>-1</sup>, respectively. These values agree with the type of motion associated with each relaxation and with the values observed in other families of polymers that have similar side groups and structures.<sup>10,14,22</sup> As shown, relaxation  $\beta$  is the one that provides the greatest contribution to the total relaxation of the material (Fig. 3 and Table II). In general, all the PAALAs studied behave similarly to PAALA-*i5*, although, showing slight differences according to the constitution of the side chain.

For PAALA-3, two overlapping relaxations can be seen at  $-91$  and  $-49^\circ\text{C}$ , which are designated  $\beta'$  and

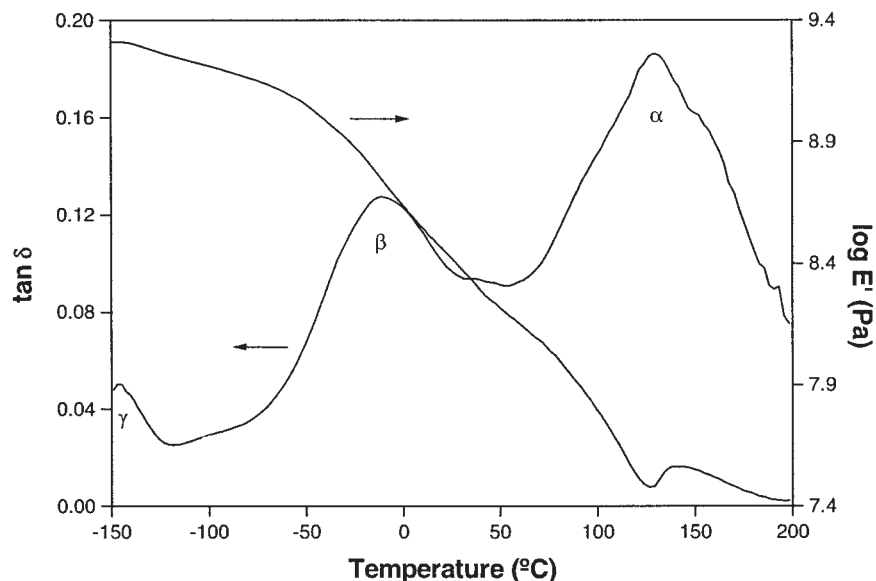


Figure 2 Temperature dependence of loss tangent  $\tan \delta$  and storage modulus  $E'$  at 10 Hz for PAALA-*i*5.

$\beta$  respectively, corresponding to the rotation of the whole side group (Fig. 4). In fact, both processes correspond to a single relaxation that occurs within a wide temperature range. This would indicate that the polymer has various domains with different levels of mobility, and that relaxation  $\beta'$  is the result of the side chain's loss of residual mobility. This double relaxation has been seen in poly( $\gamma$ -*n*-alkyl  $\alpha$ -L-glutamate)s,<sup>12</sup> and its intensity rapidly decreases as the length of the side chain increases. Other authors<sup>10</sup> have not observed relaxation  $\beta'$  for the same family of

polymers, which seems to indicate that whether this relaxation occurs or not may be determined by the packing of the helices and the thermal history.

Similarly to PAALA-3, PAALA-*i*3 shows a relaxation spectrum in which there are two relaxations associated with the rotation of the side chain (Fig. 4). There is a peak at  $-101^\circ\text{C}$  with a shoulder at  $-63^\circ\text{C}$ , which correspond to the relaxations  $\beta$  and  $\beta'$ , respectively. Relaxation  $\beta'$  has only been observed for the propyl and isopropyl derivatives. The reproducibility of the relaxation spectra and the fact that transitions  $\beta$

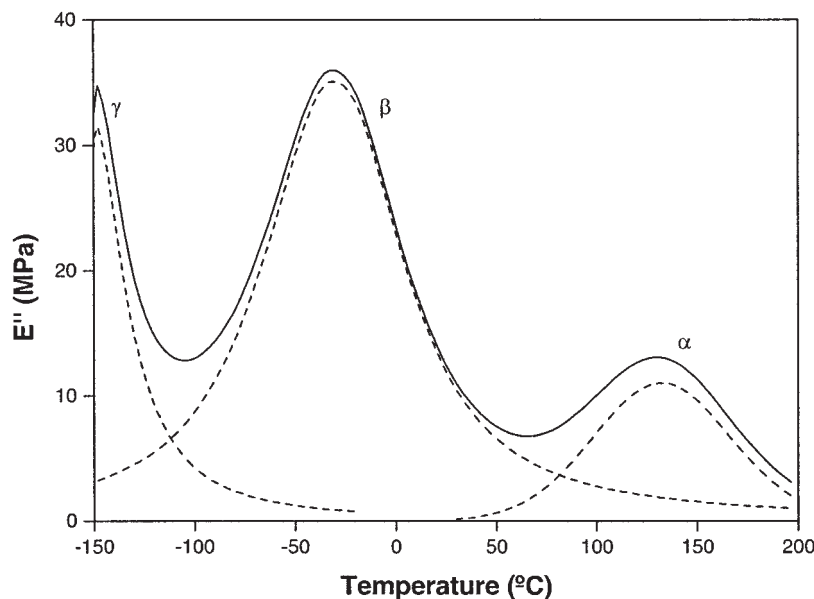


Figure 3 Temperature dependence of loss modulus  $E''$  at 10 Hz for PAALA-*i*5. Solid lines are experimental values and dotted lines are the peaks obtained by deconvolution.

TABLE II  
Temperatures of the Maximum of  $\tan \delta$ , Percentage of Modulus Storage  $\Delta E'$ , Activation Energies  $E_a$ ,  $\Delta E'/E'$ , and  $m$  Fuoss-Kirkwood Parameter for the Relaxations of the Various Polymers Studied at 10 Hz

| Polymer             | $\gamma$ -Relaxation |                 |                                 | $\beta$ -Relaxation |                 |                                 |                | $\alpha$ -Relaxation |          |                 |                                 |
|---------------------|----------------------|-----------------|---------------------------------|---------------------|-----------------|---------------------------------|----------------|----------------------|----------|-----------------|---------------------------------|
|                     | $T$ (°C)             | $\Delta E'$ (%) | $E_a$ (kcal mol <sup>-1</sup> ) | $T$ (°C)            | $\Delta E'$ (%) | $E_a$ (kcal mol <sup>-1</sup> ) | $\Delta E'/E'$ | $m$                  | $T$ (°C) | $\Delta E'$ (%) | $E_a$ (kcal mol <sup>-1</sup> ) |
| PAALA-3             | —                    | —               | —                               | -49 <sup>a</sup>    | 79              | 21                              | 2.7            | 0.128                | 170      | 21              | 78                              |
| PAALA- <i>i</i> 3   | —                    | —               | —                               | -101 <sup>b</sup>   | 63              | 17                              | 1.8            | 0.105                | 220      | 37              | 80                              |
| PAALA- <i>i</i> 4   | -146                 | 8               | —                               | 0                   | 73              | 22                              | 3.6            | 0.153                | 140      | 19              | 72                              |
| PAALA- <i>i</i> 5   | -143                 | 11              | 7                               | -13                 | 80              | 24                              | 8.5            | 0.170                | 130      | 9               | 66                              |
| PAALA- <i>neo</i> 5 | —                    | —               | —                               | 70                  | 81              | 27                              | 4.5            | 0.072                | 160      | 19              | 75                              |
| PAALA- <i>c</i> 5   | —                    | —               | —                               | 50                  | 67              | —                               | —              | —                    | 200      | 33              | —                               |
| PAALA- <i>c</i> 6 c | -65                  | 59              | 11                              | 80                  | 27              | —                               | —              | —                    | 180      | 14              | —                               |
| PAALA-Bn            | —                    | —               | —                               | 53                  | 89              | —                               | 7.6            | —                    | 160      | 11              | —                               |
| PGBLG               | —                    | —               | —                               | 38                  | 95              | —                               | 15.1           | —                    | 105      | 5               | —                               |

<sup>a</sup> For PAALA-3, a relaxation  $\beta'$  also occurs at -91°C.

<sup>b</sup> For PAALA-*i*3, a relaxation  $\beta'$  also occurs at -63°C.

<sup>c</sup> For PAALA-*c*6, the relaxation denoted  $\gamma$  in the table corresponds to the axial-equatorial conformational change of the cyclohexyl group.

and  $\beta'$  continue to appear in a second scan rule out the influence of the thermal history. Therefore, it can be concluded that in PAALAs, these transitions depend mainly on the packing of the helices.

Both PAALA-3 and PAALA-*i*3 show a relaxation  $\alpha$ , which can be attributed to motions of the main chain at very high temperatures, particularly for the branched derivative. This agrees with the high softening temperature of the material required for the preparation of the samples. No  $\gamma$  transitions occurred for either of the polymers in the temperature range studied. In poly( $\gamma$ -*n*-alkyl  $\alpha$ ,L-glutamate)s<sup>10</sup> and in poly(methacrylate)s<sup>13,14</sup> the  $T_\gamma$  decreases as the length of the side chain decreases. Because in PAALA-*i*5 relaxation  $\gamma$  occurs near -150°C, this

relaxation should be expected to occur in PAALA-3 at temperatures below -150°C. The propyl ester group is less rigid than the isopropyl ester group; therefore, it can be expected that this last derivative will not show a  $\gamma$  relaxation, just as the poly(isopropyl methacrylate).<sup>14</sup> In this sense, it should be reminded that in branched polyethylenes, relaxation  $\gamma$  only occurs when the branching has at least three methylene units.<sup>11</sup>

PAALA-*i*4 (Fig. 5) shows a relaxation spectrum similar to that of PAALA-*i*5 (Fig. 2). Indications of relaxation  $\gamma$ , which would be associated with conformational motions of the isobutyl group, appear at -146°C. Transitions  $\beta$  and  $\alpha$  occur at temperatures of 0 and 140°C, respectively.

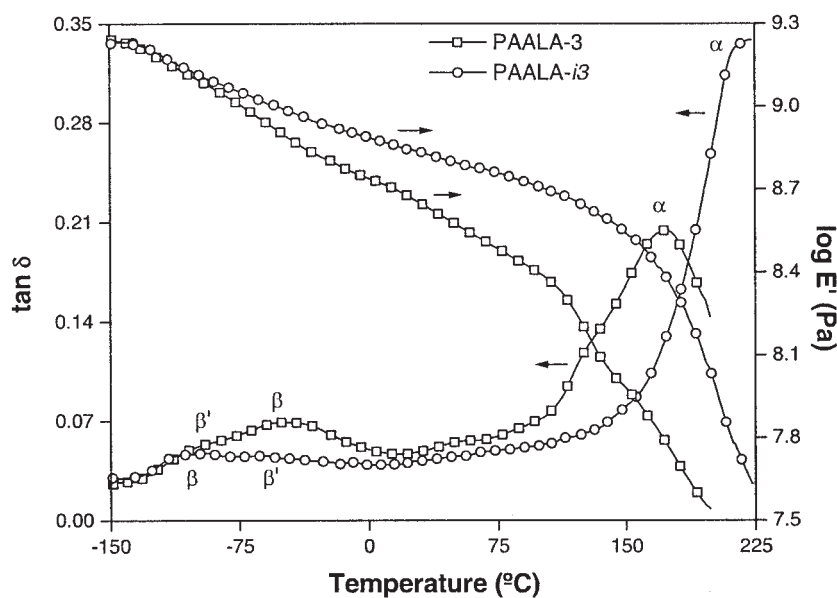


Figure 4 Temperature dependence of loss tangent  $\tan \delta$  and storage modulus  $E'$  at 10 Hz for PAALA-3 and PAALA-*i*3.

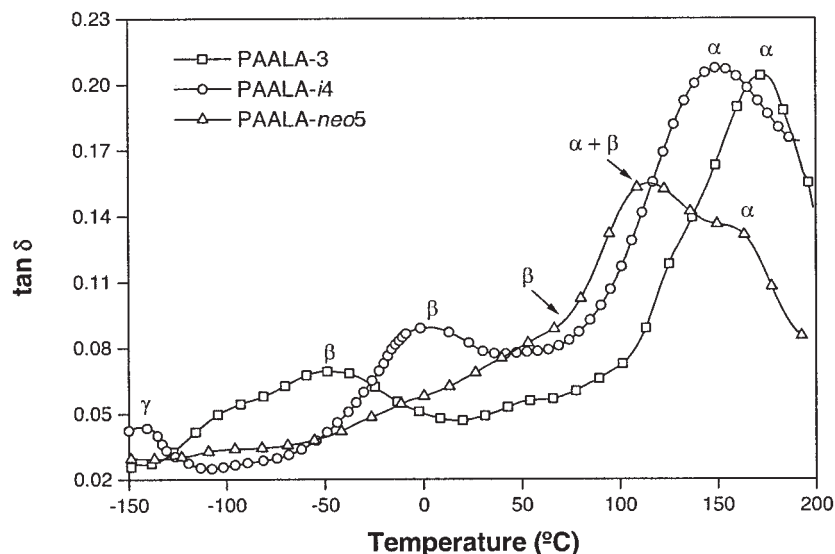


Figure 5 Temperature dependence of loss tangent  $\tan \delta$  at 10 Hz for PAALA-3, PAALA-*i4*, and PAALA-*neo5*.

As it was to be expected, PAALA-*neo5* (Fig. 5) shows no signs of relaxation  $\gamma$ , because the volume of the neopentyl group restricts its mobility, and its high degree of symmetry does not allow its alkyl units to adopt more than one spatial conformation. Relaxations  $\beta$  and  $\alpha$  overlap at high temperatures, although they can be identified as two separate processes, because they appear as an asymmetric peak with various maxima. Tentatively, we attributed a value to  $T_{\beta}$  close to 70°C. Two maxima appear at 110 and 160°C, the first of which can be attributed to cooperative motions of the side and main chains ( $\alpha + \beta$ ), respectively, and the second one to relaxation  $\alpha$  exclusively. The fact that relaxation  $\beta$  occurs at high temperatures and overlaps the relaxation of the main chain may be explained by the rigidity of the neopentyl group. Furthermore, the high packing density of PAALA-*neo5* (Table I) would also imply a high cohesive energy that would restrict conformational motions.

PAALA-*c5* has a complex mechanical relaxation spectrum with very low  $\tan \delta$  values (figure not shown). Relaxation  $\alpha$  is seen at around 200°C. A complex  $\beta$  relaxation can be sensed across a broad range of temperatures going from -130 to 100°C, with a maximum around 50°C and various shoulders at lower temperatures. The spectrum does not enable us to glean further information, although relaxation  $\beta$  may be associated both with the rotation of the side group and with conformational changes in the cyclopentyl group taking place at low temperatures.

In the relaxation spectrum of PAALA-*c6* (Fig. 6), at the low temperature of -65°C, a significant  $\gamma$  relaxation with an activation energy of 11 kcal mol<sup>-1</sup> can be observed. Relaxation  $\beta$  appears at around 80°C and slightly overlaps transition  $\alpha$  at 180°C. The similar behavior observed for poly(cyclohexylmethacrylate)s<sup>14</sup>

enables us to assign these three relaxations, in increasing order of temperature, to the conformational motions of the cyclohexyl group, the rotation of the side chain, and the motions of the entire main chain. The appearance of relaxation  $\beta$  at high temperatures is consistent with the high packing density of PAALA-*c6* (Table I), which restricts the rotation of the bulky side chain. By means of DMTA and <sup>13</sup>C CP-MAS NMR, axial-equatorial conformational change in the cyclohexyl group has been observed for the poly(cyclohexylmethacrylate) at -50°C.<sup>23,24</sup> Studies carried out on polymers with cyclohexyl groups in the side chain attribute the relaxation  $\gamma$  observed to the axial-equatorial conformational transition of the cyclohexyl group, because the activation energy associated with this relaxation, which is around 11 kcal mol<sup>-1</sup>, coincides with the energy barrier for this transition.<sup>13,25</sup> So, the relaxation at -65°C observed in PAALA-*c6* may be attributed to the exchange between the two chair conformations of the cyclohexyl group. For cyclohexane and other cyclohexyl derivatives of low molecular weight, this conformational exchange has an activation energy of 14 kcal mol<sup>-1</sup> assigned to it.<sup>13</sup> This activation energy decreases to 11 kcal mol<sup>-1</sup> in PAALA-*c6* due to the intermolecular interactions associated with packing in the polymers. For the case of PAALA-*c6*, the results obtained by DMTA are consistent with those previously obtained<sup>20</sup> for the same polymer by <sup>13</sup>C CP-MAS NMR. By means of this same technique, a second-order transition was observed at around -70°C, which implies a change in the dynamics of the cyclohexyl group. In Figure 7, curves  $E''-T$  are shown for PAALA-*c6* at various frequencies. A high value of  $E''$  for the relaxation associated with the conformational change of the cyclohexyl group can be seen with respect to relaxations  $\beta$  and  $\alpha$ .

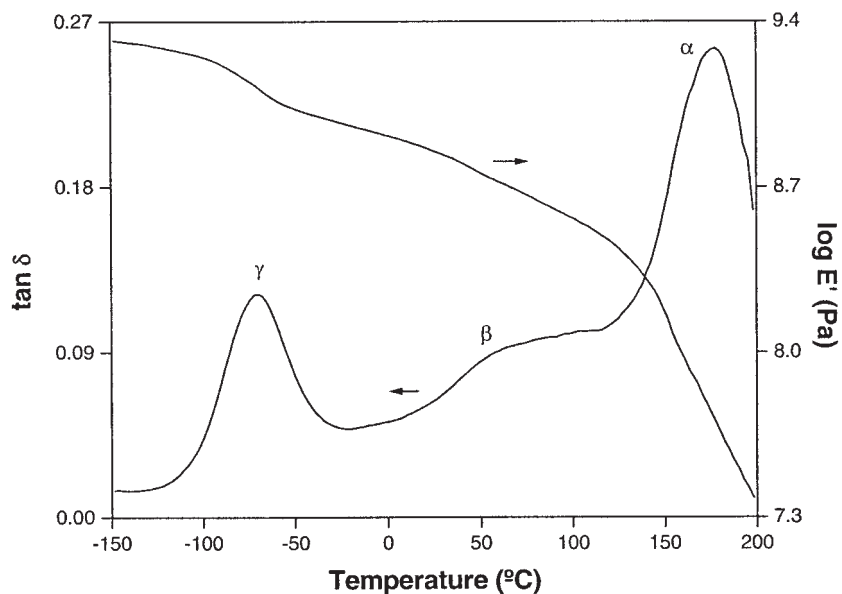


Figure 6 Temperature dependence of loss tangent  $\tan \delta$  and storage modulus  $E'$  at 10 Hz for PAALA-c6.

For most PAALAs, relaxation  $\alpha$  accounts for <20% of the total decrease in storage modulus,  $\Delta E'$  (%), whereas the relaxations associated with the side chain  $\beta + \gamma$  account for >80% (Table II). This shows the significant role played by the side chain in the dynamic mechanical properties of these polymers. The relatively low value of the  $m$  parameter of relaxation  $\beta$  is indicative of the existence of limited cooperativeness and shows that relaxation  $\beta$  can be largely attributed to the rotation of the side chain. As was to be expected, PAALA-Bn, PAALA-c5, and PAALA-c6 do not show a  $\gamma$  relaxation associated with local confor-

mational motions of the alkyl end groups of the side chain.

#### Effect of the length of the side chain

The effect of the length of the side chain for the same degree of branching can be evaluated by comparing polymers PAALA-i3, PAALA-i4, and PAALA-i5, in which the length of the side chain is increased by a methylene. As shown in Table II, relaxation  $\alpha$  appears at a lower temperature as the length of the side chain increases. This effect, which has already been demon-

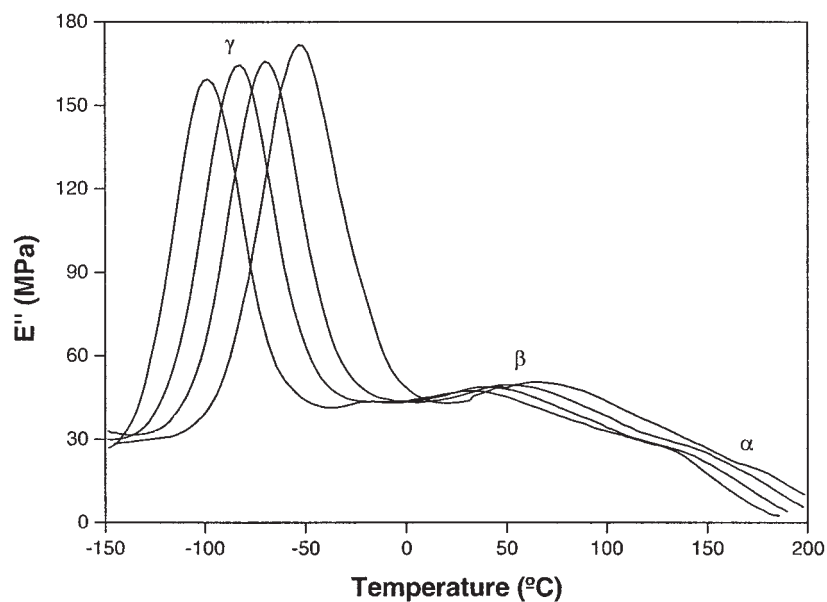


Figure 7 Temperature dependence of loss modulus  $E''$  for PAALA-c6 at several frequencies (0.1, 1, 10, and 100 Hz).

strated for a wide range of polymers, should be understood as the internal plasticizing effect exerted by the disordered side chains on the main chains.

The intensity of relaxation  $\beta$  increases as the side chain becomes longer. This effect can be seen as an increase in  $\Delta E'/E'$  (Table II) and as an increase in the intensity of  $\tan \delta$  (Figs. 2, 4 and 5). The Fouss-Kirkwood parameter  $m$  also increases as the length of the side chain increases, because there are more chemical environments involved in relaxation  $\beta$ .

In general, the increase in the length of the side chain in poly( $\gamma$ - $n$ -alkyl  $\alpha$ ,L-glutamate)s<sup>10,12</sup> and other families of polymers leads to a decrease in  $T_\beta$  and in the glass-transition temperature. This behavior can be explained by considering the fact that, when the side chain is not crystallized, there is an internal plasticizing effect that influences cooperative motions between the side chain and fragments that are close to the main chain. In our case, the temperature at which relaxation  $\beta$  occurs increases from PAALA-*i4* to PAALA-*i3*, and later decreases in PAALA-*i5*. The significant high  $T_\beta$  for the isopropyl as compared with that for the isobutyl derivatives is because a greater number of conformations are possible in the interhelical space in PAALA-*i4*. In these cases, relaxation  $\beta$  should, therefore, involve almost exclusively motions of the entire side chain. The decrease in  $T_\beta$  observed for the isoamyl derivative is more likely to be the result of the plasticizing effect on both the main chain and the side chain. In this case, relaxation  $\beta$  may also involve joint motions of the side and main chains. As the length of the side chains in the PAALAs increases, the temperature at which relaxation  $\beta$  appears can be understood as a compromise between chain size increasing and internal plasticizing effect that may also involve fragments of the main chain.

Generally, the decrease observed in the packing density in poly( $\gamma$ - $n$ -alkyl  $\alpha$ ,L-glutamate)s<sup>10,12</sup> and in other polymers as the length of the side chain increases explains the decrease observed in  $T_\beta$ . In the case of PAALAs, the existence of an additional methylene in the main chain may result in an increase in  $T_\beta$  as the side chain increases. Table I shows how, in the polymers studied, that is, in PAALA-*i3*, PAALA-*i4* and PAALA-*i5*, the packing densities increase slightly, although they are quite similar, which means that the cohesive forces between chains must be also similar. Therefore, the differences observed in terms of the relaxation spectra can be basically explained by the different sizes of the side chains and the amount of free space left between the helices.

#### Effect of the volume of the side chain

The effect of the volume of the side chain, for the same chain length, becomes evident if one compares PAALA-3, PAALA-*i4*, and PAALA-*neo5* polymers, in

which the side groups increase in volume although they are of approximately the same length. As the volume and, therefore, the rigidity of the side group increase, the temperature at which relaxation  $\beta$  occurs also increases (Table II, Fig. 5). The greater the volume of the side group, the greater the cohesive forces between chains, as their greater density indicates (Table I); there is also more steric hindrance to intramolecular rotations. Other authors<sup>14</sup> have observed this same effect for a similar series of poly(methylmethacrylate)s. The intensity of relaxation  $\beta$  increases with the volume of the side group (PAALA-3 < PAALA-*i4* < PAALA-*neo5*). Such increase is most apparent in  $\tan \delta$ - $T$  curves and in the  $\Delta E'/E'$  values.

#### Effect of the degree of branching of the side group

The effect of the degree of branching of the side group for the same number of carbon atoms is made explicit when one compares PAALA-3 to PAALA-*i3* and PAALA-*i5* to PAALA-*neo5*. PAALA-*i5* shows a greater intensity for relaxation  $\beta$  and lower  $T_\beta$  than PAALA-*neo5* (Table II), since the side group in the latter is more branched and rigid, and its mobility is, therefore, more restricted. The greater rigidity of the neopentyl group also affects the main chain:  $T_\alpha$  is higher for PAALA-*neo5*. In general, a similar behavior should be expected for polymers PAALA-3 and PAALA-*i3*. Although, in this case, the comparison is not as precise, because the relaxation of the side chain appears in two domains,  $\beta$  and  $\beta'$ ; for a wide range of temperatures, it is clear that PAALA-*i3* has a higher modulus than PAALA-3 (Fig. 4). In general, the results obtained by DMTA are consistent with the structural results. The more highly branched derivatives have a greater level of cohesion, due to their greater density (Table I), and are more rigid, and so, the motions are hindered to a greater degree. Thus relaxations  $\beta$  occur at higher temperatures and with less intensity.

#### Comparison between poly( $\beta$ ,L-aspartate)s and poly( $\alpha$ ,L-glutamate)s

A comparative study of poly( $\beta$ ,L-aspartate)s and poly( $\alpha$ ,L-glutamate)s was carried out on the benzyl derivatives of both families. Figure 8 shows the overlapping mechanical relaxation spectra of poly( $\gamma$ -benzyl  $\alpha$ ,L-glutamate), PGBLG, and of the poly( $\alpha$ -benzyl  $\beta$ ,L-aspartate), PAALA-Bn. Relaxations  $\beta$  and  $\alpha$  occur at lower temperatures in PGBLG than in PAALA-Bn. The effect of the two additional methylenes in the side group of the PGBLG is double. On the one hand, they provide the side group with mobility and, on the other, they plasticize the main chain and reduce the cohesive forces between chains by means of a spacer effect. This effect is also evident in the PGBLG's lower modulus (rigidity) value. The PGBLG, whose side



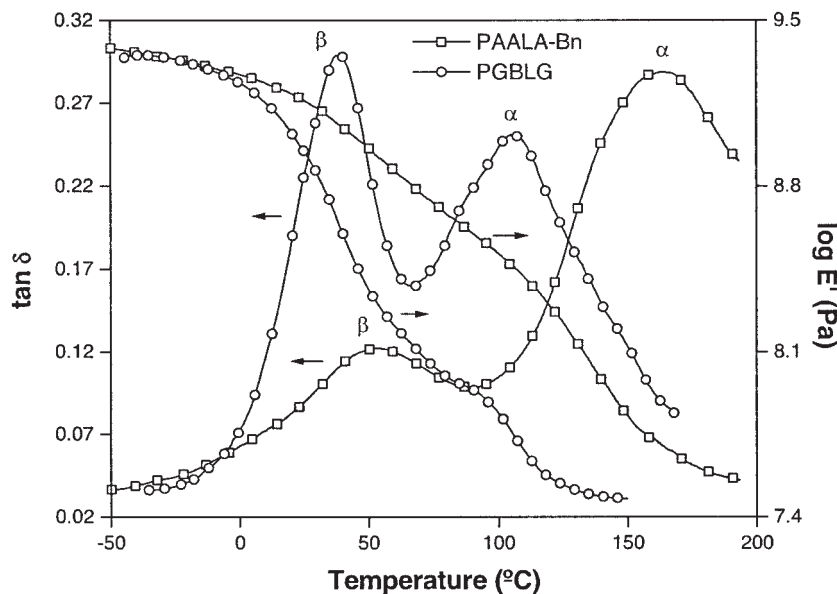


Figure 8 Temperature dependence of loss tangent  $\tan \delta$  and storage modulus  $E'$  at 10 Hz for PAALA-Bn and PGBLG.

chain is larger, shows a more intense  $\beta$ -transition. If one considers the existing background knowledge on poly( $\gamma$ -alkyl  $\alpha$ ,L-glutamate)s, the behavior observed for PAALA-Bn in comparison to that of PGBLG can be extended to the other poly( $\alpha$ -alkyl  $\beta$ -L-aspartate)s.

### CONCLUSIONS

Poly( $\alpha$ -alkyl  $\beta$ -L-aspartate)s show up to three transitions, referred to as  $\gamma$ ,  $\beta$ , and  $\alpha$ , in increasing order of temperature. Relaxation  $\gamma$  is attributed to local motions in the side chain. For PAALA-c6, this relaxation is attributed to axial-equatorial conformational changes in the cyclohexyl group. Relaxation  $\beta$  is attributed to the rotational motions of the side chain, whereas transition  $\alpha$  is related to the motions of the entire main chain.

The constitution of the side chain has a significant effect on the dynamic mechanical properties of the poly( $\alpha$ -alkyl  $\beta$ -L-aspartate)s and, therefore, on its potential applications. Specifically, the length, volume, and degree of branching of the side chain determine the intensity and temperature of relaxation  $\beta$  and, to a lesser extent, of relaxation  $\alpha$ . In general, it is the transition- $\beta$  that makes the greatest contribution to the total relaxation of the material.

As the length of the side chain increases, the intensity of relaxation  $\beta$  does so too, and  $T_\beta$  increases initially and then decreases. This behavior can be understood as a compromise between the greater size of the side group, which tends to increase  $T_\beta$ , and an internal plasticizing effect, which tends to decrease it. Long groups with limited branching tend to decrease  $T_\alpha$ .

There is a correlation between the chemical and crystalline structure of PAALAs and their dynamic mechanical properties. Thus, the crystalline structure of PAALAs that have side groups of a greater volume or with a higher degree of branching are denser and more cohesive, and relaxation  $\beta$  occurs at higher temperatures.

The absence of the two methylenes present in the side chains of poly( $\gamma$ -alkyl  $\alpha$ ,L-glutamate)s means that poly( $\alpha$ -alkyl  $\beta$ -L-aspartate)s are less mobile and more rigid, and that relaxations  $\alpha$  and  $\beta$  occur at higher temperatures.

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