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Dielectric Relaxation Phenomena in Poly(glutamic acid esters). 1. Glass Transition and Main Dielectric Relaxation in Poly(γ-*n*-alkyl L-glutamates)

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ABSTRACT: Poly(γ-methyl L-glutamate) and a homologous series of poly(γ-*n*-alkyl L-glutamates) (P*n*ALGs) including only the even (*n* = 2, 4, 6, 8, 10, 12, 14, and 16) members of the series have been studied by dilatometry, differential scanning calorimetry, and dielectric measurements. The glass transition temperature has been related to the number of methylene groups in the outer part of the *n*-alkyl side chain (including the terminal methyl) of the repeating unit. A semiempirical equation has been used that affords estimates of T_g in good agreement with the experimental data. The melting points and enthalpies of the crystalline members of the series were analyzed. For melting points a good fit of a Garner plot by a least-mean-squares procedure is obtained with $T_m° = 407$ K, $a = -6.04$, and $b = -3.49$. The contribution to the melting enthalpy per methylene unit clearly demonstrates that only part of the *n*-alkyl side chains form a crystal lattice. In amorphous members of the series, i.e. polymers with short side chains when *n* = 1, 2, 4, 6, 8, and 10, a dielectric relaxation (called β-relaxation) has been found at temperatures near and over the glass transition temperature of the side chains (T_g). In polymers with long side chains the strength of this relaxation decreases due to side chain crystallization. In polymers with shorter side chains a relaxation appears as a shoulder of the β-relaxation and at lower temperatures of T_g. By study of the strength, shape, and position of the β peak vs temperature, both relaxations were analyzed.

Introduction

Poly(γ-*n*-alkyl L-glutamates), subsequently referred to in this paper as P*n*ALGs, where *n* represents the number of carbon atoms (see Figure 1 for structural formula) in the external part of the *n*-alkyl side chain, are a series of synthetic polypeptides whose main chain adopts a stable α-helicoidal conformation. Very recently significant amounts of experimental data on their structure, properties, and behavior have been gathered and reported.

In solid-state films, these helices are packed in crystalline structures which depend to a great extent on the size, shape, and length of the *n*-alkyl side chains. The lateral paraffinic chains surround α-helical main chains.[1] From the observation of ^{13}C NMR and ^{13}C CP/MAS NMR chemical shifts in the solid state, Watanabe et al.[2,3] have reported that the main chain of P*n*ALGs assumes a right-handed α-helical conformation irrespective of side chain length and that in the side chain crystallites the *n*-alkyl chain adopts an all-trans zigzag conformation.

Some studies have been made on side chain structure and motions in PnALGs as a function of the *n*-alkyl side chain length. Above a certain temperature considerable motion occurs in the side chains, whereas the α-helical main chain remains rigid. It has been shown that when $n \geq 10$, the external part of the *n*-alkyl side chain is able to crystallize in a paraffin-like lattice.[1,4,5] Some authors also confirm that the melting and crystallization processes of the lateral *n*-alkyl chains produce a rearrangement of the α-helices.[6,7]

In the members of the series with $n < 10$ all the *n*-alkyl side chains are in the amorphous state.[8–11] For those members of the series with $n \geq 10$ only a part of the *n*-alkyl side chain remains in the amorphous state. In some of these polymers two states have been detected in the amorphous packing of the *n*-alkyl side chains, differentiated by their mobilities. They are separated by a transition which presents the same characteristics as a glass transition. This transition has been detected from a wide variety of experimental techniques including:

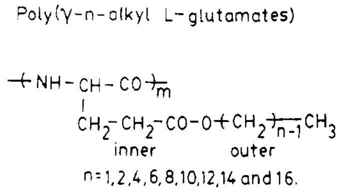

Figure 1. Schematic representation of the chemical formula for the structural unit of the investigated series of poly(γ-*n*-alkyl L-glutamates) (P*n*ALGs). See text for notation. Methylenes in $>$CH—CH$_2$—CH$_2$—CO—O— represent methylenes in the inner part of the *n*-alkyl side chains. *n* represents the number of carbon atoms in the outer part of the *n*-alkyl side chains, i.e. methylenes and terminal methyl groups. Here *m* represents the degree of polymerization.

(i) a jump in the Cp–T curve,[12] (ii) a change of slope in the specific volume vs temperature curve,[13] (iii) a change detected in the curve of the α-helix interspacing as a function of temperature,[6,14] (iv) a viscoelastic relaxation process in the transition range,[1,5,15,16] (v) a dielectric relaxation process in the same temperature interval,[12,17–19] and (vi) a NMR relaxation observed by proton spin–lattice relaxation and spin–spin relaxation over the same temperature interval.[2,3,20,21]

It has also been found that poly(γ-benzyl L-glutamate) exhibits below the ambient conditions a transition temperature structural relaxation process similar to that found in many amorphous materials where the states of the material at temperatures lower than the transition temperature are states out of thermodynamic equilibrium.[22]

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Summarizing, it can be said that the side chains which are in the interhelices space behave in the same way as an independent amorphous phase with liquid or glassy states at temperatures higher and lower than the glass transition temperature, respectively. The study of the side chain motions has attracted the attention of many research groups. The dielectric relaxation spectrum shows the existence of two relaxation processes which are denominated as γ- and β-relaxation in increasing order of temperature. The first is associated with local motions within the side group and the other, which appears at higher temperatures, is associated with cooperative motions of the side group as a whole.[4,12]

Another important area of research is to analyze the role played by the conformational characteristics of the backbone in poly(γ-*n*-alkyl L-glutamates) in the thermal properties and to determine the influence of the *n*-alkyl side chain length on these thermal properties. The conformations of the backbone of P*n*ALGs and other comblike polymers are very different from each other; the main chain conformations of P*n*ALGs are usually α-helices which are rather rigid with interchain hydrogen bonds while those of conventional comblike polymers are normally random coils. The crystallization of the side chains takes place independently of main chain stereoregularity. The main chain in poly(α-olefins) [poly(1-*n*-alkylethylenes)] crystallizes in a helical conformation and the side chains assume an orthorhombic order. Moreover the thermal behavior of the side chains for poly(α-olefins)[23-32] is similar to that obtained for many other comblike polymers where the main chain adopts a random coil conformation.[33]

However, the main task of the present work is a systematic study of the dielectric β-relaxation in a homologous series of poly(γ-*n*-alkyl L-glutamates) with *n*, 1, 2, 4, 6, 8, 10, 12, 14, and 16 in relation to the glass transition temperature determined by dilatometry and differential scanning calorimetry. For this reason the present study is not only devoted to the amorphous members of the series but also to the members which present crystallinity in the side chains due to a large part of the side chains remaining in the amorphous state. This crystallinity is a function of the number of carbon atoms in the side chain and to some extent, as with many comblike polymers, depends on the main chain structure.[33]

In some cases the two phase model had been adopted to explain the thermal behavior of some α-helical poly(α-amino acids) with side chains.[16]

Experimental Section

Compounds. The homologous series of P*n*ALGs was prepared by an ester exchange reaction (alcoholysis) of poly(γ-methyl L-glutamate) (AJICOAT-2000) with *n*-alkyl alcohols: ethyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, and *n*-hexadecyl alcohols (Merck, AG).

The reactions were carried out at 333.2 K using a mixture of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane 50/50 (v/v) as solvent and *p*-toluenesulfonic acid as catalyst. All the reactions were conducted in a homogeneous phase. The method, with some modifications, has been extensively described in the literature.[34-36]

Characterization. The molar-interchanged ratio of methyl group to *n*-alkyl group was followed for each of the members of this homologous series by determining their carbon, hydrogen, and nitrogen contents by elemental organic analysis. Elemental organic analysis of the final products is given in Table 1. As can be seen, the agreement between calculated and found values is quite good, lying within the limits of error of the determination for each of the elements.

In addition, the degree of substitution of the methyl group by the respective *n*-alkyl group was also confirmed by ^{1}H-NMR and ^{13}C-NMR spectra of the resulting polymers in trifluoroacetic acid or in deuterated chloroform. TMS was used as an internal standard. Both series of spectra were essentially similar to those reported in the literature for some of the present materials. All NMR spectra were recorded on either a 90-MHz Varian EM-930 (^{1}H-NMR spectra) or a 200-MHz Bruker AM-200 (^{13}C-NMR spectra) instrument. Since the chemical shift of the methoxy group of the poly(γ-methyl L-glutamate) used as starting material for the alcoholysis almost disappeared in the final products (3.84 ppm for ^{1}H and 51.6 ppm for ^{13}C spectra), the ester-exchange reaction was considered to be almost complete, at least within the limits of detection of the two above mentioned NMR techniques.

Table 1. Molecular Characteristics, Chemical Composition, and Organic Elemental Analysis of a Series of Poly(γ-*n*-alkyl L-glutamates) (P*n*ALGs) (n = 2, 4, 6, 8, 10, 12, 14, and 16)[a]

sample	chemical formula of structural unit	mol wt of structural unit	organic elemental analysis			
				C (%)	H (%)	N (%)
P2ALG	$C_7H_{11}O_3N$	157.80	calc	53.5	7.1	9.0
			found	53.4	7.0	8.3
P4ALG	$C_9H_{15}O_3N$	185.34	calc	58.4	8.2	5.6
			found	58.1	8.0	7.4
P6ALG	$C_{11}H_{19}O_3N$	213.38	calc	62.0	9.0	6.6
			found	61.7	8.8	6.2
P8ALG	$C_{13}H_{23}O_3N$	241.41	calc	64.7	9.5	5.8
			found	64.1	9.5	5.9
P10ALG	$C_{15}H_{27}O_3N$	269.44	calc	66.9	10.0	5.2
			found	66.9	9.9	5.5
P12ALG	$C_{17}H_{31}O_3N$	297.48	calc	68.7	10.4	4.7
			found	68.1	10.5	5.1
P14ALG	$C_{19}H_{35}O_3N$	325.51	calc	70.2	10.8	4.3
			found	70.1	11.1	4.0
P16ALG	$C_{21}H_{39}O_3N$	353.55	calc	71.4	11.0	4.0
			found	71.0	11.3	4.5

[a] Here *n* represents the number of carbon atoms in the outer part of the *n*-alkyl side chain.

Infrared spectra of the P*n*ALGs were also taken on films on a Perkin-Elmer 457 double beam spectrometer. This analysis was done to ensure that the samples were in the α-helical conformation.

The infrared spectra of films of our P*n*ALGs exhibited amide I, II, and V bands at about 1650, 1546, and 615–620 cm^{-1}, which are indicative that, in the films, the backbone chain of P*n*ALGs are in the α-helical form.[9] Films of poly(γ-methyl L-glutamate) (P1ALG) were cast on glass plates from 5–10% dichloromethane solution at room temperature. The resulting films then were dried in vacuo to constant weight. Plates for the other members of the series were obtained from the melt by hot pressing moulding around 473.2 K. Plates of thickness from 1.5 to 2.5 mm were prepared.

Thermomechanical Measurements. Dilatometric runs were carried out on a DuPont 943 thermomechanical analyzer. After cooling at 10 K/min from room temperature to 123.2 K, a probe was located on the sample. The probe was equilibrated in order to get a null pressure reading on the sample. The measurements taken as probe displacements were carried out in heating cycles at a rate of 5.0 K/min. From the displacement readings, linear expansion coefficients $\alpha = (1/l)(\mathrm{d}l/\mathrm{d}T)$ were calculated. Initial lengths for the different samples range between 1.5 and 2.5 mm.

Differential Scanning Calorimetry. The differential scanning calorimetric runs were used to furnish values of the melting enthalpies needed to estimate the percentage of side chain crystallinity following a method due to Jordan et al.[37] They were carried out at a rate of heating of 20.0 K/min on a DSC 4 Perkin-Elmer differential scanning calorimeter which is equipped with a 3700 Model acquisition data station. Calorimetric data on the members of the series for $n \leq 10$ have been described in a preceding paper,[12] and they will be commented on later.

Dielectric Measurements. Dielectric measurements were carried out in a GenRad 1620 A capacitor bridge in the range of frequencies between 500 Hz and 100 kHz. Before determination the samples were gold metalized. A measuring cell of 20-mm diameter has been used throughout the work. Samples were set in the cell and then cooled to 123.2 K. Capacity and loss tangent

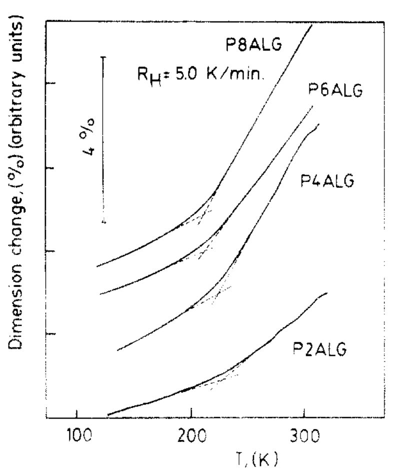

Figure 2. TMA diagrams obtained at a rate of heating of 5.0 K/min for a series of amorphous poly(γ-n-alkyl L-glutamates) with n = 2, 4, 6, and 8.

Table 2. Thermal Transitions of a Series of Poly(γ-n-alkyl L-glutamates) (n = 1, 2, 4, 6, 8, 10, 12, 14, and 16)[a]

	DSC measurements (R_H = 20.0 K/min)		TMA measurements (R_H = 5.0 K/min)		tan δ vs T (1 kHz)
sample	T_g (K)	T_m (K)	T_g (K)	T_m (K)	T_β (K)
P1ALG					272[b]
P2ALG	234		230		267
P4ALG	219		224		259
P6ALG	212		214		250
P8ALG	213		214		249
P10ALG	211	250.3		245	250
P12ALG		292.1		282.7	263
P14ALG		318.0		313.7	276
P16ALG		327.0		321.2	280
P18ALG		336.2[c]			

[a] Here n represents the number of carbon atoms in the external part of the n-alkyl side chain. Except for the member of the series with n = 1, the samples have been prepared by cooling from the bulk either to the glassy state for amorphous members of the series, i.e. n = 2, 4, 6, 8, and 10, or to the crystalline state for the crystalline ones, i.e. n = 10, 12, 14, and 16. [b] Determined on a sample obtained by evaporation of solvent at room temperature from a solution in dichloromethane. [c] Value for T_m for this member of the series has been taken from ref 4.

were measured in the isotherm form and the heating mode at temperature intervals which vary from run to run between 5 and 10 K. Temperature scale precision has been estimated to be better than ±0.2 K.

Experimental Results

Dilatometric and Calorimetric Measurements. The experimental dilatometric results for the members of the homologous series with $n \leq 8$ are shown in Figure 2. The glass transition is detected through the change in the slope of the length vs temperature plot (l vs T), i.e. through the change in the linear expansion coefficient α, between the glass and the liquid states of the n-alkyl side chains. The value of the glass transition temperature, T_g, has been estimated by the extrapolation of the glass and liquid l vs T curves as usual. The values of T_g are collected in Table 2 and plotted in Figure 3 as a function of the number of carbon atoms n, in the external part of the side chain.

As can very easily be seen, the values of T_g plotted in Figure 3 monotonically decrease as n goes from n = 2 to n = 8 *and* n = 10. These two last members of the series present almost the same glass transition temperature. It is not due to an increase of the glass transition temperature itself. It is very difficult to establish the borderline and the mutual influences between the glass transition, involving the whole side chains, and the side chain crystallinity involving the outer part of the side group. This feature will be analyzed in more detail in relation to the dielectric relaxation position later on.

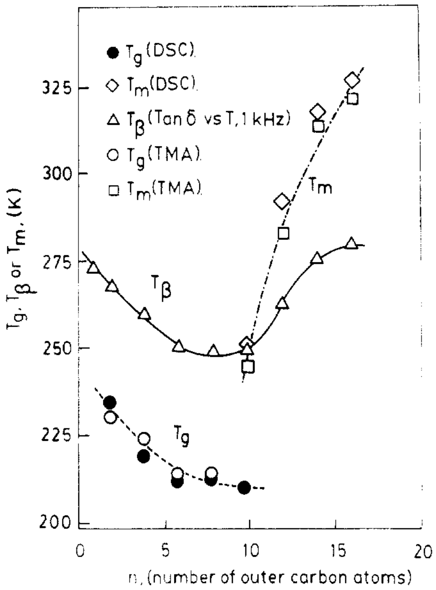

Figure 3. Glass transition temperature T_g, dielectric β-relaxation temperature T_β, and melting temperature T_m versus the number of carbon atoms in the outer part of the n-alkyl side chains n (i.e. number of outer carbon atoms) of a series of crystalline and amorphous poly(γ-n-alkyl L-glutamates). The dashed line drawn through the experimental glass transition temperature T_g data has been calculated by means of eq 1 and parameters $T_g(0)$ = 250 K, n_c = 10, and $T_g(n_c)$ = 211 K, as indicated later in the text. The dotted and dashed line drawn through the experimental melting point T_m data has been calculated by means of eq 3 and parameters T_m^0 = 407 K, a = −6.04, and b = −3.49, as indicated later in the text.

Figure 4a shows the TMA traces obtained for the polymers of the series with $n \geq 16$. These traces are characteristic of a first-order transition. In order to compare the transition temperatures determined by dilatometry and that determined by DSC, the dependence on temperature of the expansion coefficient has been calculated from the above traces and represented in Figure 4b. The maximum of the peak in the expansion coefficient has been used as the TMS melting temperature shown in Table 3. As can be seen in Figure 4b, poly(γ-n-decyl L-glutamate) (P10ALG) shows a peak around 243.2 K. The expansion coefficient value at temperatures over the transition is greater than that at lower temperatures. This could suggest the presence of two simultaneous processes occurring in the same temperature range, one of which would be the melting process of the small paraffin-like crystallites from the paraffin lattice and the other would be due to the glass transition of the amorphous regions of the side chains. The crystallization of the side chains of this polymer only involves a very small fraction of them, as can be estimated when the crystalline fraction and the number of amorphous or crystalline methylenes plus the terminal methyl is calculated from calorimetric measurements using a procedure due to Jordan et al.[37] In accordance with this interpretation, it is worthwhile noting that the thermal treatment given previously to the measurement, i.e. a fast quenching from room temperature, rules out the possibility of this overlapped peak to the glass transition being due to a structural relaxation process.

For the members of the series with $n \geq 10$ the dilatometric melting temperature increases with the lateral chain length (see Table 3); this implies an increase in size of the crystallites as the side chain length grows.

The experimental results obtained from the differential scanning calorimetry experiments show a behavior quite

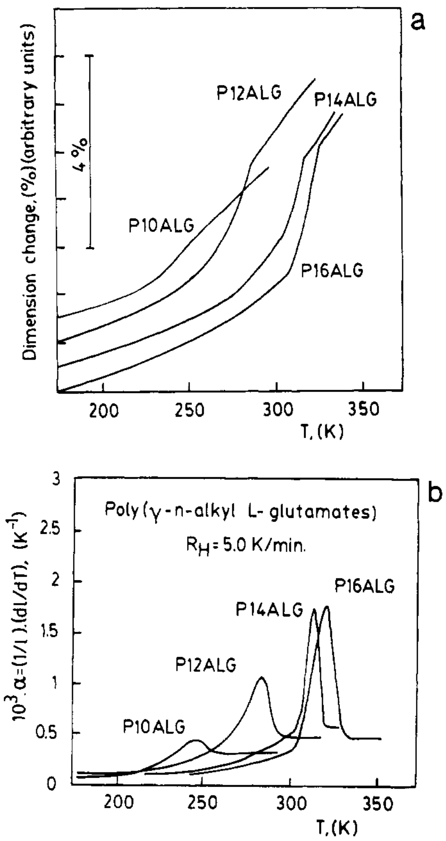

Figure 4. (a) TMA diagrams obtained at a rate of heating of 5.0 K/min for a series of crystalline poly(γ-n-alkyl L-glutamates) with n = 10, 12, 14, and 16. (b) Linear expansion coefficients $\alpha = (1/l)(dl/dT)$ measured at a rate of heating of 5.0 K/min for a series of crystalline poly(γ-n-alkyl L-glutamates) with n = 10, 12, 14, and 16.

Table 3. Apparent Heat of Melting (ΔH_f), Melting Transition Temperature (T_m), Entropy of Melting (ΔS_f), etc. of the Crystalline Side Chains and Some Other Derived Quantities of a Series of Crystalline Poly(γ-n-alkyl L-glutamates)

sample	ΔH_f (cal/g)	ΔH_f (cal/mol of structural unit)	T_m[b] (K)	ΔS_f [cal/(mol of structural unit K)]
P10ALG	0.86	231.7	250.3	0.93
P12ALG	5.30	1577.7	292.1	5.40
P14ALG	11.54	3756.0	318.0	11.81
P16ALG	12.85	4544.1	327.0	13.90
P18ALG[a]	16.72	6381.3	336.2	18.98

[a] Values for ΔH_f and T_m for this member of the series have been taken from ref 4. [b] These values have been obtained by DSC at a rate of heating of 20.0 K/min. They represent values obtained at the maximum of the melting peaks (cf. Table 2).

similar to that observed in the dilatometric measurements (see Figure 5a,b). Those members of the series with side chain lengths larger than n = 10 show a first-order transition due to the melting of the crystalline structure of the side chains, as can be seen in Figure 5a. The experimental results for the maximum of the endotherms corresponding to the melting points are plotted in Figure 3, and the experimental results for the enthalpy of melting of the side chains are collected in Table 3. The increase of the enthalpy of melting with the value of n implies a higher relative fraction of the side chains involved in the crystallization as the side chain length grows.

Figure 5b shows the DSC traces for the sample members of the series with n = 2, 4, 6, 8, and 10. These results were briefly discussed in a previous paper.[12] In Figure 3, the glass transition values obtained from these traces have been plotted. The members for this series show no sign of crystallinity, at least under the experimental conditions (thermal history) employed to determine the glass transition temperature.

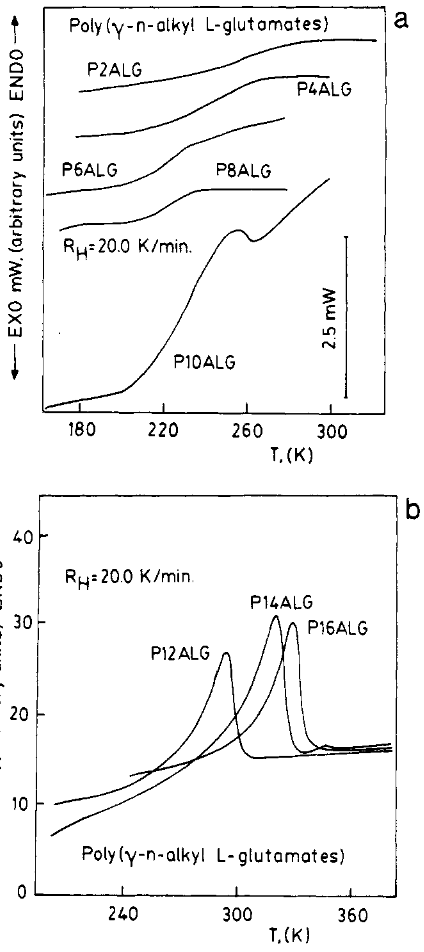

Figure 5. (a) DSC diagrams obtained at a rate of heating of 20.0 K/min for a series of amorphous poly(γ-n-alkyl L-glutamates) with n, 2, 4, 6, 8, and 10. (b) DSC diagrams obtained at a rate of heating of 20.0 K/min for a series of crystalline poly(γ-n-alkyl L-glutamates) with n = 12, 14, and 16.

Discussion of Results

Thermal Transitions. At this point, we are going to make a detailed analysis of thermal properties and some other characteristics typical of comblike polymers which give information on the structure of side chains and their relation with the main chains as well as their correlation effects; we will consider the glass transition temperature, T_g, melting point, T_m, and melting enthalpy, ΔH_m, as primary magnitudes and then we will submit the data to the same treatments given to some other comblike polymers in order to establish any differences between conventional comblike polymers and those studied in the present paper in which the main chains adopt an α-helix configuration in the solid state.

For a great number of homologous series of comblike polymers differing widely in the structure of their main chain, the T_g values as a function of n can be described according to a general equation within the limits of experimental error with the experimental values. Barrales-Rienda et al.[38-41] have examined the glass transition temperature T_g of a great number of comblike polymers as a function of the number of methylene groups plus the terminal methyl in the side chains. They have discussed their experimental results and many others from the literature in light of the following equation:

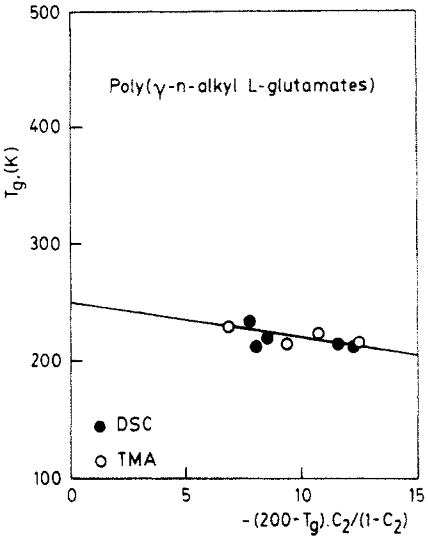

Figure 6. Glass transition temperatures T_g of a series of amorphous poly(γ-n-alkyl L-glutamates) plotted as a homologous series of ethylene–[—NH—CH(—CH—CH$_2$—CO—O—)—CO—] copolymers to estimate the glass transition temperature $T_g(0)$, i.e. the first member of the series [—NH—CH(—CH$_2$—CH$_2$—CO—O—)—CO—] and the parameter k according to the Gordon–Taylor–Wood equation.[42,44] Here C_2 represents the weight fraction of —CH$_2$— groups in the respective PnALG member of the series as indicated in the text.

$$[T_g(0) - T_g(n)]^2 = [T_g(0) - T_g(n_c)]^2\{1 - \exp[-n/(n_c - n)]\} \quad (1)$$

where $T_g(0)$ is the glass transition temperature corresponding to a carbon side chain length $n = 0$, which for the present system is [—NH—CH(—CH$_2$—CH$_2$—CO—O—)—CO—], and $T_g(n_c)$ is the glass transition temperature of the member of the series with $n = n_c$, where n_c is the number of critical methylene groups needed to initiate the crystallization of a part of the lateral n-alkyl side chains. The above equation (1) implies the following conditions $T_g(n) = T_g(0)$ for $n = 0$, $T_g(n) = T_g(n_c)$ for $n = n_c$, and $\mathrm{d}T_g(n)/\mathrm{d}n = 0$ for $n = n_c$.

However, for the application of eq 1, actual values of $T_g(0)$, $T_g(n_c)$, and n_c need to be known. They can be evaluated from the glass transition temperatures $T_g(n)$ of some members of the homologous series.

$T_g(0)$ may be obtained very accurately by applying the Gordon–Taylor equation[42,43] in the form proposed by Wood[44] and by assuming the present series of poly(γ-n-alkyl L-glutamates) as copolymers of polyethylene. Thus, the glass transition of our homologous series of comblike polymers may be considerd to be a function of its composition by weight as follows:

$$T_g = T_{g,1} + [k(T_{g,2} - T_g)C_2/(1 - C_2) \quad (2)$$

where T_g is the copolymer (comblike polymer) glass transition temperature, $T_{g,1}$ is the glass transition temperature of the first member of the series ($n = 0$), for the present system [—NH—CH(—CH$_2$—CH$_2$—CO—O—)—CO—], $T_{g,2}$ is the glass transition temperature of polyethylene, which has been recommended by Boyer[45–49] as $T_{g,2} = T_g(\mathrm{PE}) = T_g(—\mathrm{CH_2}—) = 200$ K, and C_2 is the weight fraction of the outer side chain with respect to the structural unit, i.e. the weight fraction of outer methylene groups plus the terminal methyl. Thus, for instance, for the member of the series with $n = 2$, C_2 = MW of [—CH$_2$—CH$_3$]/MW for [—NH—CH(—CH$_2$—CH$_2$—CO—O—CH$_2$—CH$_3$)—CO—] = (29.062/157.169) = 0.185.

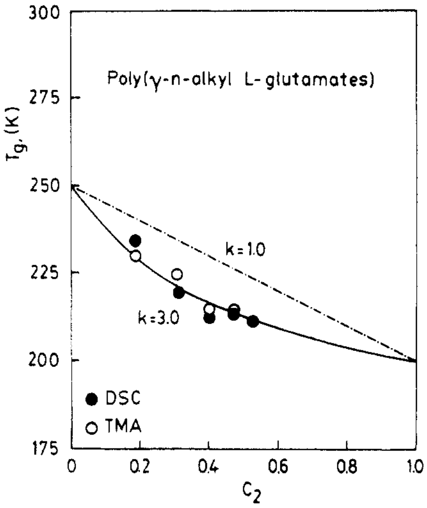

Figure 7. Glass transition temperatures T_g versus C_2 (weight fraction of —CH$_2$— groups in the respective PnALG member of the series) of a series of amorphous poly(γ-n-alkyl L-glutamates) plotted as a homologous series of ethylene–[—NH—CH(—CH$_2$—CH$_2$—CO—O—)—CO—] copolymers according to the Gordon–Taylor–Wood equation.[42–44]

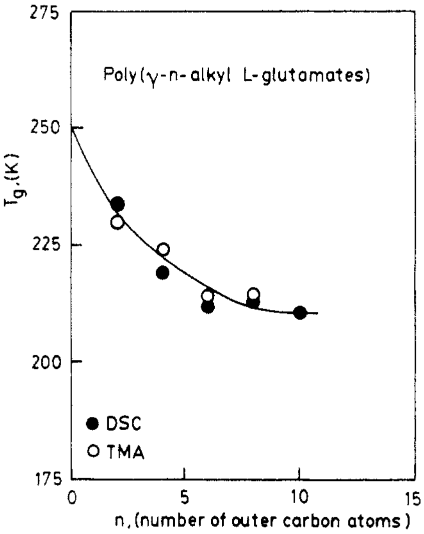

Figure 8. Glass transition temperatures T_g of a homologous series of poly(γ-n-alkyl L-glutamates) as a function of the number of methylene groups n in the outer part of the n-alkyl side chain (including the terminal methyl). The curve represents values calculated using eq 1 and parameters for $T_g(0) = 250$ K, $n_c = 10$, and $T_g(n_c) = 211$ K given in the text.

A plot of the experimental data of T_g for the present series according to eq 2 has been done in Figure 6. From this plot we have obtained values for $T_g(0) = 250$ K and $k = 3.0$. With the values of these parameters, the Gordon–Taylor–Wood equation[42–44] is plotted in the usual form, as shown in Figure 7. The good agreement found between experimental data for T_g values of the present series and the theoretical curve calculated with the above parameters from the Gordon–Taylor–Wood relation[42–44] further demonstrates both the adequacy of this equation to interpret glass transition temperatures of comblike polymers such as our poly(γ-n-alkyl L-glutamates) in which the backbone adopts an α-helicoidal conformation and the goodness of all the approximations and assumptions we have made to calculate the above parameters.

In Figure 8 a plot of T_g vs n is shown. The full line has been drawn with the following parameter values; $T_g(0)$ = 250 K, which has been obtained from the extrapolated value for $T_g(0)$ given in the plot of T_g vs $-[200 - T_g]C_2/(1 - C_2)$ given in Figure 6; $n_c = 10$ estimated from the plot given in Figure 10, where as we will see below, a value of

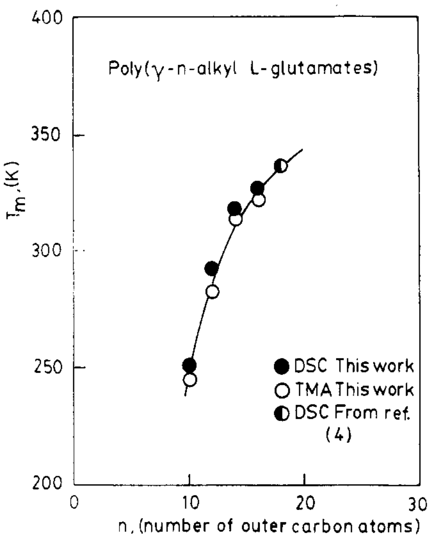

Figure 9. Plot of melting point temperatures T_m against the number of methylene groups in the outer part of the *n*-alkyl side chain (including the terminal methyl) of a series of crystalline P*n*ALGs. Experimental points for T_m have been measured by means of DSC and TMA, as is described in the text. The full line represents the calculated value according to eq 3 and using values of the parameters $T_m{}^0 = 407$ K, $a = -6.04$, and $b = -3.49$ obtained by mean least-squares curve fitting to eq 3. The value for $n = 18$ (◐) has been taken from ref 4.

10 is obtained for the number of critical methylene groups needed to initiate crystallization; and $T_g(n_c) = 211$ K, the value of $T_g(n)$ for $n_c = 10$ taken from Table 2. As can be seen, there is a good correlation and agreement between the experimental data for T_g estimated by DSC and TMA and those calculated and represented in Figure 8 by a solid line. Equation 1 is good enough to describe the dependence between $T_g(n)$ and n in the present homologous series of PnALGs.

It is well-known that melting points of compounds containing *n*-alkyl chains converge to a unique value. The relationship between T_m and n, the number of methylene groups in the *n*-alkyl chain, assuming the linearity of the enthalpy and the entropy, according to Broadhurst,[50,51] can be expressed as follows:

$$T_m = (\Delta H_{f,e} + \alpha n)/(\Delta S_{f,e} + \beta n) = T_m{}^0(n + a)/(n + b) \quad (3)$$

where α is the enthalpy of melting per mole of methylene groups, $\Delta H_{f,e}$ is the contribution due to the chain ends, β represents the contribution of each added methylene group to the entropy of melting, $\Delta S_{f,e}$ is the contribution to the entropy of the chain ends, $T_m{}^0$ is the convergence temperature or melting point of a crystal composed of fully extended chains of linear polymethylene, and a and b are two constant characteristics of the corresponding comblike polymer. Linearity is usually observed for correlations of enthalpy or entropy against chain length across short ranges of n.[37,52] The middle term of eq 3 is known as Garner's equation.[53] Variations of these equations have been extensively employed.[54-56] In Figure 9 a plot of T_m vs n is given for the crystalline members of the series. Equation 3 has been applied to our DSC and TMA melting point data included in the third and fifth columns of Table 2 for the crystalline PnALGs. The values of the parameters $T_m{}^0$, a, and b for the series have been obtained by least-squares curve fitting and are $T_m{}^0 = 407$ K, $a = -6.04$, and $b = -3.49$; these values agree fairly well with those of the same parameters given for some other comblike polymers.[33,38,57] The full line on Figure 9 has been drawn with these values for the above parameters.

Broadhurst[50,51] has also fit the melting enthalpies of a series of *n*-alkanes in the hexagonal modification to an equation of the form proposed by Flory and Vrij,[52]

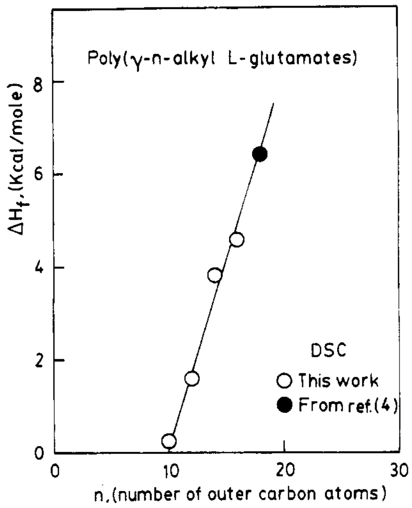

Figure 10. Plot of the apparent melting enthalpy ΔH_f per structural unit against the number of methylene groups (including the terminal methyl) in the outer part of the *n*-alkyl side chain of a homologous series of crystalline poly(γ-*n*-alkyl L-glutamates) to obtain the number of critical methylene groups n_c needed to initiate the crystallization in the *n*-alkyl side chain. The value for $n = 18$ (●) has been taken from ref 4.

$$\Delta H_f = \Delta H_{f,e} + \alpha n \quad (4)$$

where ΔH_f is the melting enthalpy, $\Delta H_{f,e}$, as already defined, is the contribution to the melting enthalpy due to chain ends, and α is the enthalpy of melting per mole of methylene groups. From the values given in Table 3 for ΔH_f a plot of these apparent melting enthalpies vs the number of methylene groups including the terminal methyl in the outer part of the *n*-alkyl side chain n for our crystalline PnALGs is given in Figure 10. From this plot an enthalpic contribution due to chain ends value of $\Delta H_{f,e} = -8.400$ cal/mol and an enthalpy of melting per mole of methylene groups value of $\alpha = 840$ cal/mol of —CH_2— and $n_c = 10$ for the number of critical methylene groups to initiate crystallization have been obtained. These values are more or less similar to those obtained by Watanabe et al.[1] for the same type of compounds of this homologous series. The value of $\alpha = 840$ cal/mol of —CH_2— is close to the value of 723 cal/mol of —CH_2— reported by Broadhurst[50] for the α-hexagonal → liquid transition in *n*-alkanes. This type of packing for *n*-alkyl side chains in a hexagonal lattice has been observed for many other comblike polymers by means of some other techniques such as X-ray diffraction and IR spectroscopy studies.[27,28,58-60]

The number of critical methylene groups n_c calculated by the method of Jordan et al.[37] and by applying eq 4 agrees fairly well. However, this agreement between both procedures is attained only if we consider the outer *n*-alkyl side chain. When the entire *n*-alkyl side chain, i.e. including the ester group —CO—O— and inner methylene groups, is considered, different values are obtained for each procedure. The same behavior has been found for some other conventional comblike polymers.[33,61] It can be concluded that only a portion of the outer part of the *n*-alkyl side chain in crystalline P*n*ALGs participates in the crystallization. Hsieh et al.[60] have proposed for the interlamellar structure in poly(*n*-octadecyl methacrylate) an intercalating arrangement with side groups pointing in opposite directions interlocking to form the side chain crystallites. In our crystalline PnALGs the crystallization of the inner part of the side chain is hindered not only by the main chain but also by the ester group, because its size

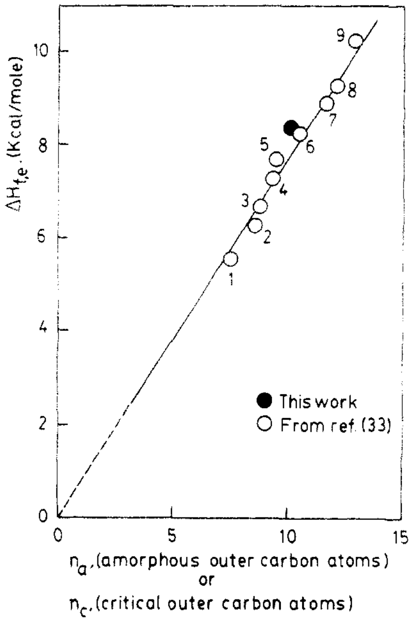

Figure 11. Plot of the melting contribution due to chain ends $\Delta H_{f,e}$ against the number n_c of critical methylene groups (including terminal methyl) in the outer part of the *n*-alkyl side chain of a series of conventional crystalline comblike polymers. Other data for $\Delta H_{f,e}$ and n_c for some other homologous series of comblike polymers have been taken from ref 33 as follows: (1) poly(1-*n*-alkylethyl oxides); (2) poly(1-*n*-alkylethylenes); (3) poly[*N*-(10-((*n*-alkyloxy)carbonyl)-*n*-decyl)maleimides] (4) poly(*n*-alkyl acrylates); (5) poly(*n*-alkyl vinyl esters); (6) poly[*N*-(*n*-alkyl)maleimides]; (7) poly[*N*-(5-((*n*-alkyloxy)carbonyl)-*n*-pentyl)maleimides]; (8) poly[*N*-(*n*-alkyl)acrylamides]; (9) poly[*N*-(((*n*-alkyloxy)carbonyl)methyl)maleimides].

and shape prevent side chain packing by impeding the insertion of a higher number of methylene groups from opposite side chains.

Our results for $\Delta H_{f,e}$ and n_c and many others for some others comblike polymers[33] with a great variety of backbone chemical structures and conformations are given in Figure 11, where a plot of ΔH_{fe} vs n_a or n_c is shown. The number of critical methylene groups needed to initiate the crystallization of a part of the lateral *n*-alkyl side chains n_c is equal to the number of amorphous methylene groups after the crystallization of a part of the lateral *n*-alkyl side chains n_a, in other words, $n_c = n_a$. To estimate the crystallinity present in the side chains, very often the number of crystalline —CH_2— group, including the terminal methyl, in the side chain is defined as n_c and therefore the number of amorphous methylene groups remaining, n_a, as $n_a = n - n_c$. In dealing with crystalline comblike polymers the meanings of n_c (critical) or n_c (crystalline) must be taken into account. Its inadequate use may introduce some confusion. In Figure 11 a good correlation between both magnitudes is obtained. The good correlation found between $\Delta H_{f,e}$ vs n_c may favor the concept that only the side chains are involved in the crystallization process for polymers with side chains in general as well as for P*n*ALGs in particular. The main chain conformation does not play any important role in side chain crystallization, apart from possibly affecting the critical number of methylene groups which initiate crystallization due to its own stiffness.

Dielectric Relaxation. Values of the dielectric loss tangent tan δ are plotted in Figure 12a,b as a function of temperature at 1 kHz for the nine members of the series studied in the present work. As can be observed, there are two relaxation zones, called hereafter β and γ in decreasing order of temperature.

The dielectric relaxations in poly(glutamic acid esters) have, usually, been designated with Greek letters in alphabetic order as the temperature decreases, so the highest temperature relaxation is called α.

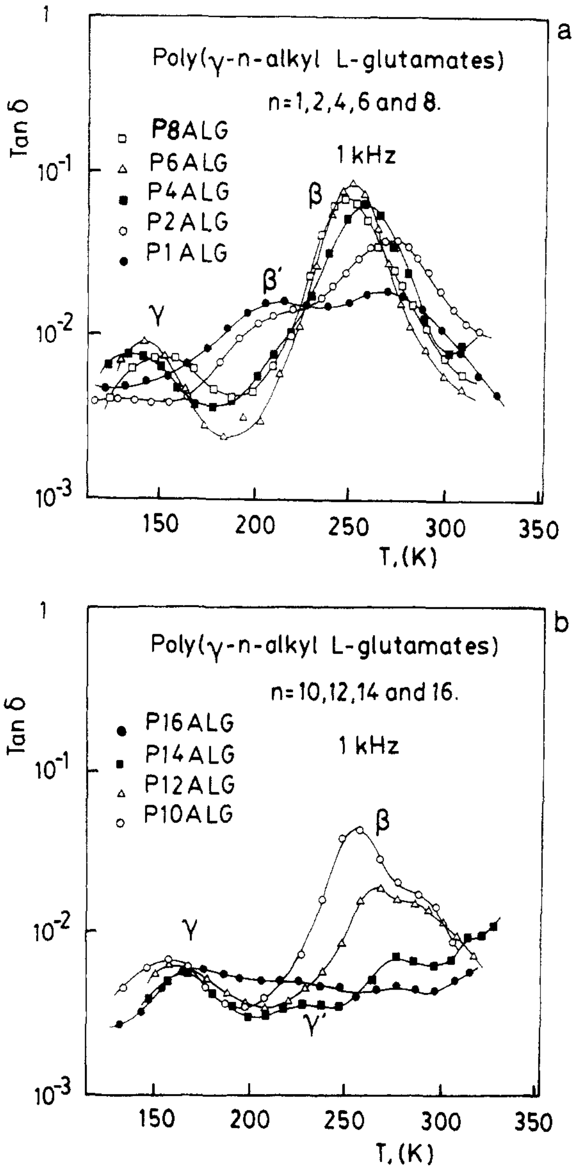

Figure 12. (a) Temperature dependence of tan δ at 1 kHz for poly(γ-*n*-alkyl L-glutamates) (n = 1, 2, 4, 6, and 8): (●) P1ALG; (○) P2ALG; (■) P4ALG; (△) P6ALG; (□) P8ALG. (b) Temperature dependence of tan δ at 1 kHz for poly(γ-*n*-alkyl L-glutamates) (n = 10, 12, 14, and 16): (○) P10ALG; (△) P12ALG; (■) P14ALG; (●) P16ALG.

In amorphous polymers the dipolar dielectric relaxation appearing at the highest temperature is the one associated with conformational motions of the main chain polymer segments closely related to the glass transition of the material. This is not the case for the polymers in this work as the main chains are highly ordered and no conformational motions are possible in them. No main chain glass transition in the sense given to the term when it refers to amorphous polymers has been detected by DSC or dielectric techniques in poly(glutamic acid esters) obtained by casting from an helicogenic solvent. From mechanical measurements Kajiyama et al.[62,63] ascribed the α-relaxation to the thermal molecular motion of the α-helices in the crystalline region. Kakizaki et al.,[19] in a recent paper, have found an α dielectric relaxation in some P*n*ALGs which has been associated with the cooperative motion of both the main chain and the side chain. This relaxation is not shown in this work because the experimental temperature interval does not reach such high temperatures.

Thus, our high temperature dielectric relaxation will be called β. The well-known relationship between the β dynamic-mechanical[15,16] or dielectric[17,18] relaxation and the side chain glass transition exists not only because it appears in the same temperature range as the glass transition detected by calorimetric or dilatometric techniques but also because of the great parallelism between the dependence on the side chain length of the temperature of the dielectric β-relaxation and the side chain glass transition on one side. We have to consider also the parallelism of the dependence on the side chain length of the intensity of the β-relaxation and the crystalline side chain fraction in the members of the series with $n > 10$.

It is widely accepted that a glass transition has a configurational origin; the change in the specific heat in the transition is due to a change in the number of configurations that the polymer segments may experience at a fixed temperature (although a contribution to the specific heat increment due to vibrational changes in the transition cannot be ruled out, as Goldstein[64] has already noted). In the polymers in this work the number of configurations in the temperature range in which the glass transition takes place depends only on the number of ways of arranging the side chains in the interhelix space. No contribution of main chains has to be expected as they are in the form of helices ordered in a pseudocrystalline lattice. The appearance of a DSC or dilatometric glass transition due to side chain motions needs these motions to be cooperative, as does the glass transition of amorphous polymers due to main chain motions. Several characteristics of the behavior of the dielectric β-relaxation that support the cooperative character of the solid chain motions will be analyzed below.

The γ-relaxation zone will be the subject of a forthcoming paper[65] it is ascribed to local motions of small groups within the side chain. At temperatures between both relaxations there appear to be some signs of a third relaxation process in the first three members of the series. We will denominate this relaxation as β'-relaxation. It appears about 80 K above the γ-relaxation in the polymers with $n = 2$ and 4 that show both relaxation processes whereas the temperature of the γ peak increases as n grows. This leads us to ascribe the β'-relaxation to the motion of the bigger groups than to the ones responsible for the γ one, as will be discussed below. There are also signs of a fourth relaxation in the members of the series with $n > 14$, which we will call γ'; the effect of the thermal treatments on this relaxation peak support the ascription of this relaxation process to local side chain motions near the crystallites formed in the side chain phase, as we will discuss elsewhere.[65]

At temperatures higher than the β-relaxation there is a shoulder or an incipient peak in the curve of tan δ vs T, which can be related to the melting process of the crystalline side chain fraction which takes place (as measured by DSC or dilatometry) in the same temperature interval. The side chains involved in the crystallites are not able to participate in the motions that produce the β-relaxation before the melting temperature, but they may contribute to the high temperature side of the β-relaxation which covers a temperature interval above the melting temperature.

Similarly to the dilatometric glass transition T_g, the maximum of the β-relaxation monotonically decreases as the length of the side chains increases for $n = 1, 2, 4$, and 6. This fact is accompanied by a rise in the height of the peaks. However for n between 6 and 10 the position and height of the maxima remain almost constant. For values of $n \geq 10$, the shift of the maxima to higher temperatures is accompanied by a rapid shortening of its height. The position of the maximum of the β-relaxation at 1 kHz is given in the sixth column of Table 2 and plotted in Figure 3 as a function of the number of carbon atoms n, in the outer part of the n-alkyl side chain. For comparative purposes the dilatometric glass transition T_g and the temperature at the maximum of the melting peak have also been included. The temperature of this β dispersion, as can be seen, decreases with the increase in the length for side chain from ethyl to decyl members, and thereafter increases. From some mechano-dynamical measurements made by some other authors[1,5,36,66] on some members of the present series it has been demonstrated that in PnALGs with longer n-alkyl groups than methyl ones, the β-relaxation temperature decreases with the increase in the side chain length from ethyl to n-octyl or n-decyl members and thereafter increases.

The isothermal curves of log ϵ'' as a function of the frequency f allow us to construct a master curve for this relaxation for polymers of this homologous series with $n < 12$. This requires the horizontal shift factor of the isotherms in the diagram of log ϵ'' vs log f and small vertical shift factors which are systematically temperature dependent. Parts of a–f of Figure 13 show the master curves for these polymers in plots in which $\log(\epsilon''/\epsilon''_{\max})$ has been represented as a function of $\log(f/f_{\max})$, where $\epsilon''_{\max}$ and $f_{\max}$ correspond to the maximum value of ϵ'' and the frequency at which this maximum appears at each temperature, respectively. The horizontal shift factors a_T have been represented in Figure 14 as a function of the reciprocal absolute temperature. log a_T has been defined in such a way that in those isotherms which show the maximum in the range of experimental frequencies $\log a_T \equiv \log f_{\max}$ is fulfilled.

At temperatures below the glass transition temperature a shoulder is detected in the P1ALG, P2ALG, and P4ALG members which is indicative of a relaxation which we will designate as the β'-relaxation. It has only been possible to determine the precise position of the maximum due to this relaxation for the member P1ALG measured at low frequencies. This polymer shows an Arrhenius behavior with an apparent activation energy of 28.5 kcal/mol.

The values of the glass transition temperature estimated by both dilatometric and calorimetric measurements can be explained in terms of the diminution with temperature of the number of available conformations in the side chains of the polymer in the interhelix space.

The relaxation times for the conformational rearrangements of the chains increase as the number of accessible conformations decreases, and a transition to a glassy state out of equilibrium is produced when these relaxation times attain a critical value which is dependent on experimental conditions.

The dielectric measurements of the β-relaxation reveal the loss of molecular mobility of the side chains of the polymer through the loss of the orientation capacity of the permanent dipole within the carboxyl group when the temperature diminishes through the transition. The permanent dipole moment is common to all the members of the series studied; therefore, the characteristics of the β-relaxation can be used to study the influence of the length of the side chains on their mobility.

The Fröhlich[67] equation

$$\epsilon_0 - \epsilon_\infty = [\mu_0{}^2 g 4\pi N 3\epsilon_0/3kT(2\epsilon_0 + \epsilon_\infty)][(\epsilon_\infty + 2)/3]^2 \quad (5)$$

allows us to determine the effective dipole moment $\mu_{\text{eff}} = (g\mu_0{}^2)^{1/2}$ which compared with the permanent dipole moment of the isolated dipole gives a measure of the loss of dipole orientation capacity in the relaxation process (it also gives a measure of the dipole–dipole correlation). The

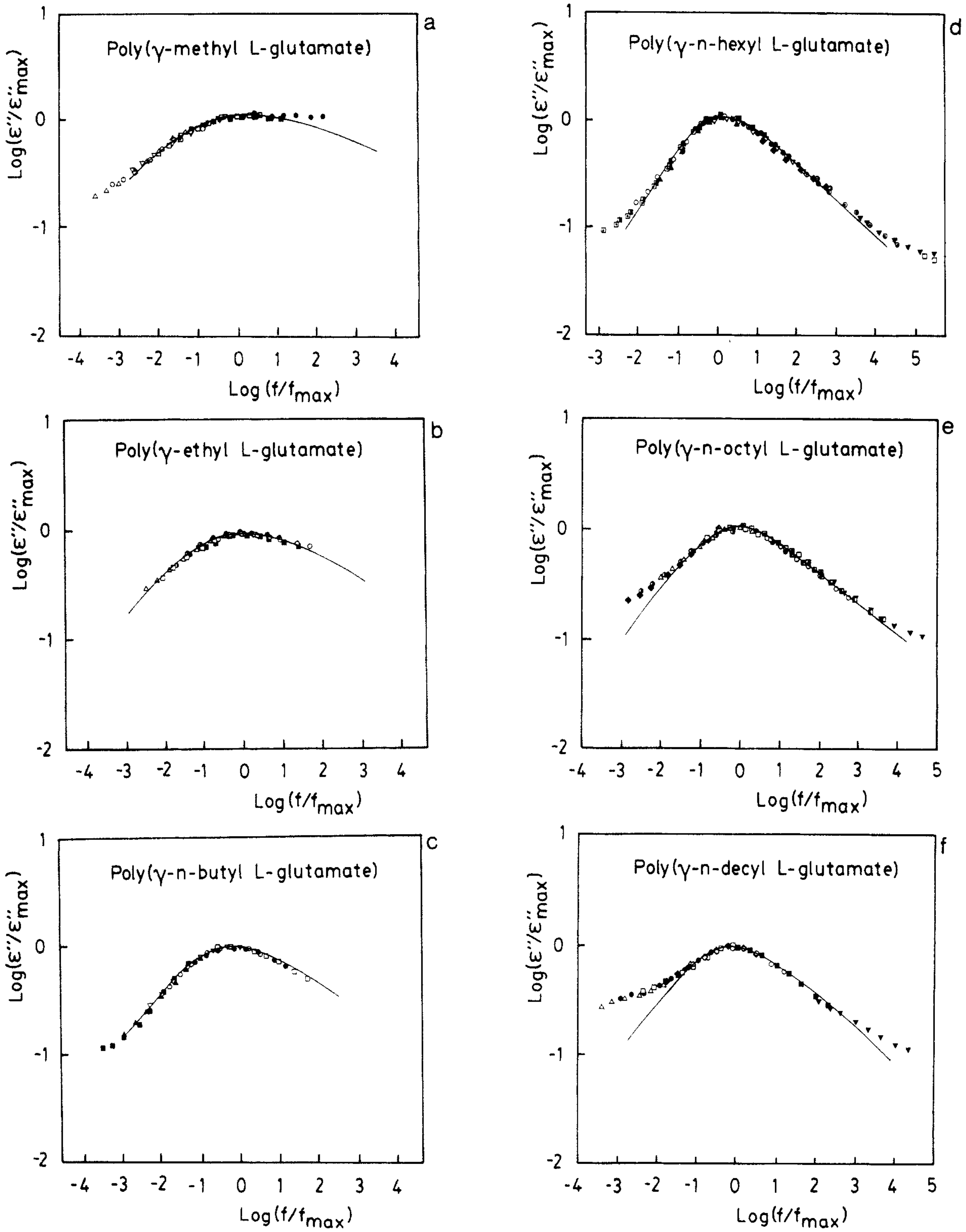

Figure 13. (a) Master curve of the loss permittivity $\log(\epsilon''/\epsilon''_{max})$ vs $\log(f/f_{max})$ for the β-relaxation in poly(γ-methyl L-glutamate): (△) 55.5 °C; (○) 47.5 °C; (▽) 35.4 °C; (□) 25.5 °C; (▼) 13.7 °C; (■) 5.5 °C; (●) −3.8 °C. Here f_{max} is the frequency for the loss permittivity maximum, ϵ''_{max}. The full line is the curve calculated with the Williams–Watts model[75] with $\beta = 0.20$. (b) Master curve of the loss permittivity $\log(\epsilon''/\epsilon''_{max})$ vs $\log(f/f_{max})$ for the β-relaxation in poly(γ-ethyl L-glutamate): (△) 31.4 °C; (□) 24.6 °C; (◑) 19.0 °C; (●) 11.7 °C; (■) 7.5 °C; (○) 2.3 °C. Here f_{max} is the frequency for the loss permittivity maximum, ϵ''_{max}. The full line is the curve calculated with the Williams–Watts model[75] with $\beta = 0.25$. (c) Master curve of the loss permittivity $\log(\epsilon''/\epsilon''_{max})$ vs $\log(f/f_{max})$ for the β-relaxation in poly(γ-n-butyl L-glutamate): (■) 27.9 °C; (▲) 17.6 °C; (▽) 8.0 °C; (○) 2.4 °C; (●) −5.3 °C; (□) −13.0 °C. Here f_{max} is the frequency for the loss permittivity maximum, ϵ''_{max}. The full line is the curve calculated with the Williams–Watts model[75] with $\beta = 0.30$. (d) Master curve of the loss permittivity $\log(\epsilon''/\epsilon''_{max})$ vs $\log(f/f_{max})$ for the β-relaxation in poly(γ-n-hexyl L-glutamate): (■) 16.7 °C; (▣) 9.8 °C; (○) 4.0 °C; (▲) −3.0 °C; (■) −8.7 °C; (●) −14.6 °C; (◆) −20.5 °C; (◐) −26.3 °C; (⊙) 40.1 °C; (▼) −48.6 °C; (□) −58.8 °C. Here f_{max} is the frequency for the loss permittivity maximum, ϵ''_{max}. The full line is the curve calculated with the Williams–Watts model[75] with $\beta = 0.40$. (e) Master curve of the loss permittivity $\log(\epsilon''/\epsilon''_{max})$ vs $\log(f/f_{max})$ for the β-relaxation in poly(γ-n-octyl L-glutamate): (◆) 11.2 °C; (◑) 5.4 °C; (△) −0.4 °C; (●) −12.1 °C; (□) −18.0 °C; (■) −23.5 °C; (○) −29.3 °C; (▣) −35.8 °C; (▼) −42.0 °C. Here f_{max} is the frequency for the loss permittivity maximum, ϵ''_{max}. The full line is the curve calculated with the Williams–Watts model[75] with $\beta = 0.35$. (f) Master curve of the loss permittivity $\log(\epsilon''/\epsilon''_{max})$ vs log (f/f_{max}) for the β-relaxation in poly(γ-n-decyl L-glutamate): (△) 21.2 °C; (●) 12.0 °C; (□) 1.9 °C; (◆) −7.6 °C; (○) −17.3 °C; (■) −26.8 °C; (▼) −36.9 °C. Here f_{max} is the frequency for the loss permittivity maximum, ϵ''_{max}. The full line is the curve calculated with the Williams–Watts model[75] with $\beta = 0.36$.

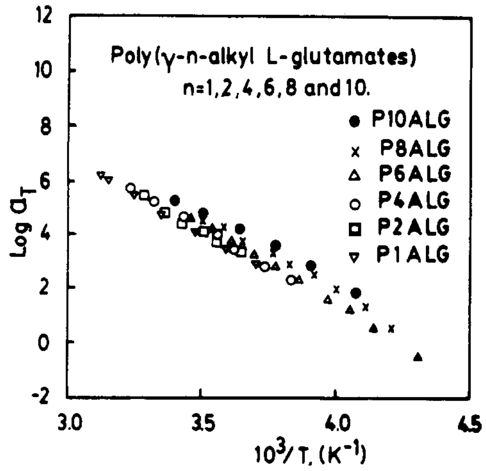

Figure 14. Horizontal shift factor a_T for the β-relaxation in poly(γ-n-alkyl L-glutamates) (n = 1, 2, 4, 6, 8, and 10) (see text) plotted against the reciprocal temperature: (▽) P1ALG; (□) P2ALG; (○) P4ALG; (△) P6ALG; (×) P8ALG; (●) P10ALG. Values for the horizontal shift factor a_T have been obtained from loss permittivity.

values of $\epsilon'_{\rm U}$ and $\epsilon'_{\rm R}$ have been determined for the polymers with $n \leq 10$ by extrapolation of the Cole–Cole[68] arcs. In Figure 15a,b some of these arcs measured on P6ALG are shown as an example. $\mu_{\rm eff}$ at 273.2 K has been calculated for all the members of the series. $\epsilon'_{\rm U}$ and $\epsilon'_{\rm R}$ were estimated at this temperature by extrapolation in the plot of $\epsilon'_{\rm U}$, $\epsilon'_{\rm R}$ vs temperature, as can be seen in Figure 16. The respective values obtained are shown in Table 4. The number of dipoles per volume unit N has been calculated by taking into account the density data on this homologous series given by Watanabe et al.[1]

The value of the effective dipole moment, as can be seen in Table 4, rises rapidly with the number of carbon atoms in the external part of the side chain on going from $n = 1$ to $n = 4$, attaining afterward a constant value around 1.25. This would suggest that when the side chains are shorter, the glass transition does not imply the complete loss of their mobility, but rather in the glassy state it is still possible to orientate the permanent dipole moment of the carboxyl group through more restricted motions than in the liquid state. The existing paralellism in behavior between the polymers studied in the present series and that of the poly(acrylates)[69] is noteworthy. The effective dipole moment increased rapidly in the α-relaxation of the members of this series PMA–PEA–PBA (n = 1, 2, and 4). That is to say, also in this latter case, in which the side chains are similar to those of the polymers studied in the present work, but the configuration of the main chains is quite different, the lateral n-alkyl side chains lose mobility in the glassy state when the side chain length is increased. In other words mobility of the side groups in the glassy state is smaller. A secondary relaxation is produced at lower temperatures, which is called the β-relaxation in the poly(acrylate) series. It is attributed to the loss of this remaining mobility of the side chains in the glassy state. The longer the length of the side chains or the effective dipole moment of the main dielectric relaxation the less intense this last relaxation. In our PnALGs the β'-relaxation must be attributed to this process of loss of mobility of the side chains in the glassy state. Its intensity decreased rapidly from n = 1 to n = 4, as in the case of poly(acrylates). The β'-relaxation appears in the dielectric results given by some other authors. Thus, for instance, Nguyen et al.[70] have shown very clearly the presence of this transition. However, it is hardly detectable in either the dielectric measurements carried out by Sasaki et al.[17] or the dynamo-mechanical measurements by Yamashita et al.[15] Nevertheless, in none of these references has a possible explanation of this relaxation process been analyzed. In addition, it must be mentioned that Tsusumi et al.[71] and Watanabe et al.[72]

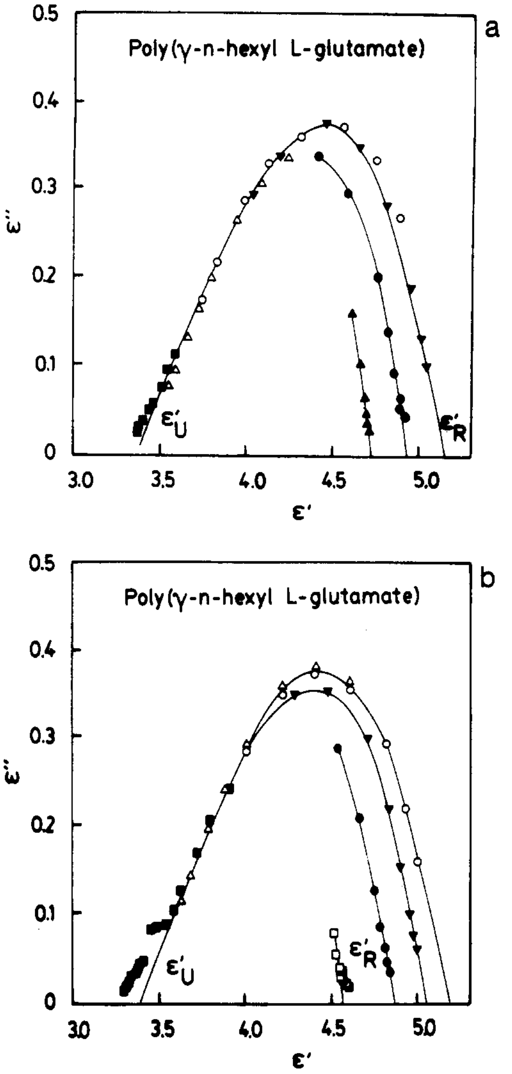

Figure 15. (a) Complex dielectric plots to calculate $\epsilon'_{\rm U}$ and $\epsilon'_{\rm R}$ for the β-relaxation of poly(γ-n-hexyl L-glutamate): (▲) 26.7 °C; (●) 9.8 °C; (▼) −3.0 °C; (○) −14.6 °C; (△) −26.3 °C; (■) −40.1 °C. See the legend for Figure 16 for the definition of $\epsilon'_{\rm U}$ and $\epsilon'_{\rm R}$. (b) Complex dielectric plots to calculate $\epsilon'_{\rm U}$ and $\epsilon'_{\rm R}$ for the β-relaxation of poly(γ-n-hexyl L-glutamate): (□) 36.8 °C; (●) 16.7 °C; (▼) 4.0 °C; (○) −8.7 °C; (△) −20.5 °C; (◪) −31.9 °C; (■) −48.6 °C. See the legend for Figure 16 for the definition of $\epsilon'_{\rm U}$ and $\epsilon'_{\rm R}$.

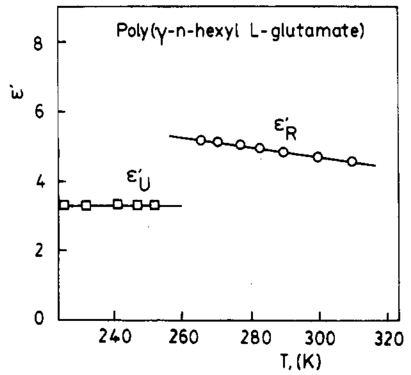

Figure 16. β-Relaxation of poly(γ-n-hexyl L-glutamate). The dielectric constants ϵ' for $\epsilon'_{\rm U}$ and $\epsilon'_{\rm R}$ values are given as a function of temperature T. $\epsilon'_{\rm U}$ (unrelaxed dielectric constant) and $\epsilon'_{\rm R}$ (relaxed dielectric constant) represent the values of ϵ' at short times and long times or times where no dependence of ϵ' on time is observed, respectively. Their difference $\Delta\epsilon = \epsilon'_{\rm R} - \epsilon'_{\rm U}$ is a measure of the orientation polarization.

Table 4. Characteristic Parameters for Dielectric β-Relaxation for a Homologous Series of Poly(γ-n-alkyl L-glutamates) (PnALGs) (n = 1, 2, 4, 6, 8, and 10)[a]

sample	ϵ_0 (°C)	ϵ_∞ (°C)	$10^{-21}N$ (cm^{-3})	μ_{eff} (D)	β
P1ALG	3.32	2.9	5.4	0.53	0.20
P2ALG	4.20	3.0	4.7	0.86	0.25
P4ALG	4.70	3.0	3.8	1.13	0.30
P6ALG	5.10	3.3	3.1	1.21	0.40
P8ALG	4.75	3.0	2.7	1.28	0.35
P10ALG	4.25	3.1	2.3	1.22	0.36

have not detected the presence of this relaxation peak. The mobility of the side chains, after a fashion, must be related to the packing of the α-helices and hence to the manner of sample preparation as well as its thermal history.

A small peak in the same range of temperatures of the β'-relaxation appears in the members of the series with n = 14 and n = 16. This process ought to be associated with the appearance of the side chain crystallization through a mechanism which may be somewhat similar to that used to explain the β'-relaxation.[4] A detailed study of this process together with the lower temperature relaxation process will be published separately.

The intensity of the β-relaxation decreases rapidly when the side chain length increases for values of $n > 10$. This feature is associated with the incipient crystallization of the side chains. The cooperative motions of the side chains are hindered because some methylene units —CH_2— of the side chains participate in the paraffin-like crystallites which form the crystalline phase around the α-helices. The β-relaxation will be produced only in those side chains with all of their methylene units in the amorphous phase. As can be seen in Table 4, the intensity of the β-relaxation decreases rapidly as the crystalline fraction increases. This indicates that the main part of the side chain partakes to some extent in the crystalline phase. As the intensity of the relaxation decreases, the temperature of the respective peak shifts to higher temperatures. A similar behavior has been found in semicrystalline polymers when the crystalline fraction increases.[73]

The glass transition temperature decreases as the number of methylene units increases for the shorter members of the series, i.e. for $n < 10$. The same effect takes place in the case of the β-relaxation. By analogy with the glass transition of the main chain in poly(acrylates) and poly(methyl methacrylates), this fact may be explained by bearing in mind that part of the side chains have a plasticization effect on their cooperative motions. This has been explained by Sasaki et al.[17] by means of a two phase model, one of which is crystalline and is formed by the α-helices and the other is the amorphous phase. Therefore, an increase in the side chain length produces an increase in the amorphous phase fraction. In semicrystalline polymers, this would normally give rise to a shift of the main dielectric relaxation to lower temperatures. It can be concluded that the β-relaxation is associated with the cooperative motion of the n-alkyl side chain residue as a whole group[17,19] and corresponds to the pseudoglass transition of the side chains.[4,22]

Many relaxation processes can be adequately described by means of a relaxation function of Kohlrausch–Williams–Watts[74,75] (KWW):

$$\phi(t) = \exp[-(t/\tau)^{\beta}] \tag{6}$$

which can be understood as the consequence of the existence of a relaxation time distribution of increasing width with lower values of β (ranging between 0 and 1). Romero Colomer et al.[22] have studied the glass transition and the structural relaxation associated with a related polymer, poly(γ-benzyl L-glutamate) (PBLG), using DSC and dielectric measurements. They show that the KWW function is applicable in both cases with a high degree of agreement in the value of the β parameter and the time relaxation–temperature curve. They found the similarity between the structural relaxation associated with the side chains of the PBLG and the characteristic glass transition of amorphous polymers. Equation 6 has been recently analyzed by means of the coupling model of Ngai et al.[76,77] in which parameter β ($0 < \beta < 1$) is a measure of the coupling produced between the different groups which move to produce the relaxation process (main chain segments in the glass transition of lineal amorphous polymers or side chains in the case of comblike polymers such as those studied in the present work) among them or with other groups. The relaxation process rate slows down with time, as a result of the coupling between the relaxing species. A value of $\beta = 1$ signifies that the process is not coupled.

The dependence of the complex dielectric permittivity on frequency at constant temperature may be expressed in terms of the relaxation function given by eq 5 as follows:

$$\{[\epsilon^*(\omega) - \epsilon_\infty]/(\epsilon_0 - \epsilon_\infty)\} = \int_0^\infty (-\mathrm{d}\phi(t)/\mathrm{d}t) \exp(-i\omega t)\, \mathrm{d}t \tag{7}$$

The integral of eq 7 has been calculated by an expansion of series proposed by Williams et al.[78] by searching for the best value of β to reproduce the master curves. The master curves together with the experimental results for polymers with n = 1, 2, 4, 6, 8, and 10 have been plotted on Figure 13a–f. The values for the best fit of β are gathered in Table 4. As can be seen, the value of β rises from 0.2 for P1ALG to 0.4 for P6ALG to give an almost constant value around 0.35 for P8ALG and P10ALG.

Concluding Remarks

From the present results we can derive the following conclusions:

(1) The glass transition temperature of amorphous PnALGs can be described with fair accuracy by a semiempirical equation as a function of the number of methylene groups in the outer part of the n-alkyl side chain in this series of PnALGs. The same equation has been shown to be very precise in describing the same relationship for some other conventional comblike structures.

(2) Members of the series with outer side chain lengths ≥10 carbon atoms display melting temperatures. Melting points and their dependence on the number of carbon atoms in the outer n-alkyl side chain were similar to those of the conventional comblike polymer in which the backbone adopts a random coil conformation. Garner's equation fits very acceptably the experimental melting point estimates by means of DSC or TMA measurements.

(3) The respective melting enthalpies ΔH_f clearly indicate that side chain crystallization takes place with part of each side chain.

(4) There exists among our present series of PnALGs and some other conventional comblike polymers a good correlation between the critical chain length in the outer part of the n-alkyl side chain needed to initiate the crystallization, n_c, and the term $\Delta H_{f,e}$ due to the chain end contribution to the melting enthalpy. This means that the effect of the main chain structure and conformation of PnALGs on the side chain crystallization is less than expected.

(5) It has been found that PnALGs present a β-relaxation which, for members of the series with n-alkyl side chains longer than methyl, decreases with the increase in the side chain length from ethyl to n-octyl or n-decyl members

and thereafter increases. This β-relaxation is associated with the cooperative motion of the *n*-alkyl residue as a whole group and corresponds to the pseudoglass transition of the side chains. The Williams–Watts[75] decay function has been used to model this dielectric relaxation in equilibrium conditions. A single parameter β defines the shape of the curves. The superposition of a master curve $\epsilon''/\epsilon''_{\max}$ vs $\log(f/f_{\max})$ for $n \leq 10$ is good at the maximum and most of the curve, and in some cases an appreciable scattering is observed on the high and/or low frequencies of the curves. Generally speaking, we can conclude that the agreement between the model and our experimental results is quite good. This relaxation process may be ascribed to conformational rearrangements of the side chains in the interhelix space.

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