Dielectric relaxation properties of linear polyesters derived from β-propiolactone

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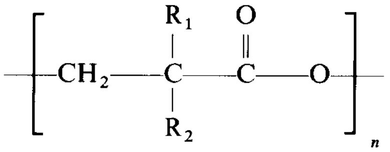
Dielectric relaxation measurements are reported over a frequency range of 0.01–50 kHz and from 100–490 K for a series of poly(α-dialkyl-β-propiolactones): poly(α-dimethyl-β-propiolactone) (PPL), poly(α-methyl-α-ethyl-β-propiolactone) (PMEPL) and poly(α-methyl-α-n-propyl-β-propiolactone) (PMPPL). First of all, the three polyesters investigated show a high temperature β-relaxation peak which is due to their glass transitions. Secondly, PPL and PMEPL exhibit a γ relaxation peak, at 275 and 210 K, respectively, which is related to the crystalline fraction of the polyester since its intensity increases with the degree of crystallinity. PMPPL does not show such a relaxation due to its low degree of crystallinity. Thirdly, a weak δ relaxation peak is observed at low temperatures (~130 K) for PMPPL and PMEPL. This peak is absent in PPL. This observation suggests that the δ peak is due to ethyl and propyl group rotations around the main chain of the linear polyester in its amorphous fraction; PPL does not show this relaxation since it has only methyl substituents and a high degree of crystallinity. Finally, the β, γ and δ relaxation data of these three polyesters were analysed using a method based on the frequency–temperature superposition principle and using the Cole–Cole representations.

(Keywords: dielectric relaxation; polyesters; crystallinity)

INTRODUCTION

Poly(α-dialkyl-β-propiolactones) having the general skeletal formula:



$$\left[-CH_2-\overset{R_1}{\underset{R_2}{C}}-\overset{O}{\overset{\|}{C}}-O- \right]_n$$

exhibit unique physical properties[1–5]. Their degrees of crystallinity range from 10 to 85% and their melting points from 300 to 515 K depending upon their substituents[1,3–8]. In addition, they can be used to produce fibres[2,4,5,9–11]. Fibres spun from poly(α-dimethyl-β-propiolactone) have excellent elastic properties, colour stability, and good resistance to heat and light as compared to nylon 6 and poly(ethylene terephthalate)[4].

The mechanical relaxation properties of several poly(α-dialkyl-β-propiolactones) have been previously investigated[12–15]. Poly(α-dimethyl-β-propiolactone), commonly called polypivalolactone (PPL), exhibits, in addition to the usual α and β relaxation peaks which are, respectively, associated to the melting and glass transition temperatures, a γ relaxation peak, at ~280 K, which was not observed with the other members of this series. This γ relaxation peak was then related to the crystalline fraction of PPL since its intensity increases with the degree of crystallinity[12].

It was also shown that poly(α-methyl-α-ethyl-β-propiolactone) (PMEPL)[8], poly(α-methyl-α-n-propyl-β-propiolactone) (PMPPL)[13] and poly(α-diethyl-β-propiolactone)[14] exhibit a low temperature δ relaxation peak, at ~130 K, which is absent in PPL. This δ peak was assigned to the rotation of ethyl and propyl substituents in the amorphous fraction of the polylactones; PPL does not show this δ peak since it has only methyl substituents.

In previous articles[16,17], it has been shown that additional information can be gained about the relaxation properties of PMPPL and PPL by using a dielectric method. This technique is particularly useful with polyesters owing to their polar groups that are dielectrically active. It allows the measurements of both kinetic parameters (activation energy and relaxation width) and equilibrium parameters (dipole correlation factor) from data taken over a wide frequency range.

In this paper, dielectric measurements are reported for a third member of the polylactone series, namely PMEPL. Measurements were made in a frequency range of 0.01–50 kHz and from 90 to 340 K. This temperature range allows the observation of the β, γ and δ relaxation regions. The main results obtained previously with PPL and PMPPL will then be recalled and the dielectric relaxation behaviour of this series of polylactones having methyl/methyl (PPL), methyl/ethyl (PMEPL) and methyl/n-propyl (PMPPL) substituents will be discussed.

EXPERIMENTAL

PMEPL and PMPPL were synthesized in our laboratory[8,18]. The third polyester, PPL, was provided by the Shell Laboratories in Amsterdam. The main characteristics of these three polylactones are given in *Table 1*: weight-average molecular weight (M_w), glass transition temperature (T_g) and melting temperature

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Table 1 Main characteristics of polylactones

Name	Acronym	Substituents	M_w (kg mol^{-1})	T_g (K)^a	T_m(K)
Poly(α-dimethyl-β-propiolactone)	PPL	Methyl and methyl	280	410	513
Poly(α-methyl-α-ethyl-β-propiolactone)	PMEPL	Methyl and ethyl	80	260	397
Poly(α-methyl-α-n-propyl-β-propiolactone)	PMPPL	Methyl and n-propyl	131	275	370

^{a}D.s.c. measurement, except for PPL which was measured dielectrically at 10 Hz

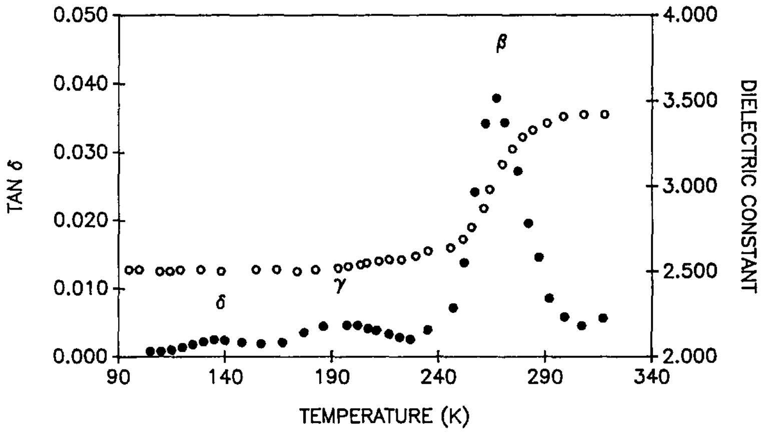

Figure 1 Temperature dependence of the dielectric loss tangent (tan δ, ●) and of the dielectric constant (○) of PMEPL at 10 Hz

(T_m). *Table 1* shows that these polyesters are semicrystalline. Their degree of crystallinity is, however, different. It is of the order of 80% for PPL[12,17], 35% for PMEPL[8] and 15% for PMPPL[13,15,16].

PMEPL films were prepared by quenching from the melt. Samples were melted at 400 K for 10 min, quenched in water and then annealed for different periods of time. They had degrees of crystallinity ranging from 31 to 36%.

The degree of crystallinity X of PMEPL samples was determined by density measurements using the following formula:

$$1/\rho = X/\rho_c + (1 - X)/\rho_a \qquad (1)$$

where ρ is the density of the sample, ρ_c (1.23 g cm^{-3}) the density of a completely crystalline PMEPL sample and ρ_a (1.07 g cm^{-3}) the density of a completely amorphous PMEPL[9].

A General Radio (model 1621) precision capacitance system was used for dielectric measurements. Polymer films were held in a three-terminal cell constructed in our laboratory using the model of McCammon and Work[19]. It has two parallel electrodes of 3.0 cm diameter. The cell was placed in an environmental chamber constructed for temperature regulation.

All series of measurements were performed starting from the lowest temperature. Cooling was accomplished using liquid nitrogen and the temperature programme was monitored by a programmable temperature controller. A copper/constantan thermocouple was mounted near the sample to monitor its temperature. A limited number of dynamic mechanical measurements were also performed using a Rheovibron DDV-II viscoelastometer (Toyo Baldwin Co.).

RESULTS AND DISCUSSION

Analysis of PMEPL

The dielectric constant (ε') and dielectric loss tangent (tan δ) of PMEPL at 10 Hz are plotted in *Figure 1* as a function of temperature. The tan δ curve shows three relaxation regions, β, γ and δ, in order of decreasing temperature. The high intensity β peak (275 K), accompanied by an abrupt increase in ε', is associated with the glass transition of PMEPL. In the γ and δ relaxation regions (210 and 110 K, respectively), the ε' curve is flat and is almost independent of temperature.

Dynamic mechanical data of PMEPL are shown in *Figure 2*, where the dynamic modulus and dynamic loss tangent are plotted as a function of temperature at 110 Hz. By comparing *Figures 1* and *2*, it can be seen that the three peaks of PMEPL appear in the same temperature region by both techniques, although they show up at slightly higher temperatures in the dynamic mechanical measurements due to the higher frequency used and are more intense. In the mechanical spectra, the δ peak is more intense than the γ peak whereas the inverse is observed in the dielectric curves. This inversion has already been observed in the literature and was attributed to different relative contributions of the dipolar and mechanical motions in the two techniques[20].

An attempt was made to determine the crystalline or amorphous origin of the γ peak of PMEPL by performing dielectric measurements as a function of the degree of crystallinity[21]. It was seen that the intensity of the γ peak increases slightly and that of the β peak decreases slightly with an increase from 31 to 40% in the degree of crystallinity. In order to correlate the relaxation

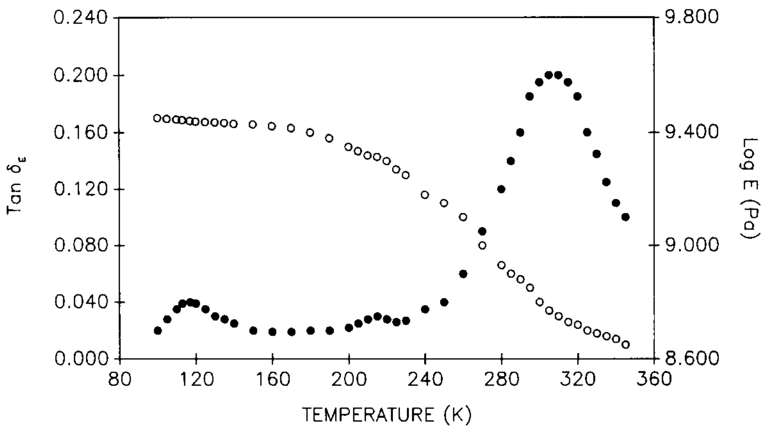

Figure 2 Temperature dependence of the mechanical loss tangent (tan δ_E, ●) and dynamic modulus (E, ○) of PMEPL at 110 Hz

parameters with crystallinity[22,23], we then attempted to construct Cole–Cole plots with the γ peak data of PMEPL. It was found that a satisfactory superposition could not be obtained due to a non-linear increase in the intensity of the peaks with increasing frequencies. One possible explanation for this unusual behaviour may lie in the presence of a second peak, in this temperature range, which would increase in intensity with frequency. Ishida *et al.*[24] also observed, for unsubstituted poly(β-propiolactone), a non-linear increase in the intensity of dielectric loss peaks with increasing frequencies in the same temperature range, but it was unexplained.

The temperature dependence of the ε' and dielectric loss (ε'') of PMEPL, at various frequencies in the β relaxation region, is shown in *Figures 3* and *4*, respectively. As expected for the glass transition region, ε'' shows a well defined peak at each frequency, whose intensity increases and shifts to higher temperatures as the applied frequency increases. The dielectric data of PMEPL in the β region were then analysed using the Davidson–Cole equation[25] for various temperatures and frequencies. Mathematically, this equation is expressed as follows:

$$\varepsilon^* = \varepsilon_u + (\varepsilon_R - \varepsilon_U)/(1 + i\omega\tau)^\beta \qquad (2)$$

where ε^* is the complex dielectric constant defined by $\varepsilon^* = (\varepsilon' - i\varepsilon'')$, ω is the angular frequency and τ the relaxation time. ε_R and ε_U are the dielectric constants at low and high frequencies, respectively, and the $(\varepsilon_R - \varepsilon_U)$ value represents the dielectric strength. β is a parameter which decreases as the absorption curve broadens. For a single relaxation time model, the Cole–Cole plot is a semi-circle of radius $(\varepsilon_R - \varepsilon_U)$ with β equal to unity. For polymers, the single relaxation time model is inadequate and Cole–Cole plots are not semi-circles but show asymmetry at the high frequency end[20,26,27].

Figure 5 shows the Cole–Cole plot for the β relaxation peak for PMEPL. The superposition of the data is satisfactory, as usually seen for amorphous polymers and semicrystalline polymers at low degrees of crystallinity[16,28]. The parameter β was determined from the method described in reference 26. The limiting dielectric constants ε_R and ε_U were taken at the points of intersection of the curve with the ε' axis. The values of β, ε_R and ε_U thus obtained for the β relaxation process of PMEPL are equal to 0.54, 3.41 and 2.55, respectively.

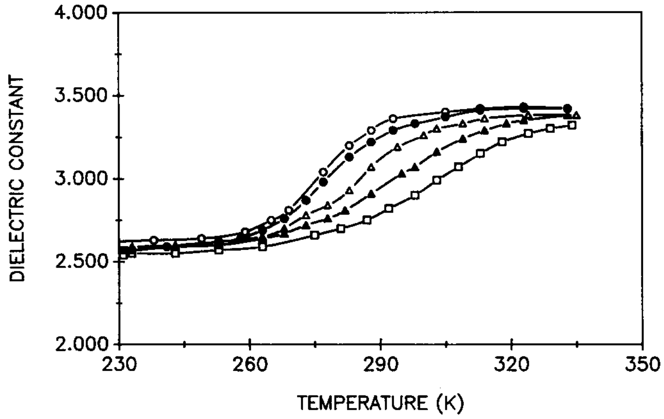

Figure 3 Temperature dependence of the dielectric constant of PMEPL at different frequencies in the β relaxation region: (○) 10 Hz; (●) 100 Hz; (△) 1 kHz; (▲) 10 kHz; (□) 50 kHz. Data were measured at eight different frequencies between 10 Hz and 50 kHz; only five series of curves are given here for the sake of clarity

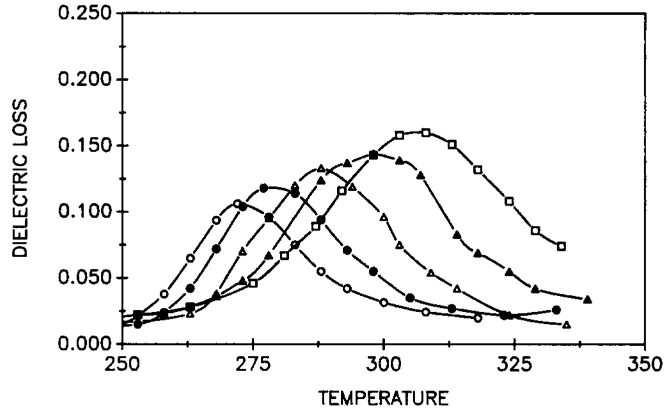

Figure 4 Temperature dependence of the dielectric loss of PMEPL at different frequencies in the β relaxation region. For symbols and further details see *Figure 3*

The parameter β of the β relaxation peak of PMEPL, unlike those of semicrystalline polymers of higher degrees of crystallinity such as poly(1,6-hexamethylene adipate)[29] and PPL[17], is not a function of temperature, suggesting the validity of the frequency–temperature superposition principle for this relaxation process. This may be related to the lower degree of crystallinity of PMEPL (~40%) as compared to PPL (~80%).

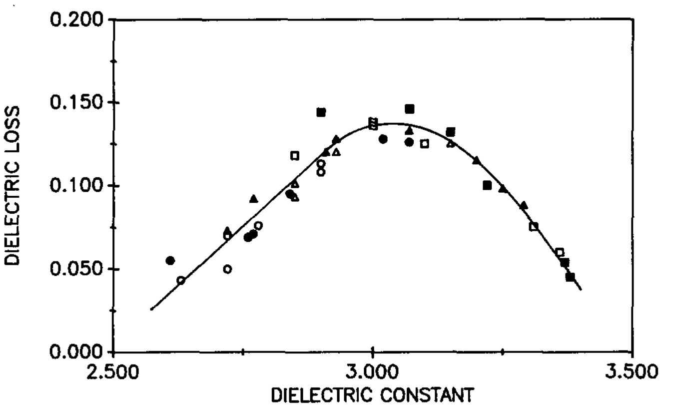

Figure 5 Cole–Cole representation of the dielectric loss data of PMEPL in the β relaxation region. In this figure, data obtained at six different frequencies, and at several temperatures are reported: (○) 273 K; (●) 278 K; (△) 283 K; (▲) 288 K; (□) 293 K; (■) 298 K

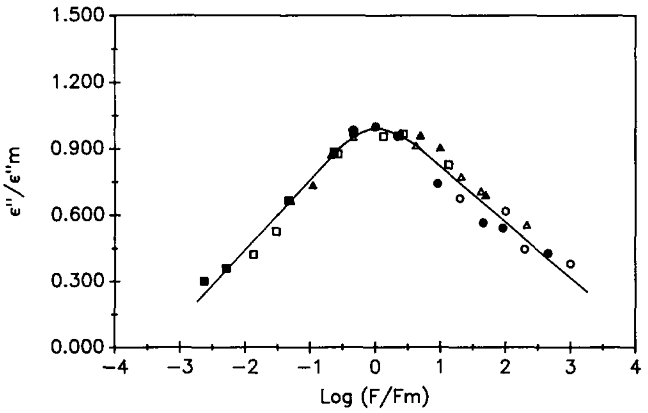

Figure 6 Normalized dielectric loss data ($\varepsilon''/\varepsilon''_m$) of PMEPL in the β relaxation region. For symbols and further details see *Figure 5*

A normalized β loss curve of PMEPL was constructed by plotting ($\varepsilon''/\varepsilon''_m$) *versus* the reduced frequency (f/f_m) (*Figure 6*) where ε''_m is the maximum value of ε'' and f_m its corresponding frequency. Within the temperature range investigated, the data superimpose satisfactorily showing that the distribution of relaxation times remains constant with temperature[30]. The width at half-height of the normalized β loss curve of PMEPL was determined and is equal to 3.8. The $\Delta H/\Delta L$ value, which represents the ratio of the distance of the high (ΔH) and low (ΔL) frequency branches of the dispersion curve, at half-height, from the log $(f/f_m) = 0$ point is equal to 1.27. $\Delta H/\Delta L$ is a measure of the asymmetry of the dispersion curve (it is equal to unity for a symmetrical curve). The experimental value of PMEPL indicates a slight asymmetry.

Dielectric data of PMPPL and PPL were analysed previously using Ferry's reduced variable method[31]. According to this method, if all contributions to the dielectric relaxations associated with dipole orientations have a magnitude inversely proportional to the absolute temperature T, and if all relaxation times change by the same factor b_T when the temperature changes from T to a reference value T_o, then measurements at any temperature could be reduced to T_o, giving ultimately a master curve[31,32]. For this purpose, the dielectric constant and dielectric loss values must be normalized in the form of $(\varepsilon' - \varepsilon_U)/(\varepsilon_R - \varepsilon_U)$ and $\varepsilon''/(\varepsilon_R - \varepsilon_U)$ functions. The resulting normalized functions must coincide with horizontal shifting, and the same values of the shift factor b_T must superpose both the real and imaginary components of the dielectric constant.

For PMEPL, the dielectric loss data were normalized and reduced to 288 K by shifting the curves horizontally. The superposition obtained is satisfactory (*Figure 7*). No vertical shift was required since the function was previously normalized in the vertical direction. The shift factor b_T was obtained empirically at each temperature and was used to reduce the ε' data (these data are not given here but they can be found in ref. 21). It was found that the same shift factors could be used for both the real and imaginary components of the dielectric constant.

An important physical property of a polymer is its apparent energy of activation (ΔE) which measures the stiffness of the chain against segment motions. Measurements of dielectric data provide a convenient way of evaluating ΔE by using the Arrhenius equation:

$$f = f_o \exp(-\Delta E/RT) \qquad (3)$$

where f is the measuring frequency, f_o is the frequency when T approaches infinity and T is the temperature corresponding to the maximum of the ε'' curve. The results thus obtained for the β process of PMEPL are plotted in *Figure 8*. A straight line is obtained from which a value of 183 ± 7 kJ mol^{-1} is calculated for ΔE.

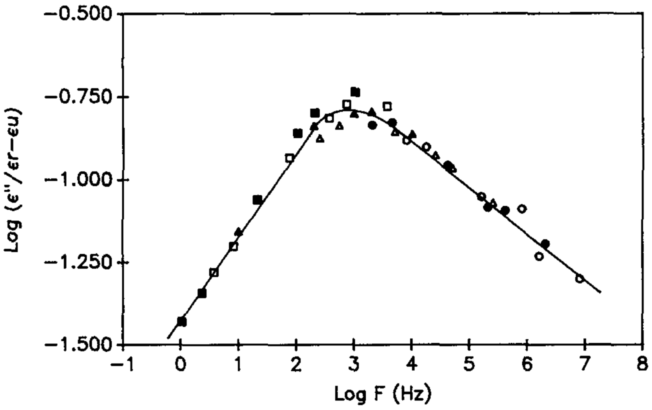

Figure 7 Dielectric loss master curve of PMEPL in the β relaxation region. For symbols and further details see *Figure 5*

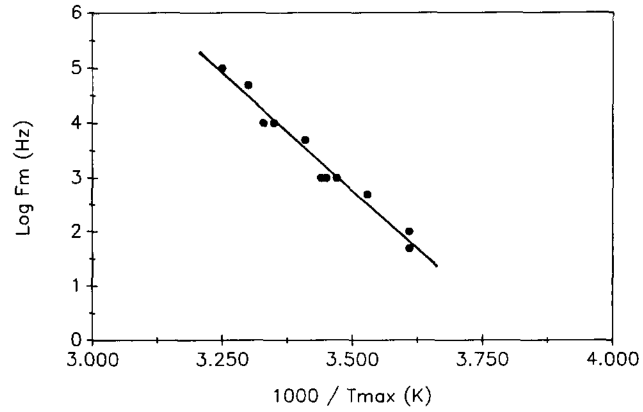

Figure 8 Arrhenius plot of the dielectric loss data of PMEPL in the β relaxation region

Analysis of PPL

Dielectric data of PPL have been reported as a function of temperature and frequency in reference 17. At 10 Hz, the tan δ curve shows a low temperature relaxation at ~275 K, which is the γ peak (*Figure 9*). The intensity of this peak is low and no significant increase in ε′ is observed in this temperature region. At ~410 K, the tan δ curve shows a high intensity β peak, accompanied by an abrupt increase in ε′. This relaxation process was associated with the glass transition of PPL[17]. Both the β and γ relaxation processes of PPL were analysed using a method based on the frequency–temperature superposition principle and using the Cole–Cole representation[17]. It was found that the frequency–temperature superposition principle is applicable to the γ relaxation peak despite the high degree of crystallinity of PPL. However, it could not be applied to the β relaxation peak except at low temperatures and high frequencies.

Analysis of PMPPL

Dielectric data of PMPPL have been reported as a function of temperature and frequency in reference 16. At 10 Hz, the tan δ curve shows two relaxation peaks, β and δ, in order of decreasing temperature (*Figure 9*). The intensity of the δ peak, at ~120 K, is low and no significant increase of ε′ is observed in this temperature region. The high temperature β peak, at ~275 K, has a high intensity and is accompanied by an abrupt increase of ε′. This peak was assigned to the glass transition of PMPPL[16]. The dielectric relaxation data of PMPPL were also analysed using a method based on the frequency–temperature superposition principle and using the Cole–Cole representation[16]. It was found that these methods are applicable to the β relaxation peak. Their validity to analyse the δ peak data could not be checked owing to its very low intensity.

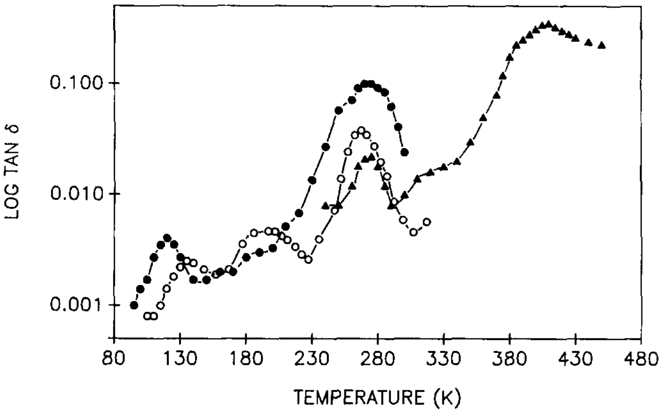

Figure 9 Temperature dependence of the dielectric loss tangent (tan δ) of PMEPL (○), PPL (▲) and PMPPL (●) at 10 Hz

DISCUSSION

A summary of the principal parameters measured or calculated from the analysis of PPL, PMEPL and PMPPL dielectric data is given in *Table 2*. The three polyesters investigated exhibit a β relaxation peak which was assigned to their T_g. Indeed, in the β region, a maximum in tan δ is observed as a function of temperature along with an increase in ε′. These assignments for PMPPL and PMEPL are in agreement with T_gs of 275 and 260 K, respectively, which were measured by d.s.c.[8,9] (see *Table 1*). PMPPL also shows a T_g of 270 K by stress-relaxation measurements and of 301 K by dynamic mechanical measurements at 110 Hz[13]. Finally, PMEPL shows a T_g of 300 K by dynamic mechanical measurements at 110 Hz (*Figure 2*). Our assignment of the β peak of PPL to its T_g is in agreement with a previously reported[17,33] T_g value of 390 K measured in the dynamic mechanical mode at 110 Hz, whereas a slightly lower value at 369 K was obtained by stress-relaxation measurements[12]. However, it must be noted that dielectric measurements show a strong and well-defined β peak whereas the mechanical measurements lead to a weak and ill-defined β peak. The low intensity β mechanical relaxation peak is due to the small amorphous fraction of PPL (degree of crystallinity ~80%) and the high intensity β dielectric relaxation peak is due to the high polarity and high concentration of ester groups on the PPL chains[17]. These T_g values are significantly larger than the $T_g(L)$ value of 270 K reported by Pratt and Geil[33], who also reported a $T_g(U)$ value of 340 K. However, in view of the T_g and T_m data reported in *Table 1* for PMPPL and PMEPL, a T_g value in the 370–410 K range for PPL seems reasonable since there is an increase of T_m of >110 degrees for PPL as compared to those of the two other lactones and,

Table 2 Comparison of dielectric parameters for PPL, PMEPL and PMPPL

Relaxation process	Polymer	T (K)[a]	Intensity[b] of tan δ	ΔE (kJ mol^{-1})	$\Delta H/\Delta L$	Width at half-height
	PPL	410	0.350	182 ± 16	–	–
β	PMEPL	270	0.038	183 ± 7	1.27	3.8
	PMPPL	275	0.112	180 ± 12	1.33	3.5
	PPL	275	0.021	154 ± 11	0.71	3.05
γ	PMEPL	210	0.005	–	–	–
	PMPPL	–	–	–	–	–
	PPL	–	–	–	–	–
δ	PMEPL	135	0.0025	–	–	–
	PMPPL	120	0.0038	–	–	–

[a] Temperature corresponding to the maximum of the tan δ curve at 10 Hz
[b] Intensity of the maximum of the tan δ curve at 10 Hz

therefore, the T_g of PPL has to be larger than those of PMEPL and PMPPL, because the smaller substituents of PPL create less free volume than ethyl and n-propyl substituents.

The relaxation peak intensity of PMPPL is equal to 0.112 as compared to 0.038 for PMEPL (*Table 2*). This higher intensity value for PMPPL is due to a low degree of crystallinity of ~15% as compared to ~40% for PMEPL (d.s.c. measurements). T_g being a property of the amorphous fraction of the semicrystalline polymer, the intensity of the β peak decreases with an increase of crystallinity. For a highly crystalline polymer like PPL, one expects a lower β relaxation peak intensity than those found with PMPPL and PMEPL. On the contrary, a very intense β peak is recorded. This unusual behaviour of PPL is unexplained at this point.

At intermediate temperatures, a γ relaxation peak was observed for PPL and PMEPL (*Table 2*). These γ peaks are related to the crystalline fraction of the polyesters (crystalline origin) since their intensity was shown to increase with the degree of crystallinity[17,21]. It is to be noted that the intensity of the γ peak of the PPL sample with a degree of crystallinity of 80% is 0.021 as compared to 0.0050 for the γ peak of the PMEPL sample with a degree of crystallinity of 40%. PMPPL does not show this γ relaxation peak because its degree of crystallinity is too low at ~15%.

One possible mechanism to explain a secondary relaxation of crystalline origin involves torsional oscillations of chain segments around the main chain axis within the crystal[26]. An increase in the degree of crystallinity then increases the intensity of this secondary relaxation peak because the fraction (size and/or number) of crystals in the sample becomes larger. A second possible mechanism to explain the γ relaxation process of PPL and PMEPL involves the motion of chain segments which are located close to the surface of the crystals. According to this mechanism, the γ process, unlike the β process, does not involve the bulk amorphous phase of the sample but only the segments at the surface of the crystals whose mobility is significantly reduced as compared to those in the bulk amorphous phase. The average crystal size and/or number increases with increasing degrees of crystallinity. At the same time, the amorphous surface area of the crystals increases and the intensity of the γ peak increases.

PMPPL and PMEPL finally show a low temperature δ peak which is absent in PPL (*Table 2*). This observation suggests that the δ relaxation peak could be due to ethyl or/and propyl group rotations around the main chain in the amorphous fraction of the linear polyester. PPL, which has only methyl substituents and a high degree of crystallinity, does not show this relaxation process. This assignment is in agreement with the observation of a δ relaxation peak with poly(α-diethyl-β-propiolactone) which has ethyl substituents[14]. A similar trend was observed by Hoff *et al.*[34] who investigated the mechanical relaxation properties of methyl, ethyl, n-propyl and n-butyl poly(methacrylates). They found that a low temperature loss peak, assigned to side-chain alkyl group rotations, occurs only in polymers having alkyl groups bigger than the ethyl group. They also found a low temperature relaxation peak, which was also assigned to rotations of side-chain alkyl groups, with n-propyl and n-butyl poly(α-chloroacrylates) but not with methyl and ethyl poly(α-chloroacrylates). These results indicate that alkyl chains containing at least two or three carbon atoms can relax at ~130 K (at 10 Hz) because they have several degrees of freedom. This relaxation process (δ peak for PMEPL and PMMPL) then involves not only local mode rotations about the main chain axis but also alkyl vibrations. In contrast, methyl groups can only relax through rotation. Activation energies for the rotation process would be low and this process would occur at much lower temperature (at a given frequency). This is the reason for the observation of the δ relaxation peak with PMEPL and PMPPL, but not with PPL.

Table 2 also gives values of the width at half-height of the normalized dispersion curves[16,17] for the β relaxation peak of PMPPL and PMEPL. Values of 3.5 and 3.8 were observed, respectively. These are typical values for semicrystalline polymers[26]. In general, the higher the degree of crystallinity, the broader the dispersion curve[35].

The broadening of the dispersion curves in semicrystalline polymers can be explained by using a modified two-phase model[36]. The regular two-phase model is made of a crystalline zone where molecular chain motions are minimal and of an amorphous zone where the chains are capable of large scale micro-Brownian motions. In the modified two-phase model, an amorphous interphase is added at the crystal surface. The movements of the chains at the interphase are restricted because these chains are linked simultaneously to the amorphous zone and to the crystalline zone. When the temperature is raised, the thermal motions of the chains start in the bulk amorphous phase where most of the mobile chain segments are found. With further rise in temperature, the chains at the interphase gradually gain motions and, meanwhile, dispersion goes on. Thus, with increasing degrees of crystallinity, the dispersion curves become broader than they are for completely amorphous polymers containing only one phase, meaning that the distribution of relaxation times is broadened in the long relaxation time region with respect to the average relaxation time[26]. Amorphous polymers often show[37] relatively sharp dispersion curves with widths at half-height ranging from 2 to 3. Semicrystalline polymers show wider dispersions depending upon their degree of crystallinity. Widths at half-height for semicrystalline polymers often range[26,38] from 3 to 5.

Table 2 also gives the $\Delta H/\Delta L$ parameter which characterizes the shape of the normalized dispersion curve. For the β peak of PMPPL and PMEPL, $\Delta H/\Delta L$ values are, respectively, equal to 1.33 and 1.27. These values are consistent with those found for a large number of semicrystalline polymers of low degrees of crystallinity[26]. For a large number of amorphous polymers[39,40], $\Delta H/\Delta L$ often ranges from 1.4 to 1.6. An increase in the degree of crystallinity is known to broaden the dispersion curve on the low frequency side and, consequently, the quantity $\Delta H/\Delta L$ decreases.

CONCLUSIONS

The three polyesters investigated in this study showed a high temperature β relaxation peak which was assigned to their T_g. The frequency–temperature superposition principle was applied to the β relaxation peak of PMPPL and PMEPL, but not to the β process of PPL due to its degree of crystallinity.

An intermediate temperature γ relaxation peak was observed for PPL and PMEPL. This γ relaxation peak was shown to be related to their crystalline fraction. PMPPL does not exhibit such relaxation due to its low degree of crystallinity. The frequency–temperature superposition principle was also found to be applicable for the γ relaxation process of PPL, but not to the γ relaxation of PMEPL due to a non-linear increase in the intensity of this peak with increasing frequency.

At low temperatures, a weak δ relaxation peak was observed for PMPPL and PMEPL. This peak was absent in PPL. The δ relaxation peak of PMEPL and PMPPL was assigned to ethyl and propyl group rotations about the main chain in the amorphous fractions of the polyesters.

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