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Viscoelastic Properties of Poly(pivalolactone)

Joseph Noah and Robert E. Prud'homme*

Département de chimie, Université Laval, Ste-Foy, Québec, Canada G1K 7P4.

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ABSTRACT: The viscoelastic properties of poly(pivalolactone) (PPL) have been investigated in the linear range using stress–relaxation and dynamic-mechanical measurements. Under the conditions that the sample was isotropic and insensitive to relative humidity, Ferry's reduction method was applied without using translations along the vertical axis. A horizontal shift factor was determined at each temperature, which satisfactorily agreed with the WLF equation in the transition region. The apparent activation energy of PPL was temperature dependent and passed through a maximum near T_g whose value was found to be 369 ± 3 K. The relaxation spectrum was calculated according to the first method of approximation of Schwarzl and Staverman, and it was found to be flat with a complicated fine structure. Two absorption peaks were determined. The low-temperature γ peak, around 300 K, was ascribed to a relaxation process in the crystalline phase of the polymer while the high-temperature β peak was related to the glass-transition process.

Among polylactones based on the skeletal formula $(\text{-CH}_2\text{CR}_1\text{R}_2\text{COO-})_n$, poly(pivalolactone) (PPL) has been the most extensively studied because of its technological importance.[1-3] The practical and technological interests appeared since the polymer has been commercially spun to give fibers.[1,2] Moreover PPL has been found to have reinforcing properties when prepared in copolymers of the general structure ABA where A represents a PPL block and B an elastomer, for example, poly(α-methyl-α-*n*-propyl-β-propiolactone) (PMPPL). The mechanical properties of PPL/PMPPL ABA copolymers were reported similar to those of commercial styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS) copolymers.[4]

More recently, it was shown that grafting of short ($M_n \sim$ 500–4000) chains of PPL onto various elastomeric backbone polymers, including ethylene–propylene–diene, alternating ethylene–ethyl acrylate copolymer, and poly(ethyl acrylate), produced a new type of thermoplastic elastomer with outstanding physical properties, such as solvent resistance resilience, abrasion resistance, and heat and aging stability.[5-9] ABA triblock copolymers containing 35–45% PPL made from polyisoprenes ($M_n \sim 40\,000$) could be melt-spun into fibers showing excellent mechanical properties.[10] In each case, the outstanding properties of these PPL-graft elastomers were related to the hard segments of PPL which act as cross-linking sites and reinforcing filler particles.

In view of the commercial importance of PPL, its thermal and crystalline properties have been investigated.[11-19] But surprisingly, its mechanical properties have not been studied despite the importance of this investigation in order to know the performance of PPL as a commercial film or fiber.

It is then the purpose of the present paper to investigate the viscoelastic behavior of PPL. On one hand, these measurements will lead to the determination of the glass transition temperature of PPL using stress–relaxation as well as dynamic methods. On the other hand, PPL is a highly crystalline material and little is known about the viscoelasticity of highly crystalline polymers. The results obtained in this study, along with investigations made on other crystalline polymers, may serve as a basis in checking up theoretical ideas in that area.

Experimental Section

The PPL sample (No. 100–36) used in this study was supplied by the Shell Laboratories in Amsterdam. Its viscosity average molecular weight, determined in a trifluoroacetic acid solution at 293 K, was 280 000 $\text{g}\cdot\text{mol}^{-1}$.[19] The polymer contained a small amount of stabilizer.

The polymer films were obtained from a laboratory press. The samples were melted at 523 K for 10 min and they were rapidly quenched in water at room temperature, annealed at 468 K for 6 h, and then used. Under these conditions, PPL is a highly crystalline material and it is uniquely found by X-ray diffraction in the α form which is characterized by a 2_1 helical conformation of the chains.[11-13] DSC measurements, using indium as calibration standard, gave an enthalpy of fusion of 118 $\text{J}\cdot\text{g}^{-1}$ which corresponds to 80% crystallinity. The specimen is very brittle reaching an ultimate elongation lower than 10% even above 440 K.

Relaxation measurements were carried out at different temperatures on an Instron tester (table Model 1130) which we used as a relaxometer. Before each measurement, the sample specimen was preconditioned at zero strain in the jaws of the relaxometer, at least 1 h at the desired temperature. All series of measurements were performed starting from the highest measuring temperature. It was found that under these conditions, the relaxation curves were reproducible. This result indicates that there is no change in the structure of the sample due to heat treatment. Moreover, the sample was found to be insensitive to relative humidity. For relaxation measurements, samples having a thickness of 90 μm were used. For dynamic mechanical measurements, thicknesses of the order of 60 μm were necessary.

In order to ascertain that the measurements were restricted in the linear range of viscoelasticity, two different tests were undertaken at 351 K. According to the hysteresis loop method,[20]

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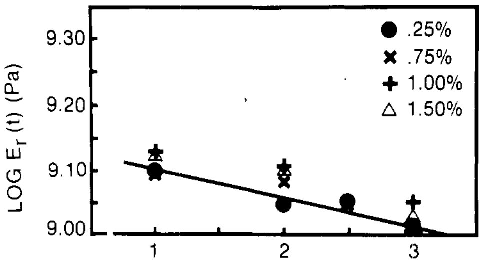

Figure 1. Test of linear viscoelastic limit at 351 K.

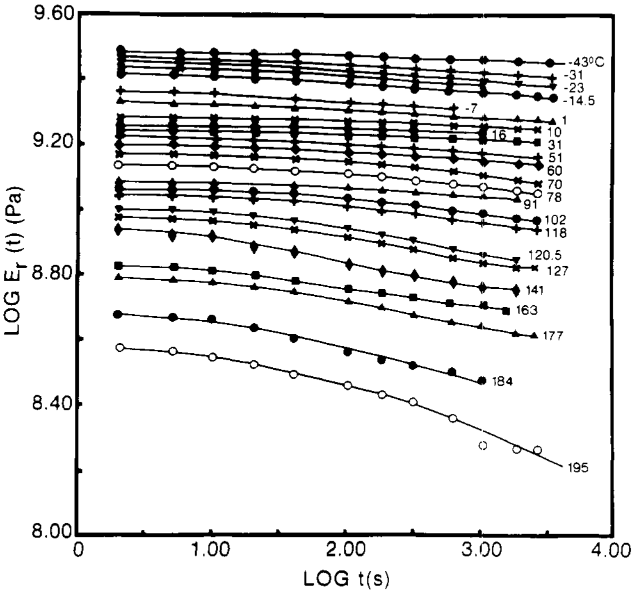

Figure 2. Stress-relaxation curves of poly(pivalolactone).

the viscoelasticity of PPL was approximated as linear from 0 to 1% elongation. From a test developed to verify the Boltzmann superposition principle[21] (Figure 1), it was concluded that levels of strain smaller than 1.5% correspond to the linear viscoelastic behavior. But all the relaxation experiments reported in this paper were done with 0.75% elongation.

Results and Discussion

1. Stress-Relaxation Data. Experimental data of stress relaxation at different temperatures, ranging from −20 to 195 °C, are shown in Figure 2, where the relaxation modulus $E_r(t)$ is plotted against time on a log-log graph. The modulus is high at most temperatures, which is characteristic of a semicrystalline polymer, or of a polymer below its T_g. However, in the T_g region, the decrease in modulus is much less important than that normally found for an amorphous polymer. The time-temperature superposition principle commonly used for amorphous polymers was applied to these results. At first, an arbitrary temperature T_0 whose value is 364 K was chosen. We used a theoretical correction factor $f(T)$ equal to $T_0\rho_0/T\rho$ for thermal expansion and for the temperature variation of elastic modulus due to rubber elasticity, where ρ_0 and ρ are the densities of the sample at temperatures T_0 and T, respectively. But we assumed the dependence of ρ with temperature to be negligible, so the effective correction factor was T_0/T. This correction was applied only for temperatures higher than 364 K for a reason that will be discussed in the next section. The curves for various temperatures were superposed to form a single composite curve or master stress-relaxation curve, as shown in Figure 3, by shifting each curve along the time axis only. A horizontal shift factor a_T was experimentally determined at each temperature and will be discussed in the next section of this paper. No vertical shifts were necessary in order to obtain satisfactory superposition.

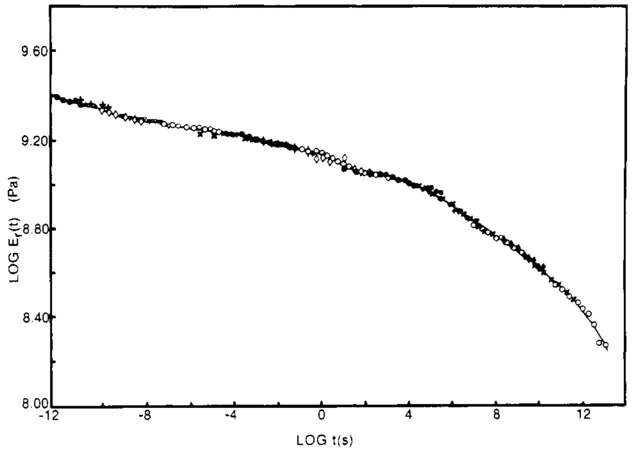

Figure 3. Master curve of stress-relaxation of PPL at 364 K.

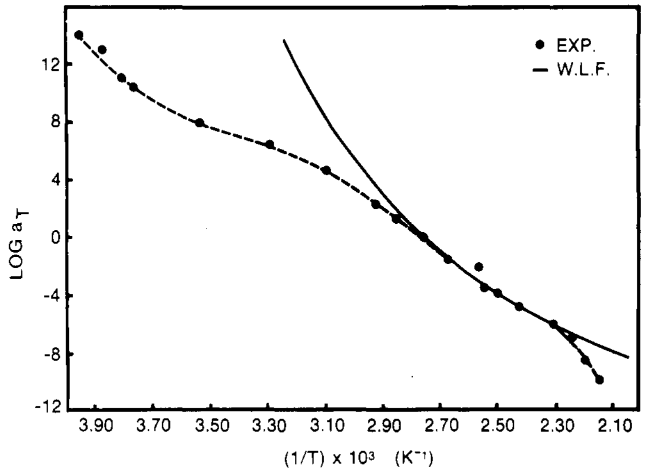

Figure 4. Experimental shift factors of PPL and WLF equation.

2. Shift Factor and Apparent Activation Energy. The logarithm of the experimental shift factor, a_T, is plotted against $1/T$ in Figure 4. The resulting curve was found to coincide with the well-known WLF equation[22] except at lower and higher temperatures where the observed values deviate systematically below the calculated curve. The WLF equation reads:

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + T - T_0} \qquad (1)$$

where a_T is the shift factor at the measuring temperature T, T_0 is the reference temperature, and C_1 and C_2 are constants having values of 15.5 and 115 K, respectively.[22] In the regions where deviations from the WLF equation occur, different relaxation processes are found. In the glassy zone, the relaxation process is due to thermal motion of the side chains or of localized small portions in the main chain. In the transition region, the relaxation process is due to the cooperative segmental diffusion of the entire molecule (micro-Brownian motion). Below T_g, the WLF theory is not applicable, so a different temperature correction should be used. A small theoretical correction has been suggested by McCrum,[23] but in general $f(T)$ is close to unity below T_g. Above T_g, the correction arises from the kinetic theory of rubber elasticity, so the correction factor is the same in the transition and rubbery regions even if the character of the relaxation processes is different in these two regions. It is postulated that the relaxation process in the rubbery zone is an intermolecular process due to the loosening of entanglements whereas the re-

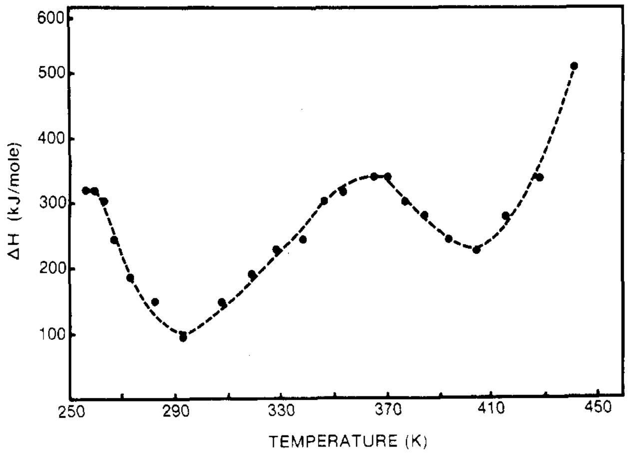

Figure 5. Apparent activation energy of PPL.

laxation process in the transition zone is an intramolecular process. These considerations explain the deviation from the WLF equation in the higher temperature range.

An apparent activation energy, ΔH, has been calculated from the data of the shift factor using the well-known equation

$$\Delta H = 2.3R\ \mathrm{d}(\log a_T)/\mathrm{d}(1/T) \tag{2}$$

where R is the gas constant. The $\log a_T$ vs. $1/T$ curve of Figure 4 was differentiated graphically and the results were substituted in eq 2 to evaluate ΔH at each temperature. Calculated values of ΔH shown in Figure 5 are then obtained and it is seen that they are temperature dependent. There is a maximum in this curve, $\Delta H_{\max}$, whose value is 343 kJ·mol^{-1}, at 365 K; this temperature is closely associated with the glass-transition temperature of the sample, and this temperature region is usually called the β relaxation transition zone. In a temperature range where a single relaxation process occurs, the activation energy associated with small amplitude motion of the chain increases with the temperature below T_g. Above T_g, the segmental cooperative diffusion (or micro-Brownian) process prevails and the activation energy decreases with temperature. Then the apparent activation energy has a maximum near T_g. The values of $\Delta H_{\max}$ reported in this work are of the same order of magnitude as those found in the literature by the stress-relaxation method. For example, values of 610 and 480 kJ·mol^{-1} have been found previously for racemic and optically active poly(α-methyl-α-n-propyl-β-propiolactone) (PMPPL), respectively.[24] The value obtained for PPL is slightly lower than those for PMPPL but this behavior is expected because the apparent activation energy increases with the size of side chains. A second transition zone, called γ, is observed in Figure 5 around 260 K. Its activation energy is 320 kJ·mol^{-1}, which is very close to the activation energy of the β process. The relaxation process associated with this γ transition will be discussed later in this paper.

3. Predicted Dynamic Properties. In order to predict dynamic data, the relaxation spectrum $H(t)$ of PPL was calculated from its relaxation master curve over 23 decades, using the first approximation method proposed by Schwarzl and Staverman[25]

$$H(t) = -\left.\frac{\mathrm{d}E_r(t)}{\mathrm{d}\ln t}\right|_{t=\tau} = -\left.\frac{E_r(t)\ \mathrm{d}\log E_r(t)}{\mathrm{d}\log t}\right|_{t=\tau} \tag{3}$$

The relaxation spectrum thus obtained is shown in Figure 6 where it is plotted with a linear ordinate scale. Over the time scale covered, the spectrum is flat; its intensity varies between $10^{7.80}$ and $10^{7.40}$ Pa and it develops a complicated fine structure on the longer relaxation times side. These features are characteristic of a highly crystalline polymer.[22]

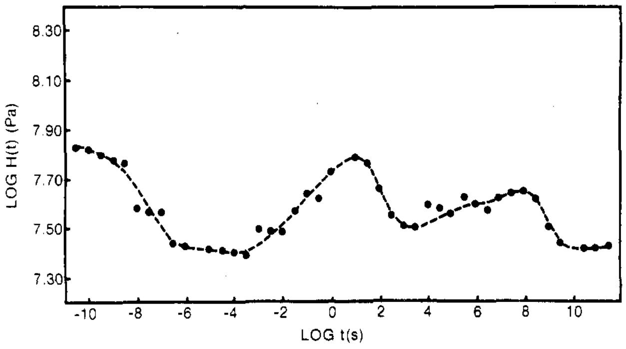

Figure 6. Relaxation spectrum of PPL.

Several mechanical data were computed using the relaxation spectrum. The real part of the complex modulus $E'(\omega)$ was approximated using an equation proposed by Catsiff and Tobolsky:[26]

$$E'(\omega) = E_r(t)|_{t=1/\omega} + \gamma(m)H_{2b}(\log t)|_{t=1/\omega} \tag{4}$$

where

$$H_{2b}(\log t) = -\left.\frac{\mathrm{d}\ E_r(t)}{\mathrm{d}\log t}\right|_{t=\tau} \Big/ \Gamma(1+m) \tag{5}$$

$$m = -\frac{\mathrm{d}}{\mathrm{d}\log t}\left\{\log\left[-\frac{\mathrm{d}\ E_r(t)}{\mathrm{d}\log t}\right]\right\} \tag{6}$$

$$\gamma(m) = 0.4343\left[\frac{\pi}{2}\csc\frac{m\pi}{2} - \Gamma(m)\right] \tag{7}$$

and Γ is the "gamma" function. In the present case, the second term of the right-hand side of eq 4 is negligibly small (less than 1% of the first term) and this second term can be omitted. So we assume:

$$E'(\omega) \approx E_r(t)|_{t=1/\omega} \tag{8}$$

Using the so-called zeroth-order approximation, one finds that the imaginary part of the complex modulus $E''(\omega)$ is related to the relaxation spectrum by the following equation.[25]

$$E''(\omega) = \frac{\pi}{2}H(\log t)|_{t=1/\omega} \tag{9}$$

Finally the mechanical loss tangent is given by:

$$\tan\delta(\omega) = E''(\omega)/E'(\omega) \tag{10}$$

Substitution of eq 8 and 9 into 10 gives the values of the mechanical loss tangent. The time–temperature superposition principle data have then been substituted in eq 5 and 6 to obtain the loss modulus, E'', and the storage modulus, E', values as a function of temperature. In Figure 7, E' and E'' are plotted against temperature. One observes an absorption peak of E'' occurring at 370 K and a dispersion of E' in the same temperature range. Based on the results of Figure 5, this peak is associated to the glass-transition process. One also observes in the E'' curve part of an absorption peak around 265 K. In Figure 8, the predicted tan δ curve is plotted against temperature. The absorption peak due to the glass transition occurs at 372 K; this value is in good agreement with the observed location of $\Delta H_{\max}$ at 365 K and that of E'' at 370 K. A small peak probably related to a secondary relaxation process is seen around 270 K; its nature will be discussed in the next section.

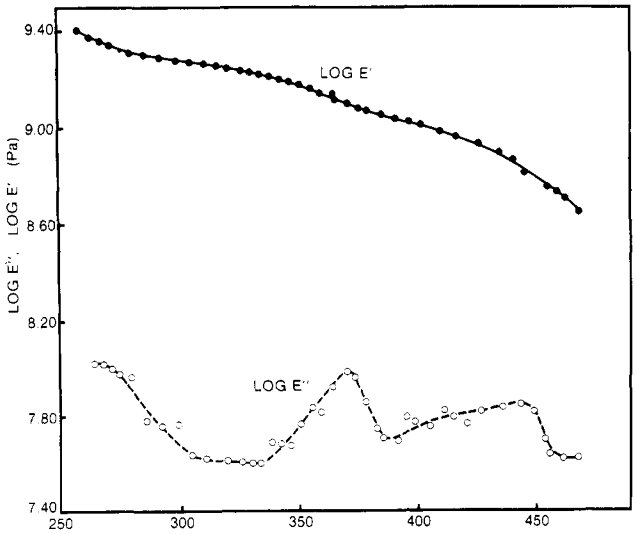

Figure 7. Predicted storage and loss moduli of PPL.

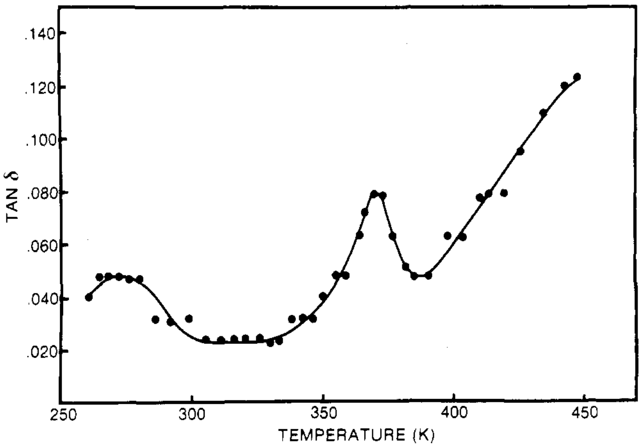

Figure 8. Predicted tan δ curve of PPL.

4. Observed Dynamic Data. In order to complete the viscoelastic data of PPL, a dynamic-mechanical analysis was done using a Rheovibron DDV-II apparatus (Toyo Baldwin Co.). The observed tan δ data were corrected according to Massa's equation.[27,28] Values at 110 Hz are presented in Figure 9, curve a. A large peak appears around 287 K, followed by a shoulder of small intensity around 373 K. Based on our stress-relaxation analysis, the shoulder at 373 K is related to the glass-transition temperature of the sample (β process) and the large peak at 287 K is associated with another relaxation process (γ transition). It is assumed that the γ peak is related to the crystalline portion of the sample since this peak is of very high intensity and that the PPL sample is 80% crystalline. In order to verify this hypothesis, a second sample with a lower degree of crystallinity (71%) was prepared. When the degree of crystallinity decreases, the intensity of the peaks due to the crystalline phase must also decrease. In fact, one observes a significant decrease of the intensity of the peak at 287 K in Figure 9, curve b. However, the intensity of the shoulder does not seem to increase. This is probably due to the fact that PPL is a highly crystalline polymer and that the peak at 370 K is the result of having a small β peak superposed to the onset of the large γ peak. Even if the decrease in the degree of crystallinity is perceptible, the total amount of the amorphous material is still too small in the second sample to contribute significantly in the increase of the peak due to T_g. We should mention here that our values are in complete disagreement with earlier measurements made by Allegrezza[4] on a PPL sample. In his work, Allegrezza found no evidence of a peak below 373 K. This peak is however obvious from our work.

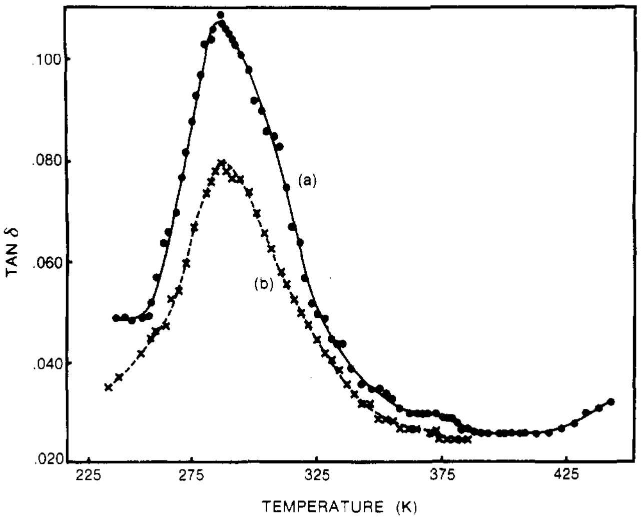

Figure 9. Observed tan δ curves of two PPL samples with different thermal histories, at 110 Hz: (a) same sample as used in the other parts of this work; (b) sample having a lower degree of crystallinity.

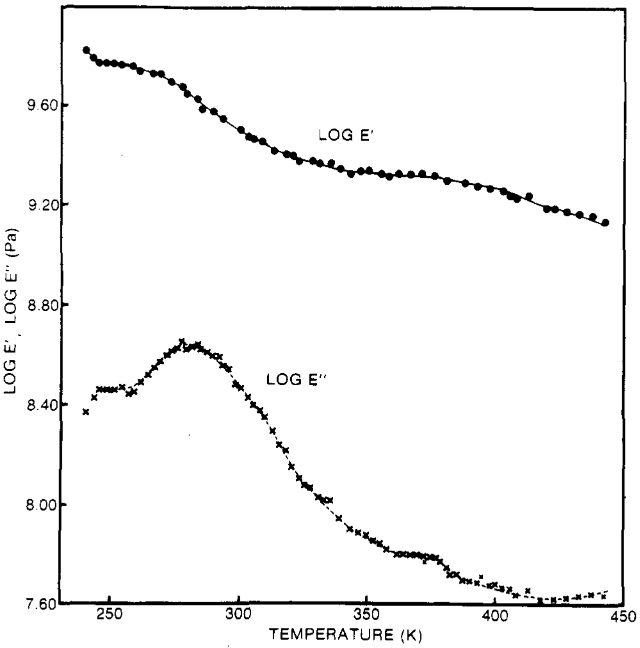

Figure 10. Experimental storage and loss moduli of PPL.

In Figure 10, the experimental values of E' and E'' are plotted against temperature. The predicted dynamic properties (Figures 7 and 8) are slightly lower than the observed ones, but the overall agreement is fairly good. The locations of the absorption peaks in Figures 9 and 10 are found at higher temperatures, which is unavoidable when comparing results obtained from dynamic and static methods.

The apparent activation energies associated with the γ and β processes were calculated using Arrhenius' equation:

$$F = F_0 e^{-\Delta H/RT} \tag{11}$$

where F is the measuring frequency, F_0 is the frequency when T approaches infinity, and T is the temperature corresponding to a maximum in the tan δ curve at measuring frequency F. Values of 212 and 219 kJ·mol^{-1} were found for the γ and β processes, respectively.

However, it is unusual that two different transitions have almost the same values of activation energies. Usually the activation energy associated with the γ process is very small when compared to the energy associated with the β process, except when the transition phenomenon involves a relaxation in the crystalline phase like that found in poly(tetrafluoroethylene) at room temperature.[29] But in the latter case, the transition implied a change of crystalline structure. From our tan δ measurements (Figure 9), the γ peak is certainly a crystalline dispersion peak for its property to increase its intensity with increase of crystallinity, and the high activation energy of the γ process suggests a crystalline transition. However, X-ray powder measurements made on the PPL sample at temperatures above and below the γ transition temperature do not show any evidence for the sort of change observed in poly(tetrafluoroethylene).

The tan δ measurements made at temperatures lower than 233 K did not reveal any other transition peak, contrary to the case of poly(α-methyl-α-*n*-propyl-β-propiolactone).[24]

Conclusion

The present work on poly(pivalolactone) showed that the simple time–superposition principle or Ferry's reduction method can be successfully applied to the highly crystalline PPL under suitable conditions, when the polymer is isotropic and insensitive to relative humidity and the measurements restricted to very low elongations. In building up the relaxation master curve of PPL, no vertical shift was required. This is also the case for poly(trifluorochloroethylene) and isotactic polypropylene. For these polymers, the simple time–temperature superposition is applicable.[29] However, this behavior is in contrast with the one observed for Nylon 6, polyethylene, and poly(tetrafluoroethylene).[29] In Nylon 6, the simple time–temperature superposition is applicable to relaxation curves obtained at 0 and 75% relative humidities, but an appropriate vertical shift is necessary to surperimpose these two relaxation master curves. In polyethylene, vertical translation originates from the change of the degree of crystallinity during the course of relaxation measurements. For poly(tetrafluoroethylene), the superposition method becomes invalid at 19 °C; this is due to transition phenomena involving a change in the structure of the sample. In our case, the PPL sample is found to be insensitive to relative humidity. Moreover, all the measuring temperatures are lower than the original annealing temperature. Then the viscoelastic properties of PPL at different temperature correspond to rheological responses at the same degree of crystallinity. It is therefore possible to compose a smooth relaxation master curve using the simple time–temperature superposition.

From static and dynamic methods, two absorption peaks were determined. The high-temperature peak corresponded to the β mechanism commonly assigned to the amorphous phase of a polymer; its intensity was low. The low-temperature peak was related to a crystalline transition in the sample (γ peak). From measurements of $\Delta H_{\max}$, E'', and tan δ, an average value of 369 K was found for the glass-transition temperature of PPL. A value of about 373 K was found at 110 Hz from the dynamic loss tangent measurements. These values are in complete disagreement with that of 263 K reported by Oosterhof,[2] but since Oosterhof does not give any details about its experimental procedure, any comparison is difficult. A possible explanation of the discrepancy may lie in a mix up between the large γ peak and the very small β peak which we have shown to occur at lower temperature, but our results agree with that recently reported by Allegrezza et al.[30]

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