(15) T. M. Birshtein, E. B. Zhulina, and A. M. Skvortsov, *Biopolymers*, in press.
(16) A. Litan and S. Lifson, *J. Chem. Phys.*, **42**, 2528 (1965).
(17) D. Poland and H. A. Scheraga, *J. Chem. Phys.*, **45**, 1456 (1966).
(18) A. M. Skvortsov, T. M. Birshtein, E. B. Zhulina, and A. A. Gorbunov, *Vysokomol. Soedin., Ser. A*, **18**, 2097 (1976).
(19) F. W. Wiegel, *J. Phys. A; Math., Nucl. Gen.*, **10**, 299 (1977).
(20) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943).
(21) G. Pôlya, *Math. Ann.*, **84**, 149 (1921); E. W. Montroll in "Applied Combinatorial Mathematics", E. Beckenbach, Ed., Wiley, New York, 1964, p 9; W. Feller, "An Introduction to Probability Theory and its Applications", Wiley, New York 1957.
(22) A. M. Skvortsov, E. B. Zhulina and T. M. Birshtein, *Mol. Biol. (Moscow)*, **11**, 380 (1977); **12**, 472 (1978).
(23) E. B. Zhulina, A. M. Skvortsov, and T. M. Birshtein, *Biopolymers*, in press.

Mechanical Properties of Racemic Poly(α-methyl-α-n-propyl-β-propiolactone)

Joseph Noah and Robert E. Prud'homme*

Groupe de recherche sur les macromolécules, Département de chimie, Université Laval, Québec 10, P.Q. G1K 7P4, Canada. *Received August 24, 1978*

ABSTRACT: Stress–relaxation and dynamic mechanical behavior of the racemic homopolymer of α-methyl-α-n-propyl-β-propiolactone (PMPPL) have been investigated. Using Ferry's reduction method, experimental shift factors that satisfactorily agree with the WLF equation in the transition region were determined. The apparent activation energy of the sample is temperature dependent, and it passes through a maximum near the glass-transition temperature whose value has been found to be 270 ± 2 K. The relaxation spectrum was calculated according to the first approximation method proposed by Schwarzl and Staverman. The slope of its wedge portion is equal to –0.28, which is the type of value often found for a semicrystalline polymer. In addition to the β transition region, a second transition zone is revealed at low temperatures by the dynamic mechanical measurements. This transition is probably due to the mobility of the propyl side group of the polymer or to a restricted motion of its main chain. Dynamic mechanical measurements were also conducted on a second PMPPL sample which is optically active. The tan δ, E', and E'' curves of the latter sample are very similar to those of the racemic polymer. These results seem to indicate that the mechanical properties are not much influenced by the change of structure of the polymer brought up by the optical activity, except for small changes which can be associated to the difference in the degree of crystallinity between the two samples.

Poly(pivalolactone) [$(CH_2C(CH_3)_2COO)_n$; PPL] has been shown to be an interesting polymer since it can be produced in the form of fibers having high melting points.[1-4] It has however several undesirable properties which are related to a crystal–crystal transition occurring upon stretching.[2,3,5] In order to avoid this problem, several studies have been devoted to the preparation of copolymers of PPL with a comonomer of lower degree of crystallinity. In particular, poly(α-methyl-α-n-propyl-β-propiolactone) [$(CH_2C(CH_3)(CH_2CH_2CH_3)COO)_n$; PMPPL] has been used.[6,7] Some attempts have also been made to prepare graft copolymers of PMPPL on elastomers.[8] In such materials, PMPPL does not present the crystal–crystal phase transition which occurs in the homopolymer,[9] similar to the PPL case. In order to explain the mechanical properties of such materials, it is necessary to determine first the mechanical properties of the PMPPL homopolymer.

It is then the purpose of the present paper to study the linear viscoelastic behavior of PMPPL homopolymer in order to obtain its rheological functions and also to determine its glass-transition temperature, T_g. This goal will be achieved by using the stress–relaxation measurements as well as dynamic mechanical methods.

Since a PMPPL sample showing optical activity was also available,[10] the dynamic mechanical measurements were conducted on this second sample as well.

Experimental Section

Two samples were used in this study. The racemic PMPPL, hereafter called PMPPL-R, was prepared using standard anionic polymerization procedures and a tetrahexylammonium benzoate initiator. It did not present any specific rotation when run in chloroform, at a 0.4% concentration, at 25 °C, and using a wavelength of 546 nm. Its molecular weight was found to be 88 000 by osmometry. The optically active PMPPL, hereafter called PMPPL-OA, was prepared using a 1–1 mixture of diethylzinc–(R)-(–)-3,3-dimethyl-1,2-butanediol "stereoelective" initiator. It gave a value of specific rotation of –0.6 in the same conditions as those used for the PMPPL-R sample. Its molecular weight was 26 000. These two samples were respectively samples No. 7 and 3 of a previous publication.[10]

Both polymers were cast into thin films by pouring their chloroform solutions in a crystallizing pan, followed by gradual evaporation at room temperature. The resulting films were dried at 318 K in a vacuum oven for 24 h. They were annealed at 335 K during 16 h and then used. Under these conditions, both polymers are semicrystalline and are found by X-ray diffraction in the α form, which is characterized by a 2_1 helical conformation of the chains.[9] DSC measurements yielded an enthalpy of fusion of 8.2 and 12.6 $J \cdot g^{-1}$ for PMPPL-R and PMPPL-OA, respectively. Even if the enthalpy of fusion of pure PMPPL crystal is not known, such a value certainly corresponds to a low degree of crystallinity probably of the order of 10%.[10] Melting points, T_m, of 366 and 375 K were determined for PMPPL-R and PMPPL-OA, respectively. These specimens reach ultimate elongations of about 750%. The strains at yield point are respectively 17 and 15% for the racemic and the optically active polymer. All these measurements indicate a significant increase in the degree of crystallinity of the optically active polymer as compared to the racemic one.

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. No dependence of the viscoelastic properties on relative humidity was noticed.

The linear viscoelastic theory implies no permanent change in microstructure, which could occur with deformation and cause a permanent hysteresis on repeated loading. To ascertain that

0024-9297/79/2212-0721$01.00/0

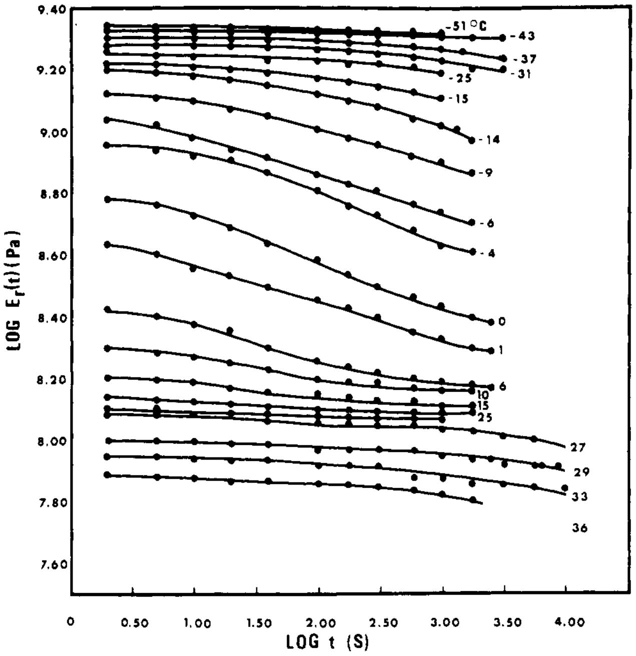

Figure 1. Stress-relaxation curves of racemic MPPL polymer.

we were in the linear viscoelastic range, two different tests were undertaken. First, the hysteresis loop method was applied.[11] From 0 to 2.5% elongation, no permanent set was recorded for both samples. The second test was designed to check the homogeneity and the linearity of the stress-strain relations. This test is a consequence of the Boltzman superposition principle which stipulates that relaxation moduli must be independent of strain magnitude.[12] Typical results indicate that log $E_r(t)$ is constant within 0.02 for strains smaller than 2.5%. This order of magnitude for the limit of linear viscoelasticity has been observed for other crystalline polymers. Nevertheless, all the relaxation experiments reported in this paper were done with 0.75% elongation.

Results and Discussion

1. Stress-Relaxation Data. Typical data of stress-relaxation of PMPPL-R at different temperatures ranging from -51 to 36 °C are shown in Figure 1, where the relaxation modulus $E_r(t)$ is plotted against time on a log-log graph. The relaxation modulus varies from the glassy value of about 10^9 Pa to the rubbery value of 10^8 Pa, passing through a transition region where it decreases sharply within a narrow range of temperature. Using Ferry's reduction method,[13] all the results were reduced to an arbitrary temperature T_0, whose value is 274 K for PMPPL-R. We neglected a correction for thermal expansion and for temperature variation of elastic modulus due to rubber elasticity. We assumed $T_0\rho_0/T\rho$ to be unity. ρ_0 and ρ are the densities of the sample at temperatures T_0 and T, respectively. Thus we composed the smooth master curve of stress-relaxation shown in Figure 2 for PMPPL-R. All the relaxation curves satisfactorily superposed by sliding them along the time axis only using an experimental shift factor a_T, at each temperature. Only a few points deviate from the master curve, and these deviations are believed to be due to experimental scatter.

At short times (log $t < -4$), the modulus values are typical of those usually found in the glassy region. At intermediate times ($-4 <$ log $t < 4$), the decrease in modulus is due to the glass transition. At long times ($4 <$ log $t < 8$), a plateau region is observed. For amorphous polymers, this plateau is generally associated with a loosening of entanglements as a result of thermal expansion. The plateau region continues until the entanglements are completely untied. When this happens, a catastrophic decrease of modulus is seen (flow zone). For semicrystalline polymers having a relatively high degree of crystallinity, the plateau zone is also characterized by a small decrease of modulus, but the time interval where it happens is generally larger than that found in amorphous polymers. The plateau region in semicrystalline polymers is rather associated to the thermal expansion of its crystalline portion. The plateau region ends when premelting occurs. At this point, a rapid decrease of modulus with time is observed. In semicrystalline polymers, loosening of the entanglements of the amorphous portion of the sample also occurs, but this phenomenon is hidden behind the larger modulus and modulus changes of the crystalline portion. However, in samples having low degrees of crystallinity, both phenomena can be observed.[14] This is exactly what happens for PMPPL. In the plateau region, at times shorter than (log t) = 8, a regular decrease of modulus is observed similar to that of polymers of high degree of crystallinity. But at (log t) = 8, a change in slope occurs. The decrease in modulus then becomes more rapid.

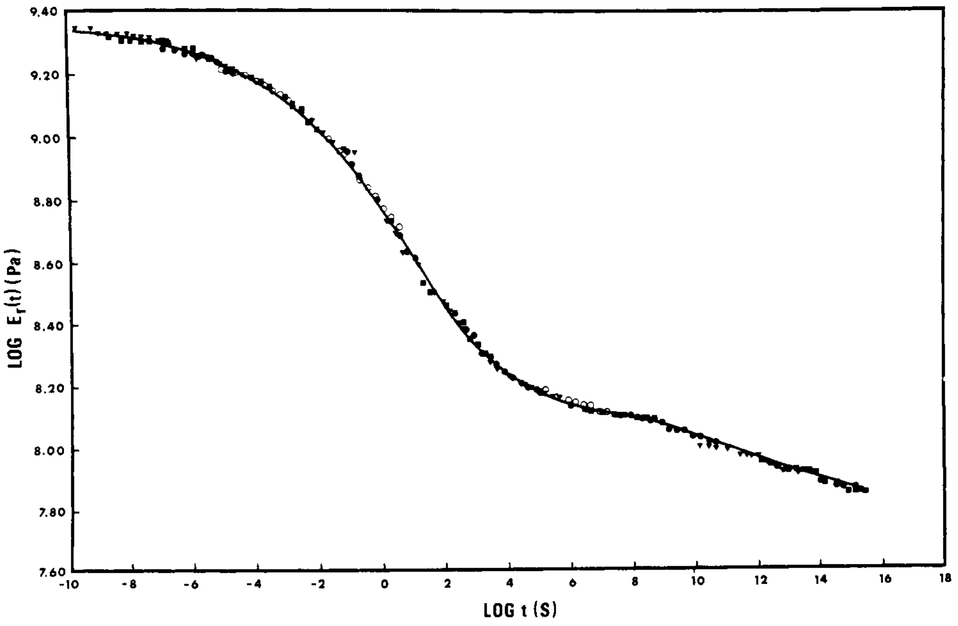

Figure 2. Master curve of stress-relaxation of racemic MPPL polymer at a reference temperature of 274 K.

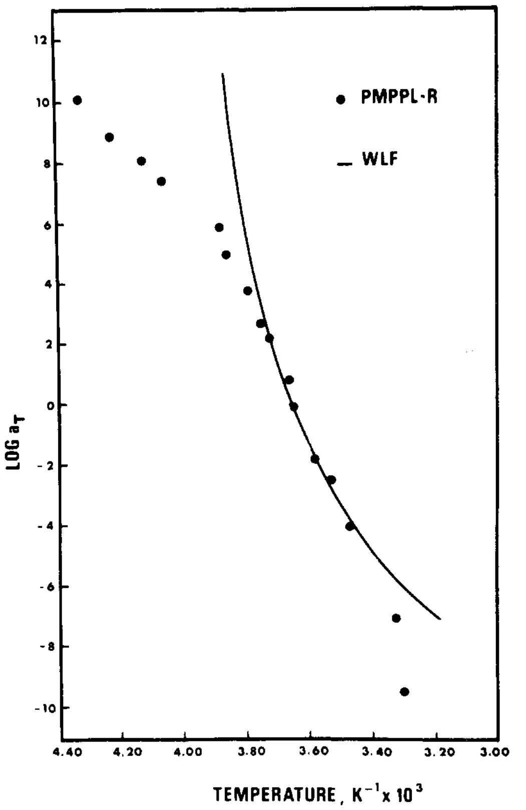

Figure 3. Experimental shift factors of the racemic MPPL polymer and the WLF equation.

At this point, the amorphous part of the sample has reached the time where its entanglements are untied. The change in modulus of the amorphous part then becomes important, and it contributes significantly to the total modulus observed. A change in slope is then seen.

Similar results have been obtained previously by Mercier and Groeninckx[14] who studied the relaxation spectra of polycarbonates having degrees of crystallinity between 0 and 20%. A change in slope similar to that observed for PMPPL is clearly seen at (log t) = 4 for samples having degrees of crystallinity of less than 11.5%. This break is then related to the non-negligeable contribution of the flow of the amorphous portion of the polymer to the total modulus. A similar interpretation holds for PMPPL.

2. Shift Factor and Apparent Activation Energy. The logarithm of the experimental shift factor a_T is plotted against $1/T$ in Figure 3. Except in the lower and higher temperature ranges where there are inflection points, the resulting curve coincides well with the well-known WLF equation:[13]

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

where a_T is the shift factor at the temperature T, T_0 is the reference temperature, and C_1 and C_2 are constants having values of 12.5 and 32 K, respectively. C_1 and C_2 were determined by using the classical graphical method suggested by Ferry.[13] The deviation from the WLF equation in the lower temperature range seems to be a common feature for all polymers. It was previously noted for other amorphous and crystalline polymers.[13] As was pointed out by Ferry et al. when studying the poly(methacrylates) series,[15,16] the relaxation process in the glassy zone is due to thermal motion of the side chains or of localized small portions in the main chain, whereas the relaxation process in the transition region is due to the micro-Brownian movement of the molecule or to short-range cooperative segmental diffusion. So it is understandable that the experimental shift factor log a_T diverges from the WLF equation in the lower temperature range since the WLF equation applies in a temperature zone ranging from T_g to T_g + 100 where the second relaxation process prevails.

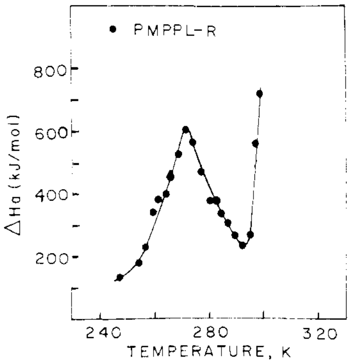

Figure 4. Apparent activation energies of the racemic MPPL polymer.

Similar considerations account for the deviation from the WLF equation in the higher temperature range. The relaxation process in the plateau region differs from that in the transition region. It is postulated that the relaxation process in the plateau zone is an intermolecular process due to the loosening of entanglements, whereas the process in the transition zone is an intramolecular process. It is reasonable to think that the validity of the WLF equation is doubtful in the plateau region even if a smooth master curve is obtained by shifting relaxation curves along the time axis.[13]

The above argument results in having agreement between the WLF equation and the experimental shift factor in a region defined between T_g and T_g + 100 for linear amorphous polymers. The presence of branching, cross-linking, or crystallinity considerably narrows this region. In Figure 3, the agreement is reduced to a range of 30 °C due to the crystallinity of the sample.

It is also possible that the deviations of log a_T from the WLF prediction be a consequence of the correction factor $f(T)$ which was not applied below T_g. In fact, no appropriate theory permits one to make this correction in the glassy state. In several instances, it is not important. But when the modulus-time dependence is as slight as it is in Figure 1 at temperatures lower than 258 K, the correction may become important and influence significantly the shift factors determined.

By treating the relaxation process as a chemical reaction, an apparent activation energy ΔH, which measures the stiffness of the chain against segments motion, can be calculated from the data of the shift factor using the well-known equation:

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

where R is the gas constant and the factor d log a_T/d$(1/T)$ is obtained by graphical differentiation. The values of ΔH calculated for PMPPL-R are shown in Figure 4, where they are plotted against temperature. The activation energy is not independent of temperature. It has a sharp maximum, $\Delta H_{\max}$, which is 610 kJ·mol^{-1} at 271 K for PMPPL-R. The maximum in ΔH suggests that the molecular motion changes at this point, and this temperature is closely related to the glass-transition temperature T_g. Below T_g, only short-range molecular motions associated with rotations of moderately small amplitude around chemical bonds are permitted. With increasing temperature, the amplitude of these rotations becomes larger, and the energy required to favor these rotations

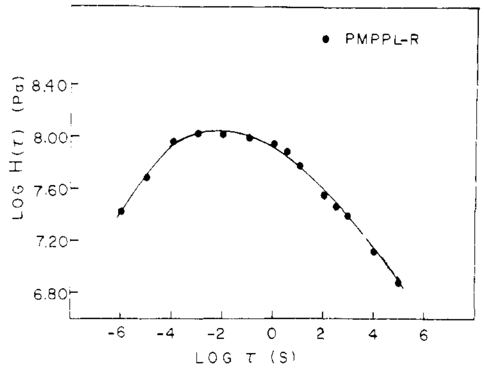

Figure 5. Relaxation spectrum of the racemic MPPL polymer at a reference temperature of 274 K.

increases. Above T_g, the molecule moves, and the energy necessary for these movements decreases with increasing temperature. Then the apparent activation energy is the result of two distinct contributions and has a maximum near T_g, which is the point where the long-range movements start, and then it is the point where the first molecular process is replaced by the second one. The value of ΔH_{max} reported above is of the same order of magnitude as those found in the literature by the stress-relaxation method. For example, values between 460 and 920 kJ·mol^{-1} are found for the methyl methacrylate-methyl acrylate copolymers[17] and values between 460 and 940 kJ·mol^{-1} are reported for acetylated poly(vinyl alcohols).[18]

3. Distribution of Relaxation Times. The distribution of relaxation times $H(\tau)$ or relaxation spectrum of PMPPL-R was obtained from its master curve using the first method of approximation proposed by Schwarzl and Staverman[19]

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

The spectrum is shown in Figure 5 on a log–log graph. Its shape consists of a high intensity plateau at shorter times and a wedge type portion with a slope of −0.28 at larger relaxation times. For an amorphous polymer, the slope of the wedge has often been observed between −0.50 and −0.66 depending upon the rigidity of the chain.[17] For a crystalline polymer, this slope is larger than −0.50, and the magnitude of the deviations seems proportional to the degree of crystallinity of the sample.[18]

4. Observed Dynamic Data. In order to confirm the stress–relaxation analysis of the PMPPL sample, dynamic mechanical properties were measured on a Rheovibron DDV-II apparatus (Toyo Baldwin Co.), at four different frequencies ranging from 110 Hz to 3.5 Hz, as a function of temperature. The experimental values of tan δ were corrected according to Massa's equation[20,21] and are presented in Figure 6. One observes a large peak around 300 K which is obviously related, based on our stress–relaxation measurements, to the T_g of the sample and part of a small peak, around 130 K, associated to a secondary relaxation of the polymer. The PMPPL-OA tan δ results, obtained at 110 Hz, are also included in this graph. Only minor differences are observed in the location of the tan δ peaks of PMPPL-R and PMPPL-OA. For example, the maxima are found at 303 and 302 K, respectively. In addition, the PMPPL-R peak is more intense than the PMPPL-OA one. This difference is certainly related to the difference in the degree of crystallinity of the two samples. The PMPPL-R sample has a lower degree of crystallinity, and since the intensity of the T_g peak is directly proportional to the amorphous content of the polymer, the PMPPL-OA sample peak needs to have a lower magnitude than the PMPPL-R one. In Figure 7, the values of E' and E'' of PMPPL-R, as obtained experimentally at 110 Hz, are plotted against temperature. A small increase in E'' around 130 K is observed, similar to that seen in the tan δ curve, Figure 6. This increase will be discussed in the next section of this paper. Above 273 K, a maximum in E'' along with a regular decrease in E' are observed. Both changes are due to the glass transition of the sample.

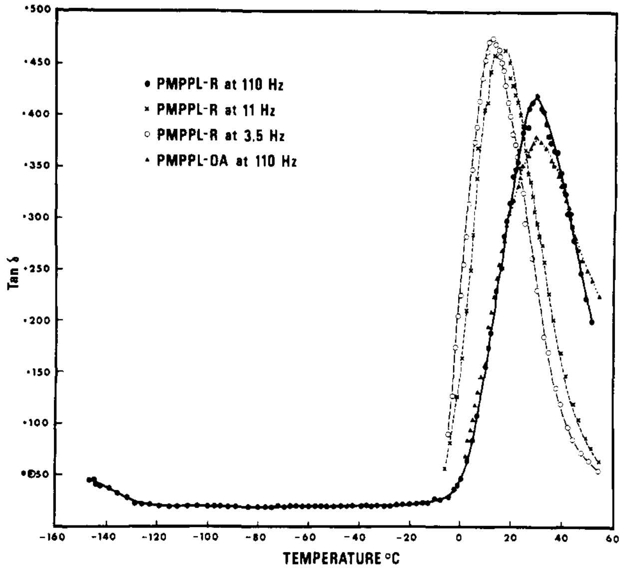

Figure 6. Observed tan δ curves of racemic and optically active MPPL polymers.

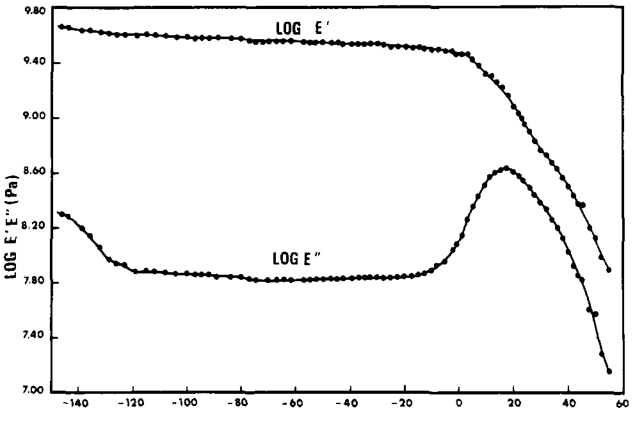

Figure 7. Elastic and loss moduli of the racemic MPPL polymer at 110 Hz.

An apparent activation energy of the process was calculated, using Arrhenius' equation:

$$F = F_0 e^{-\Delta H/RT} \tag{4}$$

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. The least-squares method applied to the results yielded an apparent activation energy of 132 kJ·mol^{-1} for PMPPL-R and 127 kJ·mol^{-1} for PMPPL-OA. The value found for the optically active polymer is then slightly smaller than that measured for the racemic one. These values are of the same order of magnitude as those reported in the literature, using a dynamic method, for other semicrystalline polymers.[22-24] But these values are considerably lower than the one obtained from the stress–relaxation measurements. A similar discrepancy was noted when comparing published results.[17,22,23] A partial explanation of the disagreement between the two kinds of methods may be due to the fact that the cyclic loading in the dynamic experiment builds up heat in the sample. Since the amount of heat generated depends heavily on the frequency used, the dynamic activation energies seem to be systematically slanted toward low values. Another alternative explanation would be to consider that in the dynamic experiment, since T_g is displaced at higher temperatures, one measures the activation energy corresponding to that higher temperature which is according to Figure 4 significantly lower than that found at the T_g of the static experiment. This latter explanation was formerly suggested when considering the relaxation β process of poly(chlorotrifluoroethylene).[22]

Conclusion

The present study of PMPPL has shown by static and dynamic methods of investigation an absorption peak corresponding to the β mechanism which is commonly assigned to the amorphous phase of the polymer. From the $\Delta H_{\max}$ curve, a value of 271 K is found for the glass-transition temperature of PMPPL-R. From the dynamic data recorded at 110 Hz, T_g values of 303 and 302 K are obtained for the PMPPL-R and the PMPPL-OA samples, respectively. It is expected to have a higher T_g by the dynamic method as compared to the one obtained by the static method since different frequencies were used in the two sets of experiments. For PMPPL-R, a value of 266 K was reported by Allegrezza[6] using a DSC technique while we obtained 269 K by the same method. The agreement is certainly satisfactory.

From dynamic measurements, a small rise in intensity has been observed at 130 K suggesting a peak at a somewhat lower temperature. Due to its position and intensity, this peak is probably associated with a γ process. It is not likely related to the crystalline phase of the polymer because the PMPPL-R has a very low degree of crystallinity. It is probably associated with a restricted motion of the main chain of the polymer (crankshaft mechanism),[25] or it is associated with the motion of the side chains. Further studies at higher frequencies are necessary to elucidate this point.

It was expected that a larger T_g for the optically active sample than for the racemic one would be found since a 13 K difference is found in their equilibrium melting points T_m^0.[10] The lower molecular weight of the optically active sample may contribute to the reversal. If PMPPL shows the same T_g–molecular weight dependence as does polystyrene, one would expect an increase in T_g of about 5 °C for the optically active polymer[26] if it had the same molecular weight as the racemic one. This would bring T_g of PMPPL-OA larger than that of PMPPL-R. But the difference between the two T_g would still be smaller than that between the T_m^0. This result suggests that T_g is less sensitive than T_m^0 to changes in stereoregularity which go along changes in optical activity.

It was also expected that differences in the relaxational mechanical properties of the PMPPL-OA sample as compared to the racemic polymer would be found. Consequently, a complete stress–relaxation study of the PMPPL-OA sample was made, but the results are not reported herein since they are very similar to those of the racemic sample, except for some small differences which can be entirely explained by the difference in the degree of crystallinity between the two samples.

Significant differences in properties between the PMPPL-R and the PMPPL-OA samples are observed by calorimetry. The PMPPL-OA polymer has a higher melting point, a larger crystallization rate, and a higher enthalpy of fusion than the PMPPL-R sample.[10] These results were interpreted in terms of the presence of short stereoblocks of *d* and *l* sequences in the racemic polymer, sequences which become larger in the optically active sample.[10] On the other hand, Marchessault et al. indicated that the X-ray diffraction pattern of the racemic PMPPL sample could be interpreted in terms of a syndiotactic model consisting of alternating *d* and *l* sequences.[8]

In any event, if the polymer contains stereoblocks, they are certainly short. Attempts have been made to determine the stereostructure of the polymer by NMR analysis.[10] But so far, the ^{13}C and ^{1}H NMR techniques have not revealed any important differences in structures between the two samples. Additional attempts are now being made using higher resolution NMR and shift reagents.

At the present time, we cannot determine quantitatively the degree of optical purity of PMPPL-OA since the pure enantiomeric polymer is not available. But its low value of specific rotation is not an indication of a low degree of optical purity. It can as well be an indication of the low value of optical rotation of the pure enantiomer. Even if we cannot make any quantitative statement about this point at the present time, it is interesting to know that a poly(α-phenyl-α-ethyl-β-propiolactone) sample (PPEPL) with high optical purity (prepared from a monomer mixture whose composition is 90% (+) and 10% (−)) has been made and that this polymer has a value of specific rotation of 1.04 at 546 nm (27.28). At a lower wavelength, for example at 405 nm, a value of 14.9 is found for PPEPL, and a value of −14.5 is observed for PMPPL-OA. This comparison does not prove the high optical purity of the PMPPL-OA sample, but it suffices to indicate that its specific rotation value is not necessarily related to low optical purity.

Acknowledgment. The authors are very grateful to Dr. N. Spassky and A. Leborgne, from the Laboratoire de chimie macromoléculaire of the Pierre et Marie Curie University, for providing them the PMPPL-OA sample used in this study. They also thank the National Research Council of Canada and the Ministry of Education of the Province de Québec (FCAC program) for the research grants that supported this work.

References and Notes

(1) N. R. Mayne, *CHEMTECH*, 728 (December 1972); N. R. Mayne, *Adv. Chem. Ser.*, **No. 129**, 175 (1973).
(2) F. W. Knoblock and W. O. Statton, U.S. Patent 3 299 171 (1967).
(3) British Patent 1 172 619 (1967).
(4) H. A. Oosterhof, *Polymer*, **15**, 49 (1974).
(5) R. E. Prud'homme and R. H. Marchessault, *Macromolecules*, **7**, 541 (1974).
(6) A. E. Allegrezza, Ph.D. Thesis, University of Massachusetts, Amherst, 1972.
(7) A. E. Allegrezza, R. W. Lenz, J. Cornibert, and R. H. Marchessault, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2617 (1978).
(8) R. H. Marchessault, J. St.-Pierre, M. Duval, and S. Perez, *Macromolecules*, **11**, 1281 (1978).
(9) J. Cornibert, R. H. Marchessault, A. E. Allegrezza, and R. W. Lenz, *Macromolecules*, **6**, 676 (1973).
(10) N. Spassky, A. Leborgne, M. Reix, R. E. Prud'homme, E. Bigdeli, and R. W. Lenz, *Macromolecules*, **11**, 716 (1978).
(11) R. J. Farris in "Polymer Networks: Structural and Mechanical Properties", A. J. Chompff and S. Newman, Eds., Plenum, New York, 1973.
(12) G. Champetier, R. Buvet, J. Néel, P. Sigwalt, and collaborators, "Chimie macromoléculaire", Hermann, Paris, 1970, Tome 1.
(13) J. D. Ferry, "Viscoelastic Properties of Polymers", 2nd ed., Wiley, New York, 1970.
(14) J. P. Mercier and G. Groeninckx, *Rheol. Acta*, **8**, 510 (1969).
(15) W. Child, Jr., and J. D. Ferry, *J. Colloid Sci.*, **12**, 389 (1957).
(16) J. D. Ferry, W. C. Child, Jr., R. Zand, D. M. Stern, M. L. Williams, and R. F. Landel, *J. Colloid Sci.*, **12**, 53 (1957).
(17) K. Fujino, K. Senshu, and H. Kawai, *J. Colloid Sci.*, **16**, 262 (1961).

(18) K. Fujino, T. Horino, K. Miyamoto, and H. Kawai, *J. Colloid Sci.*, **16**, 411 (1961).
(19) F. Schwarzl and A. J. Staverman, *Appl. Sci. Res., Sect. A*, **4**, 127 (1953).
(20) D. J. Massa, *J. Appl. Phys.*, **44**, 2595 (1973).
(21) A. R. Ramos, F. S. Bates, and R. E. Cohen, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 753 (1978).
(22) J. D. Hoffman, G. Williams, and E. Passaglia, *J. Polym. Sci., Part C*, **14**, 173 (1966).
(23) M. L. Williams and J. D. Ferry, *J. Colloid. Sci.*, **10**, 474 (1955).
(24) J.-Y. Decroix, Thèse de Doctorat, Université Claude Bernard, Lyon, 1974.
(25) I. M. Ward, "Mechanical Properties of Solid Polymer", Wiley-Interscience, New York, 1971.
(26) L.-P. Blanchard, J. Hesse, and S. L. Malhotra, *Can. J. Chem.*, **52**, 3170 (1974).
(27) C. G. D'Hondt and R. W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 261 (1978).
(28) C. G. D'Hondt, Ph.D. Thesis, University of Massachusetts, Amherst, Mass., 1976.

The Basis for Miscibility in Polyester–Polycarbonate Blends

C. A. Cruz, J. W. Barlow, and D. R. Paul*

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712. *Received March 16, 1979*

ABSTRACT: Miscible amorphous phase behavior often results when the polymer pairs are chosen to give specific interactions which lead to exothermic heats of mixing. A method for estimating miscibility, based on calorimetric measurements of heats of mixing of low molecular weight analogues of the polymer repeat units, is tested for polycarbonate blends with a series of different polyesters. Polymer blends whose analogues show negative heats of mixing usually exhibit at least partial miscibility whereas those whose analogues show positive heats of mixing are invariably immiscible. The heat of mixing data suggest that the specific interaction leading to miscibility in this series involves the physical interaction between the polyester carbonyl moieties and the polycarbonate molecule.

Physical blends of polymers which form a single amorphous phase and are therefore thermodynamically miscible usually have physical properties which vary uniquely with blend composition in a smooth and continuous fashion between the property values of the pure components. This property combination is comparable to what can be achieved by chemical means through copolymerization, but the cost of producing miscible blends may be much less since only a physical blending operation is involved. Consequently there has been a great deal of research interest in miscible polymer blend systems.

By rough count, over fifty miscible polymer binary blends are now known to exist. Given the possible tens of thousands of polymer blend combinations that could be (and perhaps have been) examined, it is fairly clear that polymer–polymer miscibility is a somewhat uncommon event. The thermodynamic analysis of Scott[1] which applied the Flory–Huggins theory[2] to mixtures of dissimilar polymers provides a conceptual framework for understanding the exceptional nature of polymer–polymer miscibility. According to Scott, the enthalpy and entropy of mixing of polymers 1 and 2 are given by

$$\Delta H_{\mathrm{mix}} = BV\phi_1\phi_2 \tag{1}$$

$$\Delta S_{\mathrm{mix}} = -\frac{RV}{V_{\mathrm{r}}}\left(\frac{\phi_1 \ln \phi_1}{x_1} + \frac{\phi_2 \ln \phi_2}{x_2}\right) \tag{2}$$

where V_{r} is a reference volume, V is the volume of the system, x_i is the degree of polymerization of species i in terms of the reference volume, ϕ_i is the volume fraction of i in the mixture, and B is the mixing energy density characteristic of the polymer–polymer segmental interactions in the blend. It is clear from these equations that the entropy of mixing is a function of the molecular sizes being mixed and that it decreases rapidly toward zero as the degrees of polymerization of the component polymers approach the values typically found in commercial materials. The enthalpy of mixing, on the other hand, is primarily dependent on the energy change associated with changes in nearest neighbor contacts during mixing[2] and is much less dependent on molecular lengths. The net result is that the free energy of mixing, $\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$, is primarily influenced by the sign and magnitude of ΔH_{mix} for high molecular weght mixtures. The general success of the regular solution theory[3] is an indication that most materials weakly interact to give positive heats of mixing. Consequently, one would expect that the free energy of mixing associated with blending randomly selected high molecular weight polymers would be positive, a situation indicative of immiscibility or multiple amorphous phase formation.

The above considerations immediately suggest that miscible polymer blends will most likely result when polymer pairs are carefully selected for their abilities to form strong interactions of a type which result in negative heats of mixing. Recently, a number of studies on several of the polymer blends known to be miscible support this viewpoint. For example, Olabisi[4] observed negative interaction parameters between miscible poly(vinyl chloride) and poly(ϵ-caprolactone) pairs by means of solvent probe techniques and spectroscopic measurements and proposed the possibility of charge-transfer interactions to account for this phenomena. Similarly, Kwei et al.[5] found that the interaction parameter for miscible polystyrene–poly(vinyl methyl ether) blends was likewise negative in the composition range, 35–65% polystyrene. Nishi and Wang[6] and Paul and Barlow et al.[7-10] have shown that the heat of mixing parameter in the classical theory of melting point depression was negative when that theory was applied to miscible blends of poly(vinylidene fluoride) and various amorphous oxygen containing polymers. The latter investigators suggest that a strong, probably dipole related, interaction between carbonyl groups and the PVF_2 segment is responsible for the observed miscibility.[10]

0024-9297/79/2212-0726$01.00/0