Dynamics of the Viscoelastic β Process in Bisphenol A Polycarbonate

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ABSTRACT: Viscoelastic properties of bisphenol A polycarbonate (PC) were determined over a range of frequencies from 0.0159 to 15.92 Hz and a temperature range of −140 to 25 °C. This experimental range is sufficiently broad to characterize the viscoelastic β-relaxation process. The complex compliance was represented in terms of a relaxation function proposed by Havriliak and Shortridge to represent the viscoelastic β process of unmodified and impact modified poly(vinyl chloride) (PVC). The parameters of the relaxation function as well as their dependence on temperature were determined by the multiresponse statistical techniques developed by Havriliak and Watts. The viscoelastic parameters are compared to those of PVC and methyl methacrylate–butadiene–styrene modified PVC. Tensile yield properties of polycarbonate are also discussed in terms of the Ree-Eyring model and the viscoelastic β-process parameters. Detailed numerical analysis shows that the β process is much too fast to cause a retardation stress to the yield stress at low temperature or at high strain rates. The β process is discussed in terms of Mansfield's hindered segment rotation and Perchak et al.'s ring flip models.

Introduction

Bauwens-Crowet et al.[1] studied the tensile yield behavior of poly(vinyl chloride) (PVC) and bisphenol A polycarbonate (PC) as a function of temperature and strain rate. They found the tensile yield behavior of PVC to be similar to that of the acrylic systems studied by Roetling;[2–4] i.e. two molecular processes were necessary to account for the experimental results. Polycarbonate was different from these polymers because only one process was necessary to account for the tensile yield behavior in the experimental temperature and strain rate range of their measurements. The activation energy for the single process in polycarbonate was found to be 75.5 kcal/mol,[1] which is much too high to be considered the β process. No explanation for this apparent discrepancy in the number of processes needed to represent tensile yield behavior was offered, although rationalization of this observation is basic to any molecular understanding of tensile yielding.

Dielectric relaxation measurements on polycarbonate over a considerable temperature of frequency range, conditioning, and material type have recently been reported by Pratt and Smith.[5] Earlier dielectric results by Watts and Perry[6] were also reviewed. Clearly there is a β process in polycarbonate showing a broad loss maximum centered at 1 Hz at about −100 °C. Although the β process depends on specific environmental conditions, it is always present. Perhaps the most recent viscoelastic measurements on polycarbonate were made by Struik,[7] who showed that the β process does not disappear upon heat treatment even when quenched from high (155 °C) to low (−150 °C) temperatures. There is some apparent change in the loss tangent above −50 °C and 1 Hz, but these are sufficient only to change the loss tangent details in the high-temperature or low-frequency regions of the β-relaxation process.

Havriliak and Shortridge[8,9] have shown that the viscoelastic β process of neat or impact modified PVC can be represented by

$$\frac{J^*(\omega) - J_\infty}{(J_{0\beta} - J_\infty)} = \{i + (i\omega\tau_0)^\alpha\}^{-\beta} \tag{1}$$

which is the viscoelastic analogue of the expression proposed by Havriliak and Negami[10] to represent the dielectric dispersions of many polymers. In eq 1, $J^*(\omega) = J'(\omega) + iJ''(\omega)$, which is the complex compliance measured at radian frequency $\omega = 2\pi f$, where f is the frequency in hertz. In the remainder of this work, radian frequency will be used in units of radians per second. $J'(\omega)$ is the real or storage part of the compliance, while $J''(\omega)$ is the imaginary or loss compliance and $i = -1^{1/2}$. The other quantities are parameters of eq 1 and may or may not be temperature dependent. J_∞ and $J_{0\beta}$ represent the high-frequency (instantaneous) and low-frequency (equilibrium value for the β process) values of the complex compliance, respectively, i.e. conditions where $J''(\omega) \rightarrow 0$. Although $J_{0\beta}$ represents the equilibrium compliance for the β process, the parameter should not be confused with the equilibrium compliance when the entire system comes to equilibrium. The equilibrium compliance for the entire system would involve not only the β process but the α as well as any other relaxation process in PC. The parameter τ_0 is the relaxation time, and its slope in an Arrhenius plot yields the activation energy. The parameters α and β are formally related to the distribution of relaxation times.[10,11] A more meaningful molecular interpretation is in terms of a time-dependent correlation function developed by Cole.[12] Mansfield[13] has more recently represented the time-dependent correlation function in terms of hindered rotations of polymer segments about their main-chain axis. For this reason, Mansfield's model interprets the α and β parameters in terms of intra- and intermolecular interactions that restrict polymer chain orientational movements. Finally Perchak et al.[14] used computer simulation techniques of simple lattice models (flexible and rigid) to conclude that a flexible lattice would allow phenyl groups to ring flip 180° about their C_1–C_4 axis.

Determination of the parameters of eq 1, as well as their dependence on temperature, using multiresponse statistical techniques as describe by Havriliak and Watts.[15,16] In this method of parameter estimates, a complete range of $J^*(\omega)$ at a single temperature, forming a complete complex plane locus, is not required. The data from a series of temperature sweeps at constant but different frequencies can be pooled together to form a database amenable to analysis. A number of models are proposed to represent the temperature dependence of the parameters, they are then analyzed, and the one which minimizes the determinant of the residuals is assumed to be the best representation of the data. In this work we extend the methodology described in ref 8, 9, 15, and 16 to the viscoelastic β process in polycarbonate.

Experimental Section

Materials and Test Specimens. The polycarbonate used in this study is Merlon 50.[17] The pellets were dried at 60 °C in

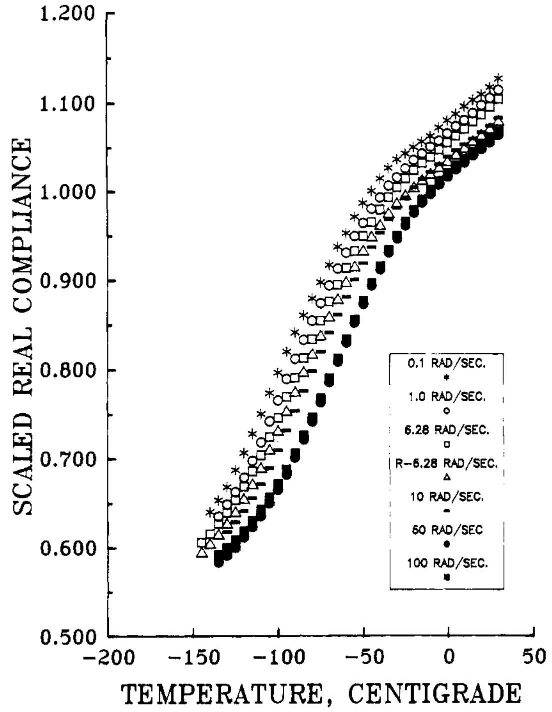

Figure 1. Temperature dependence of the real compliance in units of cm^2 N^{-1} multiplied by 10^5. The various frequencies are listed in the legend.

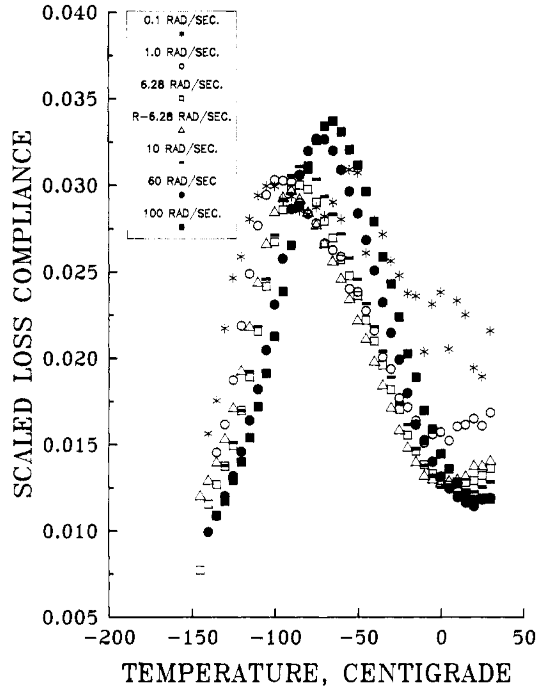

Figure 2. Temperature dependence of the loss compliance in units of cm^2 N^{-1} multiplied by 10^5. The various frequencies are listed in the legend.

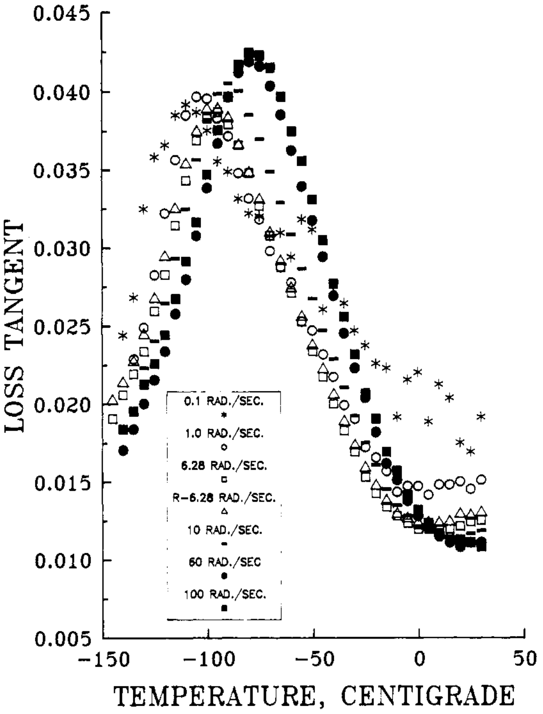

Figure 3. Temperature dependence of the loss tangent. The various frequencies are listed in the legend.

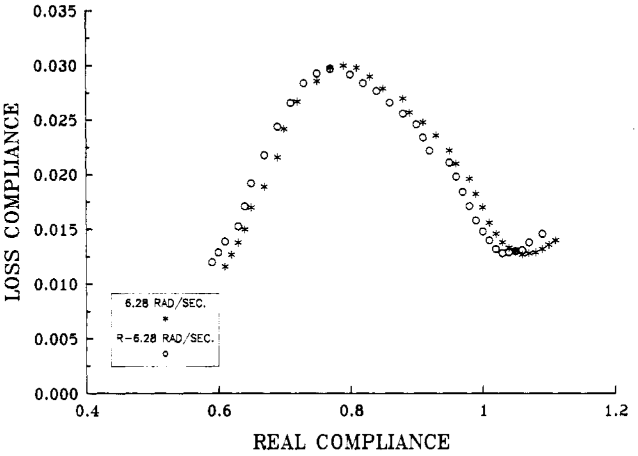

Figure 4. Complex plane plot of the reduced real and imaginary parts of the complex compliance. The frequency is 6.28 rad/s with the replicated run at the same frequency.

vacuum for 12 h. The dried resin was molded into 0.125 in. × 2 in. × 3 in. test specimens in a 1-oz Newbury injection molding machine under the following conditions: nozzle and barrel temperature = 290 °C, injection pressure = 600 psi, injection time = 15 s, overall cycle time = 40 s, and a mold temperature = 65 °C. We believe these molding conditions form stress-free parts. Test specimens, suitable for viscoelastic measurements, 0.125 in. × 0.5 in. × 2 in., were cut from the plaques.

Viscoelastic Measurements. All the viscoelastic measurements were carried out in the Rheometrics Dynamic Spectrometer RDS-770 using the techniques described elsewhere.[8,9] The sequence and number of frequencies used in this study were expanded to 6.28, 0.1, 100, 6.28, 1, 10, and 60 rad/s. The number of frequencies was increased from 4 to 7 so that a more meaningful rate plot using the temperature at which the loss tangent becomes a maximum could be constructed.

Numerical Analysis. Data were sent to an IBM Model 3090 main frame and assembled into a SAS data set.[18] All regression calculations were made by using SAS as described elsewhere.[8,9,15,16] It is important to note that except where stated, the complex compliance has been reduced by 10^5 in order to keep the numerical analysis within bounds.

Results

Preliminary Results. A plot of the real and imaginary parts of the complex compliance as well as the loss tangent with temperature for the different frequencies is given in Figures 1–3, respectively. A complex plane plot of the data taken at 6.28 rad/s as well as the repeat run is shown in Figure 4. An Arrhenius rate plot of the temperature at which the loss tangent becomes a maximum for each of the frequencies is given in Figure 5. Initial values for the critical frequency as well as its temperature dependence were estimated from Figure 5. Initial values for $J_{0\beta}$ and J_∞ as well as their dependence on temperature were es-

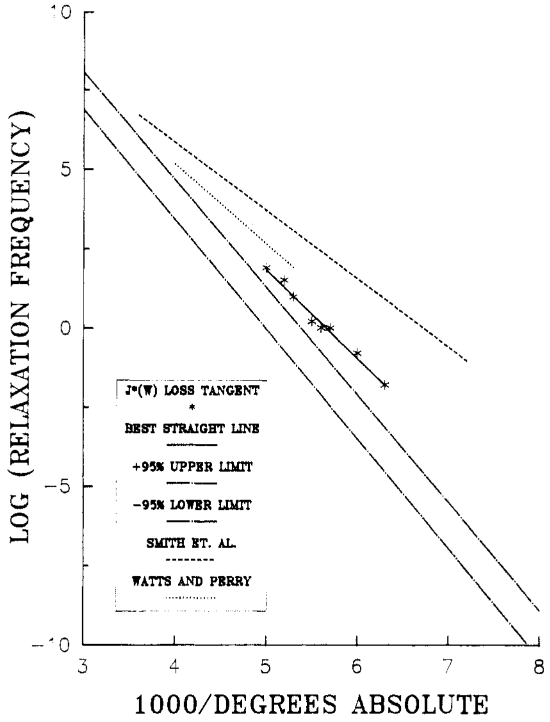

Figure 5. log of relaxation frequencies in hertz is plotted against 1000/K where K is degrees kelvin.

Table I
Summary of the Changes Made to the Complex Compliance Represented as Percentages of the Mean Value of the Compliance

parameter	PC	unmodified PVC[7]	13.05 wt % MBS modified PVC[17]
0.1 rad/s			
real	-1.2	-5	-4.2
imaginary	-6.9	-30	0
1.0 rad/s			
real			
imaginary			
6.28 rad/s			
real	0.12	0	0
imaginary	10.7	0	0
R-6.28 rad/s			
real	2.3	0	0
imaginary	0	0	0
10 rad/s			
real	0.8		
imaginary	0		
60 rad/s			
real	0.7	0	0
imaginary	0	0	0
100 rad/s			
real	0.02		
imaginary	0		
500 rad/s			
real		2	+5.3
imaginary		9	-5

Table II
Summary of the Statistical Quantities for Representing the Temperature and Frequency Dependence of the Complex Compliance of the Polycarbonate of Bisphenol A (PC) in Terms of Equation 1

parameter	PC	unmodified PVC[7]	13.05 wt % MBS modified PVC[17]
scaled determinant	3.9×10^{-8}	1.49×10^{-9}	5.4×10^{-7}
coef of variatn			
real, %	0.6	1	3
imaginary, %	20	11	20
deg of freedom	193	51	119

Table III
Equation 1 Parameters and Their Confidence Limits for Representing the Viscoelastic β Process of the Polycarbonate of Bisphenol A (PC)

parameter	PC	neat PVC[7]	13.06 wt % MBS modified PVC[17]
J_0	1.03	0.67	1.03
sd	0.01	0.01	0.02
$J_0(T)$	0.0013	0.0009	-0.0001
sd	0.0001	0.0001	0.0002
J_∞	0.57	0.32	0.43
sd	0.01	0.02	0.02
$J_\infty(T)$		-0.0009	-0.0010
sd		0.0002	0.0003
ln (f)	5.6	-1.7	-1.3
sd	0.7	0.3	1.3
ln $(f)(T)$	-7.9	-7.4	-13.6
sd	0.2	0.3	0.7
α	0.21	0.18	0.16
sd	0.01	0.02	0.01
β	0.51	0.18	0.70
sd	0.07	0.02	0.12
ref temp	-50	-50	-50

timated from the high- and low-temperature limits of the plots in Figure 1. α and β parameters were estimated from graphical parameters as given in ref 9.

Results of Regression. Initial attempts to treat all of the data failed. This failure was traced to the deviations from the complex plane behavior shown in Figure 4 at the high-temperature (high compliance value) end of the plot. These deviations are probably due to another higher temperature or lower frequency relaxation process. When the data set was truncated to temperatures below 0 °C, convergence readily occurred. Small adjustments were made to the compliance to optimize the fit. Results of the final regression analysis are give in Tables I–III. In Table I we have listed the constant corrections in percent (see ref 8) to the total compliance that was made to minimize the scaled determinant. Table II lists the statistics associated with the minimization procedure and Table III the parameters, their dependence on temperature, and their confidence limits.

Table III is organized in the following way. In eq 2, $J_{0\beta}$ is assumed to have the following dependence on temperature

$$J_{0\beta} = I_1 + C_1 T \qquad (2)$$

where C_1 is the slope or temperature coefficient in a temperature plot, °C, and I_1 is a constant or intercept. We take advantage of centering the experimental data about some reference temperature in order to minimize the magnitude of the parameters, in this case the intercept. In this particular study the reference temperature was taken to be −50 °C so that eq 2 becomes

$$J_{0\beta} = I_2 + C_2(T - 50) \qquad (3)$$

where the intercepts are different numerically while the slopes are the same. For the specific case of the three $J_{0\beta}$s listed in Table III, eq 3 can be rewritten as

$$J_{0\beta} = 1.03 + 0.0013(T - 50) \quad \text{for PC} \qquad (4a)$$

$$J_{0\beta} = 0.67 + 0.0009(T - 50) \quad \text{for PVC} \qquad (4b)$$

$$J_{0\beta} = 1.03 - 0.0001(T - 50) \quad \text{for modified PVC} \qquad (4c)$$

In this way, $J_{0\beta}$s can be estimated for any temperature. Directly under the coefficients in Table III are the

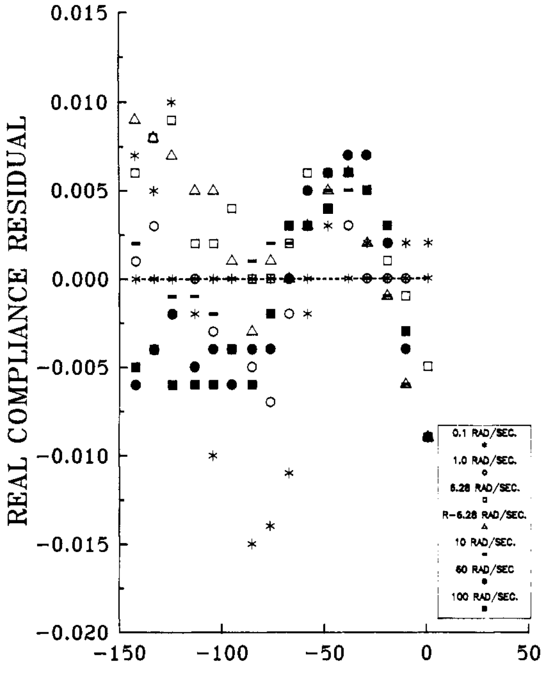

Figure 6. Dependence of real (reduced) residuals with temperature for the different frequencies listed in the legend.

standard error of estimate for the parameter. Briefly, Table III is a list of the C's and I's necessary to calculate the parameters of eq 1 at any temperature.

A reference temperature of −50 °C was chosen to facilitate comparison with impact modified and unmodified PVC. A better reference temperature would have been −75 °C, but this would have necessitated recalculating the parameters and their estimates for comparatives studies. Attempts were made to include temperature dependences for J_∞ as well as α and β, but these were found to be unnecessary. The statistical results at convergence are comparable to those of other studies (see Table II).

A plot of the real and imaginary residuals, i.e., the difference between the experimental and predicted values, is given in Figures 6 and 7, respectively. The magnitude of the real residuals is about the same as the error band associated with replication studies.[20] The magnitude of the imaginary residuals is somewhat higher but this is probably due to the nature of the regression process. The determinant that is minimized contains sums of squares of real and imaginary residuals as well as sums of their cross product. Since the magnitude of the real compliance is an order to magnitude higher than it is for the loss compliance, the minimization process lends greater relative weight to the sums of real squares than it does to the sums of imaginary squares, thereby leading to greater uncertainty in the estimation of $J''(\omega)$.

Discussion

The parameters for the viscoelastic β process of polycarbonate are different from those of neat PVC (see Table III). The equilibrium compliance for the β process, i.e., $J_{0\beta}$, is higher for polycarbonate than it is for PVC. The difference $\Delta J = J_{0\beta} - J_\infty$ is also much larger, signifying that the magnitude of the β process is much larger. Though the activation energy is the same for both materials, the relaxation frequency at the reference temperature (−50 °C) is three decades higher. The relaxation frequency at the reference temperature is related to the preexponential factor when the reference temperature in degrees kelvin is set to zero. Since the slopes of the two rate plots are nearly the same for the two materials, the relaxation frequency at room temperature will be higher by the same magnitude (see Figure 8). The β parameter is considerably larger, i.e., the relaxation process narrower, at any temperature. This increase in β tends to concentrate the β process in the impact time range at higher temperature (see Figure 12 of ref 9).

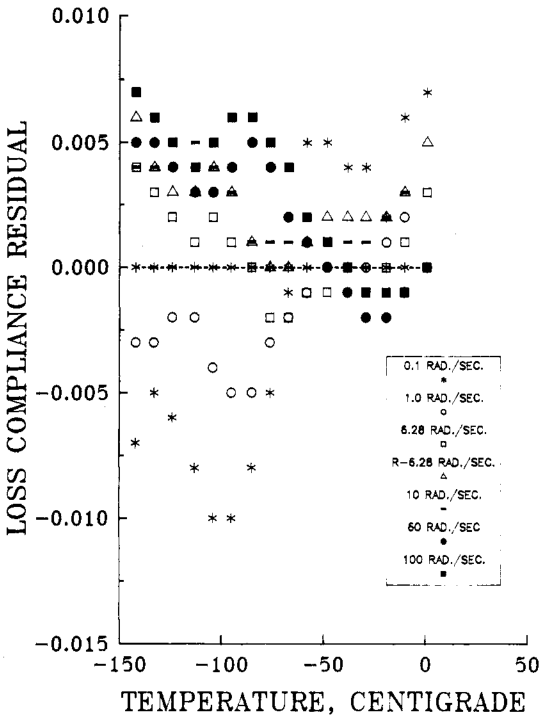

Figure 7. Dependence of loss (reduced) residuals with temperature for the different frequencies listed in the legend.

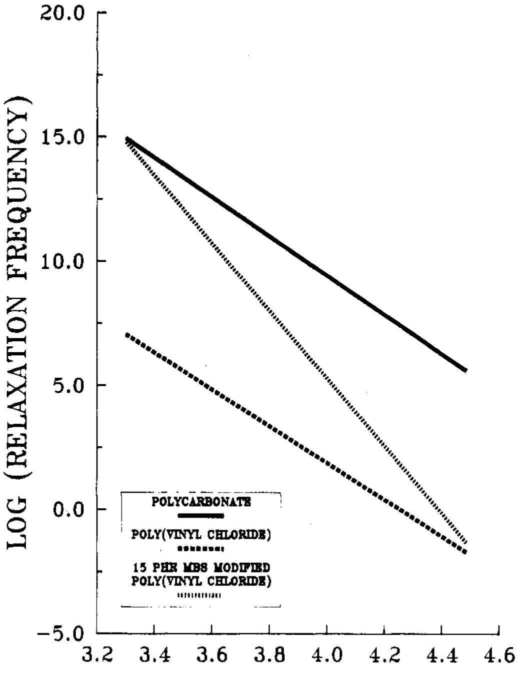

Figure 8. log of relaxation frequencies in hertz with 1000/K where K is degrees kelvin for polycarbonate, poly(vinyl chloride), and impact modified poly(vinyl chloride).

The β process parameters for polycarbonate are more similar to the parameters of modified PVC than they are to neat PVC (see Table III). The β-process equilibrium and instantaneous compliances are about the same so that the magnitude of the β processes are similar. The critical

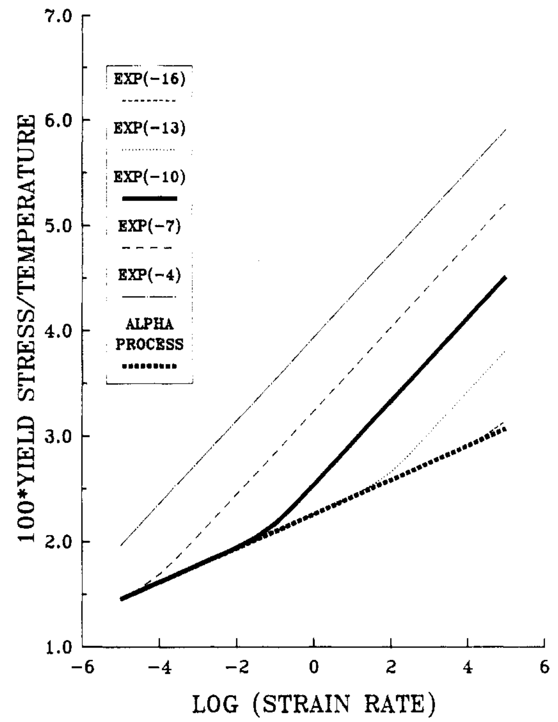

Figure 9. Dependence of the temperature reduced yield stress in kg/(mm K) with log strain rate in s^{-1}. Temperature of the calculation was taken to be 25 °C. The exponential values for C_β are listed in the legend.

frequency of the β process for polycarbonate is much faster than it is for modified PVC at -50 °C. However, the activation energy for modified PVC is much larger so that at room temperature the critical frequencies are about the same (see Figure 8). Similarity of the relaxation times suggests that the impact properties of the two systems at room temperature would be similar. However, the relaxation frequency of the modified PVC is much more temperature dependent then for polycarbonate, i.e., the brittle to ductile transition temperature is expected to be higher for modified PVC based on these arguments.

The absence of a retardation stress due to the β process for polycarbonate in the work of Bauwens-Crowet et al. can be understood from the data in Table III and the parameters for tensile yielding in PVC.[1] The expression derived by Roetling and Bauwens-Crowet et al. to represent the dependence of yield stress (σ_y) on strain rate ($\dot{\epsilon}$) and temperature (T) by extending the Ree-Eyring model to include two processes, i.e., a fast and a slow one, is given by

$$\sigma_y/T = A_\alpha\{\ln 2C_\alpha\dot{\epsilon} + (Q_\alpha/RT)\} + A_\beta \sinh^{-1}\{C_\beta\dot{\epsilon}\exp(Q_\beta/RT)\} \quad (5)$$

The following values for the constants were determined by Bauwens-Crowet et al. to represent the yield stress behavior for poly(vinyl chloride):

$A_\alpha = 7 \times 10^{-4}$ kg/(mm^2 K)

$A_\beta = 10.1 \times 10^{-4}$ kg/(mm^2 K)

$Q_\alpha = 70.5$ kcal/mol $\quad Q_\beta = 14$ kcal/mol

$C_\alpha = 10^{-38}$ s $\quad C_\beta = 4.26 \times 10^{-10}$ s

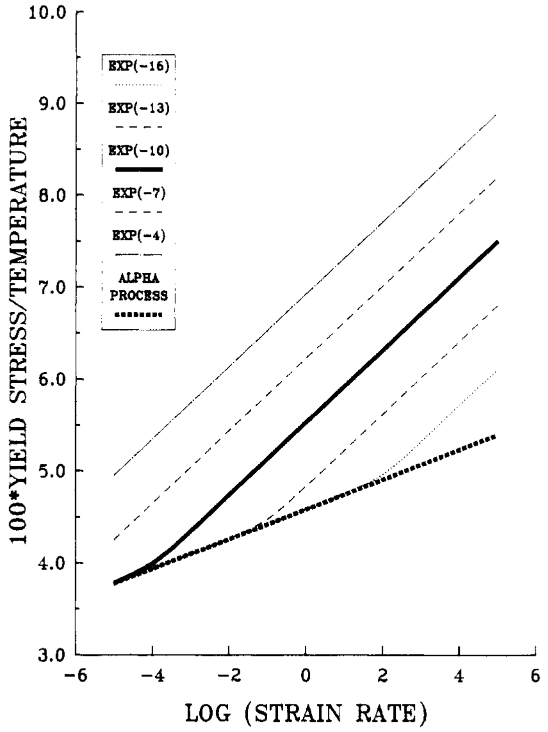

Figure 10. Calculated values and conditions are similar to those in Figure 9 except the temperature is -40 °C.

In these expressions the subscript represents the process, i.e., α or β, while Q is the activation energy, C represents the frequency factor or preexponential, and A represents a number of quantities that represent specific details about the jumping process. The β processes for polycarbonate and poly(vinyl chloride) were found to have the same activation energies but considerably different relaxation frequencies (Table III) at the reference temperature, i.e., different preexponentials. We can investigate the effect of a shorter relaxation time on yield stress by recalculating the yield stress using eq 5, the parameters cited above, and different values of C_β. We have plotted the tensile yield stress/temperature ratio as a function of log (strain rate) from -5 to +5 (see Figure 9). The range from -5 to 0 is an approximate experimental range, while the range from 0 to 5 is generally considered to be the range of high-speed tensile testing. The heavy solid line represents the predicted behavior of neat PVC, while the heavy dashed line represents the contribution of the α process, i.e., the β-process contribution has been set to zero. The calculations were be remade for exponents of C_β to be -16, -13, -7, and -3. The results of these changes at 25 °C are given in Figure 9. Choice of the exponent for the C_β term has a dramatic effect on the β-process contribution to the yield stress. For example, there is not a significant contribution from the β process to the yield stress when the exponent of C_β is -16, even in the range of high-speed tensile testing. We have plotted results of similar calculations for -40 and -100 °C (see Figures 10 and 11). At -40 °C, when the exponent of the C_β term is -16, the contribution to yield stress is in the high-speed range but negligible in the conventional range. The β process with an exponent of -16 does make a contribution in the conventional as well as the high-speed tensile testing range. At temperatures of -100 °C the contribution of the α process to the temperature-reduced stress has probably exceeded the break stress of polycarbonate. In other words, the tensile yield behavior of polycarbonate can be represented by a single (α) process because the β process is so fast that there is no retardation stress, even at very low temperatures or very high rates.

An Arrhenius rate plot of relaxation frequencies obtained from various sources is given in Figure 5. The results from the present study are represented as 95% confidence limits by the two long dashed lines in the figure.

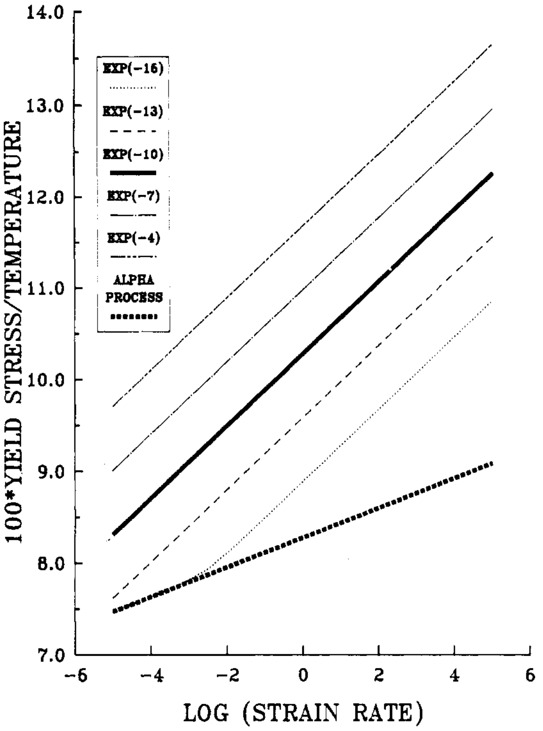

Figure 11. Calculated values and conditions are similar to those in Figure 9 except the temperature is −100 °C.

The asterisks in Figure 5 represent the loss tangent data while the shorter dashed lines represent dielectric measurements. The difference between the two methods representing viscoelastic relaxation frequencies is a matter of definition. The loss tangent maximum is always to the high-frequency side of the definition given by eq 1. The difference between the dielectric loss tangent maximum and the dielectric work of Watts and Perry is slight and may be traceable to difference in experimental error, specimen preparation, or specific polymer preparations. The differences between the two dielectric measurements was not discussed by Smith et al., therefore it is not clearly understood by us.

Mansfield's[11] Figures 11 and 12 can be overlaid to give a very crude estimates of his dynamic parameters in terms of the α and β parameters listed in Table III. For the polycarbonate case, his parameters become log $\beta C = -4$ and log $r = 0.7$. The major difference between the PVC and polycarbonate values for α and β is that β varies from 0.18 to 0.51, respectively, while α remains unchanged. Such changes in β have the effect of changing log βC from approximately 1.5 to 0.7. These changes eventually relate back to the spring constant and relaxation time, i.e., jumping times and probabilities.

More recently, Perchak et al.[14] computer simulated some simple models for the ring-flip process in polycarbonate. The phenyl groups were positioned on different types of lattices. He found flexible lattices led to ring flipping. It may be tempting to assume that ring flipping takes place during a viscoelastic measurement since the test specimen, hence the lattice, is mechanically attached to a vibrating drive. The vibration of the experiment could cause lattice distortions so that ring flipping would take place. If this was the primary mechanism, it would be difficult to account for the dielectric β process in terms of the same mechanism because the electric field is not coupled to the lattice but to the induced and permanent moments of the polymer chain. A more plausible mechanism is by means of Bueche's[21] fluctuation in free energy or volume model. In this model, fluctuations in free energy or volume supply the necessary energy and or volume for the ring jump to occur, thereby alleviating the effects of an applied field, whether it be stress or electric.

Recently Havriliak and Shortridge[11] proposed an orientation model for the viscoelastic β process in PVC. For practical purposes this mechanism could have been called "polymer chain segment-flip mechanism" or more simply segment flips. The most important feature of this model is that a portion of the PVC polymer chain rotates about the main-chain axis from one equilibrium position to another. Another interesting observation that was made in that work is that the activation energy for the viscoelastic β process of PVC is about 1.5–2.0 times that of activation energies observed of rotation barriers in simple alkyl halides.[11]

The segment-flip mechanism is not new, since it was used to describe the β dielectric relaxation mechanism in syndiotactic poly(methyl methacrylate) (s-PMMA) by Havriliak.[22] A careful examination of infrared absorption spectra made on test specimens undergoing thermal cycling exhibited hysteresis effects which led to the conclusion[23] that the side chains were not free to move independently of the main chain as first proposed by Reddish.[24] The ester groups were found to be rigidly coupled to the main chain below the glass transition temperature. Construction of trial structures consistent with infrared dichroisms of the ester groups, some structural interpretation of the spectra, and the effective dipole moment estimated from dielectric measurements led to a small number of hypothetical structures which could rotate (segment flip) about the main-chain axis. In other words the β process of s-PMMA was described in terms of segment-flips.

Conclusions

It is gratifying that specific and detailed analysis of viscoelastic data can account for the tensile yield behavior of polycarbonate because Mansfield[12] has given a reasonable molecular model for dielectric and viscoelastic relaxation processes in polymers in terms of inter- and intramolecular interactions. Such a connection between macroscopic and molecular behavior is the goal of any structure–property relationship study. It is the objective of this and other works from our Laboratory.

Acknowledgment. The writers express their appreciation to L. Walters whose expertise was an important part of this study.

Registry No. (Bisphenol A)(PC) (copolymer), 25037-45-0; (bisphenol A)(PC) (SRU), 24936-68-3.

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Molecular Modeling of Polymers. 6. Intramolecular Conformational Analyses and Molecular Dynamics of Syndiotactic Polystyrene

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ABSTRACT: Fixed valence geometry molecular mechanics conformational analyses of syndiotactic polystyrene (sPS) were performed. The PRIMM method was employed to measure relative conformational stability as a function of the number of nearest monomer neighbor interactions considered. Only two stable ordered conformations of sPS were identified. These are the all-trans conformation (T_4) and the trans-trans-gauche-gauche (T_2G_2) structure. Two crystalline phases of sPS have been observed. The diffraction pattern of one form has been interpreted in terms of a T_4 chain conformation. The other crystalline phase is postulated to have chains in the T_2G_2 conformation. Preliminary molecular dynamics (MD) simulation studies also indicate that the T_4 and T_2G_2 conformations are the only stable intrachain structures. The interconversion energy barrier between T_2G_2 and T_4 is estimated to be about 2–3 kcal/mol from both conformational analysis and MD simulation. A T_2G_2-to-T_4 transition was observed in the MD trajectory, but not the reverse transition.

Introduction

The recent development of successful schemes for the synthesis of syndiotactic polystyrene, sPS,[3] raises the issue of possible commercial uses of this polymer and/or its homologues. Thus, it is of interest to determine the physicochemical properties of sPS. Similarities of sPS to isotactic polystyrene, iPS, and to other syndiotactic vinyl polymers are of particular interest.

Relatively little information has been published on the physicochemical properties of sPS. Ishihara and coworkers[3] note that the characteristic IR signals in the region 1450–1180 cm^{-1} associated with iPS are absent for sPS. However, a new signal at 1200 cm^{-1} for sPS is attributed to its ordered chain conformation. The crystallization rate of sPS is extremely high compared to iPS. The crystal melt temperature is about 270 °C, about 40 °C higher than iPS.[3]

Two crystalline phases, termed α and β,[5] have been observed for sPS. The α phase has a fiber axis repeat of 5.0–5.1 Å.[3-5] The all-trans chain conformation, T_4, has been postulated for the α phase[3-5] by analogy to other crystalline polymers, such as polyethylene, which have fiber axis repeat units of about half-multiples of 5.0 Å and are in the T_4 chain conformation. The same reasoning has been applied to the β phase of sPS where the fiber axis repeat unit is about 7.5 Å,[5] which is characteristic of a trans-trans-gauche-gauche (T_2G_2) conformation as found, for example, in one of the crystalline forms of syndiotactic polypropylene (sPP).[6] The other crystalline form of sPP is, interestingly, T_4.[7] The α phase is obtained by annealing the melt-quenched glass, while the β form is formed by casting from solution.[4,5] The β form converts to the α phase when heated to 180–190 °C.[5] There is some evidence that two different modes of chain packing occur in the α phase depending upon the method of crystallization.[4]

Table I
Selected Values of θ_1 and θ_2 and the Nearest Structural Repeat Unit Conformational Energies, E_i,[a] for the T_4 and T_2G_2 Conformations

conformation	θ_1	θ_2	E_0	E_1	E_2	E_3	E_p
T_4	109.5°	109.5°	16.45	−3.96	−0.26	−0.02	12.21
	112.0	114.0	14.51	−3.05	−0.23	−0.01	11.22
T_2G_2	109.5	109.5	18.89	0.07	33.43	−0.26	52.13
	112.0	114.0	15.73	−1.15	−2.79	−0.23	11.56

[a] In kcal/mol/structural repeat unit. [b] E_p is the energy of the infinite polymer using up to three nearest structural repeat unit interactions.

Since there has not been extensive structural characterization of sPS, we thought that this might be a good opportunity to use computer-aided molecular modeling[8] to predict some properties of sPS that might facilitate corresponding laboratory experiments.

This paper reports the results of the intrachain conformational analyses of sPS. Subsequent papers will deal with the characterization of the intermolecular structure of sPS.

Method

The repeat unit geometry used in the conformational analyses of sPS is shown in Figure 1. The equivalence rule[1] was applied in the conformational analyses and is based upon the structural (as opposed to chemical) repeat unit geometry. With the exception of the backbone bond angles θ_1 and θ_2, all other bond lengths and angles were assigned standard values. The choices in θ_1 and θ_2 are given in Table I and are based upon suggested values for iPS.[2,9,10] There have been different viewpoints regarding what values of θ_1 and θ_2 best fit the crystal data for iPS. The strategy in our choosing different θ_1 and θ_2 is to hypothesize that these variables may also be problematic for sPS and to see how sensitive the conformational profiles of sPS are

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