

# Molecular dynamics of the beta process in the polycarbonate of bisphenol-A

S. Havriliak Jr and T. J. Shortridge

Modifiers Research Department, Rohm and Haas Co., Bristol, PA 19007, USA

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The experimental dielectric relaxation data of Pratt and Smith on the polycarbonate of bisphenol-A (PC) in the experimental range of its beta process, i.e. 0.1 to  $10^6$  Hz and  $-150$  to  $25^\circ\text{C}$ , is represented in terms of an analytical expression proposed by Havriliak and Negami. The parameters and their dependence on temperature were determined by the multi-response techniques developed by Havriliak and Watts. These parameters are then compared with the corresponding viscoelastic beta process parameters for PC recently reported by Havriliak and Pogonowski. The parameters for the dielectric and viscoelastic process are similar and some of them are within the 95% confidence limits for the parameter estimates. Some of the differences that are observed may be due to proprietary difference in ostensibly the same generic material. The dynamics of the dielectric beta process is discussed in terms of the polarizability of the *para*-substituted phenyl groups in PC as they undergo ring flips as proposed by Perchak *et al.*

(Keywords: polycarbonate; bisphenol-A; dielectric; viscoelastic; relaxation ring flips)

## INTRODUCTION

Havriliak and Pogonowski<sup>1</sup> have recently reported on the viscoelastic properties of bisphenol-A polycarbonate (PC) in the region of its beta process, i.e. a frequency range of 0.0159 to 15.9 Hz and a temperature range of  $-140$  to  $20^\circ\text{C}$ . The complex compliance was represented in terms of a five-parameter relaxation function proposed by Havriliak and Shortridge<sup>2,3</sup>. In the former study<sup>1</sup>, a comparison was made between the relaxation time of the viscoelastic beta process as defined in refs. 2 and 3 with the relaxation time of the dielectric process defined as the temperature at which the loss tangent at a particular frequency becomes a maximum. No other comparisons could be made because the dielectric relaxation data of Pratt and Smith<sup>4</sup> as well as the data of Watts and Perry<sup>5</sup> were not represented in terms of the dielectric expression proposed by Havriliak and Negami<sup>6</sup>. For these reasons a detailed comparison between the dielectric and viscoelastic beta process in PC is incomplete.

A mathematical simulation of the beta process in PC as a ring-flip process of phenyl groups about their C(1)–C(4) bonds was reported by Perchak *et al.*<sup>7</sup>. They studied the ring-flip process on rigid or flexible lattices. The flexible lattice allowed ring flips to take place, while a rigid lattice inhibited the process.

A basic understanding of the beta process in PC is important because it is this mechanism that permits tensile yielding to take place at very high strain rates or at low temperatures<sup>1,8</sup>. In this work we analysed the data of Pratt and Smith<sup>4</sup> since both the real and imaginary parts of the complex dielectric constants are reported. The data of Watts and Perry<sup>5</sup> are not treated because they only reported the loss part of the dielectric constant.

## NUMERICAL METHODS

Havriliak and Negami<sup>6</sup> proposed equation (1) to represent the complex dielectric constant  $\epsilon^*(\omega)$  as a function

of radian frequency  $\omega = 2\pi f$  (where  $f$  is in Hz) at constant temperature:

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = [1 + (i\omega\tau_0)^\alpha]^{-\beta} \quad (1)$$

In this expression,  $\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$  is the complex dielectric constant,  $\epsilon'(\omega)$  is the real or storage part of the complex dielectric constant while  $\epsilon''(\omega)$  is the imaginary or loss part of the complex dielectric constant, and  $i = \sqrt{-1}$ . The other quantities are parameters of the equations and need to be evaluated. The quantities  $\epsilon_0$  and  $\epsilon_\infty$  represent the equilibrium and instantaneous dielectric constants. The left-hand side of equation (1) represents the magnitude of the relaxation process. The parameter  $\tau_0$  is the relaxation time while the parameter  $\alpha$  represents the width of the relaxation process and  $\beta$  represents its skewness. The right-hand side of equation (1) represents the dynamic parameters. The usual method of determining these parameters is to construct a complex-plane plot at a single temperature, determine the parameters graphically and then repeat the analysis for other temperatures. In this way, the temperature dependence of the five parameters could be determined.

Havriliak and Watts<sup>9,10</sup> have developed a much more powerful statistical technique based on multi-response methods. In this method the variation of the complex dielectric constant with frequency and temperature is pooled to form a single data set. The complex dielectric constant is assumed to be given by equation (1) and the temperature dependence of the five parameters is assumed to be given by the equations:

$$\epsilon_0 = I_1 + C_1(T - T_0) \quad (2a)$$

$$\epsilon_\infty = I_2 + C_2(T - T_0) \quad (2b)$$

$$\log_e(\tau_0) = I_3 + C_3(RK - RK_0) \quad (2c)$$

$$\alpha = I_4 + C_4(T - T_0) \quad (2d)$$

$$\beta = I_5 + C_5(T - T_0) \quad (2e)$$

In these expressions  $T$  is in  $^{\circ}\text{C}$ ,  $T_0$  is a reference temperature, chosen to centre the experimental data at  $T - T_0 = 0$ ,  $RK = 1000/(273 + T)$ ,  $RK_0 = 1000/(273 + T_0)$  and finally  $\tau_0 = 1/f_0$ , or  $\log_e(\tau_0) = -\log_e(f_0)$ . These equations, except for (2c), assume a linear dependence of the parameter on temperature, while equation (2c) is essentially an Arrhenius plot. The statistical techniques used to evaluate the parameters, derivatives of equation (1) and other important numerical techniques are described in refs. 9 and 10. In this way it is not necessary to have a complete frequency range to define the parameters at a single temperature.

RESULTS

The frequency dependence of the real and imaginary parts of the complex dielectric constant in the beta process region, taken from the work of Pratt and Smith<sup>4</sup>, is given in Figures 1 and 2. The symbols in Figures 1 and 2 represent the values picked off the graphs while the lines simply connect the points and have no other meaning. The data at low frequencies and temperatures deviated significantly from the expected behaviour and were deleted from the analysis. The data were not smooth prior to the regression analysis. A complex-plane plot of the data is given in Figure 3. Trial values for the parameters were made by the graphical techniques described in ref. 6. The quality of the fit was improved by the addition or subtraction of small quantities that depended on frequency but not temperature; see Figure 4. The real correction term is about 0.03% while the imaginary correction term is about 12%. The real

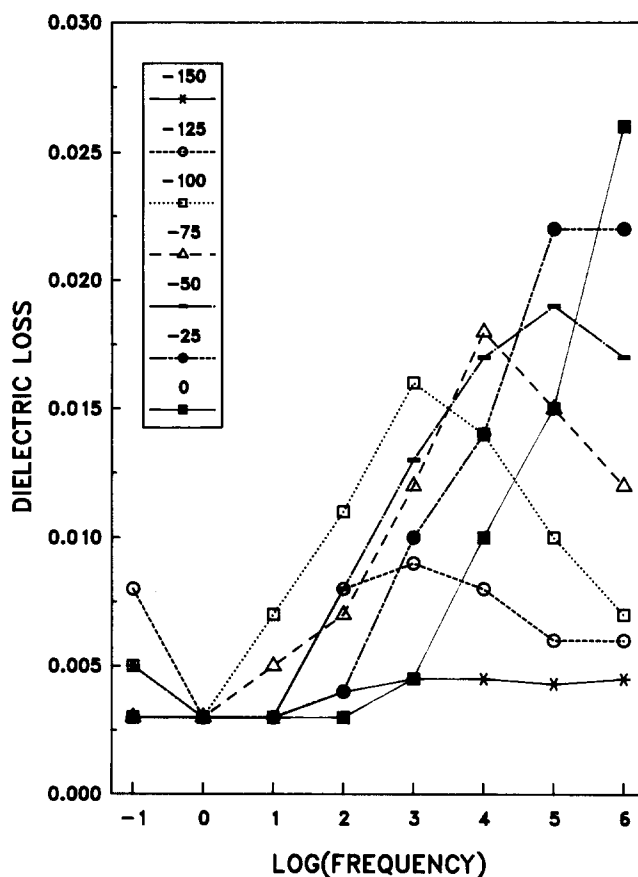


Figure 2 Dielectric loss plotted against log[frequency (Hz)] at various temperatures ( $^{\circ}\text{C}$ )<sup>4</sup>

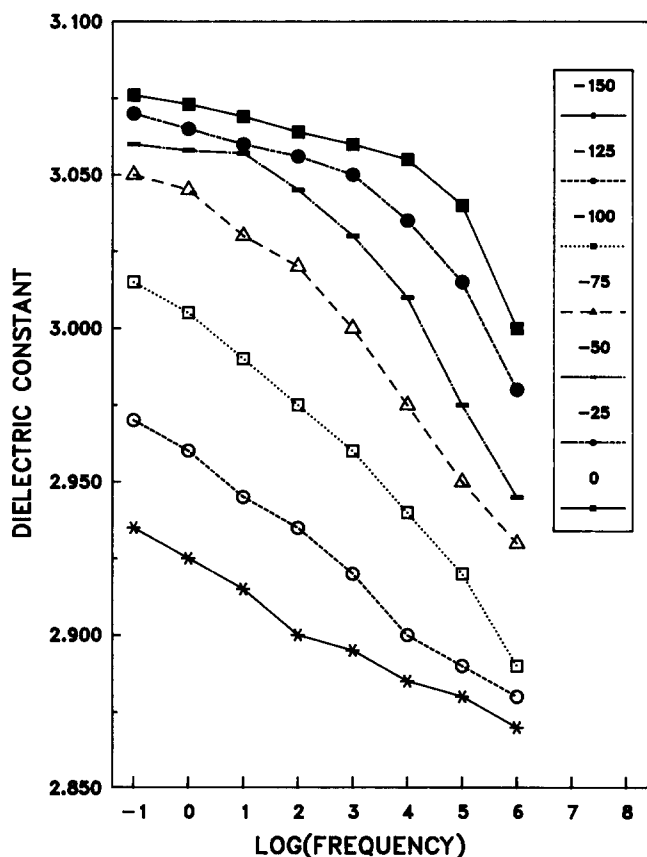


Figure 1 Dielectric (real) constant plotted against log[frequency (Hz)] at various temperatures ( $^{\circ}\text{C}$ )<sup>4</sup>

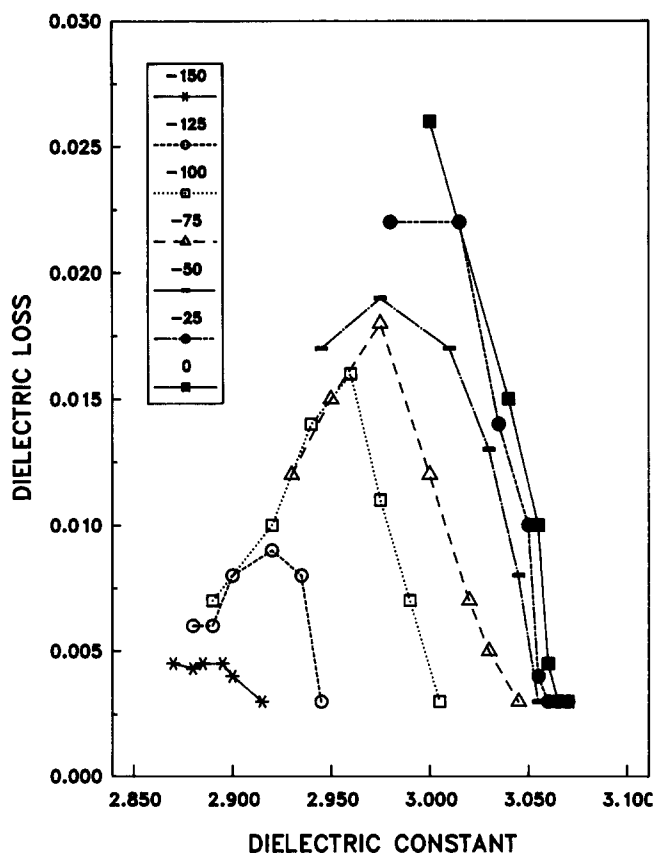


Figure 3 Complex-plane plot of the data shown in Figures 1 and 2

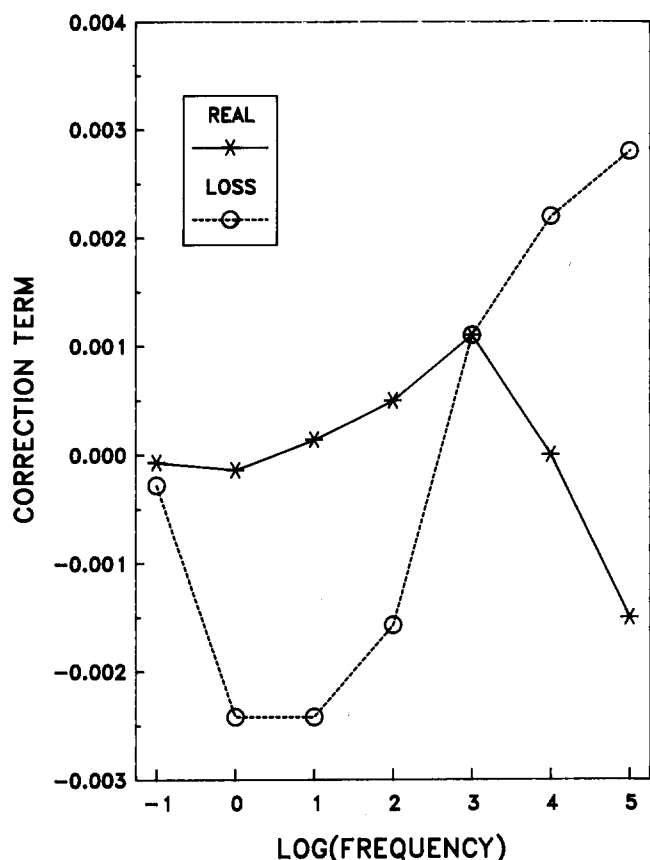


Figure 4 Plot of the corrections made to the data in Figures 1 and 2 to optimize the regression results

correction term is certainly within acceptable limits while the value for the loss is high. A possible reason for this is discussed below. The systematic trends in the correction terms suggest a systematic error in the measurements rather than some random error. The statistical results of the regression are listed in Table 1 while the  $C$  and  $I$  values for equations (2a) to (2e) are given in Table 2.

The scaled determinant (SD) in Table 1 represents the magnitude of the scaled determinant divided by the number of observations at convergence and is useful in determining the level of regression. In the present study the level of regression for the dielectric and viscoelastic analysis has been brought to about the same level. The next quantity in that table is the variance (Var), which has two components, i.e. a real and an imaginary one. It is defined as the mean sum of squared residuals. In other words the differences between the experimental and calculated quantities (i.e. residuals) are squared, then summed and finally divided by the degrees of freedom (DOF). Taking the square root of Var leads to the model standard error of estimate, listed as MSE in Table 1. This parameter is probably the most important statistical quantity in Table 1 because it is a summary of the fit. MSE has the same statistical significance as does the experimental standard deviation associated with a mean of replicated measurement. The regression has reduced the difference between the calculated and experimental quantities to about the same level so that the regression process has not favoured either quantity. Mean is simply the average of the real or imaginary quantities. The coefficient of variation (COV) is defined as the ratio of MSE to mean times 100. The differences between the real

and imaginary COV reported in Table 1 are due to the large differences in the mean since the real mean is about 10 times larger than the loss mean. Plots of the real and imaginary residuals as functions of temperature for the different frequencies are given in Figures 5 and 6 respectively.

The coefficient of variation of the real part is within acceptable limits. The coefficient of variation of the imaginary part of the dielectric constant is poor, about 34%. This poor value comes about for two reasons. First, the beta process in PC is small and the loss is probably near the limits of the measuring equipment. Secondly, the determinant that is minimized contains sums of squares of real residuals, loss residuals and their product. Since the real part of the dielectric constant is about 10 times that of the loss, there is an emphasis on the real part.

Table 1 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	Dielectric relaxation PC	Viscoelastic relaxation PC
SD	$9.3 \times 10^{-9}$	$3.9 \times 10^{-8}$
Var		
real	0.000033	
imag.	0.0000068	
MSE		
real	0.0056	
imag.	0.0026	
Mean		
real	2.99	
imag.	0.007	
Cov		
real (%)	0.19	0.6
imag. (%)	34	20
DOF	42	193

Table 2 Equation (2) parameters and their confidence limits for representing the viscoelastic beta process of the polycarbonate of bisphenol-A (PC)

Equation (2) parameters	Dielectric relaxation PC <sup>4</sup>	Viscoelastic relaxation PC <sup>1</sup>
$I_1$	3.062	1.03
s.d.	0.004	0.01
$C_1$	0.0004	0.0013
s.d.	0.0001	0.0001
$I_2$	2.836	0.57
s.d.	0.008	0.01
$C_2$	-	-
s.d.	-	-
$I_3$	10.2	5.6
s.d.	1.5	0.7
$C_3$	-5.4	-7.9
s.d.	0.2	0.2
$I_4$	0.26	0.21
s.d.	0.04	0.0
$C_4$	-	-
s.d.	-	-
$I_5$	0.43	0.51
s.d.	0.16	0.07
$C_5$	-	-
s.d.	-	-
Reference temperature (°C)	-50	-50

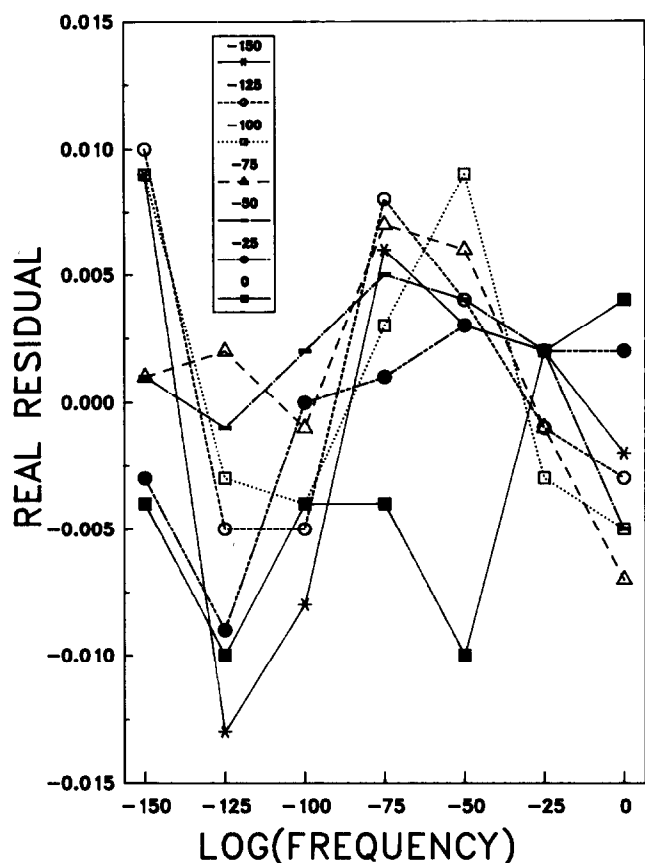


Figure 5 Plot of the real residuals with  $\log$ [frequency (Hz)] for various temperatures ( $^{\circ}\text{C}$ )

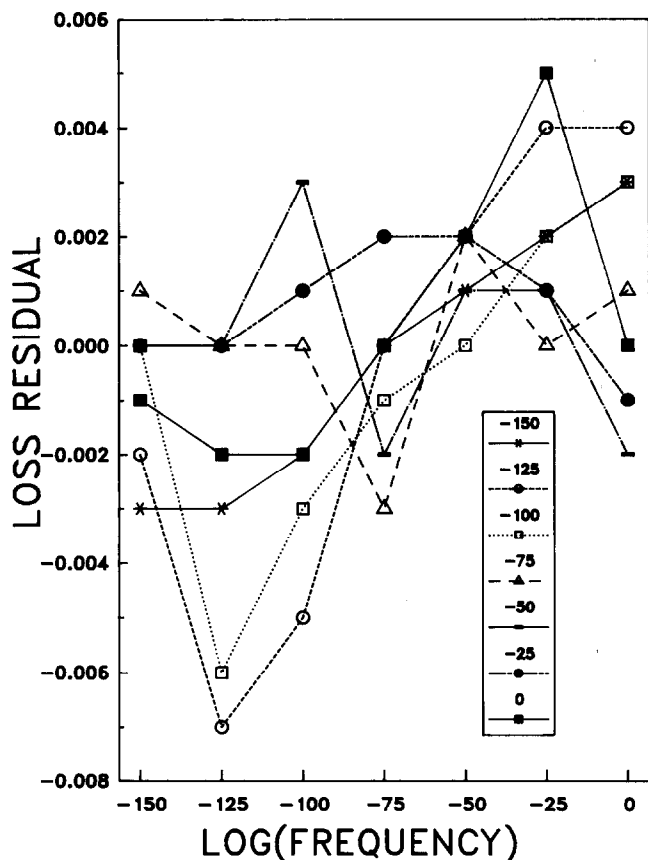


Figure 6 Plot of the loss residuals with  $\log$ [frequency (Hz)] for various temperatures ( $^{\circ}\text{C}$ )

## DISCUSSION

The parameters for the viscoelastic  $\beta$  process in PC reported in ref. 1 are also listed in Table 2. A number of parameters are similar within their experimental confidence limits. The equilibrium and instantaneous parameters are not expected to be the same for the dielectric and viscoelastic processes since the former may be related to the polarizability of the phenyl group while the latter is probably related to its shape. What is important to note is that neither requires the existence of a temperature coefficient for the instantaneous parameter, while both equilibrium parameters require temperature coefficients; although numerically different, they are quite similar. Both coefficients indicate that the magnitude of the  $\beta$  process, i.e.  $\tau_0 - \tau_{\infty}$  and  $\epsilon_0 - \epsilon_{\infty}$ , increases with temperature. The similarity is further enhanced if one estimates a scaled coefficient of expansion for each process. This estimation for the dielectric process is  $(\epsilon_0 - \epsilon_{\infty})/C_1 = (1.8 \pm 0.4) \times 10^{-3}$  and for the viscoelastic process is  $(J_0 - J_{\infty})/C_1 = (2.8 \pm 0.2) \times 10^{-3}$ . These results suggest strongly that the changes in the magnitude of the  $\beta$  process with temperature are probably the same. Perchak *et al.*<sup>7</sup> found that rigid lattices prohibit ring flips while flexible lattices permit them. As the temperature is decreased, one would expect this hypothetical lattice to stiffen and thereby reduce the number of ring flips, hence reducing the magnitude of the  $\beta$  process.

The parameters  $\alpha$  and  $\beta$  for the dielectric process are essentially the same as the corresponding parameters in the viscoelastic process. This result suggests that the time-dependent correlation functions<sup>3</sup> describing the two processes are also the same. This result is valid within experimental error, not only in general, but also with respect to specific dynamic models such as Mansfield's<sup>11</sup> hindered rotation model. In other words, the path towards equilibrium after a physical disturbance is the same in phase space, whether the disturbance is an electric or a mechanical stress field.

Under these conditions one would expect the pre-exponential factor and the activation energy in an Arrhenius rate plot of the relaxation time (related to the parameters in equation (2c)) to be the same. The results in Table 2 suggest that the parameters are different. The reason for this discrepancy is uncertain. One possible explanation is that the two sets of measurements were made under quite different sets of circumstances, i.e. a freely supported viscoelastic test specimen in a nitrogen stream vs. a dielectric test specimen clamped between metal electrodes. In addition, the measurements were made on test specimens prepared from two very different polycarbonates, albeit the same generic material. In other words the specimens may contain low-level and different additives that affect the response of the system. Finally, as has already been pointed out, there is significant disagreement between the dielectric rate plots of Smith *et al.* and Watts *et al.* In fact, the results reported in ref. 1 suggest that the rate plot parameters of the viscoelastic process are the same as those of Watts *et al.*

Watts *et al.* estimated rate plot parameters by determining the areas under the loss-temperature plots. For this procedure<sup>12</sup> to yield reliable results,  $\alpha$ ,  $\beta$  and  $\epsilon_0 - \epsilon_{\infty}$  must be independent of temperature. The results in Table 2 show that the first two assumptions are valid while the third is not. Estimates based on Table 2 show that  $\epsilon_0 - \epsilon_{\infty}$  is 0.226 at the reference temperature of  $-50^{\circ}\text{C}$ . The

temperature coefficient is such that this difference will change by 0.04 over a 100°C range, leading to a 20% error in the area estimation. One of the advantages of the techniques used in this work is that these parameters are independently evaluated.

Watts *et al.* set out to estimate the fraction of segments that orients with respect to the electric field. In his analysis he assumed that equation (3) is approximately 1. Substitution of the parameters from Table 2 shows that:

$$\frac{(\varepsilon_{\infty} + 2)^2 \varepsilon_0}{2\varepsilon_0 + \varepsilon_{\infty}} = 7.99 \neq 1 \quad (3)$$

The remainder of his argument is therefore suspect. One other difficulty with his discussion is that he assumed the alpha and beta processes to be related, which they may not be. For example, the alpha process may involve the moment associated with the carbonate group while the beta process may involve just the phenyl groups.

Watts *et al.* application of the Onsager equation<sup>12</sup> to the beta process is nevertheless a useful approach. Substitution of the equilibrium and instantaneous dielectric parameters, which are given in Table 2 at the reference temperature, into the Onsager expression:

$$\mu^2 = \frac{3kT}{4\pi N} \frac{(2\varepsilon_0 + \varepsilon_{\infty})}{3\varepsilon_0} \left( \frac{3}{(\varepsilon_{\infty} + 2)} \right)^2 (\varepsilon_0 - \varepsilon_{\infty}) \quad (4)$$

yields, at  $-50^\circ\text{C}$ ,  $\mu \approx 0.02\text{D}$ . In other words the dipole moment associated with the beta process is too small to be a dipole moment associated with the carbonate group except for the fortuitous case of nearly antiparallel arrangements of carbonate groups surrounding the central one in Kirkwood's model ( $g \approx 0$ ) for polar liquids<sup>12</sup>. The magnitude of the estimated dipole moment is, however, about the correct size to be considered as an induced moment arising from the polarizability of phenyl groups.

A better approach might be to interpret the data from the Mosotti-Clausius<sup>13</sup> point of view, which is based on the pioneering work of J. C. Maxwell. They derived an expression relating the polarizability  $\alpha_p$ , at very low optical frequencies to the refractive index,  $n$ , at comparable frequencies:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N \rho}{3M} \alpha_p = A \quad (5)$$

where  $A$  can be referred to as the molar polarization. Under the conditions of very low optical frequencies and very high electrical frequencies,  $n^2 \rightarrow \varepsilon_{\infty}$ . Under the present circumstances both  $\varepsilon_0$  and  $\varepsilon_{\infty}$  satisfy these conditions. Substitution of  $\varepsilon_0$  and  $\varepsilon_{\infty}$  from Table 2 leads

to:

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = A_0 = 0.736 \quad (6a)$$

$$\frac{\varepsilon_{\infty} - 1}{\varepsilon_{\infty} + 2} = A_{\infty} = 0.702 \quad (6b)$$

The two estimates of the molar polarization have two slightly different meanings.  $A_0$  is larger than  $A_{\infty}$  because the former parameter was obtained under those conditions where the flipping phenyl groups could move about their C(1)-C(4) bond to respond to the electrical field, while the latter parameter represents a frozen-in condition.

## CONCLUSIONS

One of the advantages of the numerical techniques described in this work is that a more detailed comparison can be made of relaxation processes by means of equation (1) than by comparing Arrhenius rate plots. In fact, since equation (1) is uniquely related to the time-dependent correlation function<sup>3</sup>, then the right-hand side of equation (1) uniquely determines the molecular dynamics of the beta process. Although some of the dynamic parameters for the dielectric and viscoelastic processes are slightly different, the differences may be due to experimental artifacts and not to any inherently different path in phase space. One reason for this view is that the differences noted above are similar to those between Pratt *et al.*<sup>4</sup> and Watts *et al.*<sup>5</sup>. Only measurements made on identically prepared specimens can distinguish between the alternatives.

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