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Mechanical Spectroscopy of the β Relaxation in Poly(vinyl chloride)

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ABSTRACT: The dynamic mechanical behavior of linear and slightly cross-linked poly(vinyl chloride) was studied in the region of the β relaxation. The relaxation spectrum has been described by an alternative relaxation time distribution based on a log normal function. By this method we have obtained distributions of the activation energy and entropy. We have found a very large distribution for the activation energy but not for the activation entropy. Moreover, cross-linking removes the high-energy components of the β relaxation process.

I. Introduction

Generally, amorphous polymers show at least two relaxations: the main one, named the α relaxation, is related to the glass transition. The relaxations occurring at lower temperature are called secondary (or sub-T_g) relaxations. The secondary relaxations are labeled, β, γ, and δ in order of decreasing temperature.

Secondary relaxations manifest neither a very noticeable change in the state of the material (such a change from the "glassy" to the "rubbery" state) nor a high jump in the heat capacity (C_p). Nevertheless, significant changes are observed in the physical properties of amorphous polymers going through secondary relaxations (for instance, physical aging).[1] The existence of β relaxation in a glass is actually regarded as a result of thermally activated molecular motions at local sites which are randomly dispersed in the disordered structure. In this structure the fluctuations of density remain frozen in all along measurements.[2]

Most mechanical and dielectric studies of poly(vinyl chloride) (PVC) have been made on the conventional polymer. These studies have shown that at least two relaxation processes, α and β, occur.

Many works have been published about β relaxation in PVC. It is generally accepted that this relaxation is due to a movement of small segments of the main chain since the chlorine substituents in PVC are attached rigidly to the main polymer chain.[3–5] Moreover, Havriliak et al.[6] have found that the intermolecular relaxation time is about 1/1000 that of the intramolecular value. These results suggest that the restrictions to segmental orientation come from chain stiffness and not from chain-to-chain interactions. The activation energy of the β relaxation is of about 50–65 kJ/mol.[4]

It is well-known that the structure of PVC is complicated and sensitive to processing conditions. However, the main features of the β relaxation are not strongly affected by crystallinity, microstructure, tacticity, molecular weight, and the thermal history of the samples.[7,8] Several authors have reported the existence of two β relaxations in PVC. Kakutani et al.[3] had found two relaxations (β_1 and β_2) for PVC polymerized at −30 °C. Since this polymer has a high syndiotacticity, they had concluded that the β_1 and β_2 processes are related respectively to the ordered and amorphous regions in PVC. del Val et al.[7,9] had determined two compensation laws by thermally stimulated depolarization current measurements, which suggest that two different microscopical mechanisms could be involved in this relaxation. In addition, they concluded that the microscopical origin of the β and α relaxations in PVC seems to be different. Diaz Calleja et al.[10–12] had observed a relaxation between the α and β relaxations, but these observations can be explained in terms of physical aging since this "relaxation" disappears with a heat treatment.

It is clear from this discussion that a good understanding of β relaxation in PVC requires information about fundamental characteristics of this process, i.e., the distributions of relaxation times, energy, and entropy.

The purpose of this paper is to report a detailed and systematic study of the β relaxation of PVC. A description derived from an approach previously used in the case of PMMA[13] is applied to our results. Then we propose a relaxation time distribution function which provides meaningful values about distribution in terms of both the activation energy and activation entropy for this relaxation process. In addition, the effect of cross-linking on the β relaxation will be discussed.

II. Experimental Methods

PVC used was a suspension polymer made by Marvylan. The average molecular weights of the polymer were determined by gel permeation chromatography (GPC) in THF at 298 K, using a standard Waters GPC apparatus. $M_n = 54\,100$ and $M_w = 107\,100$ ($M_w/M_n = 2$). The following basic formulation was used for linear PVC (L-PVC): PVC, 100 phr; dialkyltin dioctylthioglycolate by Ciba-Geigy as stabilizer, 2 phr; waxes of polyethylene, 0.7 phr; stearic acid by Merck, 0.1 phr, as lubricants. For cross-linked PVC (C-PVC), 8 phr 1,2-diethoxydibutyltin ($Bu_2Sn(OCH_2)_2$) and 4 phr calcium ethyleneglycolate ($Ca(OCH_2)_2$) were added. After dry mixing in a Henschel mixer at high speed (1000 rpm) for a few minutes at 378 K, the mixture was extruded in a LSM 30–40 mm Leistritz intermeshing counter-rotating twin screw extruder at 453 K, molded at 473 K, and cooled at room temperature. Cross-linking was performed in a Lescuyer pressing machine after extrusion of the mixture at 463 K by 10 min, as has been given elsewhere.[14]

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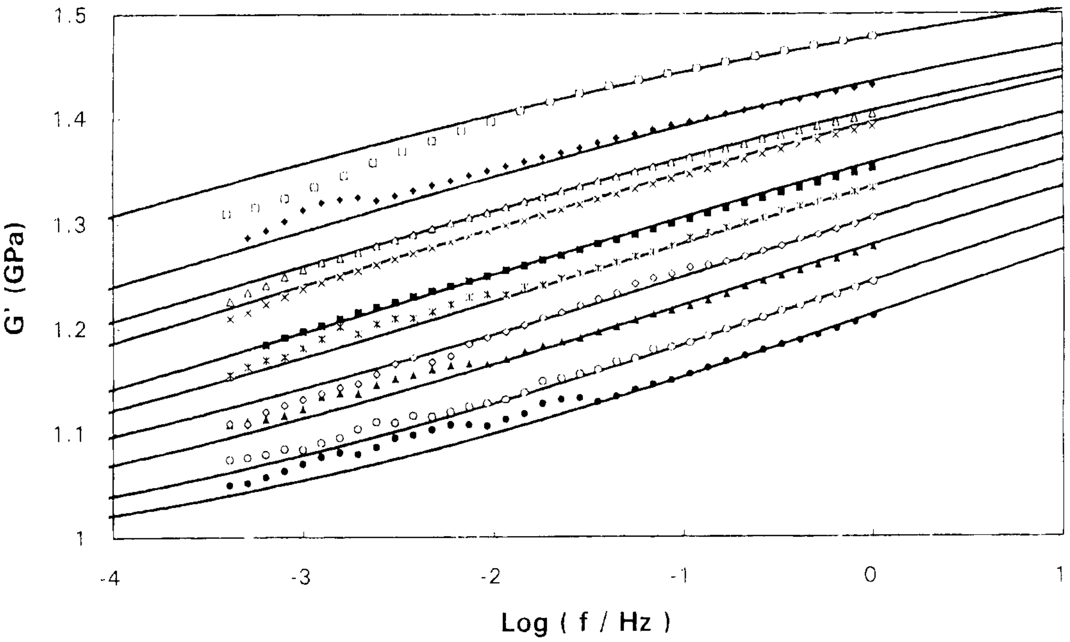

Figure 1. Isothermal spectra of G' for the β relaxation process in L-PVC at (□) 165, (◆) 175, (△) 180, (×) 185, (■) 190, (*) 195, (◇) 200, (▲) 205, (○) 212, and (●) 217 K. The continuous line is calculated from the relaxation time distribution function with parameters given in Table 1. The maximum discrepancy between theoretical and experimental results is about 2%.

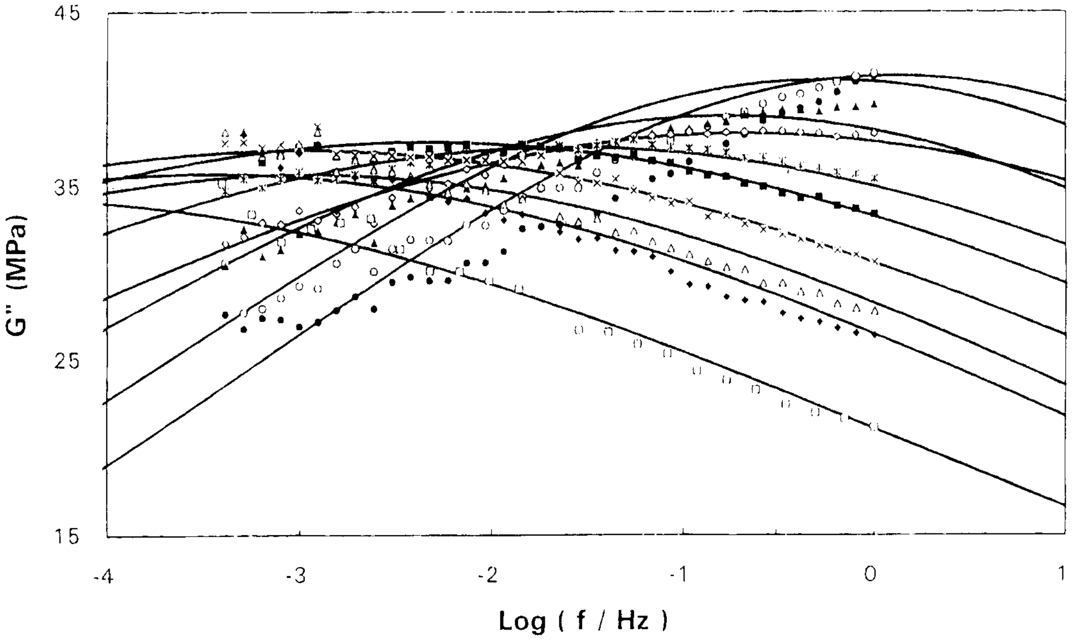

Figure 2. Isothermal spectra of G'' for the β relaxation process in L-PVC at (□) 165, (◆) 175, (△) 180, (×) 185, (■) 190, (*) 195, (◇) 200, (▲) 205, (○) 212, and (●) 217 K. The continuous line is calcualted from the relaxation time distribution function with parameters given in Table 1. The maximum discrepancy between theoretical and experimental results is about 8%.

The mean molecular weight between cross-links (M_c) was determined from the swelling rate after immersion of polymer in THF for 48 h:[15]

$$M_c = \frac{V_1 \varrho_2\left(\frac{v_2}{2} - v_2^{1/3}\right)}{\ln(1 - v_2) + v_2 + \chi_1 v_2^{2}}$$

where $1/(2M_c)$ = molar number of cross-links per gram of polymer, V_1 = molar volume of THF (76.33 mL/mol), v_2 = volume fraction of PVC in the gel (0.071), ϱ_2 = density of PVC (1.4 g/mL), and χ_1 = interaction parameter of a PVC/THF system (0.14).

For C-PVC we have at least one cross-link per chain of polymer (M_c = 21 000).

Mechanical behavior is measured with the help of a mechanical spectrometer developed in our laboratory[16] and is available from Metravib Instrument (Ecully, France); it consists of a forced oscillation pendulum, working in the temperature range 100–700 K and frequency range 5×10^{-5}–5 Hz. The mean strain is less than 10^{-4}, and the viscoelastic behavior of polymer materials appears to be independent of the applied stress over the whole strain amplitude range in all the temperature range used for experiments. The temperature of the sample remains constant to within 0.2 K.

This setup provides the storage (G') and loss (G'') moduli of the complex shear modulus (G^*) and the internal friction tan $\phi = G''/G'$ as a function of frequency (isothermal conditions) or temperature (isochronal conditions, for some fixed frequencies between 1 and 10^{-2} Hz). Resolution is better than tan $\phi = 5 \times 10^{-4}$, with an accuracy which is about ±5%, while

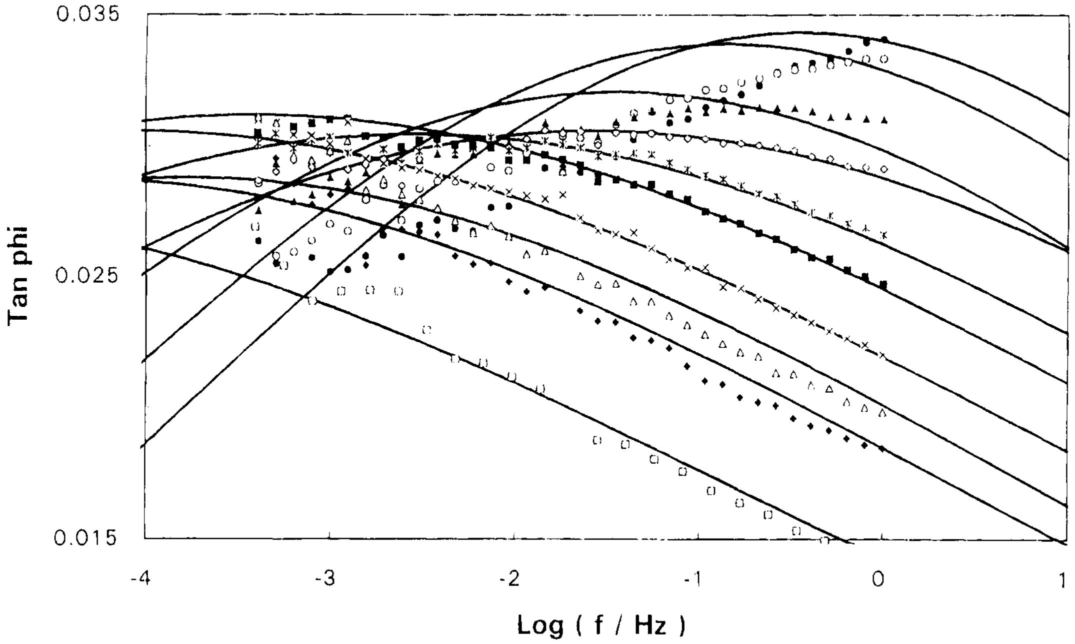

Figure 3. Isothermal spectra of tan ϕ for the β relaxation process in L-PVC at (□) 165, (◆) 175, (△) 180, (×) 185, (■) 190, (*) 195, (◇) 200, (▲) 205, (○) 212, and (●) 217 K. The continuous line is calculated from the relaxation time distribution function with parameters given in Table 1. The maximum discrepancy between theoretical and experimental results is about 10%.

relative changes in G'(Pa) lower than 10^{-3} can be easily detected.

III. Results

The isothermal behavior of G', G'', and tan ϕ in the temperature range of 165–217 K for L-PVC are shown in Figures 1–3. The figures show that, as the temperature increases, G' decreases and its spectrum shifts toward the high-frequency side. Both G'' and tan φ exhibit a peak whose position also shifts toward the high-frequency side and whose height increases as the temperature increases. This increase in height means that a horizontal shift along the frequency plane would not allow a superposition of the G', G'', and tan φ data, and therefore the time–temperature superposition of the spectra cannot be satisfactorily applied. This behavior is well recognized, and it is probably due to the solvation of plasticizer molecules in the amorphous phase.[3]

The logarithm of the frequency f_m at which G'' reaches a maximum value at different temperatures of measurements (isotherms at 200, 195, 190, and 185 K) is plotted against the reciprocal temperature in Figure 4. In the same figure, we can find the results reported by Ishida,[5] Diaz Calleja,[10] Tanaka,[17] and Dyson,[18] as well as the three data points obtained from measurements at fixed frequencies of 0.01, 0.1, and 1 Hz. As can be seen, there is a good agreement among different results and techniques: the frequency f_m varies according to the Arrhenius equation,

$$f_m = f_0 \exp(-E_\beta/RT) \qquad (1)$$

with $f_0 = 10^{15}$ Hz and $E_\beta = 62$ kJ/mol (from a linear regression, with a correlation coefficient of 0.92). Beyond the data from literature used in Figure 4, it is worth noting that this value of E_β agrees fairly well with the value obtained by Havriliak et al.[6]

Similar results were obtained at isothermal conditions for C-PVC as shown in Figures 5–7. In Figure 8, f_m is plotted against the reciprocal temperature as has been made for L-PVC. In the Arrhenius equation (eq 1), we have determined $f_0 = 4 \times 10^{14}$ Hz and $E_\beta = 55$ kJ/mol (correlation coefficient: 0.98) for this polymer.

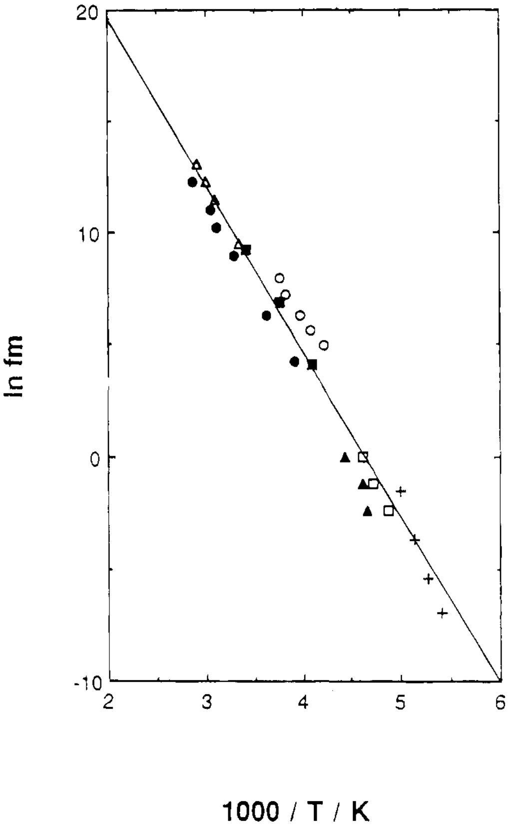

Figure 4. Frequency of the isothermal maximum of G'' and tan ϕ for the β relaxation process in L-PVC plotted against the reciprocal temperature. Data for the plot were obtained from (▲) tan ϕ isochronal peaks, (+) G'' isothermal peaks, (□) G'' isochronal peaks, (●) Ishida,[5] (■) Diaz,[12] (○) Tanaka,[17] and (△) Dyson.[18]

IV. Discussion

Viscoelastic relaxations in solids or liquids are always broader than a Debye relaxation. This broadening can

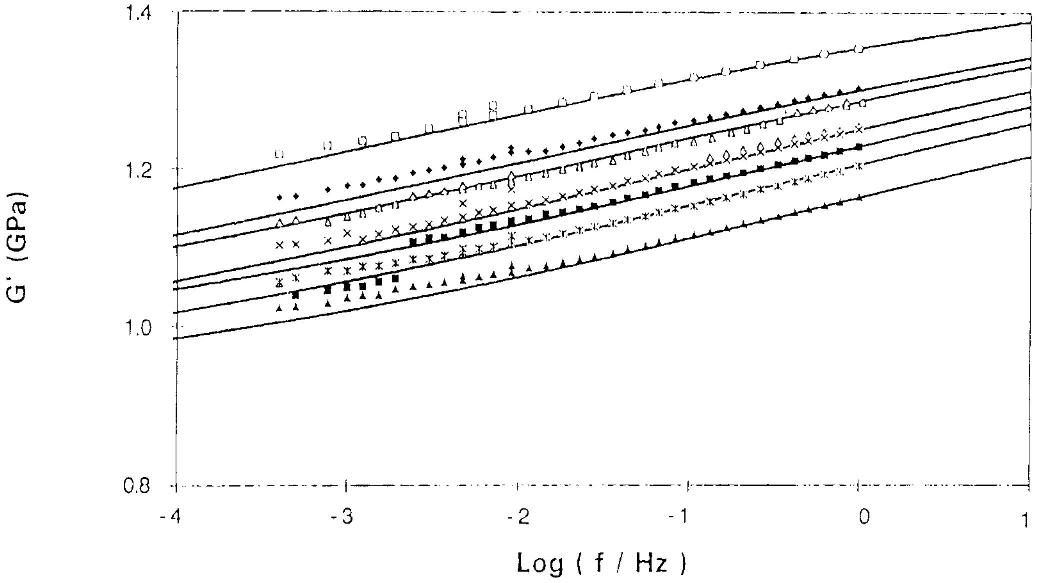

Figure 5. Isothermal spectra of G' for the β relaxation process in C-PVC at (□) 173, (◆) 184, (△) 189, (×) 194, (■) 198, (*) 203, and (▲) 208 K. The continuous line is calculated from the relaxation time distribution function with parameters given in Table 2. The maximum discrepancy between theoretical and experimental results is about 2%.

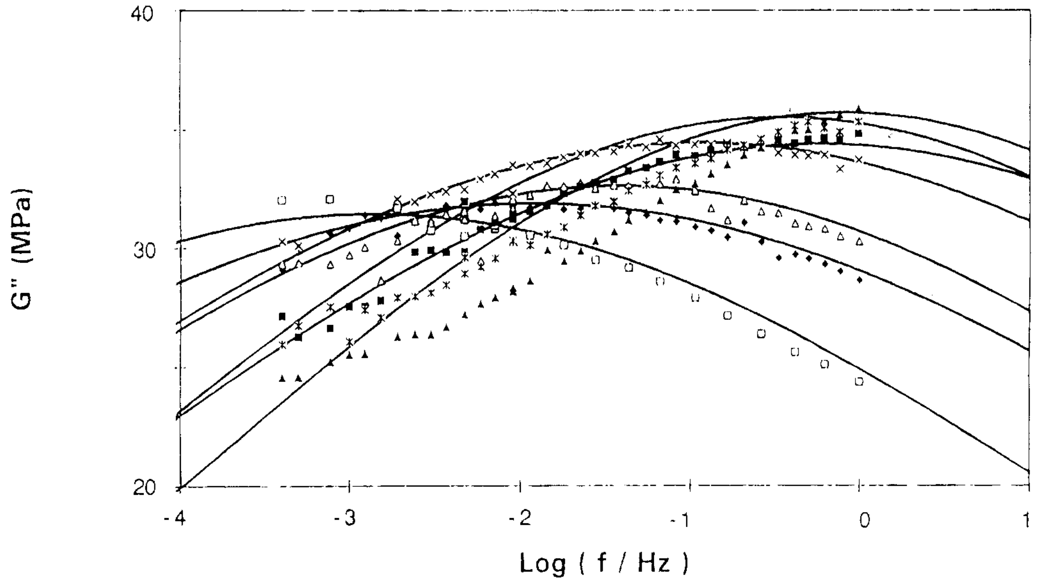

Figure 6. Isothermal spectra of G'' for the β relaxation process in C-PVC at (□) 173, (◆) 184, (△) 189, (×) 194, (■) 198, (*) 203, and (▲) 208 K. The continuous line is calculated from the relaxation time distribution function with parameters given in Table 2. The maximum discrepancy between theoretical and experimental results is about 8%.

be expressed in many different ways, such as distribution of relaxation times[4] or a stretched-exponential function.[19,20] A distribution of relaxation times might in turn reflect a distribution of activation energy, a distribution of preexponential factor, or both of them.

The quantity $\phi(\ln \tau)\, d \ln \tau$ is the fraction of the relaxation process having relaxation times between $\ln \tau$ and $(\ln \tau + d \ln \tau)$. Thus

$$\int_{-\infty}^{+\infty} \phi(\ln \tau)\, d(\ln \tau) = 1 \qquad (2)$$

In a dynamic mechanical experiment, the storage and loss moduli, G' and G'', are

$$G'(\omega\tau) = G_r + (G_u - G_r)\int_{-\infty}^{+\infty} \phi(\ln \tau)\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\, d(\ln \tau) \qquad (3)$$

and

$$G''(\omega\tau) = (G_u - G_r)\int_{-\infty}^{+\infty} \phi(\ln \tau)\frac{\omega\tau}{1+\omega^2\tau^2}\, d(\ln \tau) \qquad (4)$$

where G_u and G_r are the unrelaxed and relaxed moduli, ω is the angular frequency, τ is the relaxation time, and $\phi(\ln \tau)$ is the relaxation time distribution function.

There are a number of approximations for obtaining the relaxation spectrum from experimental data. One possibility is to describe the shape of the β relaxation spectra by the log normal relaxation time distribution function, based upon the Gaussian function:

$$\phi(\ln(\tau/\tau_m)) = \frac{1}{B\pi^{1/2}} \exp\left[-\left(\frac{\ln(\tau/\tau_m)}{B}\right)^2\right] \qquad (5)$$

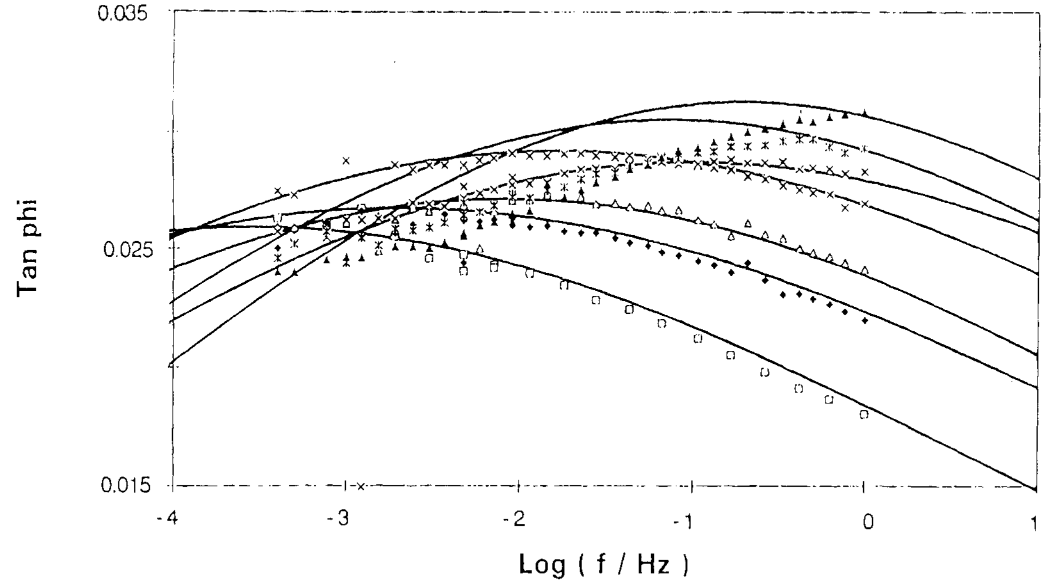

Figure 7. Isothermal spectra of tan ϕ for the β relaxation process in C-PVC at (□) 173, (◆) 184, (△) 189, (×) 194, (■) 198, (*) 203, and (▲) 208 K. The continuous line is calculated from the relaxation time distribution function with parameters given in Table 2. The maximum discrepancy between theoretical and experimental results is about 8%.

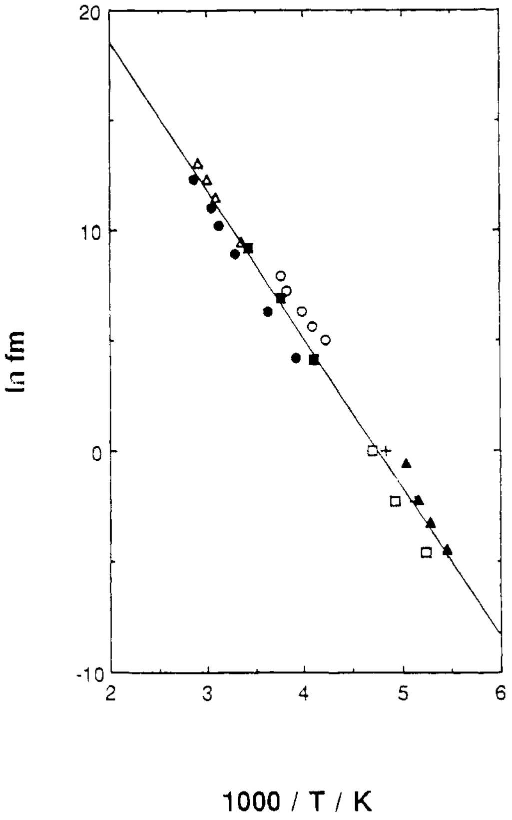

Figure 8. Frequency of the isothermal maximum of G'' and tan ϕ for the β relaxation process in C-PVC plotted against the reciprocal temperature. Data for the plot were obtained from (□) tan ϕ isochronal peaks, (△) G'' isothermal peaks, (+) G'' isochronal peaks, (●) Ishida,[5] (■) Diaz,[12] (○) Tanaka,[17] and (△) Dyson.[18]

where B is a parameter which corresponds to the width of the Gaussian distribution and τ_m is the most probable value of τ, corresponding to f_m that is the maximum in the G'' spectrum. As mentioned before,[13] it is more meaningful to describe the shape of the relaxation spectra in terms of a such a distribution of relaxation times because it reflects a distribution of activation energy, a distribution of preexponential factor, or both depending on the temperature variation of B with temperature. It should be noted that since the function in eq 5 is used through a numerical computation, the storage and loss moduli must be written in the forms:

$$\frac{G'(\omega) - G_r}{G_u - G_r} = \frac{\sum\left\{\frac{\omega^2\tau^2}{1 + \omega^2\tau^2}\exp\left[-\left(\frac{\ln(\tau/\tau_m)}{B}\right)^2\right]\right\}}{\sum\left\{\exp\left[-\left(\frac{\ln(\tau/\tau_m)}{B}\right)^2\right]\right\}} \tag{6}$$

and

$$\frac{G''(\omega)}{G_u - G_r} = \frac{\sum\left\{\frac{\omega\tau}{1 + \omega^2\tau^2}\exp\left[-\left(\frac{\ln(\tau/\tau_m)}{B}\right)^2\right]\right\}}{\sum\left\{\exp\left[-\left(\frac{\ln(\tau/\tau_m)}{B}\right)^2\right]\right\}} \tag{7}$$

As discussed by Nowick and Berry,[21] if ln τ_0 and E_β are independent of each other, B is given by:

$$B = [B_0 + (B_u/RT)^2]^{1/2} \tag{8}$$

where B_0 is a dimensionless quantity representing the width of the distribution in the parameter ln τ_0 and B_u has the dimension of energy and represents the width of distribution in E_β. However, when both ln τ_0 and E_β vary with a single parameter which may be a property of a material, B can be expressed by:

$$B = B_0 + B_u/RT \tag{9}$$

We use eqs 6 and 7 to calculate the spectra of G'' and G' for various values of $\Delta G = G_u - G_r$, G_r, and B until the calculated curves match the experimental data in both G' and G''. For the spectra where G''_{max} is not observed, f_m was determined from an extrapolation of the Arrhenius plots of Figures 4 and 8. Finally we can find tan $\varphi = G''/G'$.

The calculated spectra for G', G'', and tan φ are shown in Figures 1–3 in the case of L-PVC. Figures 5–7 show

Table 1. Parameters of the Fit of Data for Dynamic Mechanical Spectra of the β Relaxation of L-PVC by a Gaussian Distribution

T (K)	f_m (Hz)	B	ΔG (GPa)	G_r (GPa)	G_u (GPa)
217.0	1.26	10.5	0.50	0.97	1.47
212.0	0.56	11.0	0.52	0.97	1.49
205.0	0.17	12.0	0.54	0.97	1.50
200.0	0.21	14.2	0.62	0.96	1.57
195.0	0.02	14.7	0.62	0.94	1.56
190.0	4.4×10^{-3}	15.5	0.66	0.90	1.56
185.0	9.8×10^{-4}	15.7	0.66	0.91	1.57
180.0	1.1×10^{-3}	14.0	0.57	0.98	1.55
175.0	3.3×10^{-4}	14.5	0.59	0.97	1.56
165.0	2.5×10^{-5}	15.0	0.59	0.98	1.57

Table 2. Parameters of the Fit of Data for Dynamic Mechanical Spectra of the β Relaxation of C-PVC by a Gaussian Distribution

T (K)	f_m (Hz)	B	ΔG (GPa)	G_r (GPa)	G_u (GPa)
208.0	5.96	11.0	0.47	0.97	1.44
203.0	2.55	12.3	0.50	0.97	1.47
198.0	0.58	13.5	0.53	0.95	1.48
194.0	0.11	14.0	0.55	0.92	1.47
189.0	0.04	13.0	0.48	0.97	1.46
184.0	0.01	14.3	0.52	0.95	1.47
173.0	1.3×10^{-3}	13.5	0.48	0.98	1.47

these results for C-PVC. Calculated curves correspond fairly well to experimental ones since the deviation is lower than 2% for G'; although less good, the fit for G'' data is not so bad since a maximum deviation of 10% is observed with isotherms 217 (Figure 2) and 208 K (Figure 6) with a square error of about 6% for those curves. Parameters used in these simulations are given in Tables 1 and 2, and they are plotted against the temperature in Figures 9 and 10. As can be seen, this analysis provides a realistic temperature dependence of G_u which is known to decreases when temperature increases. On the other hand, ΔG is observed to decrease with increasing temperature for both L-PVC and C-PVC; this agrees with the observation made by Havriliak et al. that the difference between unrelaxed and relaxed compliance increases with temperature (see Figure 13, ref 6).

One important aspect is the analysis of B because, as mentioned above, B in eqs 6 and 7 has a physical significance in terms of the distribution of activation energy or (and) entropy. From Figure 10, the variation of B with temperature is given by eq 9 with B_0 between 0 and 2 and B_u between 17 and 21 kJ/mol. Then, as presented in the following, calculations will be made for both polymers with $B_0 = 1.3$ and $B_u = 19$ kJ/mol. In other words, energy and entropy are distributed, but the former much more than the latter: the activation energy of the β process for L-PVC is 62 ± 19 kJ/mol and $\ln(\tau_0/\mathrm{s})$ is -36 ± 1.3 and for C-PVC $E_\beta = 55 \pm 19$ kJ/mol and $\ln(\tau_0/\mathrm{s}) = -35 \pm 1.3$. It is worthwhile to note that the contrary was observed in the case of PMMA.[13] This could be understood considering the easier local molecular movement in defective sites[22] which imply lower E_β in completely amorphous regions than in more ordered regions which are recognized to exist in PVC. By another way, we have almost found the same behavior for L-PVC and C-PVC.

The self-consistency of the analysis in terms of a log normal distribution of relaxation times with the use of eqs 6 and 7 can be tested by calculating the variation of G' and G'' with temperature for a fixed frequency, using the parameters given in Tables 1 and 2 and the values of E_β and $f_0 = 1/\tau_0$ in the Arrhenius equation (eq 1). This variation expressed as $\tan \varphi = G''/G'$ for 0.09 Hz is shown in Figure 11 for L-PVC. In the same figure we can find results at 0.1 Hz for C-PVC. Calculated curves are in reasonably good agreement with the experimental isochronal curves, a rather demanding test, which supports the validity of our analysis. In short, analyzing data obtained in isothermal conditions gives us information about variation of G_u, ΔG, and B with temperature, and by means of this information we can predict the entire relaxation process at any temperature or frequency (in isothermal and isochronal conditions as well).

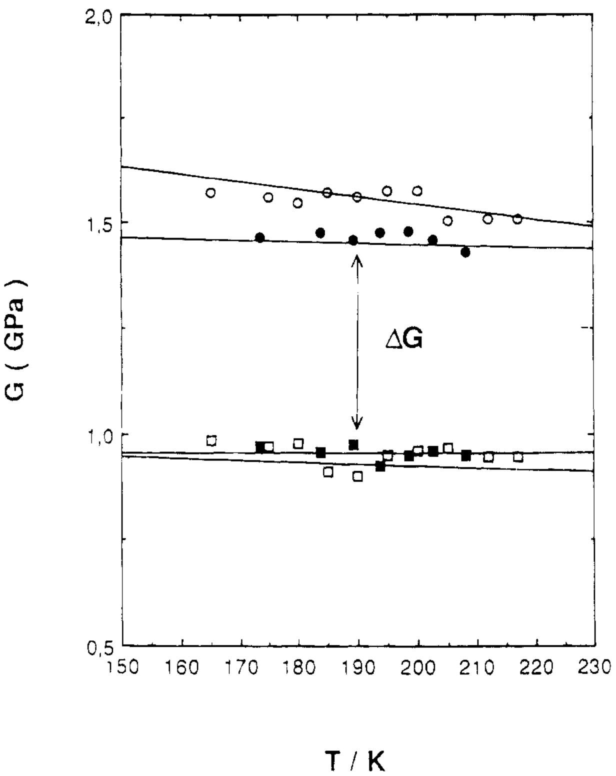

Figure 9. Variation as function of temperature of (□) G_r, (○) G_u in L-PVC and (■) G_r, (●) G_u in C-PVC for the β relaxation process. Data are obtained from the analysis using the relaxation time distribution function with parameters given in Tables 1 and 2. The least-squares linear fitting (solid lines) gives $G_u(\mathrm{Pa}) = 2 \times 10^9 - 1.8 \times 10^6 T$, $G_r(\mathrm{Pa}) = 9.6 \times 10^8 - 4 \times 10^4 T$, and $\Delta G = 9.3 \times 10^8 - 2 \times 10^6 T$ for L-PVC and $G_u(\mathrm{Pa}) = 1.5 \times 10^9 - 4 \times 10^5 T$, $G_r(\mathrm{Pa}) = 1.0 \times 10^9 - 4.0 \times 10^5 T$, and $\Delta G = 5 \times 10^8 - 4 \times 10^3 T$ for C-PVC. For all the cases, the correlation coefficient (r^2) was higher than 0.98.

Muzeau et al.[13] had used the same method to study β relaxation in poly(methyl methacrylate) where it was deduced that the distribution was mainly in the activation entropy. So, it is clear that the use of a relaxation time distribution function based on a log normal function is a powerful tool for describing the β relaxation in polymers as far as data obtained in isothermal conditions are available.

Recently, Starkweather[23] has developed a procedure based on the Eyring theory of absolute reaction rates for the analysis of relaxations. In a previous work,[13] it was shown in the case of PMMA that both analyses led to similar conclusions, but the comparison was easy due to the high relaxation strength of the β relaxation in PMMA ($\tan \varphi_{\max} \cong 0.1$); in the present work concerning PVC, the relaxation strength, about 0.035, is about 3 times lower; consequently, it was hardly possible to

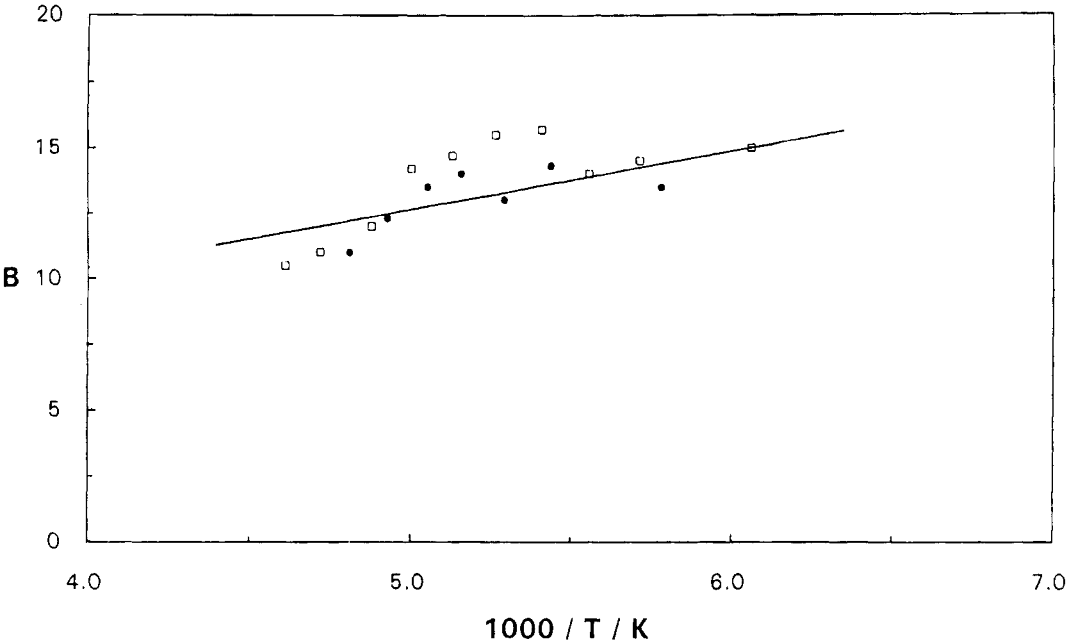

Figure 10. Temperature dependence of B, a parameter which is a measure of the width of the Gaussian distribution for L-PVC (□) and C-PVC (●). The solid line gives $B = 1.3 + 2254/T$. Scatter about the value of B corresponds to ±0.5.

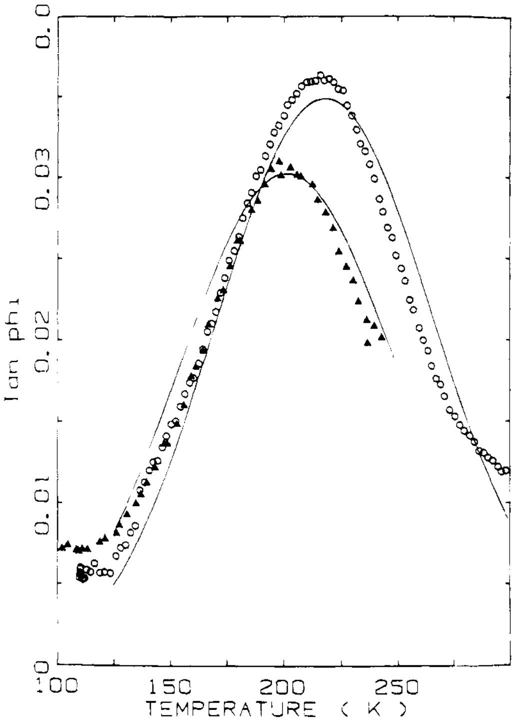

Figure 11. Isochrones of tan ϕ for the β relaxation in L-PVC (○) at 0.09 Hz and in C-PVC (▲) at 0.1 Hz. Solid lines are the calculated curves by using the temperature dependence of G_r, G_u, and B as shown in Figures 9 and 10.

apply Starkweather's method, mainly because, as mentioned earlier, variations in intensity of the relaxation process did not allow construction of a "master" curve yielding ΔS_β. This behavior is typical of a material which is not "thermorheologically simple". This characteristic of PVC can be seen by plotting the variation of G'' and G' in the complex plane or Cole–Cole plot as shown in parts a and b of Figure 12. A similar behavior in the Cole–Cole plot was observed by Havriliak et al. (see Figure 14, ref 6). In the same figures we have plotted theoretical results obtained by the analysis described here: we can see that there is a good correspondence between calculated and experimental results (maximum deviation about 10%). The use of the parameter B could suggest some similarities with the Cole–Cole function ($\beta = 1$ for a Gaussian loss curve): this would be the case if B was constant; in fact B is shown to be temperature dependent and this results in a slightly asymmetrical curve in the Cole–Cole plot as is shown in parts a and b of Figure 12. Then, by means of the parameter B dependent on temperature, our analysis takes variations observed in the spectra into consideration (compare isothermal curves calculated for 165, 190, and 217 K with experimental data). Nevertheless, Starkweather's analysis was considered as follows:

(i) From the diagram E_β–T, ΔS_β was deduced by comparing the experimental point to the curve given by the equation[23] $E_\beta = RT'[1 + \ln(k/2\pi h) + \ln(T')]$. The value ΔS_β = 43 J(mol·K) is obtained (see Figure 13, inset).

(ii) The data of Figure 2 are presented in the diagram $\Phi = 2G''/\pi\Delta G$ with $\Delta G = G_u - G_r$ = 585 MPa (average value: see Table 1), as a function of $\Delta H_\beta = RT[\ln(k/2\pi h) + \ln(T/f)] + T\Delta S_\beta$ (see ref 23).

(iii) A master curve is expected: actually, Figure 13 shows it is practically the case; from that, we deduce $\Delta H_\beta(\Phi_{\max})$ = 59 kJ/mol, that is, E_β = 60.9 kJ/mol (which is to be compared to the value E_β = 62 kJ/mol mentioned above).

(iv) Moreover, the width of distribution of ΔH_β (about ±20 kJ/mol) is also comparable to that of E_β (62 ± 19 kJ/mol): actually, it is worthwhile to notice that considering a Gaussian distribution of ΔH_β such that $\Phi = \Phi_{\max} \exp[-((59 - \Delta H_\beta)/B_u)^2]$ with B_u = 19 kJ/mol as given above, we obtain the interrupted curve of Figure 13, exhibiting a deviation with data which is never higher than 9%.

That could justify the use of a log normal distribution of relaxation times corresponding mainly, in the case of PVC studied here, to a Gaussian distribution of activation energy.

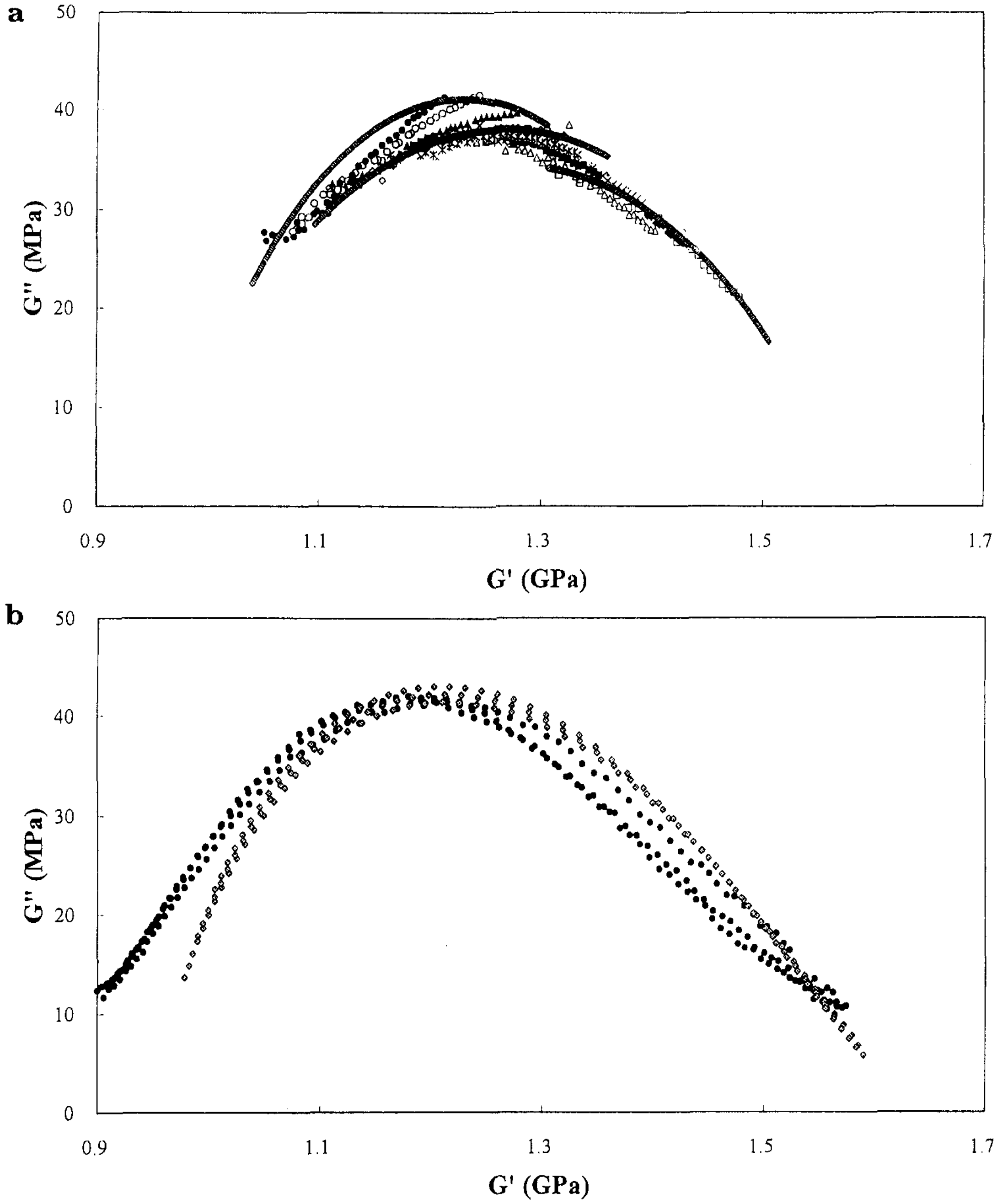

Figure 12. Cole–Cole plot in the β relaxation range for L-PVC. (a) Isothermal conditions: (symbols) experimental data as in Figure 1; (dotted diamonds) calculated values for 165, 200, and 217 K. (b) Isochronal conditions: (black dots) experimental data for 1, 0.3, and 0.09 Hz; (dotted diamonds) calculated values for the same frequencies.

Moreover, the comparison of results in isochronal conditions shows us that the low-temperature side of the loss peak of L-PVC and C-PVC is the same, but it differs markedly on the high-temperature side. It seems that cross-linking removes the high-energy components of the β relaxation. In order to verify this assumption, a more cross-linked PVC was prepared (3C-PVC, with almost three cross-links per chain of polymer, M_c = 10 400) and isochronal experiments at 1 Hz over the temperature range of 100–250 K were made. Results of tan φ for L-PVC, C-PVC, and 3C-PVC are shown in Figure 14. As can be seen, cross-linking density decreases the high side of the β relaxation of these systems. Flores[24] observed a similar behavior in cross-linked PVC/PMMA blends. $Bu_2Sn(OCH_2)_2$ causes cross-linking in PVC through nucleophilic substitution (SN_2 reaction) of chlorine atoms (especially over the isotactic sequences). Maybe these sequences are the sites of the highest energy relaxation, and when they disappear (by cross-linking reaction), we change the characteristics of the relaxation: diminution of E_β (therefore T_β) and modification of the high-temperature side of the relaxation peak. It is worth noting that simulation is in agreement with these observations because calculated curves using a lower mean value of E_β correspond reasonably well to experimental ones.

V. Conclusions

It is recognized that a log normal distribution of relaxation times for β relaxation in polymers could reflect a distribution of activation energies and (or) a distribution of the preexponential factor (i.e., the activation entropy, that is, the degeneracy of paths used during the molecular relaxation over energy barriers).

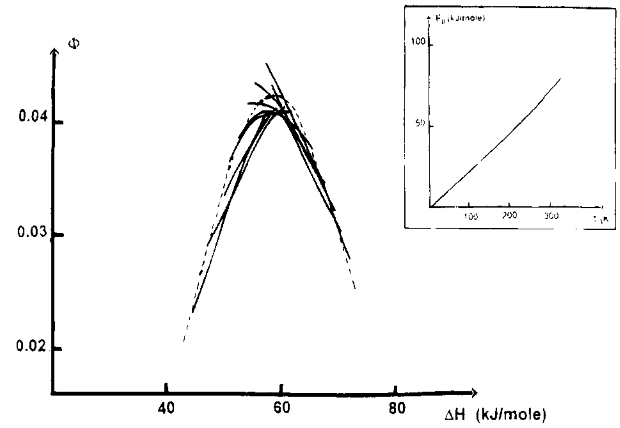

Figure 13. Plot of the whole set of curves shown in Figure 1 in the diagram Φ versus ΔH. The interrupted curve corresponds to a Gaussian distribution of ΔH (see text). In the inset, diagram E_β versus T: experimental point and curve with $\Delta S_\beta = 0$ (see text).

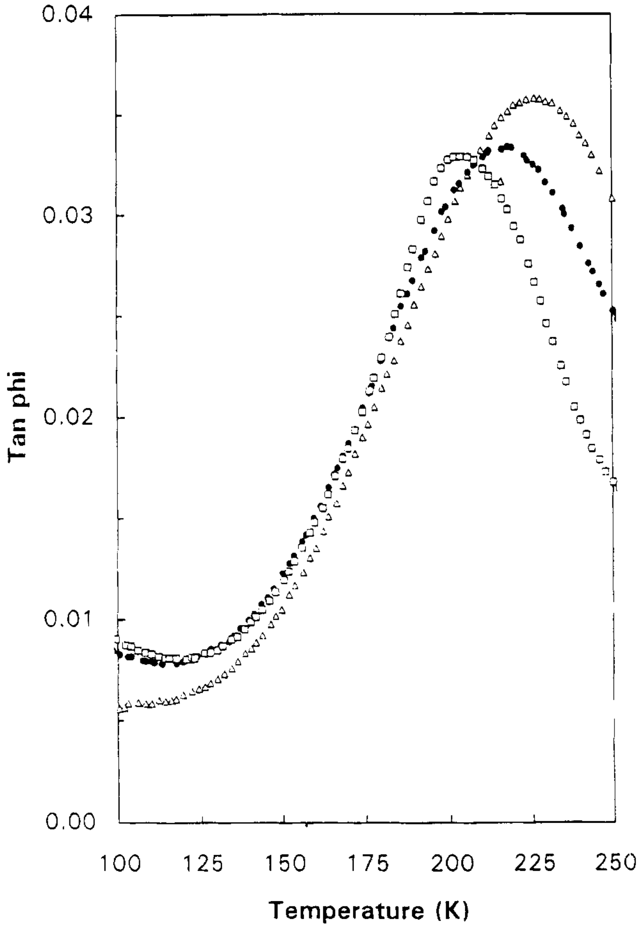

Figure 14. Isochrones of tan ϕ for the β relaxation in L-PVC (△), C-PVC (●), and 3C-PVC (□) at 1 Hz.

Applied to isothermal data, information about variation of G_u, G_r, and B (width of distribution) as a function of temperature can be obtained.

In the case of PVC, the energy distribution effect is predominant; the large distribution of the activation energy for the β relaxation could result from the microstructure of polymer (tacticity, cross-linking); actually, cross-linking of PVC by 1,2-diethoxydibutyltin ($Bu_2Sn(OCH_2)_2$) removes the high-energy components of the β relaxation.

Then, by means of a log normal distribution of relaxation times, we can predict the dynamic mechanical behavior of PVC in the entire range of the β relaxation process for isothermal or isochronal conditions as well (in other words, at any temperature or frequency).

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