Thermally stimulated depolarization study of polymer relaxation parameter distributions at normal and high pressures

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An analysis has been performed of the thermally stimulated depolarization (t.s.d.) currents in the vicinity of the glass transition temperature (T_g) of poly(vinyl chloride), poly(vinyl acetate), poly(methyl methacrylate), poly(trifluorochloroethylene) and nylon-6 at hydrostatic pressures ranging from 0.1 to 200 MPa. A technique for the transformation of t.s.d. curves into relaxation parameter distributions has been developed and substantiated. On the basis of this technique, the distributions of glass transition temperatures, relaxation times, frequency factors and activation energies and volumes were studied. It was shown that the distributions of all relaxation parameters are adequately described by exponential functions.

(Keywords: thermally stimulated depolarization; high pressure; relaxation parameter distributions; activation volumes)

INTRODUCTION

Thermally stimulated depolarization (t.s.d.) techniques have recently been used widely to study relaxation processes in polymers[1,2]. T.s.d. is a low-frequency technique working in the range 10^{-2}–10^{-4} Hz. One of its advantages is high resolution, allowing one to separate and study relaxation processes that overlap in the range of high frequencies. A combination of t.s.d. with high hydrostatic pressures was shown to enhance this resolution[3], since relaxation processes differ in their baric coefficients of relaxation times ($\partial\tau/\partial p$).

Another advantage of t.s.d. is the possibility of analysing the distributions of relaxation parameters, such as relaxation times, activation energies and frequency factors. The techniques used for this purpose are briefly covered in the next section of this article.

Using high pressures allows one to determine another important relaxation parameter, the activation volume $V^* = -RT\ (\partial \ln \tau/\partial p)$, which is the minimum volume of fluctuation of the 'hole' near a kinetic unit, required for its motion. Dielectric relaxation[4] and photon correlation spectroscopy[5,6] were used to obtain the V^* values of segmental motion in some polymers. In refs. 3 and 7 this parameter in nylon-6 and copolymers of vinyl chloride and vinyl acetate was determined by the t.s.d. technique. The relaxation parameters were calculated making no allowance for the distribution in frequencies of segmental motion.

The objective of the present work was to analyse the distribution in the basic relaxation parameters, activation volumes included. For this purpose we studied the t.s.d. currents at normal and high pressures in the region of the glass transition temperature (T_g) of amorphous poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVA) and crystalline poly(trifluorochloroethylene) (PTFCE) and nylon-6 (N6) polymers.

THEORETICAL TREATMENT

In the case when the thermal motion of all dipoles in the system is characterized by a single relaxation time τ, i.e. when the condition of a monorelaxational process is satisfied, the following relationships of the t.s.d. theory are valid[1,2].

The temperature dependence of current I is

$$\begin{aligned} I(T) &= -P_0\tau^{-1}\exp\left[-b^{-1}\int_{T_0}^{T}\tau^{-1}\,\mathrm{d}T\right] \\ &= -\frac{P_0}{A}\exp\left[-\frac{U}{RT}-\frac{1}{bA}\int_{T_0}^{T}\exp\left(-\frac{U}{RT}\right)\mathrm{d}T\right] \end{aligned} \qquad (1)$$

where P_0 is the initial polarization, b is the heating rate, T_0 is the initial temperature, U is the activation energy and A is the frequency factor. The t.s.d. current reaches a maximum if

$$\tau_m = RT_m^2/bU \qquad (2)$$

where T_m is the temperature at the peak's maximum. Equation (2) may be used to estimate the relaxation times at the temperature of the t.s.d. curve's maximum. Thus, a shift of the temperature maximum on the t.s.d. curves obtained at various heating rates (b_1, b_2) yields

$$U = \frac{R}{(T_m)_2^{-1} - (T_m)_1^{-1}} \ln\frac{b_1 (T_m)_2^2}{b_2 (T_m)_1^2} \qquad (3)$$

Activation energy can also be obtained from the initial section of the t.s.d. curve by using the expression derived

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from equation (1)

$$\ln I = \text{constant} - U/RT \tag{4}$$

One can also estimate U from the halfwidth of the peak (ΔT)

$$U \approx 2.5RT_{\mathrm{m}}^2/\Delta T \tag{5}$$

To calculate the relaxation times at any point of the t.s.d. curve, the following expression is used

$$\tau = P(t)/I(t) \tag{6}$$

where $P(t)$ and $I(t)$ are the residual polarization and current at time t. The current at the maximum of the t.s.d. curve is related to the number of dipoles N involved in the relaxation by

$$I_{\mathrm{m}} = EN\mu^2Ub/3\mathrm{e}R^2T_{\mathrm{m}}^3 \tag{7}$$

where E is the poling field, μ is the dipole moment and e is the base of natural logarithms. The t.s.d. curves for systems with a wide distribution of dynamic parameters (τ, U, A), to which polymers belong, represent an envelope of a set of narrow peaks yielded by dipole groups differing in relaxation times τ, and can be described by the following equation:

$$I(T) = -P_0\int_0^\infty \frac{F(\tau)}{\tau}\exp\left(-b^{-1}\int_{T_0}^{T}\frac{\mathrm{d}T}{\tau}\right)\mathrm{d}\tau \tag{8}$$

where $F(\tau)$ is the relaxation time distribution function.

It is clear that equations (1) and (4)–(6) are inapplicable for data treatment of systems with dynamic parameter distributions. Only equations (2) and (3) are valid to estimate the most probable values of τ and U, since the maximum of the experimental t.s.d. curve, as a rule, coincides with that of the distribution function[8-10].

Three main approaches are used to reconstruct the distribution function on the basis of experimental t.s.d. curves: the fitting method, the fractional method and the direct transformation of a t.s.d. curve into a distribution function.

In the fitting method the analytical expressions of the known distribution functions (Fuoss–Kirkwood, Cole–Cole, Havriliak–Negami, etc.) are substituted into equation (8), satisfactory agreement between the experimental and calculated t.s.d. curves being achieved through varying the width parameter of the function[1,2,11,12].

Fractional techniques are based on developing experimental conditions under which narrow dipole groups with close values of dynamic characteristics are involved in the relaxation process[1,10,13,14]. In this case a continuous distribution is approximated by a discrete set of monorelaxational processes analysed using equations (1)–(7).

The most accessible and attractive technique is that of a direct transformation of t.s.d. curves into a distribution function. This approach was adopted by Pfister and Abkovitz[9] and boils down to the following. Each point on the experimental t.s.d. curve with coordinates I_i, T_i is assumed to represent the maximum of the depolarization current $(I_{\mathrm{m}})_i$ for a narrow group of dipoles with a single value U_i and A_i or τ_i. For each of the arbitrarily selected points, the condition (2) is satisfied. This condition can be written as

$$T_i^2 = U_i\tau_i b/R \tag{9}$$

A combination of equation (9) with the Arrhenius equation $\tau = A\exp(U/RT)$ yields

$$T_i^2 = (bU_iA_i/R)\exp(U_i/RT_i) \tag{10}$$

This relationship is used to estimate A_i or U_i under the assumption that only one of these parameters varies, the other being constant for all dipole groups (the so-called one-dimensional distribution). To obtain the distribution function of the frequency factor, the value of U = constant was determined by a heating-rate-dependent shift in the t.s.d. curve maximum, making use of equation (3). As has already been pointed out, this equation is valid for estimating the most probable values of dynamic parameter distributions. Having obtained the frequency factor distribution function, one can use its most probable values to construct $F(U)$.

To determine the relative number of dipoles in ensembles N, equation (7) is used according to which

$$N \approx IT^3/bE$$

where E is the intensity of the polarizing field. Frequency factor or activation energy distribution functions are obtained from the dependences of $I_iT_i^3/bE$ on U or on $\ln A$.

The transformation method is most suitable for treatment of data obtained under conditions of high pressure where fractional techniques are not suitable. It should be noted that in contrast to f.t.s.d., the transformation method allows one to obtain many more experimental points for constructing the distribution functions, whereas the order of approximation used in both techniques is the same. A limitation of the approach adopted in ref. 9 is the necessity to introduce the concept of a one-dimensional distribution, which contradicts the experimental results. As a rule, in studying the kinetics of physical and chemical processes in polymers, a correlation between the activation energy and the logarithm of the pre-exponential factor, the so-called 'compensation effect', is observed[15,16].

The transformation method used in the present work was based on different approximations that did not need use to be made of the model of a one-dimensional distribution and thus simplify the analysis. In this approach the relaxation times at the maxima of the peaks (the sum of which yields the experimental t.s.d. curve) are assumed to be equal, while differences in the positions of these maxima on the temperature scale are assumed to be due to those in U and A. The condition of the equality of relaxation times at the maxima of individual peaks follows from equation (6). Since the residual polarization is determined by the area under the t.s.d. curve, for the maximum point it is proportional to the product of the current and the peak's halfwidth. Consequently, the relaxation time at the maximum depends only on the peak's width (b = constant). Thus, for narrow peaks of an individual relaxation process the value of τ may be considered as constant. This assumption is confirmed by f.t.s.d. data analysis. The τ values at the maxima of fractional peaks in the range of polystyrene T_g differ by no more than a factor of 1.5 (ref. 14).

It follows from condition (2) that for all peaks of individual relaxation processes at τ = constant and b = constant,

$$U_m/T_m^2 = \text{constant} \qquad (11)$$

This equation allows one to transform the temperature axis into the energy axis provided the value of the 'constant' is known. In the present work the constants were determined from the shift of the maximum of a common t.s.d. peak at various heating rates by using equation (3). The expression allowing one to calculate the activation energies at other T_i takes the form

$$U_i = U_m T_i^2 / T_m^2 \qquad (12)$$

where U_m and T_m are the values of U and T at the maximum of the common t.s.d. peak.

With regard to the applicability of equation (12) to real polymer systems, the following considerations can be made. (1) In polymers the experimental dependences of the activation energy on the temperature of the current maxima of fractional t.s.d. are close to parabolic[14]. (2) The t.s.d. curve near the polymer T_g is actually the distribution curve of the glass transition temperatures (see the next section). Therefore, to check the validity of equation (12), the latter should be compared to empirical dependences $U = f(T_g)$ reported in ref. 17. The analysis shows that in many polymer systems the dependences of U on T_g^2 are nearly linear.

On the strength of these data, condition (11) can be considered as valid for polymeric systems. Having used this condition to determine U_i and τ_i values for all T_i, we can calculate the frequency factor at each temperature.

The relative number of species in each dipole group in accordance with equations (7) and (9) is determined from

$$N_i \sim I_i T_i \qquad (13)$$

Thus, the plots of dependences of IT on U, τ and A yield distribution functions in the corresponding dynamic parameters.

It should be noted that, for the description of temperature dependences of τ, two equations—Arrhenius and Williams–Landel–Ferry (WLF)—are commonly used. The first equation is valid for linear dependences $\ln\tau = f(1/T)$ and the second for nonlinear. The dependences are nonlinear for α-relaxation in a wide temperature region of some polymers (i.e. PVC, PVA) and hence the WLF equation is preferable for these[18]. However, in the narrow temperature and frequency range near T_g, linearity of $\ln\tau$ *versus* $1/T$ dependences is observed for most polymer systems, including those studied in this work. For this reason, and in order to obtain the distributions in activation energies, we used the Arrhenius equation.

EXPERIMENTAL

Discs of PVA, PVC, PMMA, PTFCE and nylon-6 22 mm in diameter and 50–100 μm thick were cut from films obtained by moulding. The deviation of width from the average value did not exceed 5%. The electrically conductive coating on the samples was obtained by vacuum spraying of aluminium (PVA, PVC, PMMA) or by coating the samples with a thin aluminium foil (PTFCE, nylon-6). Different techniques were used because of the different coating adhesion to the polymer surface. The samples were polarized in a d.c. electric field of 10 kV cm^{-1} for 15 min at normal pressure and $T = T_g + 30$°C. The cooling rate of the samples in the electric field was 7°C min^{-1}.

The high-pressure chamber was designed to register the t.s.d. currents. The chamber consisted of a highly resistant steel body and two screw caps each fitted with six electric inputs, and it was fitted out with heating electrodes with an in-built thermocouple and a platinum resistance thermometer. The chamber was linked to a liquid compressor by a steel capillary, transformer oil serving as the pressure-transmitting liquid. Maintained to better than 5%, the pressure in the system was measured by an external manometer. The heating rates were 2, 4, 6 and 12°C min^{-1}.

The t.s.d. curves of the samples recorded in the oil and in the air coincided fully. The metal coating on the sample surface prevents plasticization by the working liquid. No alterations were observed in the t.s.d. curves recorded before and after keeping the samples at pressure up to 200 MPa for 30 min in the temperature range from 293 to 450 K.

RESULTS AND DISCUSSIONS

The range of normal pressures

For all five polymers studied, the t.s.d. current temperature dependences near T_g exhibit smooth peaks with one maximum and no remarkable overlapping with the peaks due to other relaxational processes (*Figure 1*). The temperatures at the maxima (T_m) are in good agreement with the glass transition temperatures evaluated by dielectric techniques at low frequencies[17]. In the previous section, it was pointed out that the temperature dependences of the t.s.d. current near the polymer's T_g can be presented as a sum of monorelaxational process peaks which are due to segmental motions in the amorphous regions. Consequently, the width of a t.s.d. peak correlates with that of a distribution in glass transition temperatures. To obtain the distribution function $F(T_g)$ the current scale shown in *Figure 1* should be transformed into the scale of the relative number of species in ensembles (or into a quantity proportional to this number). This can easily be done using equation (13). The distribution functions obtained are shown in *Figure 2a*. They are seen to be bell-shaped with the width and asymmetry depending on the polymer. These distributions are described quite adequately by exponential equations of the following type:

$$F(T_g) = \begin{cases} C\exp[(T_g - T_g^m)/\alpha(T_g)] & \text{at } T_g < T_g^m \\ C\exp[(T_g - T_g^m)/\beta(T_g)] & \text{at } T_g > T_g^m \end{cases} \qquad (14)$$

where T_g^m is T_g at the distribution maximum, and $\alpha(T_g)$ and $\beta(T_g)$ are the halfwidths of the distribution at 1/e height in the ranges $T_g < T_g^m$ and $T_g > T_g^m$ respectively (*Figure 2b*).

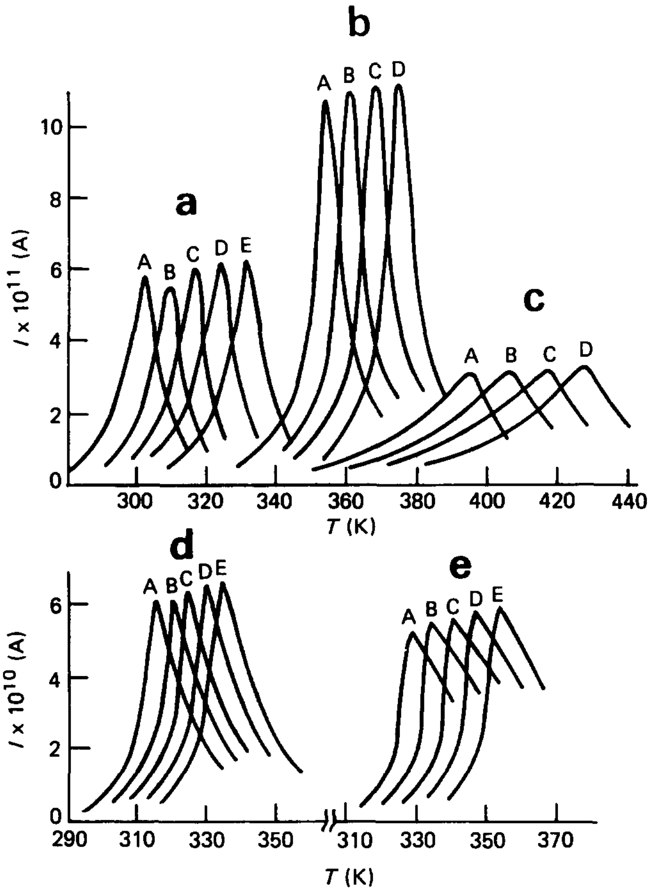

Figure 1 Dependences of t.s.d. current on temperature for (a) PVA, (b) PVC, (c) PMMA, (d) N6 and (e) PTFCE at 0.1 MPa (curves A), 50 MPa (curves B), 100 MPa (curves C), 150 MPa (curves D) and 200 MPa (curves E). Heating rate $b = 4°\text{C min}^{-1}$

According to equation (14), in semilogarithmic coordinates the T_g distributions should transform into the triangular-shaped ones. *Figure 2b* demonstrates that insignificant deviations of the experimental points from equation (15) are observed only near the top. The $\alpha(T_g)$ and $\beta(T_g)$ values are listed in *Table 1*. These data indicate that the full width $\alpha(T_g)+\beta(T_g)$ of distributions in the glass transition temperatures varies from 13°C (PVC) to 36°C (PMMA). Differences in the distribution width appear to indicate the degree of structural nonuniformity of these polymers.

To assess the distribution asymmetry we made use of the $\alpha(T_g)/\beta(T_g)$ ratio (*Table 1*). For amorphous PVC and PVA the distributions are close to symmetrical ($\alpha(T_g)/\beta(T_g) \simeq 1$). With crystalline polymers PTFCE and N6, the T_g distributions exhibit a steeper high-temperature branch as compared to the $T_g < T_g^m$ range, and are characterized by a lower value of the asymmetry parameter. This seems to be accounted for by a considerable fraction of amorphous regions with a chain packing similar to that in the crystalline phase.

A distinctive feature of the T_g distribution in PMMA is a steeper branch in the low-temperature range as compared to the $T_g > T_g^m$ range. This corresponds to a higher value of the asymmetry parameter[1,4]. It is evident that in this polymer the fraction of the regions with a dense packing is small.

It should be noted that an increase in the heating rate shifts the maximum of the T_g distribution to higher temperature without a significant change in their shape and width (*Figure 2b*).

As shown in the previous section, equation (12) allows one to transform the temperature axis of the t.s.d. curve into that of the activation energy and thus, instead of the T_g distribution, to obtain the U distribution. Then, deriving τ and A from (2) and the Arrhenius expression, one can easily obtain these parameter distributions. The value of U_m/T_m^2 required for these operations was calculated using equation (3) on the basis of data obtained at various heating rates. With PMMA it amounts to 2.26, with PVA to 1.98, with PTFCE to 1.91, with N6 to 1.5, and with PVC to $3.33\ \text{J mol}^{-1}\ \text{K}^{-1}$.

The U, A and τ distributions are adequately approximated by functions similar to those used for the T_g distribution:

$$F(X)=\begin{cases} C\exp[(X-X_m)/\alpha(X)] & \text{at}\, X<X_m \\ C\exp[(X-X_m)/\beta(X)] & \text{at}\, X>X_m \end{cases} \qquad (15)$$

where X stands for U, $\ln\tau$ or $\ln A$ of the corresponding distribution functions, X_m is the value of these parameters at the distribution function maximum, and $\alpha(X)$ and $\beta(X)$ are halfwidths of distributions at the $1/e$ height at $X<X_m$ and $X>X_m$ respectively.

Figures 3 and *4* show the activation energy, relaxation time and frequency factor distributions.

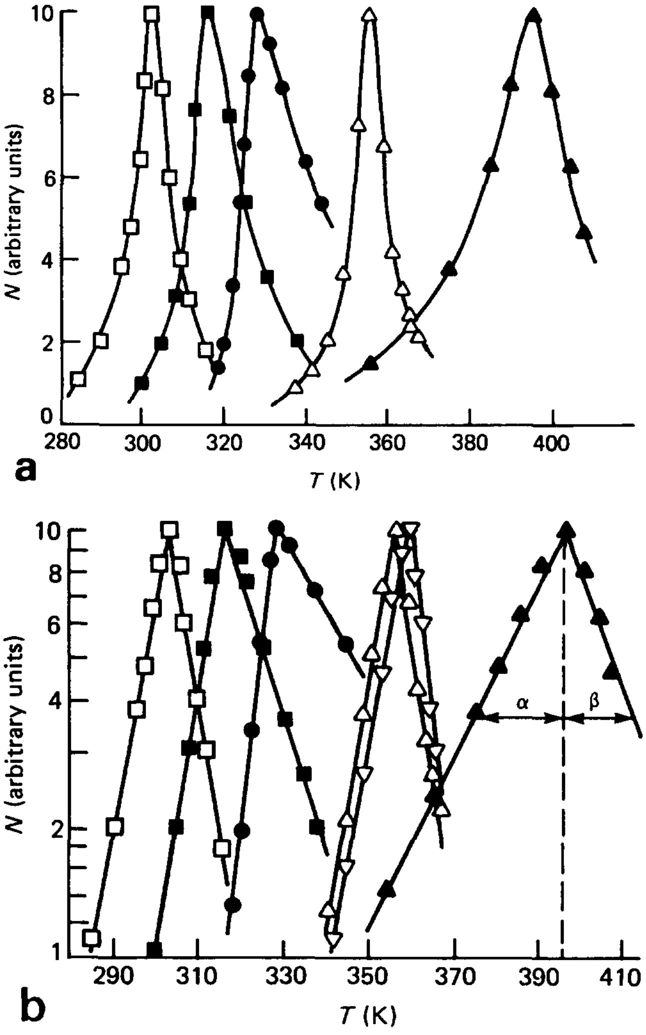

Figure 2 (a) Distributions in glass transition temperatures and (b) their logarithmic plots for PVA (□), N6 (■), PTFCE (●), PVC (△, ▽) and PMMA (▲). Heating rates $b = 4°\text{C min}^{-1}$ (□, ■, ●, △, ▲) and $12°\text{C min}^{-1}$ (▽)

Table 1 lists the parameters of the distribution functions studied. The most probable values of the activation energies for the five studied polymers (U_m) are 150–422 kJ mol^{-1}, which corresponds to the U values obtained through other relaxational methods[17].

The most probable values of the relaxation times at T_g depend on the polymer, and range from 36.6 s (PVC) to 83 s (N6) ($b=4$°C min^{-1}). The distribution width in all relaxational parameters varies systematically from polymer to polymer. The widest distributions are typical for the segmental motion in PMMA and PTFCE, the most narrow for PVA and N6. It should be noted that the values of the asymmetry parameter for all distributions in the same polymer are close, thus indicating that these distributions are due to the same structural nonuniformity of the amorphous regions in polymers. The values of the frequency factor have no physical meaning (10^{-22}–10^{-60} s), indicating that the experimental parameters U and A are effective.

Table 1 Parameters of the distribution in glass transition temperatures T_g, activation energies U, relaxation times τ and frequency factors A of the segmental motion in polymers

	Polymer				
Parameter	PVC	PVA	PMMA	PTFCE	N6
T_g^m (K)^a	356	303	396	328	316
$\alpha(T_g)$ (K)	7	8	21	5.5	7
$\beta(T_g)$ (K)	6	7	15	25	14
$\alpha+\beta$ (K)	13	15	36	31	21
α/β	1.2	1.1	1.4	0.22	0.5
$\ln[\tau_m$ (s)$]$	3.6	4.1	4.0	4.2	4.4
$\alpha(\tau)$	2.8	1.8	5.3	1.1	1.3
$\beta(\tau)$	2.6	1.6	4.2	5.9	2.7
$\alpha+\beta$	5.4	3.4	9.5	7.0	3.0
α/β	1.1	1.1	1.3	0.18	0.48
U_m (kJ mol^{-1})	422	182	355	205	150
$\alpha(U)$ (kJ mol^{-1})	16	9	37	6	7
$\beta(U)$ (kJ mol^{-1})	15	8	28	32	13
$\alpha+\beta$ (kJ mol^{-1})	31	17	65	38	20
α/β	1.1	1.1	1.3	0.19	0.54
$\ln[A_m$ (s)$]$	139.0	68.14	103.7	71.0	52.5
$\alpha(A)$	2.8	1.9	5.6	1.1	1.3
$\beta(A)$	2.7	1.6	4.2	6.4	2.5
$\alpha+\beta$	5.5	3.5	9.8	7.5	3.8
α/β	1.0	1.2	1.3	0.17	0.52

^{a} The heating rate is 4°C min^{-1}

The correctness of the approach adopted in the present work can be tested through a comparison of the distribution functions obtained with the results of other methods. The relaxation time distributions near T_g on the basis of dielectric relaxation data for PVA were analysed in ref. 12. It was found that these distributions are adequately described by the Havriliak–Negami function. *Figure 5* shows the relaxation time distributions in PVA obtained in this work and presented in ref. 12. As can be seen, the shapes of the distributions obtained by both techniques are identical. The differences in the distribution widths are not greater than 12%. Taking into account possible differences in the structure of the PVA samples, the correlation of the data can be considered satisfactory. An analysis of these distributions reveals that they can be successfully described by both the Havriliak–Negami and the exponential functions (15) suggested in this work.

The range of high pressure

Uniform compression of the polymers shifts the t.s.d. peaks to higher temperatures (*Figure 1*). The values of

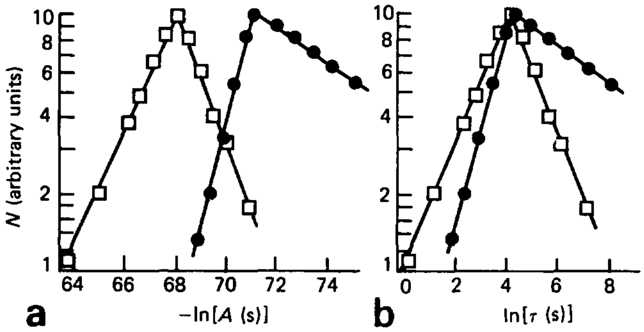

Figure 4 Distributions in (a) A and (b) τ for PVA (□) and PTFCE (●) at $p=0.1$ MPa, $b=4$°C min^{-1}

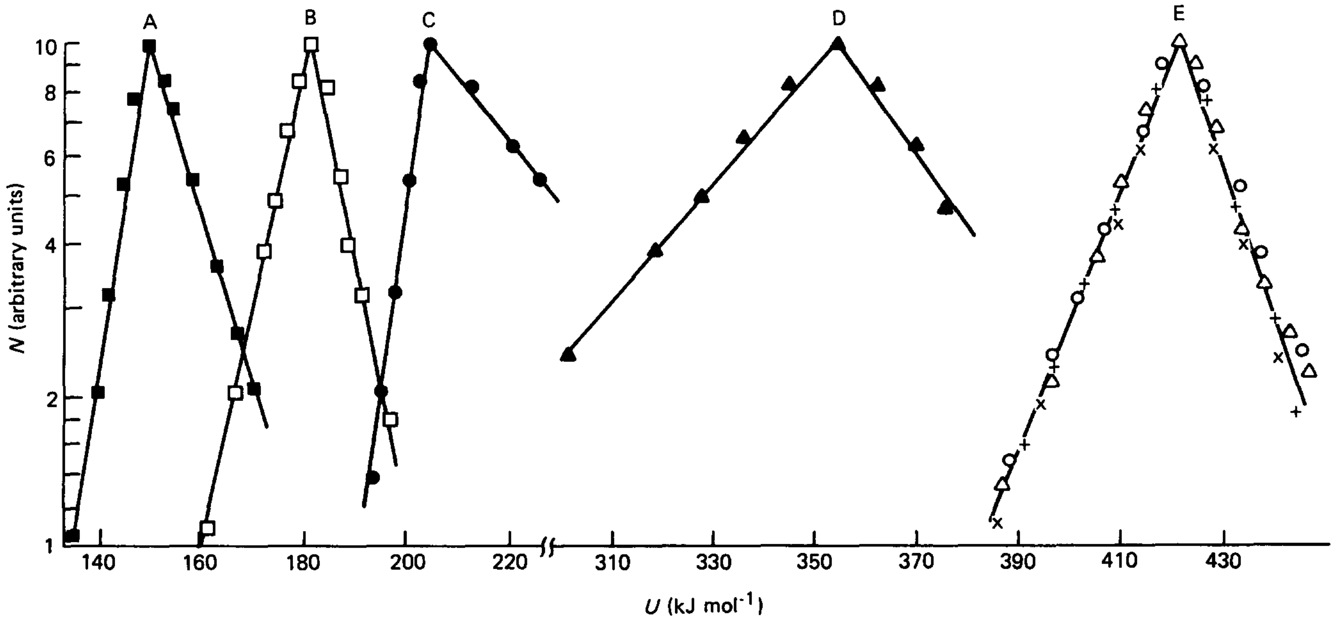

Figure 3 Activation energy distributions at $p=0.1$ MPa: curve A, N6, heating rate $b=4$°C min^{-1}; B, PVA, $b=4$°C min^{-1}; C, PTFCE, $b=4$°C min^{-1}; D, PMMA, $b=4$°C min^{-1}; E, PVC at heating rates $b=2$°C min^{-1} (○), 4°C min^{-1} (△), 6°C min^{-1} (+) and 12°C min^{-1} (×)

dT_m/dp listed in *Table 2* are in a good agreement with the results of other techniques[19]. *Figure 6* demonstrates the T_g distributions under pressure, obtained through the technique considered above.

As is seen from *Figures 2* and *6* in all polymers the distribution width in T_g slightly increases, while the asymmetry remains unchanged with variation of the pressure. On the basis of these results one can estimate the activation volumes of segmental motion and their distribution.

To calculate the activation volumes V^*, the Frenkel–Erying equation[20,21] is used:

$$\tau^p = A\exp[(U^0 + pV^*)/RT] = \tau^0\exp(pV^*/RT) \quad (16)$$

where U^0 and τ^0 are the values of activation energy and relaxation time as $p \to 0$.

According to equation (17) the external pressure increases the relaxation time due to an increase of the process activation energy by pV^*, i.e. by the energy of activation volume formation.

The most probable V_m^* value can be determined in one of three ways:

(1) Through an increase with pressure of the most probable value of the apparent activation energy estimated from equation (3). It should be noted, however, that at V_m^* values of $(100\text{–}400) \times 10^{-6}\ \text{m}^3\,\text{mol}^{-1}$ characteristic of segmental motion and at pressure $\leqslant 200$ MPa, the pV^* value is 10–20% of the average U, which is close to the experimental error.

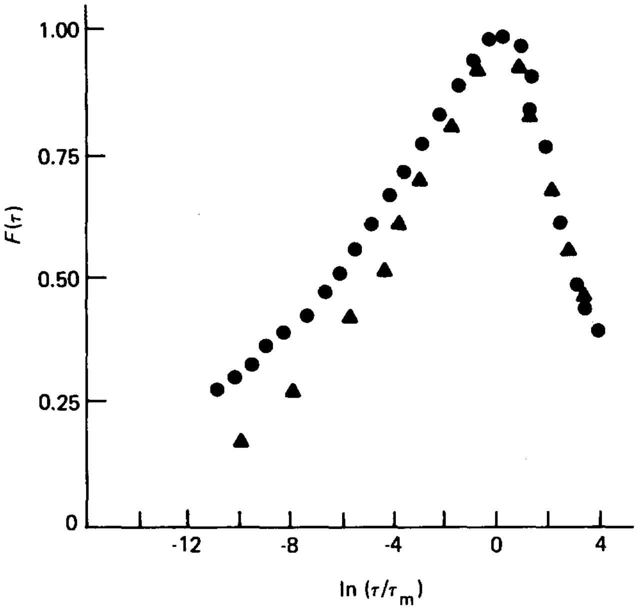

Figure 5 Relaxation time distributions at T_g of PVA on the basis of the present work (▲) and dielectric relaxation data (●)[12]

(2) Through a change with pressure of relaxation time at T = constant, using equation (16). Taking into consideration that the maximum of the t.s.d. curve shifts with pressure, i.e. $T_m = f(p)$, the values of τ at the peak maximum should be extrapolated to one temperature (for instance to the temperature of the maximum as $p \to 0$).

(3) By using the expression for the maximum of the t.s.d. curve. It follows from equations (2) and (16) that

$$\tau^p = R(T_m^p)^2/b(U^0 + pV^*)$$

Provided that the shift of the t.s.d. peaks under the external pressure is due to an increase of the activation energy of the relaxation process by pV^* at constant relaxation time at the maximum τ_m (see section headed 'Theoretical treatment'), we can write

$$(T_m^p)^2/(U^0 + pV^*) = (T_m^0)^2/U^0$$

and

$$(T_m^p)^2/(T_m^0)^2 - 1 = pV^*/U^0 \quad (17)$$

Thus, the average value of the activation energy can easily be determined from the slope angle of dependences of $[(T_m^p)^2/(T_m^0)^2 - 1]$ on p.

In the present work we made use of the third way of calculating V^*. *Figure 7* shows the baric dependences of the temperature maxima. It is seen that they can be adequately described by equation (17). The values of activation volumes calculated using the most probable values of the activation energy (*Table 1*) are listed in *Table 2*. The obtained values of V^* range from 93×10^{-6} to 462×10^{-6} m mol^{-1}, in good agreement with the results

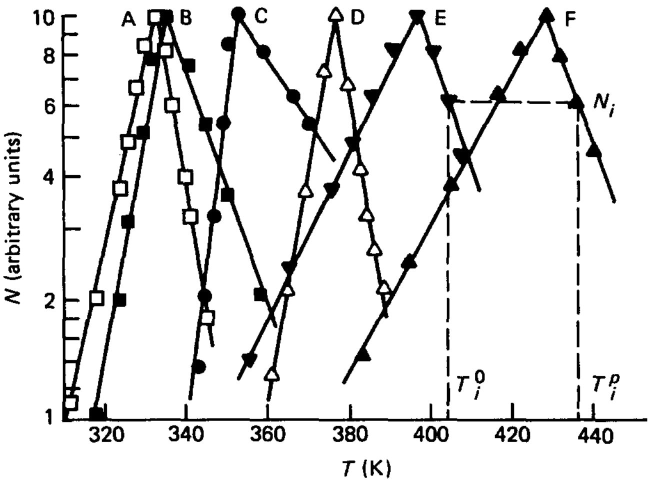

Figure 6 T_g distributions for PVA (curve A), N6 (curve B), PTFCE (curve C), PVC (curve D) and PMMA (curves E, F) at pressures of 200 MPa (A, B, C), 150 MPa (D, E) and 0.1 MPa (F). Heating rate $b = 4$°C min^{-1}

Table 2 The values of dT_m/dp and parameters of distribution in activation volumes of segmental motion in polymers

Polymer	dT_m/dp (K MPa^{-1})	$V_m^* \times 10^6$ (m^3 mol^{-1})	$\alpha(V^*) \times 10^6$ (m^3 mol^{-1})	$\beta(V^*) \times 10^6$ (m^3 mol^{-1})	$(\alpha+\beta) \times 10^6$ (m^3 mol^{-1})	$\frac{\alpha}{\beta}$
PVC	0.14	342	13	12	25	1.1
PVA	0.15	186	9.5	8.5	18	1.1
PMMA	0.22	398	38	29	67	1.3
PTFCE	0.12	162	5	24	29	0.2
N6	0.10	93	5	10	15	0.5

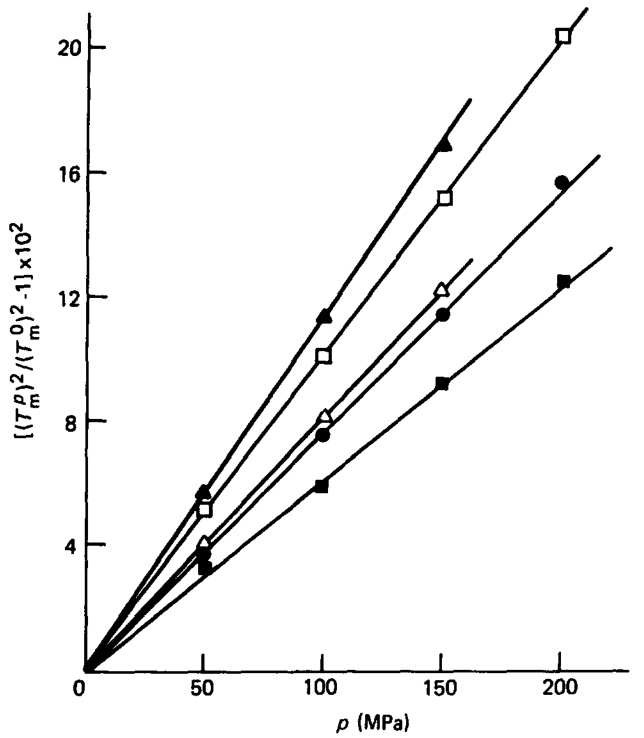

Figure 7 The dependence of $(T_m^p)^2/(T_m^0)^2 - 1$ on pressure. See the legend to *Figure 2*

obtained using the technique of dielectric relaxation in alternating fields. For instance, the activation volume of the relaxation process in the region of the PVC glass transition equals $321 \times 10^{-6}\, m^3\, mol^{-1}$, and with PVA $V^* = 139 \times 10^{-6}\, m^3\, mol^{-1}$ (ref. 4).

To obtain the activation volume distribution $F(V^*)$ it is necessary to determine V_i^* at various points of the T_g distribution curve. To this end, equation (17) should be written as follows

$$(T_i^p)^2/(T_i^0)^2 - 1 = pV_i^*/U_i^0$$

Here T_i^p and T_i^0 are *x*-coordinate values of a given point on $F(T_g)$ curves obtained at p and $p \longrightarrow 0$ at one and the same *y*-coordinate value ($N_i^0 = N_i^p$) (*Figure 2*); U_i is the value of the activation energy corresponding to a given N_i (*Figure 3*).

The V^* distributions obtained by this technique are shown in *Figure 8*. An analysis of these distributions reveals that they can be adequately described by analytical functions of the same type as those used for distributions in other relaxation parameters (equation (15)). *Table 2* lists the characteristic parameters of V^* distribution. The width of these distributions $\alpha(V^*) + \beta(V^*)$ is 10–20% of the most probable value of the activation volume and changes from polymer to polymer proportionally to the width of the activation energy distributions (*Table 2*). The asymmetry parameter in this case is the same as for other relaxation parameter distributions.

CONCLUSIONS

The analysis of the t.s.d. currents carried out in this work for five polymeric systems in the region of the glass transition temperatures and at hydrostatic pressures ranging from 0.1 to 200 MPa allows us to draw the following conclusions:

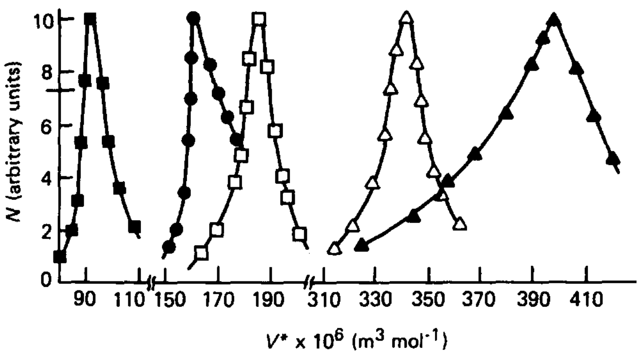

Figure 8 The activation volume V^* distributions for polymers. For notations, see *Figure 2*

The t.s.d. peaks in polymers in the region of their T_g represent the glass transition temperature distribution functions.

Distributions of glass transition temperatures, relaxation times, activation energies and volumes, and frequency factors of segmental motions in polymers are adequately approximated by exponential functions (16). The advantages of these analytical expressions, as compared to other functions used to describe the bell-shaped distributions, lie in the possibility of using them to describe both symmetrical and asymmetrical distributions, in the simplicity of calculating the characteristic parameters (average values, width and asymmetry) and plotting functions based on them. It should be noted that the conclusion on the validity of using exponential functions to describe distributions in relaxation parameters is in good agreement with the results of the t.s.d. current analysis in poly(vinylidene fluoride)[9] and f.t.s.d. data[10].

The distribution width in U, T_g, τ, A and V^* depends on the polymer. The widest distributions in all relaxation parameters are observed with PMMA and PTFCE. The most narrow distribution in glass transition temperature is typical of PVC; the narrowest in activation energy and frequency factor, relaxation times and activation volumes are typical of PVA and N6.

Distributions in all parameters for PVC and PVA are close to symmetrical. With PMMA the steeper branch is observed in the range of lower values of U, V^*, T_g, τ and A. With crystalline polymers (PTFCE and N6) the steeper branch of distributions is observed in the range of higher values of relaxational parameters, which seems to be related to a higher content of densely packed chains in the amorphous phase of these polymers. For a particular polymer, all the distributions are characterized by close values of the asymmetry parameter.

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