Thermal sampling in polymers with distributed relaxations: PMMA

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The thermal sampling (t.s.) technique, a modification of thermally stimulated discharge (t.s.d.), has been applied to investigate molecular motions in poly(methyl methacrylate) and to compare the results with the theory of t.s. It was found that the distribution of relaxation times is represented by a distribution in activation energies and the temperature dependence of relaxation times is governed by the compensation law. A statistical test confirmed the validity of the compensation effect in the case of glass transition in PMMA. A theory based on self-diffusion has been applied to explain this effect and good agreement of the calculated expansion coefficient with the dilatometric data was obtained.

INTRODUCTION

Thermally stimulated discharge (t.s.d.) is currently widely used to investigate the dielectric properties of polymers[1–9]. Recently a modification of this method, thermal sampling (t.s.), has been developed. Thermal sampling was originally proposed by Bucci[10] and was used to investigate the relaxation processes in various polymers[3–9]. Due to its high resolution the technique is particularly suitable for analysis of complex and distributed relaxation processes.

Dispersions in polymers can be described by the Debye model of relaxation if the distribution function is introduced. Such functions have been proposed to describe the results of dielectric measurements[11]. The distribution function can be calculated directly from the shape of the t.s.d. peak[1,2]; one has to assume, however, which of the relaxation parameters (pre-exponential factor, α_0, or activation energy, A) is distributed.

Recent theoretical studies[12,13] show that thermal sampling makes it possible to describe in detail the distribution function of the relaxation process and to show which of the parameters (α_0 or A) is distributed.

In the present work thermal sampling was applied to investigate the relaxation processes in poly(methyl methacrylate), a model polymeric material for dielectric investigations. The relaxation properties of this polymer have been extensively investigated by means of classical dielectric techniques[11,14] as well as by t.s.d.[1,2,15,16]. Several dispersion regions were found, labelled $\alpha, \beta, \gamma, \delta$, in order of descending temperature[11]. They are ascribed to cooperative motions of the backbone chain (α transition), rotation of the ester side group (β transition), methyl group rotation (γ transition) and ester methyl group motion (δ transition)[17]. Some authors found another relaxation, α' [2,14,18], which is probably due to the local mode relaxation, or represents the glass transition of the isotactic portion of the radically polymerized material.

The aim of this work was to obtain an insight into the detailed structure of the multiple relaxations by means of t.s. and to obtain some information about the possible nature of the distributions.

THEORY

The theory of thermal sampling has been derived for the dipolar mechanism of polarization which dominates in polar homogeneous polymers. Generally, however, other mechanisms, such as build-up of a space charge or the Maxwell–Wagner polarization can take place as well, and the theory can be extended to include the other mechanisms.

The t.s. experiment includes polarization of the sample at constant temperature, T_p, for a certain time, t_p. This causes orientation of permanent dipoles and all molecular motions for which the relaxation time $\tau(T_p)$ is of the order of t_p or smaller, become oriented. In the next step the temperature is lowered to T_d and the sample is partly depolarized in short circuit during a period of time, t_d. As a result, only a small fraction of the molecular motion processes, for which the relaxation times lie within a certain range, become frozen-in with permanent polarization. Finally the temperature is lowered to T_0 and the sample is heated linearly, the current being recorded vs. temperature (this step is identical to the standard t.s.d. experiment). Variations of electric field, temperature and current during the t.s. experiment are schematically presented in *Figure 1*.

In our previous work[12] we discussed the theoretically derived t.s. spectra for the possible cases of single, multiple and distributed Debye relaxation processes. Here we shall focus our attention on the most interesting case of a distributed relaxation. The current density during the thermal sampling experiment is given by:

$$j = E\epsilon_0(\epsilon_s - \epsilon_\infty) \times \int_0^\infty \alpha_0 a(T)|1 - \exp(-\alpha_0 x)|\exp(-\alpha_0 y)\, f(u)\mathrm{d}u \qquad (1)$$

where E is the applied field, ϵ_0 is the permittivity of vacuum, ϵ_s and ϵ_∞ are the static and high frequency dielectric constants, α_0 and $a(T)$ are the natural frequency and the tem-

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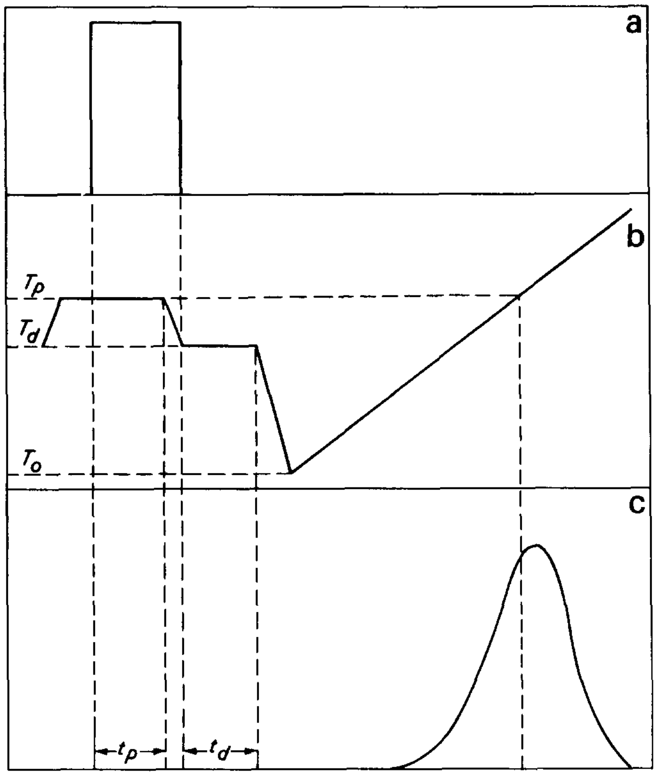

Figure 1 Scheme of electric field, temperature and current variations with time during t.s. experiment. (a) E; (b) T; (c) j

perature shift of the relaxation frequency, $\alpha = \alpha_0 a(T)$. In the case of the Arrhenius shift, $a(T) = \exp(-A/kT)$, where A is the activation energy and k is the Boltzmann constant.

$$x = a(T_p)t_p + s_1 \int_{T_d}^{T_p} a(T)\mathrm{d}T \qquad (2)$$

and

$$y = a(T_d)t_d + s \int_{T_0}^{T} a(T)\mathrm{d}T \qquad (3)$$

s_1 is the reciprocal of the cooling rate after polarization; s is the reciprocal of the heating rate and $f(u)$ is the normalized distribution function fulfilling the condition:

$$\int_0^{\infty} f(u)\mathrm{d}u = 1$$

The distribution of relaxation times can be represented either as a distribution in natural frequencies, α_0, or in activation energies, A. In the first case the formal parameter, u, in the distribution function $f(u)$ will be replaced by α_0, while in the second it will be replaced by A.

In the t.s. experiment the temperature window, $\Delta T = T_p - T_d$, is small, usually in the range of 5K, while in t.s.d. it is chosen as wide as to cover the whole relaxation process. The t.s.d. spectrum of a distributed Debye process is much broader than that of a single process, and the t.s. spectrum approaches the peak due to the single Debye process[12]. This makes it possible to utilize the simple method of calculating the activation parameters of the process, i.e. the Bucci plot[10], where $\log \alpha(T)$ is plotted vs. $1/T$ and

$$\alpha(T) = j \Bigg/ \int_t^{\infty} j(t)\mathrm{d}t \qquad (4)$$

Introducing some specific distribution functions (e.g. Cole–Cole or Fuoss–Kirkwood functions) we have performed model calculations on the t.s. spectra[12,13]. It was found that the results were different for the distribution in α_0 and in A. In the former case the value of α_0 calculated from single t.s. peaks varied significantly with polarization temperature, while in the latter case they remained almost constant. The reverse applied to the distribution in activation energies. These results led us to the conclusion that the t.s. technique makes it possible to distinguish whether there is a distribution in α_0, in A or in both.

EXPERIMENTAL

Films of poly(methyl methacrylate), ~36 μm thick, were cast from 3% solution in chloroform, and then vacuum dried to remove the residue of the solvent. The samples were supplied with vacuum evaporated gold electrodes (area, 1.5 cm^2).

The t.s. experiments were performed in a vacuum of ~5×10^{-5} torr; the heating and cooling parameters were $s = 6.7$ sec/K and $s_1 = 0.6$ sec/K. The polarization field was $E = 1.3 \times 10^7$ V/m, the polarization and depolarization times were $t_p = t_d = 180$ sec and the temperature window $\Delta T = 5$ K. The polarization temperature was scanned every 10K from liquid nitrogen temperature to 360K.

RESULTS

The set of current maxima obtained in a series of t.s. experiments is shown in *Figure 2a*. The envelope of the curves exhibits the typical features of the t.s.d. spectrum of PMMA, i.e. a broad β maximum at about 240K and an increase in peak amplitudes tending to the α maximum at about 370K. The temperatures of the t.s. maxima, T_m, increase linearly with increasing polarization temperatures, T_p, (*Figure 2b*), and the slope is close to unity, which is in good agreement with theoretical predictions[12] for the flat continuous distribution.

Each t.s. maximum was analysed numerically to obtain the Bucci plot of $\log \alpha(T)$ vs. $1/T$. The plots were linear at least up to the halfwidth temperature and for higher temperatures they deviated towards lower values of α, which was to be expected for the distributed relaxation[1]. The values of α_0 and A were deduced from the linear portion of the plots, and the dielectric strength, $\Delta\epsilon = \epsilon_s - \epsilon_\infty$, was calculated from the total charge released in a t.s. experiment:

$$\Delta\epsilon_{\mathrm{t.s.}} = \frac{1}{E\epsilon_0} \int_{t_0}^{\infty} j(t)\mathrm{d}t \qquad (5)$$

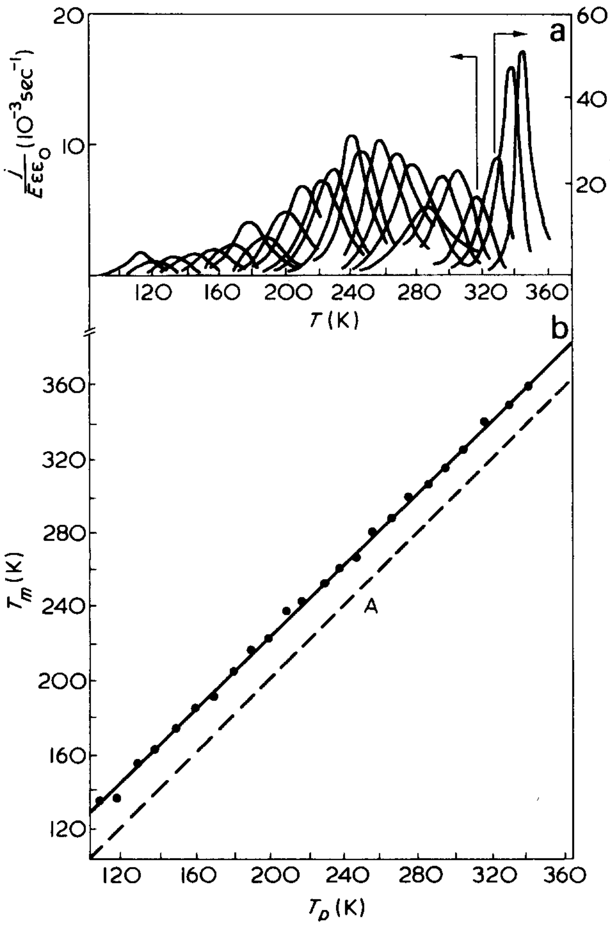

Figure 2 (a) Series of thermal sampling maxima in PMMA. The temperature window ΔT = 5K, the polarization temperature T_p is scanned every 10K. (b) Temperatures of the maxima plotted vs. polarization temperatures. A, $(T_m = T_p)$

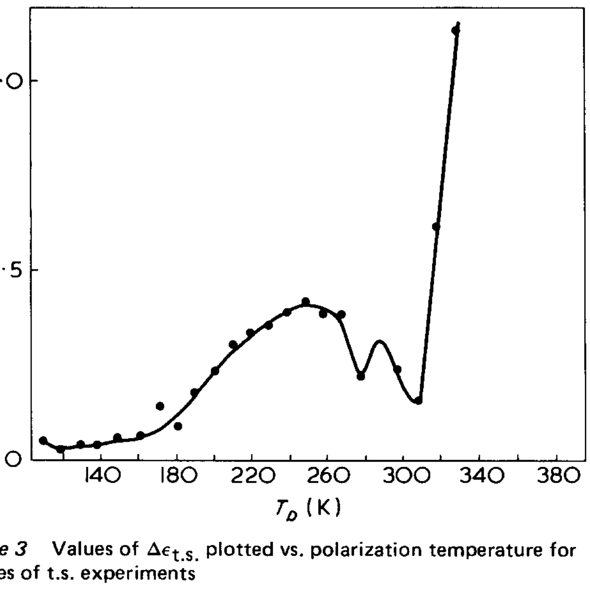

Figure 3 Values of $\Delta\epsilon_{t.s.}$ plotted vs. polarization temperature for a series of t.s. experiments

The plot of $\Delta\epsilon_{t.s.}$ vs. polarization temperatures is presented in *Figure 3*.

The values of the parameters α_0, A and $\Delta\epsilon$ obtained can be attributed to distinct 'portions' of the relaxation process. It is by no means claimed that they represent any discrete or physically distinguishable relaxations, but they are only samples of the distributed relaxation. Nevertheless, they can give comprehensive information about the relaxation process, giving the local values of relaxation times, their temperature dependence and relative contribution to the total process ($\Delta\epsilon_{t.s.}$). They can easily be converted into the classical plots of ϵ' and ϵ'' *versus* frequency or temperature[4,7,12] (which is rather difficult in the case of a standard t.s.d. experiment[1]), thus permitting direct comparison with the dielectric data. Such a conversion, calculated for a series of experiments covering the β relaxation region is presented in *Figure 4*. The plots of ϵ'' vs. frequency (T = constant) and vs. temperature (ω = constant) are very similar to those obtained in dielectric measurements, exhibiting a shift of the maximum with temperature and frequency. For lower temperatures or lower frequencies, respectively, the plots are found to be resolved into two maxima. This remains in agreement with the $\Delta\epsilon_{t.s.}$ plot which also shows an additional maximum between α and β processes. This maximum is ascribed to the α' process[2]. Thus the ϵ'' plots apparently show the maxima corresponding to β and α' which have been resolved by means of thermal sampling.

The temperature dependence of the relaxation parameters α_0 and A derived from t.s. experiments is presented in *Figure 5*. Both plots are similar consisting of steps and sloping portions of the line. The plot of activation energy is close to that obtained by the partial heating technique[15,19] where the flat parts of the plot represent the activation energies of the relaxation processes. According to the theory of t.s.[12] the sloping portions of the plot are interpreted as representing the distribution. The distribution of

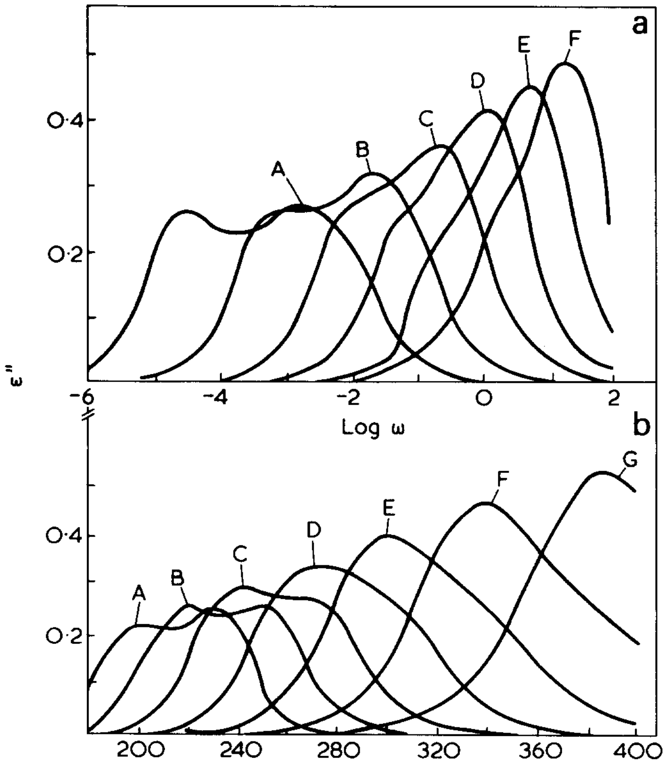

Figure 4 Plots of the imaginary part of complex dielectric constant calculated according to ref 12 from the t.s. data for the β and α' relaxation region (T_p in the range 180 to 310K): (a) ϵ'' *versus* log frequency with temperature as a parameter: A, 225K; B, 250K; C, 275K; D, 300K; E, 375K; F, 350K; (b) ϵ'' *versus* temperature, frequency as a parameter. ω values: A, 0.0001; B, 0.001; C, 0.01; D, 0.1; E, 1; F, 10; G, 100

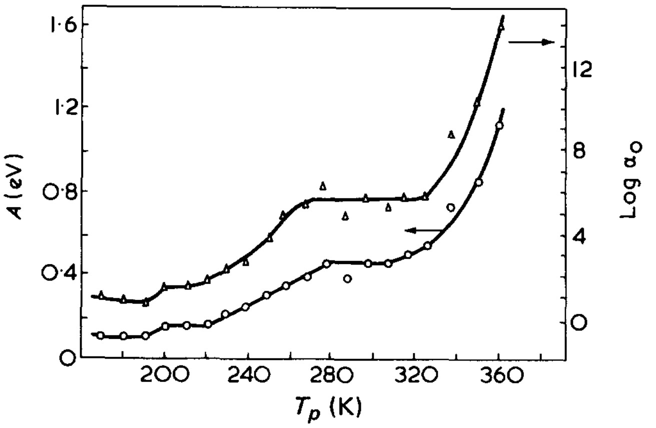

Figure 5 Activation energies, A, and natural frequencies α_0 derived from t.s. peaks plotted vs. T_p

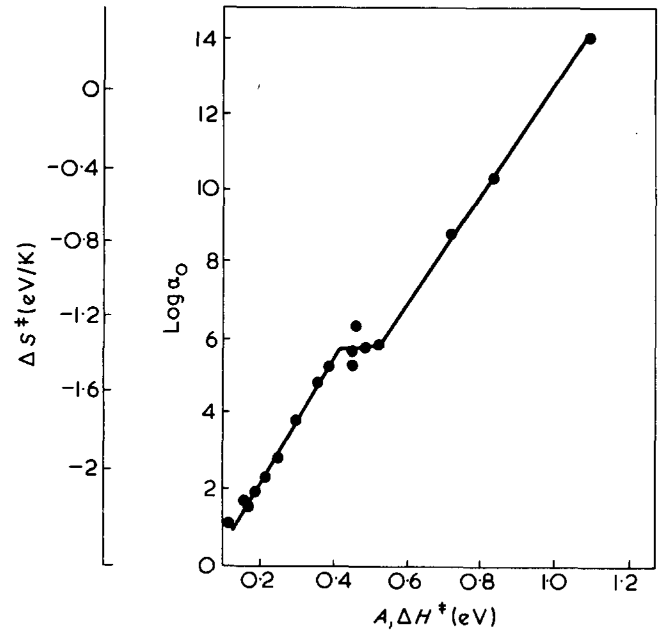

Figure 6 The plot of activation parameters $\log \alpha_0$ and $\Delta S^{\ddagger}$ *versus* A or $\Delta H^{\ddagger}$ for a series of t.s. experiments

natural frequencies cannot be the case here, however. The α_0 factor calculated from the t.s. peaks should be a decreasing function of polarization temperature[12], where a distribution in natural frequencies is concerned. In our case, however, both activation energy and natural frequency are increasing functions of the polarization temperature in the same temperature ranges.

To elucidate this point the logarithm of α_0 was plotted against A (*Figure 6*). The plot shows proportionality between $\log \alpha_0$ and A, and consists of two branches with different slopes. Such behaviour is well known in kinetic measurements and is called the isokinetic relationship or the compensation law; it is observed in chemical kinetic analysis[20–22], in electrical conductivity measurements[23,24] as well as in relaxation phenomena[25–27]. In the case of solid polymers this effect is observed only if data for different materials are compared, and by means of thermal sampling this effect can be observed in one polymer[3,5] thus making it possible to eliminate the inevitable source of errors due to differences in composition, structure and preparation of different samples.

The two segments of the plot in *Figure 6* represent two temperature ranges corresponding to the β relaxation and the α relaxation regions. Expressing the compensation relationship as:

$$\ln \alpha_0 = \ln \beta_0 + WA \tag{6}$$

we can calculate the parameters β_0 and W for both relaxations. The mean values of these parameters are $\beta_0 = 0.05$ Hz and $W = 37.9\ (\text{eV})^{-1}$ for the β relaxation, and $\beta_0 = 1$ Hz and $W = 31.3\ (\text{eV})^{-1}$ for the α relaxation.

DISCUSSION

Interpretation of the distribution

The concept of distribution of relaxation times or frequencies is widely employed in mechanical and dielectric measurements to explain the deviations from the Debye model of relaxation[11]. Assuming the Arrhenius-like temperature dependence of relaxation times, the distribution can be treated either as a distribution in natural frequencies or as a distribution in activation energies[1]. Schematic representation of both extreme cases is presented in *Figure 7a* and *7b*, where the line segments represent the temperature dependences of several subrelaxations chosen from the continuous distribution. They are parallel in the case of the distribution in α_0, and intersect at one point at $1/T = 0$ in the case of the distribution in A. In the experimental case, however, where the compensation law is fulfilled, the lines have different slopes but intersect at a point whose coordinates are β_0 and $1/T_0$. We may thus say that we are dealing with the distribution in activation energies only, and not the Arrhenius law $\alpha = \alpha_0 \exp(-A/kT)$ but the compensation law:

$$\alpha = \beta_0 \exp \left| -\frac{A}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right|$$

where T_0, the isokinetic temperature, governs the temperature dependence of the relaxation frequency, α.

The chief argument against the concept of the distribution of relaxation times[28] was that in many cases the required distribution spanned a range of as many as 6 to 10 decades of frequency, which could hardly have a physical meaning. However, the activation energy range necessary to cover such a range of relaxation times is much smaller and can be reasonably explained.

The Debye model was originally defined for a set of noninteracting dipoles which are free to rotate except for a

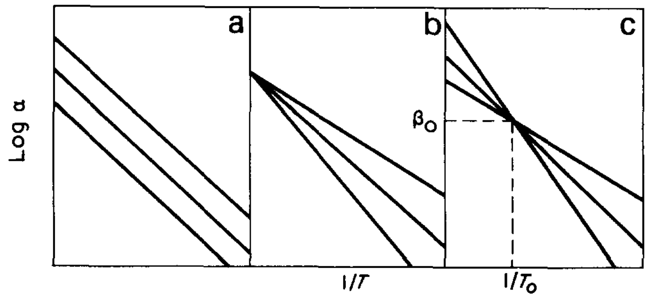

Figure 7 Schematic representation of distributions: (a) in natural frequencies; (b) in activation energies and (c) experimental distribution. The line segments represent the subrelaxations chosen from a continuous distribution

frictional torque opposing their motion. Microscopically this friction is due to the conformational barrier of a rotating molecule. If there are no interactions, all the barriers have the same height and we are dealing with a single, Debye-like relaxation. In a solid polymer, however, one may expect interactions with the neighbouring polymer segments, and these interactions lower or raise the conformational barrier. Due to the more or less random packing of chains in an amorphous polymer we have a case of a distribution of the barriers hindering the rotation of a polymer segment, thus yielding a macroscopic distribution in activation energies.

Compensation effect

In order to interpret the compensation law we shall refer to the Eyring theory representing the temperature dependence of the relaxation frequency:

$$\alpha = \frac{kT}{h} \exp\left(-\frac{\Delta G^\ddagger}{kT}\right)$$

where h is Planck's constant, $\Delta G^\ddagger$ is the Gibbs free energy of activation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

and $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are the activation enthalpy and entropy. The compensation law can be then represented as the linear $\Delta S^\ddagger - \Delta H^\ddagger$ relationship (*Figure 6*).

Most of the criticism directed against the physical significance of the compensation law[20,29,30] arises from the fact that there exists a large covariance between the $\Delta S^\ddagger$ and $\Delta H^\ddagger$ values and the propagation of experimental errors itself produces a linear $\Delta S^\ddagger - \Delta H^\ddagger$ relationship. It has been shown[30] that in the case of purely statistical compensation dependence one obtains a line with the slope $T_0 = T_{hm}$, where T_{hm} is the harmonic mean of the measurement temperatures T_i:

$$T_{hm} = n \Big/ \sum_i \frac{1}{T_i} \tag{9}$$

and n is the number of experiments.

On the basis of this finding a 'test for the hypothesis' has been devised[30]. It makes it possible to eliminate the cases where the hypothesis that the observed compensation law is only a consequence of the propagation of experimental errors cannot be rejected at a given level of significance. To test this hypothesis, the experimental slope T_0 is compared with T_{hm}

$$T_0 = \frac{\Sigma(\Delta H^\ddagger - \overline{\Delta H^\ddagger})(\Delta S^\ddagger - \overline{\Delta S^\ddagger})}{\Sigma(\Delta S^\ddagger - \overline{\Delta S^\ddagger})^2} \tag{10}$$

where the bar denotes the mean value, e.g. $\overline{\Delta S^\ddagger}$ is the mean of observed values of $\Delta S^\ddagger$. An approximate $r \times 100\%$ confidence interval for T_0 is:

$$[T_0 + t_r(V)^{1/2}, T_0 - t_r(V)^{1/2}]$$

where

$$V = \frac{\Sigma[\Delta G^\ddagger(T_0) - \overline{\Delta G^\ddagger}(T_{hm})]^2}{(n-2)\Sigma(\Delta S^\ddagger - \overline{\Delta S^\ddagger})^2} \tag{11}$$

and t_r is the statistical dispersion limit for r, the confidence interval.

The test has been applied independently to the high temperature (α relaxation), and low temperature (β relaxation) parts of the experimental data, representing two branches in *Figure 6*. The 95% confidence intervals of T_0 are compared with T_{hm} in *Table 1*. For the β relaxation the harmonic mean of experimental temperatures is included in the 95% confidence interval of T_0, thus the null hypothesis $T_0 = T_{hm}$ cannot be rejected at the 5% level of significance. However, for the α relaxation the reverse is true and we may expect a real extrathermodynamic compensation relationship, and not only the propagation of experimental errors. An additional argument confirming this statement is the linearity of the plot $\Delta H^\ddagger - \Delta G^\ddagger(T_{hm})$ found for this data set, which is expected only for the true compensation effect[31].

Interpretation of $\Delta H^\ddagger - \Delta S^\ddagger$ *relationship*

A theory explaining the linear relations between the two constants $\Delta H^\ddagger$ and $\Delta S^\ddagger$, has been developed for self-diffusion processes in inorganic solids[32,33] and it has been applied to the relaxations in various polymers[26]. Recently the theory has been modified[34] to allow direct application to polymeric solids, yielding the relationship:

$$\Delta H^\ddagger = \frac{1}{9\Delta\alpha_{te}} \Delta S^\ddagger + \Delta H^\ddagger_{tor} \tag{12}$$

where α_{te} is the isobaric coefficient of thermal expansion; $\Delta\alpha_{te}$ represents the difference in α_{te} between the rubbery and glassy state (for the α relaxation) and $\Delta H^\ddagger_{tor}$ corresponds to the internal torsional energy of a polymer chain. This equation was found to fit our data for the α relaxation in PMMA, which, in accordance with previous discussion, exhibited the real compensation effect. Values of the parameters obtained were $\Delta\alpha_{te} = 3.0 \times 10^{-4}\ \mathrm{K}^{-1}$ and $\Delta H^\ddagger_{tor} = 0.97$ eV. The values of thermal expansion coefficients calculated from dilatometric data for PMMA [14] are: for the rubbery state, $\alpha_{te} = 5.95 \times 10^{-4}\ \mathrm{K}^{-1}$; and for the glassy state, $\alpha_{te} = 2.79 \times 10^{-4}\ \mathrm{K}^{-1}$. The difference is thus $\Delta\alpha_{te} = 3.16 \times 10^{-4}\ \mathrm{K}^{-1}$, and is in good agreement with the value of this parameter obtained from t.s. experiments. We may conclude that the theory dealing with the self-diffusion processes is valid for the glass transition in PMMA and the application of the compensation equation to describe the data is well justified here.

CONCLUSIONS

Thermal sampling was applied to investigate the relaxation processes in poly(methyl methacrylate). It was shown that the dispersions in this polymer are continuously distributed.

Table 2 Comparison of statistical and experimental compensation temperatures for α and β relaxations in PMMA

Relaxation	T_{hm} (K)	T_0 (K)	95% Confidence interval for T_0 (K)
α	312	370	327/412
β	210	306	21/591

Activation energy is the parameter which undergoes a distribution, and it is not the Arrhenius law but the compensation law that governs the temperature dependence of relaxation times. A statistical test showed that in the case of the α relaxation the observed compensation cannot merely be a result of propagation of experimental errors and a true extrathermodynamic effect was detected. Application of the theory developed for self-diffusion processes gave a good agreement of the obtained expansion coefficient with the dilatometric one, thus confirming the validity of the compensation law.

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