

Study of rotational mobility of a polar molecule in polystyrene by the thermally stimulated depolarization method

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The rotational mobility of *paranitroparadimethylamino* azobenzene in polystyrene has been studied by a thermally stimulated depolarization (TSD) method at temperatures less than T_g . The frequencies and activation energies of the rotation of particles, as well as the parameters characteristic of the distribution over rotational relaxation times, and their temperature dependence have been studied.

Keywords Thermally stimulated depolarization; polystyrene; rotational relaxation; *paranitroparadimethylazobenzene*

INTRODUCTION

The rotational diffusion of low molecular weight particles in polymers has been extensively studied in recent years, since it effects the kinetics of chemical reactions responsible for the lifetimes of polymeric materials¹⁻². At the present time a large body of data on the rotational mobility of organic molecules in polymers are obtained with the help of dielectric relaxation and spin probe techniques³⁻⁷. These data may be successfully utilized for predicting the frequencies, activation energies and anisotropy of rotation of molecules that differ in the size and form, as well as predicting the dependence of these parameters on the structure and physical properties of a polymer. Much less information, however, is available on the other important dynamical characteristic, namely the distribution of rotational frequencies of molecules in polymers. The spread in rotational frequencies is reflected by the changes in e.s.r. spectra of spin probes⁴⁻⁷ and in peaks of dielectric absorption³ and is responsible for specific characters of reaction kinetics in polymers¹.

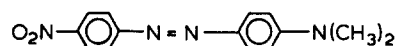
This paper is devoted to the analyses of the rotational relaxation times spectra of low weight molecules in a polymer. For this purpose a relatively new thermally stimulated depolarization method (TSD) was used⁸⁻¹⁶.

The method is based on the analysis of currents which arise when the rotational thermal motion of dipoles, polarized and frozen in the external electric field, unfreeze with increasing temperature. The TSD method can be used to determine the rotational relaxation times over the range 10^2 – 10^4 seconds and the rotation activation energies. The method also enables analysis of the parameters responsible for the distribution of relaxation times and activation energies¹³⁻¹⁵. The system: a non-polar polymer (polystyrene)–polar additive (*paranitroparadimethylamino* azobenzene) was chosen for the investigations.

EXPERIMENTAL

An atactic polystyrene (PS) with a density of 1.05 g cm^{-3} , obtained by emulsion polymerization, was used in the

experiments. A polar additive—*paranitroparadimethylamino* azobenzene ($\mu = 8\text{D}$)



was introduced into a solution of the polymer in toluene. Polymer films were obtained by evaporation of the solvent *in vacuo* with subsequent pressing at 120°C . The PS samples containing no additives were treated under the same conditions. The additive concentration in the polymer was 2.5×10^{-3} mols per mole of styrene.

Aluminium electrodes were deposited *in vacuo* on discs 4.5 cm^2 in area and 100μ in thickness. The samples were placed in a temperature-controlled chamber between two metal plates connected to a high voltage supply. The thermoelectrets were prepared at different temperatures and exposure times in an electric field of 20 kV cm^{-1} . The temperature regime in the chamber was controlled by a flow of liquid nitrogen vapour, previously passed through a heater. The temperature scan linearity was controlled by a programming device with a platinum resistance thermometer.

The polarized samples were cooled at a rate of 30 deg min^{-1} with regimes: $2.2 \pm 0.2 \text{ deg min}^{-1}$ and $4.5 \pm 0.2 \text{ deg min}^{-1}$. The depolarization current over the temperature range -160° to $+100^\circ\text{C}$ was measured by an electrometer of sensitivity 1.10^{-15} A , connected with a recorder.

Methods for treatment of experimental data

The theoretical principles of the TSD method have been described in detail elsewhere⁸⁻¹⁶. We shall consider briefly the methods and equations, used in this paper for the calculation of the main parameters.

The discharge current at a constant temperature is

$$I = \frac{dP}{dt} = -\frac{P}{\tau} \quad (1)$$

where P is the polarization at time t , τ is the relaxation time.

The TSD experiments are usually carried out under the

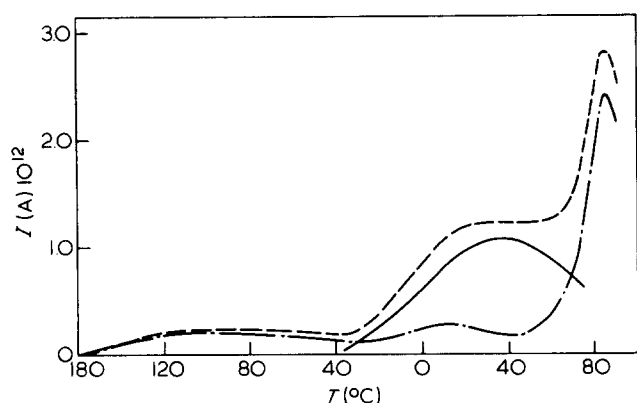


Figure 1 TSD curves for PS (---) and PS with the additive (—). The solid line shows the additive peak. Experimental conditions: $T_p = 90^\circ\text{C}$, exposure time is 30 min, $E_p = 20\text{ kV cm}^{-1}$, $b = 4.6\text{ deg min}^{-1}$

conditions of a linear temperature scan $T = T_0 + bT$, where T_0 is the initial temperature, b is the heating rate. In this case the TSD curve is described by the equation

$$I = P_0 \tau^{-1} \exp\left[-b^{-1} \int_{T_0}^T \tau^{-1} dT\right] \quad (2)$$

Provided the temperature dependence of τ obeys the Arrhenius equation $\tau = \tau_0 e^{W/kT}$, expression (2) takes the form of:

$$I = -\frac{P_0}{\tau_0} \exp\left[-\frac{W}{kT} - \frac{1}{b\tau_0} \int_{T_0}^T e^{-\frac{W}{kT}} dT\right] \quad (3)$$

Here

$$P_0 = \frac{N\mu^2 E_p}{3kT_p} \quad (4)$$

is the polarization at T_0 , N is the concentration of dipoles with a magnitude μ , E_p is the polarizing field strength and T_p is the polarization temperature.

The relaxation time τ can be obtained at various temperatures using equation (1). The value of P is determined by integrating the discharge current with respect to time from t to t_∞ . Thus,

$$\tau = \frac{\int_t^{t_\infty} I dt}{I} \quad (5)$$

The activation energy is obtained using the Arrhenius equation.

The value of W can also be determined from the initial part of the TSD curve. Taking the logarithm of equation (3) and assuming that the last term is constant at the start of the depolarization process, one gets:

$$\ln I = \text{constant} - \frac{W}{kT} \quad (6)$$

The relaxation time at the TSD peak maximum is determined by the relation

$$\tau_{\max} = \frac{kT_{\max}^2}{bW} \quad (7)$$

obtained by differentiation of the equation (3).

The parameter W can also be obtained from the displacement of the discharge current maximum at various heating rates b .

It should be noted that all the above expressions hold only in the case of a single-relaxation process.

DISCUSSION

Pure polystyrene

A TSD curve for the PS sample without an additive consists of two peaks (Figure 1). The intensive peak with a maximum at 87°C is due to α -transition in a polymer (glass-transition). According to data of the dielectric and mechanical relaxation methods¹⁷, the transition in PS at frequencies 10^{-2} – 10^{-3} Hz takes place in the temperature range 78° – 88°C . A second, less intense peak with a maximum at 13°C is due to a β -process. This transition, connected with the unfreezing of the rotational motion of smaller chain elements, should occur, as follows from the data of the relaxation methods, in the low frequency range at $T = 10^\circ$ – 20°C .

Table 1 lists the relaxation times of the peak maxima, as obtained by the TSD and dielectric and mechanical relaxation techniques. It can be seen from the Table that the results for these three methods show fair agreement.

Besides the α - and β -processes, high-frequency relaxation processes (γ and δ) also occur in PS, and are caused by small-scale motions or by the presence of impurities. However, since the temperature coefficient of these processes is low, these have to unfreeze at the TSD frequencies at very low temperatures. For instance, according to previous data¹⁷, the γ -transition would occur below -150°C .

The nature of thermally stimulated currents in a low-polar polymer such as polystyrene ($\mu = 0.4\text{ D}$) is of some importance. This current can be induced by two factors: (1) the thermal destruction of the dipole polarization or (2) the motion of charged impurity particles. The fact that the relaxation times determined from the TSD peaks agree satisfactorily with the values obtained by other methods, is in favour of the first mechanism. Additional information can be obtained by approximate estimation of the effective dipole moment of a kinetic chain segment responsible for the α process. The value of $N\mu^2$, as calculated by equation (4) from the peak in the glass-transition region, is $1.10^{20}\text{ D}^2\text{ cm}^{-3}$. To determine the

Table 1 Relaxation times obtained by the methods of TSD, and dielectric and mechanical losses

Peak	T_{\max} ($^\circ\text{C}$)	$\tau^a 10^{-2}$ (s)	$\tau^b 10^{-2}$ (s)
α	87	1.4	1.2–1.3
β	13	3.3	3.2–3.5
Additive	38	5.0	—

^a Calculated at the maximum temperature by equation (5)

^b Determined by extrapolation of the dielectric and mechanical losses data to the maximum temperatures¹⁹

Table 2 Parameters of the peaks due to the α process and the rotational relaxation of the additive

T_p ($^{\circ}\text{C}$)	T_{\max} ($^{\circ}\text{C}$)	Exposure time (s) 10^{-2}	I_{\max} 10^{13} (A)	τ_{\max}^c 10^{-2} (s)	τ_{\max}^d 10^{-2} (s)	W (kJ mol $^{-1}$)
α transition						
Fractional peaks ^a						
25	39	9.6	1.5	5.0	3.8	56.7
42	49	6.0	2.5	4.6	3.7	60.0
61	66	3.6	3.2	4.5	4.1	70.1
90	87	3.0	5.0	3.6	2.4	120.0
Total peak ^b						
90	87	12.0	24.0	1.4	2.3	60.2
Additive						
Fractional peaks ^a						
-20	-18	24.0	2.3	6.4	8.2	18.0
0	5	18.0	2.7	7.8	6.1	28.3
20	18	12.0	3.8	7.2	5.1	37.0
39	28	6.0	4.3	5.3	4.9	42.0
60	50	6.0	4.6	6.3	4.8	47.0
90	64	3.0	4.3	4.3	4.5	55.0
Total peak ^b						
90	38	12.0	10.5	5.0	4.3	26.0

^a The heating rate is 2.2 deg min $^{-1}$

^b The heating rate is 4.6 deg min $^{-1}$

^c Calculated by equation (5)

^d Calculated by equation (7)

effective dipole moment, data on the length of a kinetic segment are needed. The segment length can be estimated using the values of activation volumes (ΔV^\ddagger), obtained in ref 18 for the glass-transition point of amorphous polymers from the data on compressibility and activation enthalpy. For PS $\Delta V^\ddagger = 836 \text{ cm}^3 \text{ mol}^{-1}$, and the unit volume, in accordance with ref 19, is equal to $104 \text{ cm}^3 \text{ mol}^{-1}$. If the activation volume is comparable with the geometrical volume of the relaxing element, the segment near T_g should consist of 8–10 units. In this case the effective dipole moment is 1.3 D which seems quite reasonable.

Background observed over the temperature range -160° to $+30^{\circ}\text{C}$ seems to be connected with the motion of charged particles in a polymer.

PS with additive

The main difference in the shape of TSD curves for pure PS and for a sample with a polar additive is that in the second case the high-temperature peak has a broad shoulder in the temperature range -40° to $+70^{\circ}\text{C}$. The TSD peak of the polar additive was obtained by graphical subtraction of the spectra (Figure 1). The maximum of this peak appears at 38°C . Thus, the rotational mobility of a molecule introduced into a polymer matrix unfreezes at a lower temperature than does the segment motion responsible for the α process. The differences seem to be due to the difference in the activation volumes of these relaxators. Since the position of the α peak does not change upon introduction of the additive, the polymer filling can be considered to result in no plasticization.

The relaxation time at the temperature corresponding to the additive peak maximum is 500 s (Tables 1 and 2).

The distribution over relaxation times

Analysis of the TSD peak widths shows that reorientation both of the additive molecules and the macromolecule segments is not a mono-relaxation process, but is described by a set of relaxation times. By

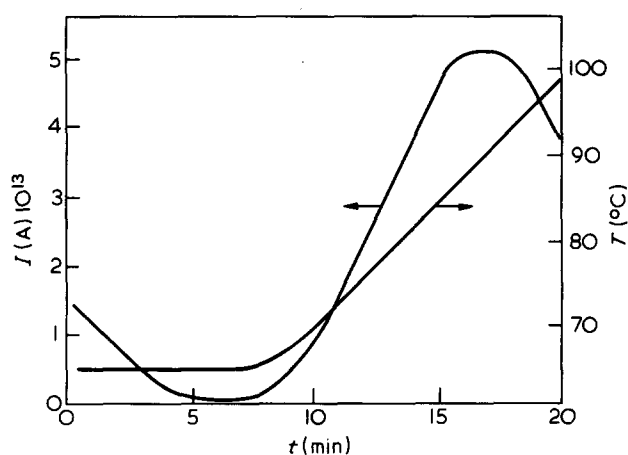


Figure 2 Fractional peak in the α -transition region. The peak parameters and the polarization conditions are given in Table 1 ($T_{\max} = 87^{\circ}\text{C}$)

differentiating equation (3), it is possible to obtain the expression for the peak half-width provided the process is described by a single relaxation time¹⁶: $\Delta T/2 \leq 0.85 T_{\max}^2/W$. The calculation gives the additive peak half-width $\leq 25^{\circ}$ and a half of the α -relaxation peak should be no wider than 8° . The experimental values of the peak widths in both cases considerably exceed the calculated ones (the half-width of the additive peak is 80° , and that of the α process is greater than 40°). For the analysis of the relaxation time distribution we used a fractional polarization technique, obtaining peaks with a half-width of $\sim 20^{\circ}$. Polarization was carried out at various temperatures, T_p , lying within the limits of the TSD peak to be analysed over a time close to the relaxation time at the corresponding temperature. The sample was then cooled to a temperature T_0 , 15° – 20° below T_p , and kept at T_0 until the complete disappearance of the charges having shorter relaxation time. After that the TSD peak was obtained by increasing the temperature at a rate 2.2 deg min^{-1} (Figure 2). Maxima of the

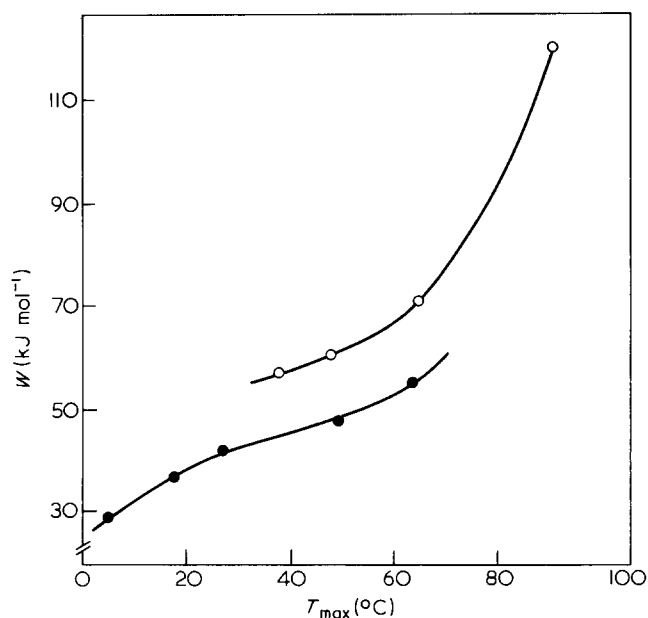


Figure 3 Activation energy as a function of the temperature of fractional peak maxima for rotation of the additive (●) and the α -transition (○) in PS

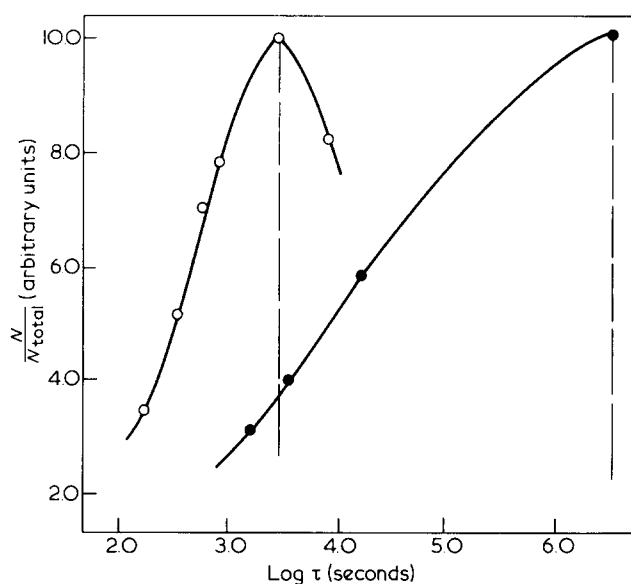


Figure 4 Regions of the relaxation time spectra for rotation of the additive (○) and of the segments of macromolecules (●)

fractional peaks were observed near the polarization point. The fractional peaks for the PS sample without the additive were obtained under the same conditions in order to allow for the background corresponding to relaxation processes in a pure polymer and to isolate the peak of the additive. The relaxation time distribution corresponding to the peaks obtained in such a way can be regarded as narrow. The polarization conditions and the parameters of individual peaks are given in Table 2.

The effective activation energy for the rotational motion of the additive molecules and of the polymer segments increases with the polarization temperature (Figure 3). This dependence is the result of the distribution over τ and W existing in the polymer: the increase in temperature promotes the reorientation of molecules and segments having greater values of rotational relaxation

times and activation energies. Using equation (4) for the maximal polarization, the number of particles corresponding to each peak can be calculated, and the distribution function over τ can be obtained for various temperatures using the temperature dependences of the relaxation times. Figure 4 shows the calculated results for 20°C. A half of the distribution function is shown, since only the initial part of the TSD curve can be treated reliably (because of the peak overlapping at temperatures higher than T_{max}). The results of investigation of a number of polymers, carried out by the TSD¹³⁻¹⁵ and electrochromism²⁰ methods, have shown that the distribution over τ is nearly symmetrical.

Figure 5 shows the temperature dependence of the half-width of the distribution over τ for reorientation of the additive particles and of polymer segments. The difference in the values of τ , calculated from the fractional peaks obtained near the maximum and in the initial part of the TSD curve, was taken as the half-width.

As follows from Figure 5, the half-width of distribution for the additive particles and for the α process strongly depends on temperature. Such a dependence seems to be a direct consequence of the existence of a set of activation energies for the rotational motion of the relaxators.

It should be noted that the effective activation energy obtained from the total TSD peak in both cases is close to the minimal value of W obtained from the fractional peaks, and is not the mean value of W (Table 2). For a set of relaxation times the TSD curve is an envelope of individual peaks, and this results in a broadening of the temperature range, in which the depolarization current increases (peak broadening), and this consequently results in a decreasing temperature coefficient of the rotation frequencies. This effect should be revealed when the relaxation times are calculated either from the initial part of the TSD curve (6), or from the charge, by integration of the curve parts (5). The effective activation energies calculated from the shift of the TSD maxima obtained at various heating rates seem to be closer to the values determined by the dielectric and mechanical loss techniques.

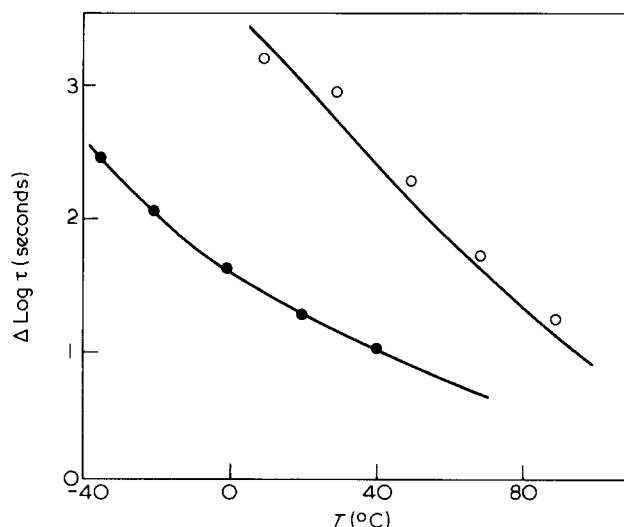


Figure 5 Half-width of the spectrum vs. τ for the additive (●) and for the α process (○) in PS

CONCLUSIONS

The results obtained show that unfreezing of rotational motion of bulk organic molecules at frequencies of the TSD method is observed over the temperature range between the maxima corresponding to α and β transitions in PS, which seems to be due to the relationship between the activation volumes of the relaxing elements of macromolecules and probe molecules. The rotational motion of low-molecular weight particles in a polymer and macromolecular segments is found to be widely distributed over the relaxation times. The width of the relaxation time spectrum depends on the temperature, which follows from the existence of a set of activation energies. As the temperature increases, the τ spectrum narrows from 5–6 frequency orders at $T = T_g - 50^\circ\text{C}$ to 1–2 orders near T_g . Thus it may be concluded that in the high-elasticity region of a polymer the relaxation time spectrum is narrow and is no wider than the order 1 frequency. This conclusion is qualitatively confirmed by the spin probe data^{3–5}, showing that at $T > T_g$ the e.s.r. spectra of the probes in polymers do not reveal, in most of the cases, the superposition of wide and narrow lines, which are characteristic of systems with a wide set of τ^{21} .

Comparison of the TSD and spin probe data reveals significant differences in the values of the rotational frequencies obtained by these methods at $T < T_g$. These differences can attain many orders of magnitude. The reasons for the discrepancy between the results for the two methods are not clear. It can only be suggested that this is due to the fact that in the low-temperature range the spin probe method gives information on the high-frequency branch of the relaxation time spectrum. However, since the rotational diffusion tensor is anisotropic for asymmetrical particles, and the direction of the dipole moment in the particles used as probes in this research coincides with the large axis of the ellipsoid of rotation, the TSD method gives us information on the lowest-frequency tensor component.

It should be noted in conclusion that rotational frequencies obtained by TSD method for the molecule used are close to those obtained by classical dielectric

measurements for a number of organic molecules in PS³ provided the sizes of rotators are close.

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