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# On the amplitude of molecular motion and mechanism of relaxational processes in polymers

**A.L. Kovarskii*[*] and S.A. Mansimov**

Institute of Chemical Physics, Academy of Sciences of USSR, Moscow, V-334, USSR

## SUMMARY

The activation volumes of $\alpha$ and $\beta$ relaxational processes in polymers have been studied on the basis of data obtained through thermally stimulated depolarization technique. Both relaxational processes were shown to be caused by the motion of the same kinetic elements of macromolecules, comprising 2-10 monomeric units. A correlation found between the activation volumes of relaxational processes and the charges isolated upon thermally stimulated depolarization of polymers is discussed. It was concluded that the correlation is due to the difference in the amplitudes of rotational motion of kinetic elements of macromolecules. The rotational motion of segments at $T<T_g$ occurs within the cone with an apex angle not exceeding $10\text{-}15^{\circ}$. Devitrification of the polymer is accompanied by a structural rearrangement which leads to a sharp increase in the amplitude of rotational motion, which manifests itself as $\alpha$-relaxational process.

## INTRODUCTION

In recent years our understanding of the mechanisms of $\alpha$ and $\beta$ processes in polymers has come to be questioned. Experimental studies failed to provide explicit evidence in support of purely polymeric specificity of $\alpha$ and $\beta$ processes and the difference in the scale of the kinetic elements of these processes. Dielectrical relaxation studies made by Johari and Goldstein (1) have most convincingly shown that in vitrescent liquids there are also two types of rotational motion of rigid molecules with no intrinsic degrees of freedom (pyridine, chlorobenzene, chloronaphthalene, o-terphenyl, etc.). These two types of molecular motion have different frequencies, whereas the pattern of treir temperature dependencies is the same as with $\alpha$ and $\beta$ processes in polymers. Still earlier, studies of the temperature dependence of the dielectric losses tangent for anthrone molecules in polystyrene revealed two relaxation area (2). Similar features were observed with rotational relaxation of a number of aromatic molecules in polyethylene (3).

These results clearly indicate that two types of rotational motion of molecules as the whole is a fundamental features of all amorphous compounds both low- and high-molecular-weight.

The difference in the mechanisms of the two types of molecular motion remains basically unclear. There are two main concepts explaining these specificities. The first of them is based on the motion of

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[*] To whom offprint requests should be sent

structural-dynamic nonhomogeneity of glasses, i.e. the existence of molecular packings with various densities or density fluctuations of various size (1,4). The other one is based on the cooperative nature of molecular motion (5). Neither of them, however, provides the answer to the basic question of what are the differencies in the kinematics of molecular motions responsible for relaxational processes.

The answer to this question can be obtained through an analysis of the activation volume of molecular motion, determined upon the uniform compression of a compound (6).

The activation volume is the baric coefficient of molecular motion frequencies $\nu$ (or relaxation times $\tau$):

$$V^* = -RT(\partial \ln \nu / \partial p) \qquad (1)$$

## EXPERIMENTAL

The technique of registering and analyzing t.s.d. currents and the experimental set-up were described in detail in the preceding work (7). Samples of polyethylene terephthalate (PETPh), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), polychlorotrifluoroethylene (PCTFE) and polystyrene (PS) were cut into discs 22 mm in diameter and 50-100 $\mu$ thick.

The dye - diethyl aniline (I) or paranitroparadimethylaminoazobenzene (II) - was introduced into PS from solution in amount of approximately 1 mM/kg and polymer was then dried in vacuo.

The charges isolated upon depolarization were determined from the areas under t.s.d. peaks using the correlation

$$Q = b^{-1} \int_{T_i}^{T_t} i \, dT \qquad (2)$$

where b is the heating rate, $T_i$ and $T_t$ are the initial and terminal temperatures of the peak. Activation volumes were calculated via the equation obtained in (7):

$$V^* = \frac{E}{P} \left[ \frac{(T_m^p)^2}{(T_m^o)^2} - 1 \right] \qquad (3)$$

Here E is the activation energy calculated in the present work by the peak maximum shift as a function of the heating rate, $T_m^o$ and $T_m^p$ - the temperature of peak maximum at normal pressure and pressure P.

The times of spin probe rotational relaxation in PS were calculated from EPR spectra following the standard technique (8).

## RESULTS AND DISCUSSION

Let us first of all consider the question of the size of kinetic elements of macromolecules (segments). This can be determined from the ratio of activation volumes to the proper volume of the molecules. The value of $V^*/V$ is known for the dynamics of additives in polymers from spin probe EPR spectroscopy data (6, 8). It was shown that $V^*/V$ is weakly dependent on the polymeric matrix properties and the size of particles, being at the same time clearly affected by the different types of molecular motion, e.g. translational and rotational.

As it was pointed out in the introduction there are two types of rotational motion and the task is to determine the value of $V^*/V$ for both types. To this end we studied the relaxation of the dye molecules in PS through t.s.d. technique. Fig. 1 shows two temperature ranges of relaxation which corresponds to the data obtained through dielectrical relaxation studies in alternating fields (2,3).

The t.s.d. technique makes it possible to broaden considerably the frequency and temperature range of studies. Besides, the technique is particularly appealing due to its high resolution with respect to relaxation processes under study, which is characterized by the ratio of peak maximum temperatures for $\alpha$ and $\beta$ processes. The lower $T_\beta/T_\alpha$, the higher the resolution. T.s.d. studies yield for $T_\beta/T_\alpha$ the value of approximately 0.6 which is markedly lower than the value yielded by the dielectrical relaxation technique in alternating fields (0.75 at f = 100 Hz (9)).

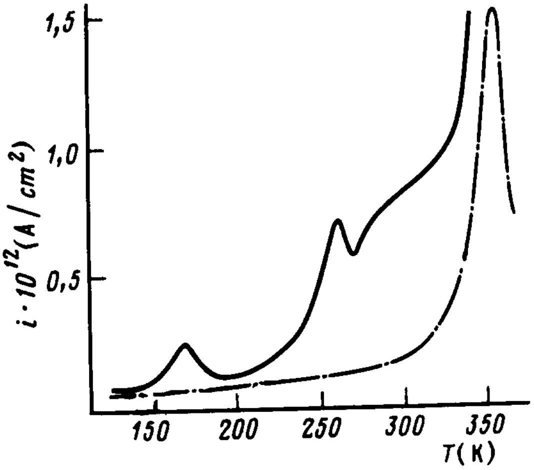

Figure 1: T.S.D. curves for polystyrene (dash line) and polystyrene with added paranitroparadimethylaminoazobenzene (approximately 0.1%) (full line).

Fig. 2 shows the temperature dependencies of rotational relaxation times for various molecules in PS, obtained using di-electrical relaxation, t.s.d. and spin probe EPR spectroscopy. It is seen than the two types of rotational motion have drastically differing temperature coefficients. Both relaxational processes merge at the area of high frequencies. In this way there exist common regularities in the rotation frequency temperature dependencies for additives in polymers, molecules in vitrescent liquids, and segmental dynamics of macromolecules ($\alpha$ and $\beta$ -processes). The existence of common regularities for molecules of different structure can be explained by close values of their molecular weights and volumes and it is precisely these parameters which largely determine the frequencies and activation energies of molecular motion (8).

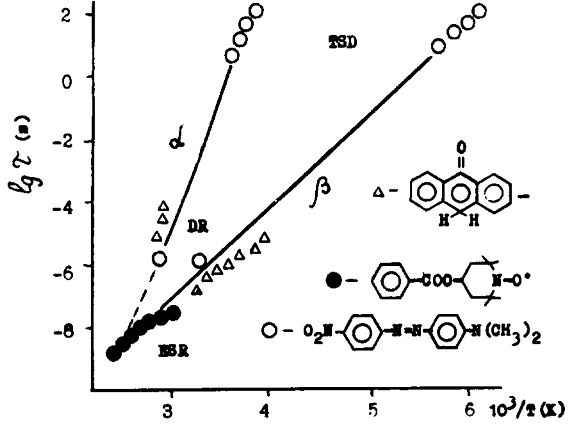

Figure 2: The Arrhenius dependence of rotational relaxation times for small molecules in polystyrene obtained through t.s.d., dielectrical relaxation and spin probe EPR spectroscopy techniques. Data on anthrone were taken from (2).

Table 1 lists the activation parameters characterizing the rotational relaxation of the additives. For high-temperature branch of rotational relaxation the ratio $V^*/V$ makes 0.18 which is within the range of values $V^*/V = 0.1$-$0.2$ obtained for spin probes in various polymer systems. This result is yet another confirmation of the fact that this parameter is but weakly dependent on the structure of molecules. With low-temperature branch $V^*/V$ is markedly higher ammounting to 1.3-1.5.

Table 1

Rotational relaxation activation parameters for additives in polymers

| Type of additive, Type of rotational motion | E, kJ/mol | $V^*$, $cm^3/mol$ | V, $cm^3/mol$ | $V^*/V_w$ |
|---|---|---|---|---|
| 1. High-frequency form ($\beta$ process) | | | | |
| dye II in PS | 34 | 27 | 149.98 | 0.18 |
| spin probes in polymer glasses according to (6,8) | 30-60 | 10-20 | 100-200 | 0.1-0.2 |
| 2. Low-frequencies form ($\alpha$ process) | | | | |
| dye 1 in PS | 101 | 157 | 105.27 | 1.5 |
| dye II in PS | 149 | 194 | 149.98 | 1.3 |
| dye III in PS | 172 | 278 | 185.3 | 1.5 |

Note: The Van der Waals volume was calculated by the technique of group contributions.

Using the values of $V^*/V$ let us calculate the Van der Waals volume of kinetically independent macromolecular segments on the basis of the known activation volumes. The results listed in Table 2 allow a conclusion to be made that both processes are caused by the motion of chain sections close in size and including from 2 to 10 monomeric units. This is in agreement with the calculations made by Bershtein et all. (10) who determined the segments' size through analyzing the activation energies of $\alpha$ and $\beta$ processes depending on the number of monomeric units in the chain.

What is the reason for this difference in the frequencies and activation energies of the two relaxation processes? Table 1 shows that the high-frequency form of molecular rotation requires activation volumes amounting to 10-20% of the molecules' proper volume, i.e. rather insignificant excess free volume. The low-frequency rotation form requires considerably higher fluctuations of the free volume. This unambiguously indicates that there are differencies in the rotational motion amplitudes of the relaxators. The conclusion is confirmed by the earlier obtained correlation (11) between the activation volumes of relaxation processes and depolarization currents isolated in them (Fig.3).

The mechanism responsible for this correlation is, in our view, as follows. The rotational motion of dipoles at $T < T_g$ can not be achieved through large free volume fluctuations due to the rigidity of the glass structure and the motion is restricted by the low value of the critical

Table 2

The Van der Waals volumes of monomeric units $V_w^m$, kinetic units $V_w^k$, and the number of monomeric units in them - n

| Polymer | $V_w^m$, $cm^3/mol$ | Process | $V^*$, $cm^3/mol$ | $V_w^k$, $cm^3/mol$ | n |
|---|---|---|---|---|---|
| PVC | 28.63 | $\alpha$ | 342 | 228 | 8 |
| | | $\beta$ | 25 | 125-250 | 4-9 |
| PMMA | 56.1 | $\alpha$ | 398 | 265 | 5 |
| | | $\beta$ | 21 | 105-210 | 2-4 |
| PETPh | 94.18 | $\alpha$ | 518 | 345 | 4 |
| | | $\beta$ | 31 | 155-310 | 2-3 |

angle of rotation (angle $\theta$ in Fig.4). This low-amplitude rotational motion is characterized by small values of activation parameters $V^*$ and E. To get the dipole moment vector out of the area restricted by the limiting angle $\theta$ a high potential barrier must be overcome, and this is hardly probable. It is clear that such low-amplitude motions can destroy only part of polarization created in the polymer by an electrical field. When the temperature in the area of $T_g$ is inceased the start is given to intensive processes of structural rearrangement and conditions realized which make it possible for dipoles to turn by larger angles. These large-amplitude rotations are $\alpha$ - process. They cause total destruction of residual polarization and require large values of $V^*$ and E. Thus, both the activation volumes and isolated charges depend on one and the same parameter - the amplitude of rotational segmental motions.

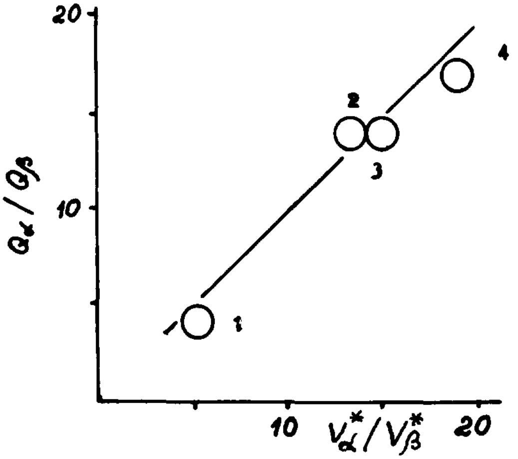

Figure 3: The dependence of charges isolated in depolarization in $\alpha$ and $\beta$ processes in PCTFE (1), PVC (2), PETPh (3), PMMA (4), on the ratio of activation volumes.

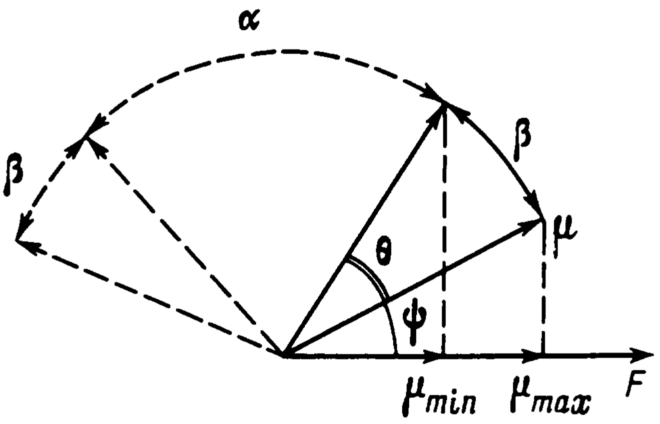

Figure 4: A diagram of reorientation of dipole in $\alpha$ and $\beta$ processes

To estimate the values of $\theta$ angle one can do the following. Fig.4 shows that the total charge isolated in $\alpha$ and $\beta$ processes is determined by:

$$Q_\alpha + Q_\beta = \frac{n\mu_{max}}{S} = \frac{n\mu\,\overline{\cos}\,\psi}{S} \tag{4}$$

where $\psi$ - the average angle of dipole arrangement in the electrical field H, depending on the field's strength, S - the area of the sample, n - the concentration of dipoles. The charge isolated in $\beta$ process is equal to:

$$Q_\beta = \frac{n}{S}(\mu_{max} - \mu_{min}) = \frac{n\mu}{S}\quad \overline{\cos}\,\psi - \overline{\cos}\,(\theta + \psi) \tag{5}$$

The charge ratio is determined by

$$Q_\alpha / Q_\beta = \frac{\overline{\cos}\,(\theta + \psi)}{\overline{\cos}\,\psi - \overline{\cos}\,(\theta + \psi)} \tag{6}$$

Fig. 5 shows the dependencies of $Q_\alpha/Q_\beta$ on $\theta$ calculated for different $\psi$ using this equation. The only thing that can be said about the dipole arrangement angles in weak fields is that they are sufficiently large, apparently larger 60°. At least experimental values of $Q_\alpha/Q_\beta$ (4-20) correspond to the theoretical curve obtained at $\psi$ = 75°. It follows from Fig.5 that the maximal value of $\theta$ makes up 10-15°.

There is a few data in the literature on determining the angle of rotation cone, to which one can oompare the results obtained in this work. These are spin probe EPR spectroscopy data (12) and that of the double electron-electron resonance (ELDOR) (13). The first paper has established that rotation of the spin probe rigidly linked to PE macromolecules at low temperatures, occurs in the cone whose apex angle does not exceed 10-25°.

The ELDOR experiments yield even more accurate values of the apex angle of rotation cone in $\beta$ processes. Using this technique Bendersky and Piven have shown that there exists the most probable value of rotation angle for particles in liquids and polymers below $T_g$. In other words the model of equiprobable noncorrelated jumps does not work. For a peroxy macroradical in PS, the root-mean-square value of rotation angle is 0.15 rad. The probability of jumps over large angles falls exponentially.

The ELDOR data also allows one to make a conclusion to the effect that the most probable angles of rotation are increased with temperature and decreased with cooling. Correspondingly, the rotation mode changes from jump-like to diffusional. The results obtained in our works also indicate that the activation volumes of high-frequency rotation of spin probes in polymers decrease sharply below $T_g$, which strongly suggests the narrowing of the rotation cone. With PVA, for instance, the activation volume of probe (tetramethylpyperidineoxyl) rotation changes from 25 to 30 cm$^3$/mol at $T > T_g$ to 8-10 cm$^3$/mol at $T < T_g$ (14).

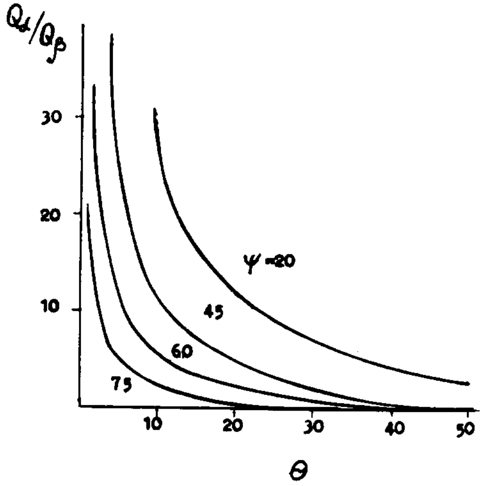

Figure 5: The dependence of $Q_\alpha/Q_\beta$ ratio on the limiting rotation angle $\theta$, calculated via equation (3) at different arrangement angles $\psi$.

Thus, the results obtained from the analysis of molecular rotation activation volumes are in agreement with the results of radiospectroscopic techniques.

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