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The Nature of β-Relaxation in Polymers

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SUMMARY

An activation analysis of relaxational β-transition in polymers, oligomers and simple molecular glasses has been made with the aid of DSC and the internal friction (IF) on the specimens under static load. On the basis of the results obtained, literature data and the correlations found, a conclusion has been drawn that β-transition in the linear polymers is defined by the rotation of the chain portion commensurable with Kuhn's segment as well as the intermolecular potential barriers.

INTRODUCTION

Beta-transition closest to the glass transition temperature ($T_\beta \lesssim T_g$) and fitting the simple Arrenius relation $\nu \approx 10^{(13\pm1)} exp(-Q/RT)$ occurs in various non-crystalline solids (JOHARI and GOLDSTEIN) polymers included (McCRUM et al. 1967). In literature the origin of β-relaxation in polymers is explained differently: by the side groups motion, the internal vibrations in them, the motion of 1÷2 monomeric units, the short chain portions, or impurities (McCRUM et al. 1967, BOYER 1976, BARTENEV and ZELENEV 1976, HEIJBOER 1977). There is direct evidence, however, that in the temperature range from T_β to T_g there appear motions of the main chains portions in linear polymers (WENDORF 1977, PERTSEV and BERSHTEIN 1981, 1982), formation of the fluctuation holes (FISCHER 1977) and the molecular re-arrangements (the "physical ageing") – (STRUIK 1976) being observed. The experimental results given below alongside with the analysis of a large amount of literature data is, in our opinion, evidence in favour of a general nature of β-relaxation as an important relaxational transition in polymers.

EXPERIMENTAL

The effective activation energy for β-transition (Q_β) was obtained by DSC method using the DSC-2 "Perkin-Elmer" calorimeter. Primarily, the temperature range

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from the beginning of β-relaxation up to T_g (the region of the "enthalpy relaxation") was recorded by the DSC curve deviations for the annealed sample and the sample quenched from $T \approx T_g + 100K$ into liquid nitrogen. A short- term annealing of the quenched samples at the β-relaxation start temperature enabled us to obtain the endothermal peak at temperature T_β. To determine Q_β samples were heated with different rates $V = 0{,}3 \div 40$ degree·min^{-1}, its value being estimated by the displacement of T_β, the linear dependencies $\ln V(1/T_\beta)$ obtained and in accordance with the formula (MOINIHAN et al. 1974):

$$Q = - \frac{R \, d\ln V}{d(1/T)} .$$

DSC was used for finding Q_β in oligomers and polymers of styrene (PS) and α-methyl styrene (PMS) as well as in PAN, PCHMA, PDMS, PDES, PMPhIPhA, PE, isopropyl benzene and glycerol (see Fig.2 caption). In all other cases the most reliable values of Q_β from the literature data available on mechanical and dielectric relaxation were used. Values of Q_β obtained by these methods and DSC were in good agreement.

According to the definition of β-transition as the closest to T_g, its temperature location has been specified in some cases. Thus, in PCHMA it covers the relaxation region at $\sim 10 \div 20^\circ C$ and not the transition at $-80^\circ C$ (1 Hz) due to the motion in the cyclohexane ring (HEIJBOER 1977). In the high-crystalline polymers (PE, PP, PTFE, PTFCE) the transition under study corresponds to "γ-relaxation" in the amorphous microvolumes since the term "β-transition" is usually used here to denote glass transition (McCRUM et al. 1967). It has been shown by experimental studies (BERSHTEIN et al. 1972) that it is wrong to relate β-transition appearance in polyamides to the absorbed water presence alone. It should be noted that question of β-relaxation in the comb-like polymers is of special interest, however, it is not regarded here.

The temperature dependencies of the effective activation volumes of the relaxation $v_{act}(T)$ were found from the IF spectra (torsional vibrations, 1 Hz) both in the absence and under the simultaneous application of a static load (the shear stress $t \approx 1$ kg/mm^2), the measuring technique is described in (BERSHTEIN et al. 1980a,1981). The magnitudes of the cohesion energy E_{coh} and the experimental values of Kuhn's segments were taken from literature.

Alongside with PS and PMS polymers, the "monomer" - isopropyl benzene and oligomers with the average number of the monomeric units in the molecule n = 4,5,7, 9,14 and 20 were used, the latter were synthesized by means of the anionic polymerization of α-methyl styrene (LAVRENKO et al. 1981) and styrene (with organo-lithium initiator). The peak molecular mass estimated by the exclusive liquid chromatography, the narrow fractions of polystyrene standards ($\bar{M}_w$ / $\bar{M}_n \lesssim$ 1,1) being also used.

RESULTS and DISCUSSION

Beta-transition was discovered by DSC in all the compounds including "monomer" and oligomers. This confirms the idea that β-transition is a general phenomenon in non-crystalline solids preceeding the glass transition as was suggested JOHARI and GOLDSTEIN (1970,1976). Fig.1 shows experimental dependence $Q_\beta(n)$ for the polymers of styrene (PS) and α-methyl styrene (PMS). Within the error limits $\Delta Q_\beta / Q_\beta \approx 10\%$ the points fit the same curve, the values of T_β varying from ~130 to 390K(for PMS) being ~20÷60° below T_g. Especially conspicuous is the extensive Q_β growth up to n = 9 and a slight "jump" at n=14÷20, the further course of Q_β remaining unchanged up to $n \approx 3 \cdot 10^4$. The "critical" molecule dimension $n \approx 10$ proves to be commensurable with the Kuhn's segment (n_K) in PS and PMS, which equals nearly to 8 units (TSVETKOV et al. 1967, LAVRENKO et al. 1981).

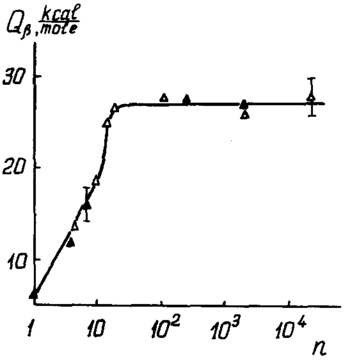

Fig.1. The dependence of the effective activation energy for β-transition in PS (light triangles) and PMS (dark triangles) on the number of monomeric units in the molecule

This result enabled us to suggest the following: if β-relaxation in simple molecular glasses is provided by the rotational-translational displacement of the molecules as a whole, it is defined in polymers (at $n > n_K$) by the same motion of the chain parts approximately equal to Kuhn's segment (the correlation part of the chain). It would be not irrelevant to say that the chain low-frequency vibrations in polymers ($\nu \approx$ ≈ 150–300 cm^{-1}) according to (BERSHTEIN and RYZHOV 1982) are also controlled by the chain portion displacements commensurable with Kuhn's segments as well as by the barriers of the molecular interactions (E_{coh}).

It has been found that for the molecular glasses with different character of intermolecular bonds and the molecular stiffness the dependence $Q_\beta \approx \frac{1}{3} \cdot E_{coh}$ is observed (Fig.2a). In fact, it is similar to Eyring's relation for the viscous flow activation energy in

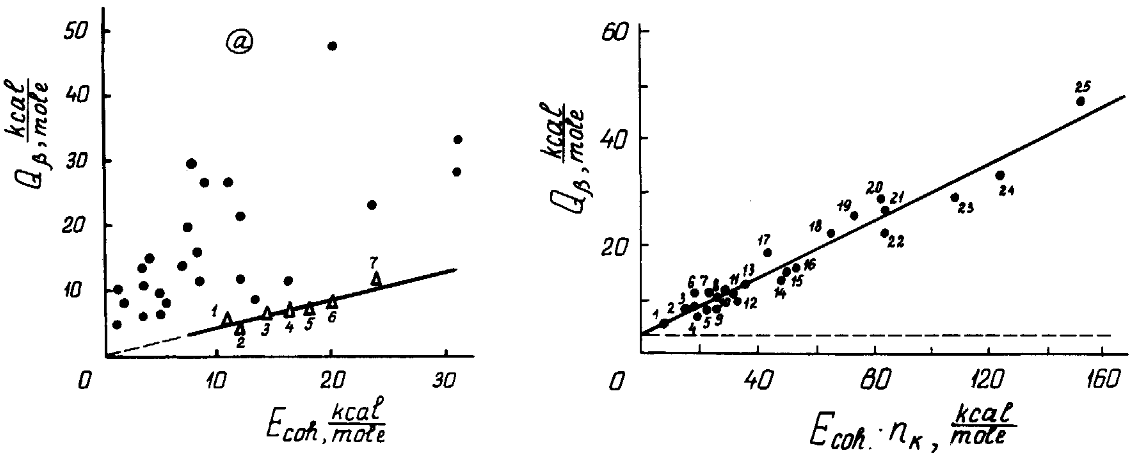

Fig.2. The dependencies of the activation energy for β-transition in simple molecular glasses (triangles) and the polymers of various chemical structures (the dark circles) on the cohesion energy (a) or the cohesion energy of Kuhn's segment (b).

a: 1 – isopropyl benzene, 2 – 2-pentanol, 3 – decaline, 4 – 5-methyl-3-heptanol, 5 – diethyl phthalate, 6 – glycerol, 7 – o-terphenyl

b: 1 – polychlorotrifluoroethylene (PCTFE), 2 – polyethylene (PE), 3 – polyisoprene (PI), 4 – polydimethylsilicone (PDMS), 5 – polydiethylsilicone (PDES), 6 – polyoxyphenylene (POP), 7 – polyethylene terephthalate (PET), 8 – polytetrafluoroethylene (PTFE), 9 – polycarbonate (PC), 10 – polyamide-6 (PA6), 11 – polypropene (PP), 12 – polymethyl acrylate (PMA), 13 – polyvinyl fluoride (PVF), 14 – polyvinyl acetate (PVA), 15 – polyvinyl chloride (PVC), 16 – polyvinyl alcohol (PVAl), 17 – polymethyl methacrylate (PMMA), 18 – polydiphenyl oxyphenylene (PDPOP), 19 – polystyrene (PS), 20 – polyacrylonitrile (PAN), 21 – poly-α-methyl styrene (PMS), 22 – polycyclohexyl methacrylate (PCHMA), 23 – polyimide-1, 24 – polyimide-2, 25 – poly-m-phenylene isophthalamide (PMPhIPhA) liquids: $Q_\eta \approx (1/4 \div 1/3) \Delta H_{evap}$, where the evaporation heat $\Delta H_{evap} = E_{coh} + RT$. This shows that in non-crystalline solids the β-relaxation events obviously occuring in the places of the less close packing correspond to the elementary events of the molecular motion in liquids.

In polymers there is no uniform dependence between Q_β and E_{coh} (kcal per the monomeric unit mole) – (Fig. 2). However, consideration of the polymer as a "mixture of Kuhn's segments" proved that for 25 polymers in question the same regular relation Q_β (kcal per the segment mole) with the segment cohesion energy was observed: $Q_\beta \approx \frac{1}{3} \cdot E_{coh} \cdot n_K + B$, where $B \approx 2 \div 5$ kcal/mole. Of special interest is the fact that the elementary events of β-relaxation and the high-temperature viscous flow for polymers seem to be principally similar too: the magnitudes of Q_β given in this paper for PS, PMS, PVA, PA6, PE, PP and PI are close to that of Q_η for the same polymers (VINOGRADOV and MALKIN 1977).

Experimental dependencies obtained v_{act} (T) are given in Fig.3. The arrows show the temperature of the β-relaxation maximum at 1 Hz; for four polymers $v_\beta \approx$ $\approx 500 \div 1500$ Å^3 . As is seen from the Table the v_β is comparable with Kuhn's segment volume.

The facts described here are consistent with the above mentioned hypothesis on the nature of the β-relaxation in polymers. Unlike the molecular glasses, in polymers the conformational transition is obviously involved in β-relaxation. Firstly, this agrees with the presence of the term $B \approx 2 \div 5$ kcal/mole in the relation for Q_β corresponding in value to the internal rotation barrier (Fig.2b). The possibility of the conformational transitions in β-relaxation was also shown spectroscopically by the authors for PS from absorption bands intensity change in the range 500 - 600 cm^{-1}. Thus, the model of the local motion in polymer chains suggested in (GOTLIB and DARINSKII 1970, SKOLNICK and HELFAND 1980) seems to us most preferable for describing the β-relaxation event. This model includes the $G \rightleftarrows T$-transition with units of the adjacent chain part rotating at different angles.

The obtained correlations result in a number of essential consequences. It is natural to suggest that the segmental motion in polymers begins locally not with glass transition but with β-transition. It is significant that $Q_\beta(n)$ dependence has a likeness with Eyring's dependence $Q_\eta(n)$ which allowed to establish the segmental nature of the viscous flow in polymers (VINOGRADOV and MALKIN 1977). The relations obtained make possible to tentatively predict the temperature and activation parameters of β-transition in polymers of various chemical structures.

It is of primary importance that the correlation part of the chain (Kuhn's segment) is revealed in presence of the molecular interactions and may determine

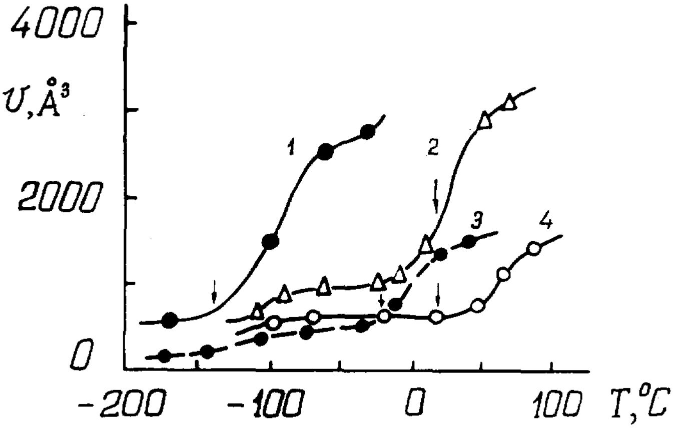

Fig.3. Temperature dependencies of effective activation volumes of relaxation in PE (1), PS (2), PVC (3) and PMMA (4)

TABLE ONE

The comparison between the effective activation volume of β-transition and Kuhn's segment volume (in the monomeric units number)

Polymer	V_β	n_K
PS	10 - 15	8
PVC	8 - 12	12
PMMA	4 - 6	6
PE	10 - 15	8

the motion unit peculiar to β-relaxation and the viscous flow in polymers. New data (BERSHTEIN et al., in press) give some grounds to consider the glass (α-) transition as an intermolecularly co-operated processes of β-relaxation.

In the framework of the interpretation suggested for β-transition temperature T_β seems to be in some way "thermodynamically" dependent on the equilibrium chain flexibility and corresponding to the inception of chain conformational changes. At $T \geqslant T_\beta$ density fluctuation also increases (FISCHER 1977). Thus, knowledge of the physical nature of T_β allows to discuss again the origin of the following two characteristic temperatures:

a) $T_2 < T_g$ in the theory of glass transition (GIBBS and DiMARZIO 1958, ADAMS and GIBBS 1965) corresponding to the zero configuration enthropy and

b) T_0 in Fulcher-Tamman's equation for the viscosity as the magnitudes of T_0 for a number of polymers

(VINOGRADOV and MALKIN 1977 and MILLER 1981) are close to the experimentally found values of T_β .

If the quasi-independent or co-operative motion of the chain parts comparable with Kuhn's segment controls the main relaxation (β - and α -) transitions, i.e. the chain conformational mobility in a wide temperature range, this motion must determine many properties of polymers. Indeed, the activation energy for deformation of glassy polymers in compressing $Q_{def} \approx \frac{1}{3} \cdot E_{coh} \cdot n$, where n is the number of monomeric units forming the activation volume of the process (BERSHTEIN et al. 1980b), the latter at $T \lesssim T_\beta$ being commensurable with Kuhn's segment volume (BERSHTEIN et al. 1980c).

Thus, the understanding of the ganeral origin of β-transition in different polymers opens up new opportunities for investigating and predicting their properties.

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