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The role of thermal analysis in revealing the common molecular nature of transitions in polymers

V.A. Bershtein *, V.M. Egorov, L.M. Egorova and V.A. Ryzhov

A.F. Ioffe Physico-Technical Institute of the Russian Academy of Sciences, 194021 St. Petersburg (Russian Federation)

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Abstract

A brief review of the authors' studies on the molecular nature of the β, α (glass) and "liquid–liquid" (ll) transitions in flexible-chain polymers using different thermal analysis techniques is presented. DSC, far infrared spectroscopy versus temperature and dynamic mechanical analysis of statically loaded samples have been used. They enabled, for the first time, the common nature and fundamental interrelationship of the above-mentioned transitions in polymers of different structure to be established experimentally. It was found that the moving segment remained practically invariable over a wide temperature range, for temperatures $T \gtrsim T_\beta$, and was close to the magnitude of the statistical (Kuhn) segment. Simple relationships between transitions parameters and main molecular characteristics of polymers have been found that offer a new approach for the prediction of transition characteristics, including the manifestation of the glass transition in multicomponent and plasticized polymeric systems, on the basis of the molecular parameters.

1. INTRODUCTION

The physical properties of polymeric materials and the chemical processes in them are determined to a considerable extent by molecular mobility, namely, by torsional vibrations and large-amplitude rotations of atomic groups differing in size. Of special significance are the motions of chain segments accompanied by rotation-isomeric transitions, i.e. the conformational mobility in a block of polymer. These motions have been detected and studied by a variety of techniques and manifest themselves as the δ, γ, β, α (glass) and "liquid–liquid" (ll) transitions, for instance, in the mechanical loss spectrum (Fig. 1(a)). Figure 1(b) shows schematically the frequency dependence of the transition temperatures (relaxation maps) covered by the experimental techniques indicated within a broad range of frequencies $\nu \approx 10^{-4}$ to 10^{11} Hz (see, for example, refs. 1–3).

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* Corresponding author.

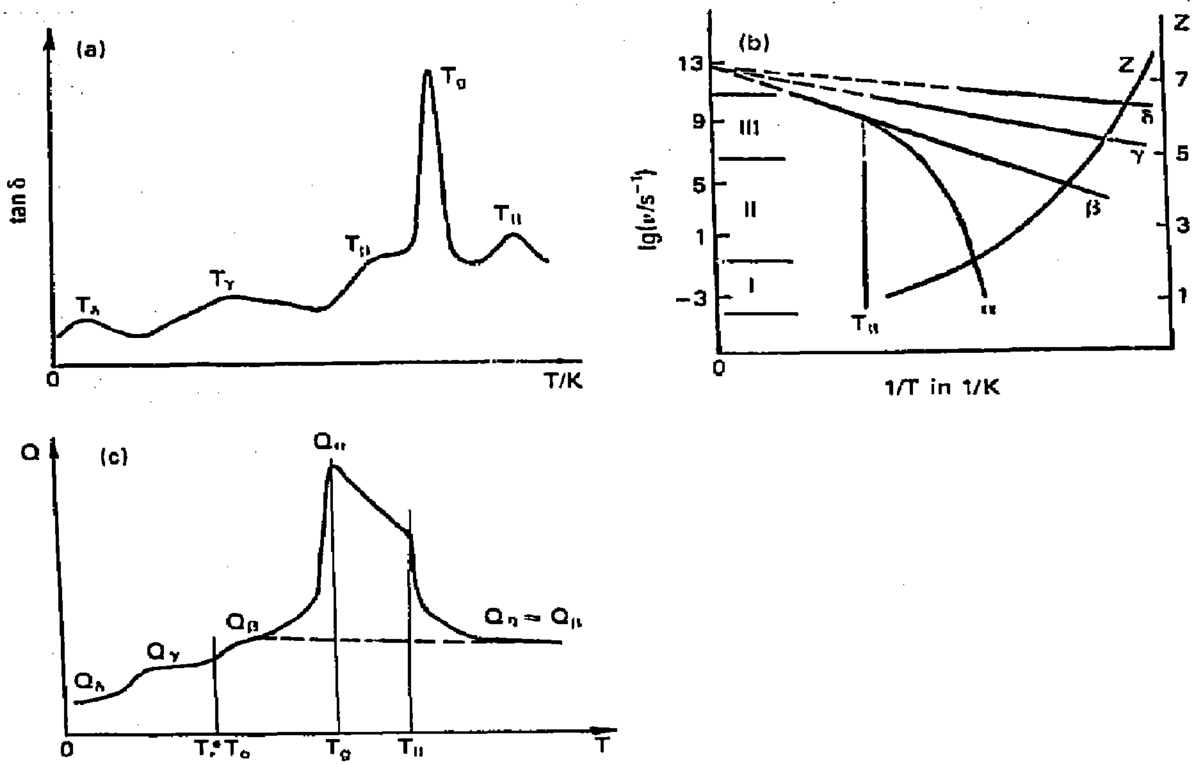

Fig. 1. Schematic representation of transitions in flexible-chain amorphous polymers: (a) mechanical loss spectrum, (b) relaxation map and the parameter of segmental cooperativity Z vs. T^{-1} (Experimental techniques: (I) DSC, thermally stimulated depolarization current, dynamic mechanical analysis (DMA), radiothermoluminescence, creep rate spectra [65]; (II) DMA, dielectric relaxation (DR), NMR; (III) ESR (probe method), Mandelshtam–Brillouin scattering, DR, acoustic measurements. NMR techniques including two-dimensional NMR comprise a very wide frequency range [3].), and (c) temperature dependence of the effective activation energy of the molecular motion.

For relaxations below T_g the lg ν versus T^{-1} plots are close to linear; they relate to kinetically simple, quasi-independent motional events and obey the Arrhenius expression for the frequency of jumps of the kinetic units, namely

$$\nu \approx 10^{13} \exp(-Q/RT) \qquad (1)$$

where Q and T are the activation energy and temperature of the transition. The relevant expression for the mean relaxation time is $\tau \approx \nu^{-1}$. The δ, γ and β relaxations may be termed Arrhenius or non-cooperative ones, although several atoms participate in a motional unit event.

At the same time, the unit event of the glass transition is a cooperative one, and over a broad range of frequencies it does not obey eqn. (1); in essence, T_g increases almost linearly with rise in lg ν only up to about

10^5 Hz, followed by a line of decreasing slope at higher frequencies. An important fact is that at $\nu \approx 10^6$ to 10^8 Hz the cooperative α transition degenerates and merges with the β transition just at T_{ll} (Fig. 1(b)).

The β, α and ll transitions should be considered as the major ones. Indeed, the sharp change of polymer properties in the glass transition range is well known. The ll transition approximately determines the boundary between the rubber-like and fluid state. Its practical significance, especially when materials are processed, is also obvious. However, the β relaxation being the closest to T_g and satisfying eqn. (1), is usually less intense than the α transition by about an order of magnitude; moreover, it is sometimes identified with difficulty. However, the fundamental role of this transition could be presumed to be the activation barrier of solid-phase reactions, deformation, flow, diffusion, physical ageing, etc. and frequently turns out to be approximately equal to the activation energy of the β transition [4].

Despite the gigantic number of studies dedicated to the above transitions, which have been summarized in a number of books [1,5–8] and review papers [9–14], the fundamental problems regarding the essence of their general molecular mechanisms and the existence of their interrelationships and relationship to basic molecular characteristics still remained obscure or were in dispute until recently. Hence, quite different and incompatible viewpoints regarding the origin of β relaxation have been proposed. It was associated with the vibration of one or two monomer units, with the same for polar side group, the motion within this group, the torsional vibrations of short chain portions, and the motion of impurities (water or monomer), etc. (see references cited in ref. 4). Furthermore, it remained unclear whether this situation could be explained by the absence of the common β transition mechanism for polymers varying in structure or by a lack of understanding of this phenomenon because of the paucity of direct experimental data.

The α process in the vicinity of T_g in flexible-chain polymers is known to be determined by segmental motions with the participation of rotation-isomeric transformations in chains. The relationship of T_g to the intermolecular interaction energy [15] or chain rigidity [16] for some polymers has been noted. However, the questions concerning the real size of a motional segment, the nature and degree of cooperativity of motion, the connection between the α and β transitions, etc. remained open for discussion. The absence of an experimental solution for the above questions and for the common relations between transition parameters and main molecular characteristics of polymers hindered prediction of the transitions.

During the last decade a large series of experimental studies entirely dedicated to revealing the molecular nature in addition to prediction of their parameters has been carried out by the authors [17–46]. These data enabled us to arrive at certain conclusions concerning the matter in question. The information gained by thermal analysis techniques has been of paramount importance therein, and the main results obtained are briefly reviewed below.

2. EXPERIMENTAL

Our experiments have mostly been performed by three techniques, DSC, dynamic mechanical analysis of the statically loaded polymers (DMA(σ)) and far-infrared (FIR) spectroscopy including spectra versus temperature measurements. A DSC-2 Perkin-Elmer calorimeter, a FIS-21 Hitachi spec-trometer and an original setup for DMA(σ) analysis were used. Figure 2 shows schematically a list of problems which have been solved by these techniques. Below we shall briefly concern ourselves only with the original methodical points.

As known, the effects commensurable in magnitude with those observed in the range of the α transition or of melting, are generally absent in the β relaxation region in the DSC curves. For this reason we devised a procedure for "revealing" this transition which is described below [18, 19, 21, 22].

It was found that when glassy polymer samples differing in history (quenched, annealed or prestrained), i.e. in enthalpy, were heated in a calorimeter their DSC curves no longer coincided, starting from the temperature of the onset of the β transition range. As shown schematically in Fig. 3, the temperature interval of this divergence or enthalpy relaxation extended from T_1 to T_2; some small effects of this kind were sometimes evident at temperatures up to $T_{\rm ll}$.

The short-term holding of a quenched or prestrained sample at a temperature of T_1 resulted in the appearance of an endothermic peak with a maximum at T_β on the DSC curve. However, if these samples had been annealed for different times at various temperatures T_i (where $T_g > T_i > T_\beta$), the relevant peaks in the range between T_β and T_g appeared in the DSC curve, their temperature T_i increasing with the temperature and duration (in proportion to $\ln t$) of the annealing treatment. Each of these peaks corresponded to unfreezing of the molecular motion mode prevailing at a given temperature T_i, i.e. to the so-called "intermediate relaxation".

The T_g was determined as the temperature at half-height of the ΔC_p heat capacity step. The peculiarities of the ll transition on the DSC curves depended on a number of factors which are discussed in refs. 4, 11 and 23, but the most typical and "pure" case of that (including the reproducibility of repeated scans) is an endothermic change in the slope of the C_p versus T curve beginning from $T_{\rm ll}$ (Fig. 3).

The effective activation energies of transitions under study, viz. the Q_β, Q_α, Q_i, $Q_{\rm ll}$, were found by the displacement of the peak maximum

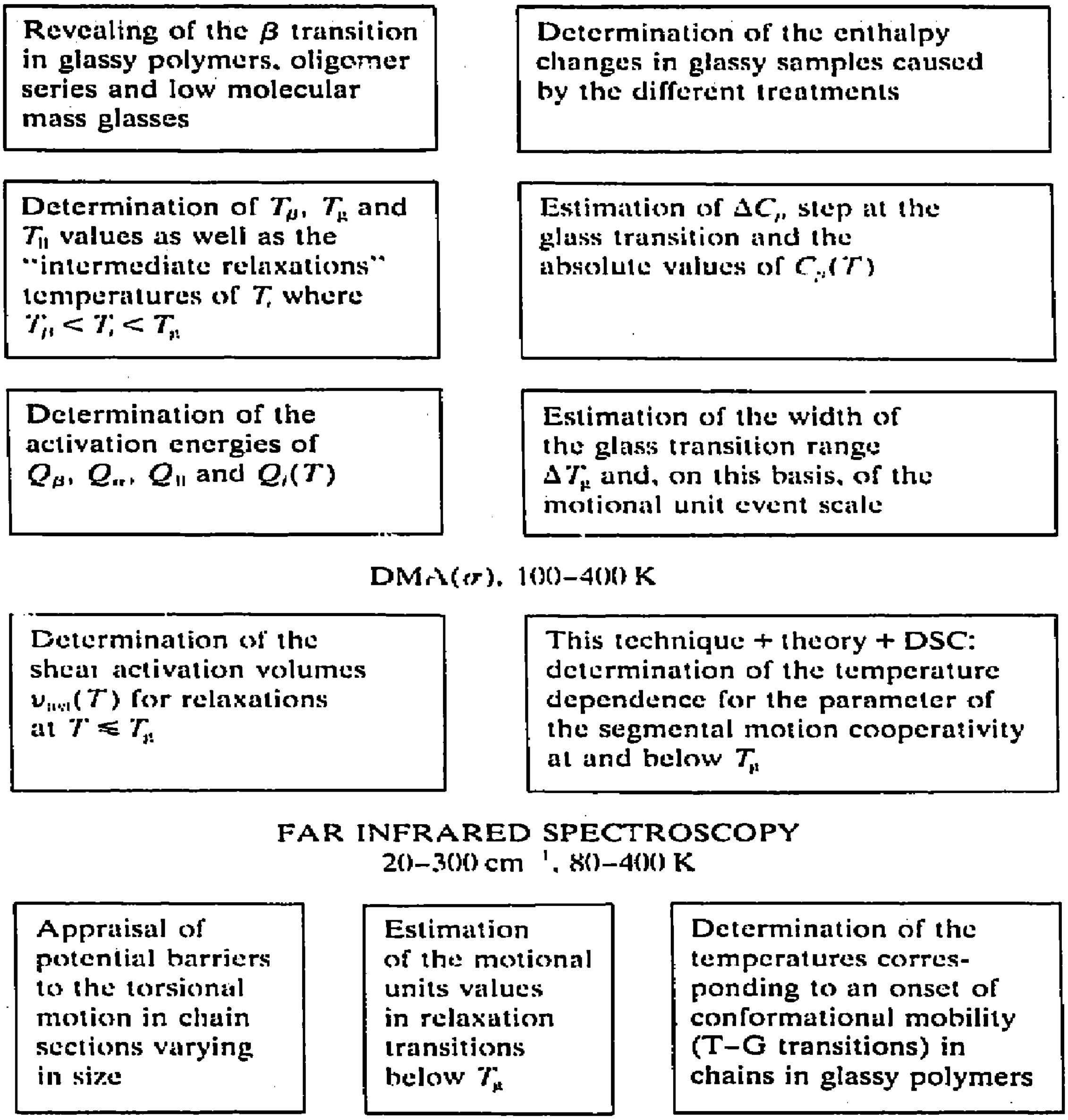

Fig. 2. A list of problems solved by the three experimental techniques employed.

temperature or of the ΔC_p step for T_g, or of the C_p curve slope change for T_{ll}, when varying the heating rate V from 2.5 to 40 K min^{-1} and using the obtained ln V versus T^{-1} linear dependences and the equation

$$Q = -R\frac{\mathrm{d}\ln V}{\mathrm{d}(1/T)} \tag{2}$$

The test conditions corresponded to the frequency range from about 10^{-2} to 10^{-1} Hz. The influence of thermal lag was taken into account [4] and the relevant corrections were made.

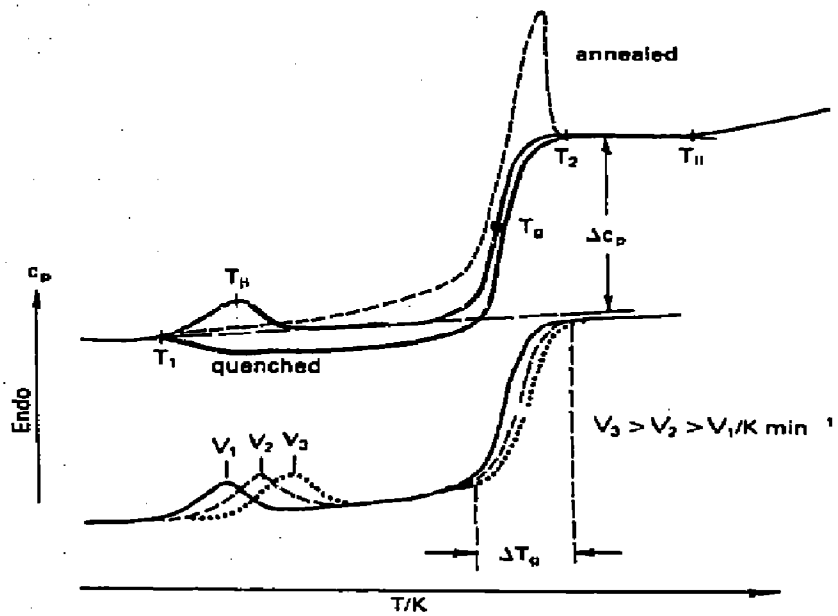

Fig. 3. The scheme of the manifestation of the main transitions in the DSC curves (see text).

Figure 4 shows, as an example, the DSC curves for an atactic PMMA sample with a various degrees of annealing, the ln V versus T^{-1} plots for β, α and "intermediate" transitions, and the temperature dependence obtained for the activation energy of molecular motion over the range T_β to T_g.

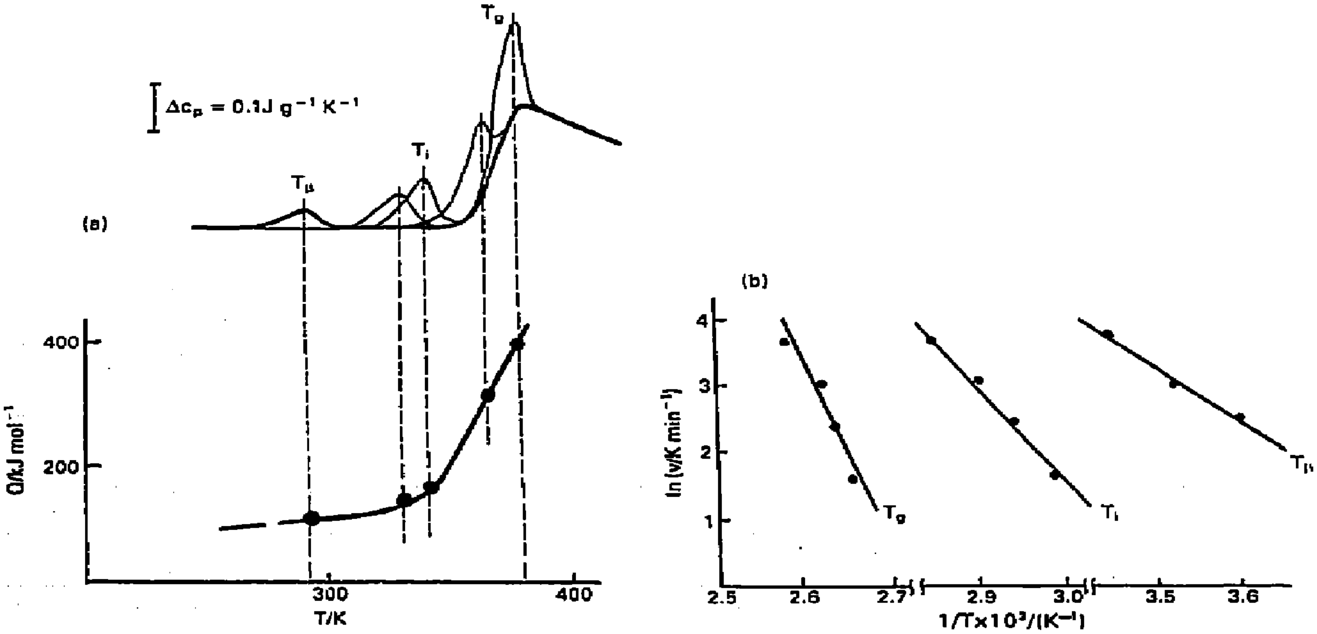

Fig. 4. DSC data for atactic poly(methyl methacrylate) [4, 21]. (a) DSC curves of samples with a different degree of annealing and the activation energy of segmental motion vs. temperature plot. (b) Transition temperatures vs. heating rate plots.

DSC also made it possible to estimate the scale of the cooperative event of the motion at T_g, viz. the volume v_{coop} of the substance participating in such an event, using Donth's formula [7, 47, 48]

$$v_{coop} = kT_g^2 \Delta C_p^{-1} / \rho(\delta T)^2 \tag{3}$$

where

$$\Delta C_p^{-1} = \frac{1}{C_{p(T<T_g)}} - \frac{1}{C_{p(T>T_g)}} = \frac{\Delta C_p}{C_{p(T<T_g)} C_{p(T>T_g)}}$$

and ρ is the density of the polymer, $C_{p(T<T_g)}$ and $C_{p(T>T_g)}$ are the heat capacities before and after the ΔC_p jump at T_g, and $\delta T = \Delta T_g/2$ is the half-width of the glass transition interval measured on cooling the melt.

The original DMA(σ) technique and the relevant analysis were elaborated in refs. 24 and 25. The internal friction spectra $Q^{-1}(T)$ have been determined by measuring the damped torsional oscillations of a pendulum at $\nu \approx 1$ Hz under conditions of simultaneous static loading of the polymer sample. The pendulum system consisted of a two-filament sample with an inertial load in its middle. The static shear stress τ_{sh}, which provided a quasi-elastic strain in the sample, was applied by turning one of the clamps through a certain angle at each test temperature. The influence of the static stress magnitude on the damped oscillations has been studied in a temperature range from 100 K up to T_g in a vacuum of 10^{-3} Torr.

The application of τ_{sh} during the dynamic experiment led to pronounced changes in the mechanical loss spectra of glassy polymers. Depending on different factors (the test temperature, the value of static stress, the general duration of the sample holding under static load and the "rest" time after unloading) diverse effects of the influence of the static field were observed [24–27]. However, at $T \leq T_{max}$ (where $T_{max} = T_g$, T_β, etc.) and short times of static loading the mechanical activation of molecular mobility in polymers, viz. the shifts of the relaxation peaks to lower temperatures, depending on the magnitude of static stress τ_{sh}, have been clearly demonstrated; see, for example, the data for PVC in Fig. 5.

An analytical description enabled us to obtain an expression for the estimate of the effective relaxation time in a field of static stresses that accounted for all the effects observed and in particular, the temperature shifts of the relaxation peaks [24, 25]. A satisfactory agreement between theory and experimental data was obtained, even though a process with a single relaxation time was considered, while the relaxation peak corresponded, in fact, to some dispersion of relaxation times.

Of importance for our objective is that this analysis permitted the use of

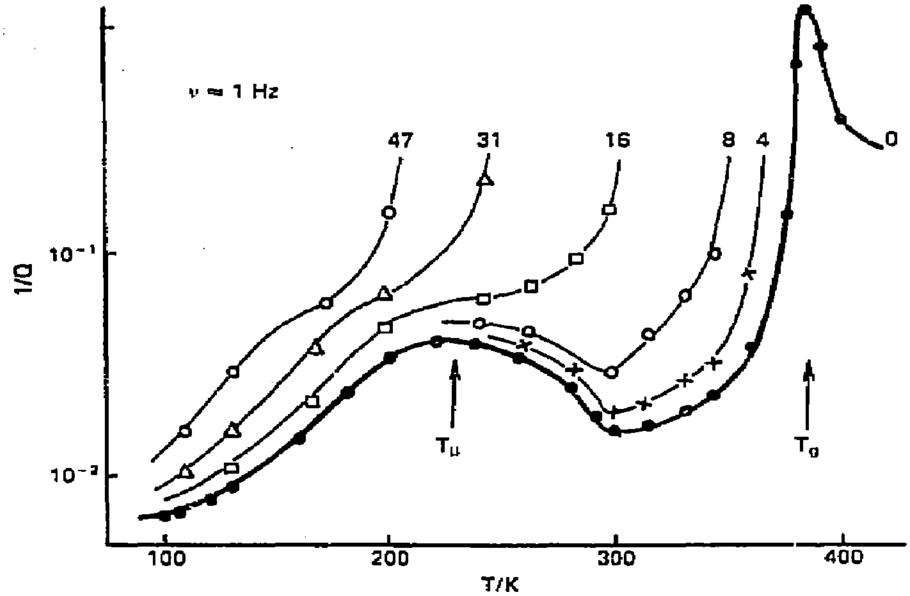

Fig. 5. Mechanical loss spectra of statistically loaded PVC samples [27]. The figures indicated the magnitudes of static shear stress τ_{sh} in MPa.

mechanical relaxation spectra of statically loaded polymers to find the effective activation volumes $v_{act}(T)$ in the relaxation processes, i.e. also (independently of DSC) to characterize the scale of motional events. At $T \leq T_{max}$ and the duration of static loading $t < 1$ min

$$v_{act} = \frac{kT}{\tau_{sh}}\left[12\left(\frac{Q^{-1}_{\tau_{sh}}}{Q_0^{-1}} - 1\right)\right]^{1/2} \tag{4}$$

where Q_0^{-1} and $Q^{-1}_{\tau_{sh}}$ are the internal friction values without or with static loading, respectively.

All the experiments have been carried out for a large number of samples: over two dozen flexible-chain polymers, a number of low-molecular organic glassses (see the caption to Fig. 7), crosslinked and multicomponent systems, and also for oligomer series of polycarbonate (PC), poly(dimethyl siloxane) (PDMS), polystyrene (PS) and poly(α-methyl styrene) (PMS).

3. RELAXATIONAL β TRANSITION

The DSC technique and the approach described above enabled us to detect and characterize the β transition for all the samples studied, i.e. polymers, oligomers and low-molecular glasses, even when it was not found by other methods [4, 18, 19]. The examples of the β and α transitions

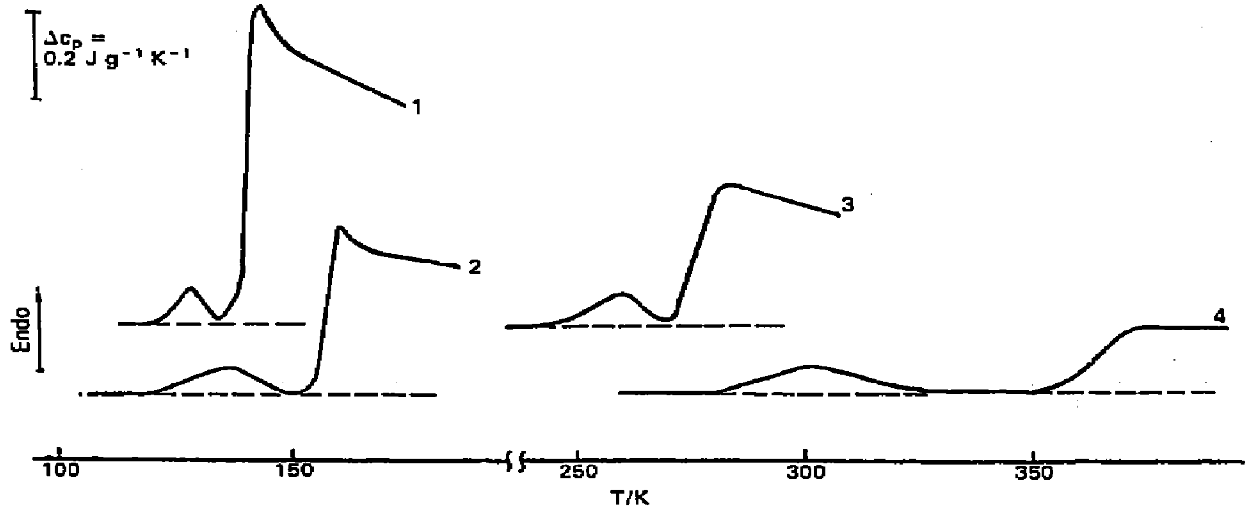

Fig. 6. DSC curves for (1) isopropylbenzene, (2) poly(dimethyl siloxane), (3) pentastyrene, and (4) poly(cyclohexyl methacrylate) [19]. The samples were treated to reveal the β transition (see text) as follows: first the sample was quenched from $T > T_g$ into liquid nitrogen; then it was held for 15 min at 118 K (1); 15 min at 123 K (2); 2 h at 233 K (3); 1 h at 263 K (4). Lastly it was cooled at 320 K min^{-1} followed by heating at 10 K min^{-1}.

appearing in DSC curves are shown in Fig. 6. A peak maximum of T_β was usually observed at temperatures about 20–100 K lower than T_g, while for low-molecular glasses the range of $T_\beta - T_g$ never exceeded 10–20 K. Only in the anomalous case of PC, was the enthalpy relaxation range of an extraordinary width, viz. $T_\beta \approx 200$ K was about 220 K lower than T_g.

Consequently, the DSC data have confirmed Goldstein and Johari's idea [2, 49] of the β transition as a general phenomenon and an indispensable precursor of the glass transition in solids with a disordered structure. Satisfactory agreement was observed between the T_β and Q_β values obtained by DSC and by the conventional relaxation methods.

A long time ago Eyring and co-workers [50] found a regular relaxationship between the flow activation energies Q_η and cohesion energies Q_{coh} for simple liquids composed of small molecules

$$Q_\eta \approx (0.30 \pm 0.05) E_{\mathrm{coh}} \qquad (5)$$

Hence it follows that the potential barrier to rotation-translational motion of a molecule in a condensed phase equals about one-third of the total energy of intermolecular interactions. Meanwhile, we found [18, 19] for 11 low-molecular vitrified simple organic liquids and short-chain oligomers that the activation energies Q_β and E_{coh} values satisfied, in essence, a similar relation (Fig. 7)

$$Q_\beta \approx (0.4 \pm 0.1) E_{\mathrm{coh}} \quad \text{or} \quad Q_\beta \approx Q_\eta \qquad (6)$$

Remarkably, for 12 flexible-chain polymers of different type the approximate equality (with an accuracy of 10–20%) of Q_β values obtained for the Q_η values estimated at temperatures $T > T_{ll}$ was also found [4, 19], which means that the unit events in a flow of liquid and the β relaxation in a glassy solid are similar, i.e. the latter is realized as a local liquid-like motional event at the site of reduced close packing with increased enthalpy and entropy ("islet of an increased mobility" [2]). Moreover, it shows that for polymers the β transition, like the flow process, is of a segmental nature.

Further, it was discovered [19] that in polymers there was no regular relation of Q_β to the cohesion energy E_{coh} per mole of monomer units. Meanwhile, the experimental data obtained for 26 flexible-chain polymers obeyed a relationship of the type (Fig. 7)

$$Q_\beta \approx (0.30 \pm 0.05)E_{\mathrm{coh}}S + B \tag{7}$$

where Q_β is in kJ per mole of kinetic units (segments), and a small supplement $B \approx 10 \pm 5$ kJ mol^{-1} corresponds to the internal rotation barrier in chains. The parameter S is the number of monomer units in a statistical

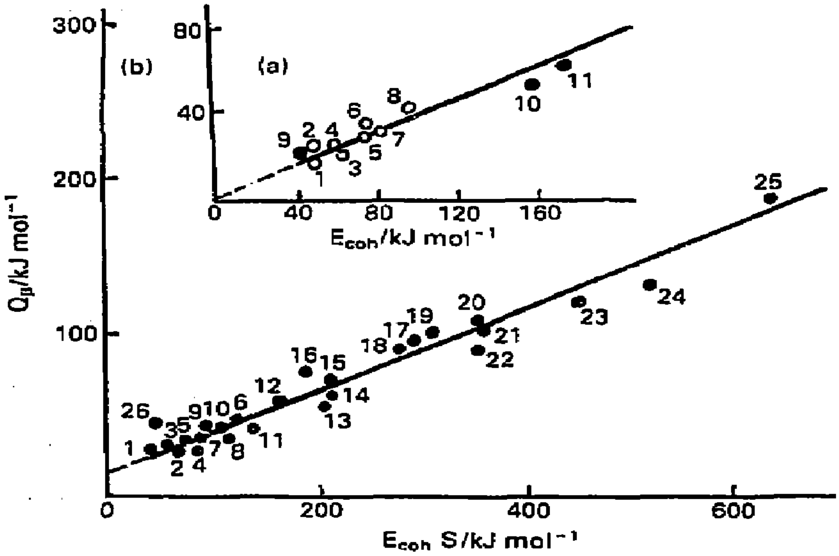

Fig. 7. Activation energy of β transition in (a) low-molecular glasses and (b) linear polymers vs. the cohesion energy or cohesion energy of a statistical segment, respectively [17–19]. (a) 1, Pentanol; 2, isopropylbenzene; 3, 5-methyl-3-heptanol; 4, decalin; 5, 1,1-diphenylpropane; 6, diethyl phthalate; 7, glycerol; 8, o-terphenyl; 9, hexamethyl disiloxane; 10, tetra-α-methylstyrene; 11, pentastyrene. (b) 1, Polyethylene, 2, polyisoprene; 3, poly(dimethyl siloxane); 4, poly(diethyl siloxane); 5, poly(phenylene oxide); 6, poly(ethylene terephthalate); 7, polytetra-fluoroethylene; 8, polycarbonate; 9, polyamide 6; 10, polypropylene; 11, polymethacrylate; 12, poly(vinyl floride); 13, poly(vinyl acetate); 14, poly(vinyl chloride); 15, poly(vinyl alcohol); 16, poly(methyl methacrylate); 17, poly(diphenyl oxyphenylene); 18, poly(butyl methacrylate); 19, polystyrene; 20, polyacrylonitrile; 21, poly(α-methyl styrene); 22, poly(cyclohexyl methacrylate); 23, polyimide I; 24, polyimide II; 25, poly(meta-phenylene isophthalamide); 26, polyisobutylene.

(Kuhn) segment. As is known, S is determined experimentally from the dimensions of the undisturbed shape of a macromolecule in a dilute θ-solution at θ-temperature and characterizes the thermodynamic, equilibrium rigidity of a chain [51, 52]. As the β relaxation obeys eqn. (1), the expression for its temperature (in kelvin) reads

$$T_\beta \approx Q_\beta(0.250 - 0.019 \lg \nu)^{-1} \qquad (8)$$

where the difference in parentheses includes the gas constant R in kJ mol^{-1} K^{-1}. Thus, eqn. (7) for Q_β in polymers differs only slightly, in essence, from eqn. (6) for low-molecular glasses provided the Kuhn segment is considered as a quasi-molecule. The barrier Q_β is controlled simultaneously by two factors, (i) the energy of intermolecular interactions, and (ii) the thermodynamic chain rigidity. The presence of the extra term B allows the participation of a trans–gauche (T–G) transition to be represented in an event of β relaxation.

In good accord with the latter result is the experimental dependence of Q_β on the average polymerization degree n for four oligomer–polymer series [19, 21, 22]. As seen in Fig. 8, the Q_β values increased only up to a definite limit for each polymer and then remained invariable. These "critical" sizes of molecules are close to the lengths of the statistical segments in relevant polymers.

The determination using eqn. (4) of a second kinetic parameter, the effective activation volume v_{act}, which is plotted versus T in Fig. 9, is also of interest for characterizing the β relaxation. The physical meaning of the term "activation volume", as applied to relaxations, is discussed below but here we only emphasize that the values of v_β were found to be rather close to those of the volumes of statistical segments in polymers (Table 1).

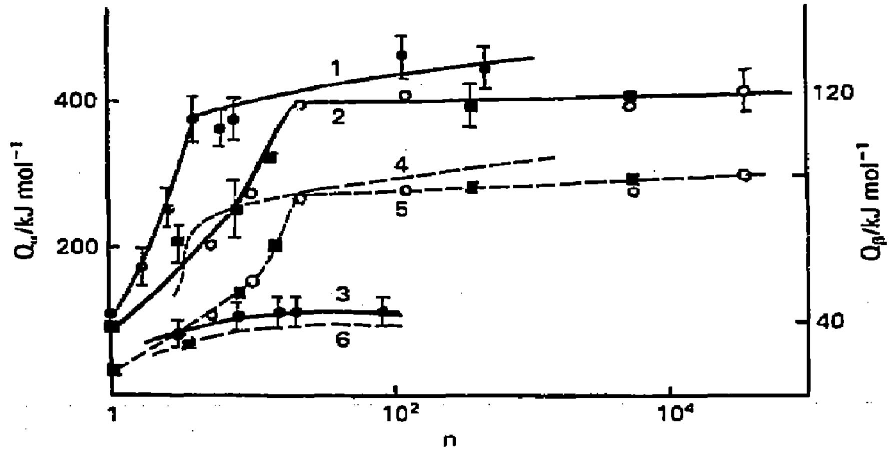

Fig. 8. Activation energies Q_α (curves 1–3) and Q_β (curves 4–6) vs. the average number of monomer units in molecules of PC (curves 1, 4), PS (○) and PMS (■) (curves 2, 5), and PDMS (curves 3, 6). The values of $Q_{\beta'}$ are given for PC, $T_{\beta'} \approx 300$–360 K [4, 21, 22].

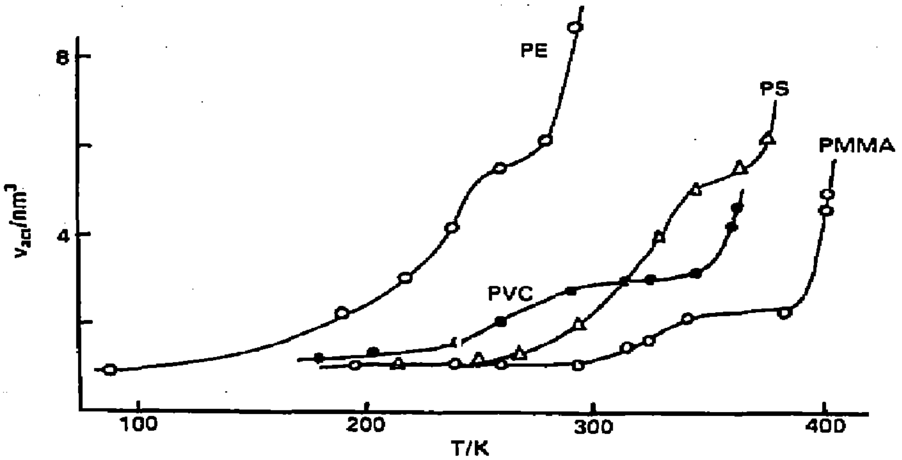

Fig. 9. Shear activation volumes of relaxation processes vs. temperature plots for PE, PVC, PS and PMMA [27].

The above thermal analysis data enabled us to advance a hypothesis for the common mechanism of β relaxation for different flexible-chain polymers [17–19] as a local liquid-like segmental motion realized by the hindered rotation in a chain section close in size to a Kuhn segment, with surmounting of chiefly intermolecular potential barriers, and participation of a T–G transition in each motional unit event.

It was assumed from the set of torsional–vibrational motions in chain sections varying in size (the broad rotational angle distribution has recently been confirmed by two-dimensional NMR data [53, 54]), with the advent of a sufficiently energetic thermal fluctuation and rotation of some monomer units through a greater amplitude (T–G transition), that a correlation

TABLE 1

Comparison of the shear activation volumes of β and α transitions with the scale of cooperative motion at T_g (DSC data) and statistical segment volume in glassy polymers [4, 27]

Polymer	v_β/nm³	v_α/nm³	v^{DSC}_{coop} at T_g/nm³	Kuhn segment size		Approximate relations		
				S/units	v_s/nm³	$\frac{v_\alpha}{v_s}$	$\frac{v^{DSC}_{coop}}{v_s}$	$\frac{v_\alpha}{v_\beta}$
PVC	0.9–1.2	2.5–3.0	4.6	12	0.9	3	5	3
PS	1.0–1.3	4.0–4.5	3.3	8	1.3	3	3	4
PMMA	0.8–1.0	2.0–2.5	1.4	6	0.8	3	2	3
PC	0.8–0.9	2.7–3.0	2.4	1–2	0.4–0.7	5 ± 2	5	3
PVA	–	–	4.4	7	1.2	–	4	–

chain section adjoining the rotation axis must unconditionally be involved in this motional event. Therefore, the Kuhn segment is "singled out" as a kinetic unit in a β transition and, simultaneously, in the conformational mobility of the chain. Such a motional event, being similar to that of segmental relaxations in a polymer melt, can be realized at the sites of free volume (packing defects) in a solid polymer.

We presumed that the motion of the chain segment in the β transition could be described best of all by a model which is the most used at present for conformational isomerization in macromolecules [55–57]. Indeed it includes a single-barrier T–G transition with forced adjustment of a small chain section in an energetically profitable way, viz. each monomer unit of this section is displaced only slightly regarding its nearest neighbour, within the amplitude torsional vibrations, and the entire chain section twists during a motional event. The displacement of the monomer units from their initial positions diminishes with increasing distance from the point of rotation and vanishes, in our interpretation, at a distance close to the statistical segment.

This hypothesis of a general mechanism for the β transition was confirmed, apart from the correlations considered, by (i) the experimental findings obtained by FIR spectroscopy and summarized in a review paper [46], and (ii) the successful prediction of the main relaxation transitions proceeding from the idea of the common nature of the β and α transitions (see Section 6).

FIR spectra of glassy polymers at frequencies $\nu < 130\,\mathrm{cm}^{-1}$ exhibit, just as in simple liquids, an absorption band caused by a small-angle torsional vibration (libration) of the monomer unit in the chain [28, 29, 31]. It was shown that the characteristics of this absorption were determined by the dipole moment and cohesion energy values for this unit, and this type of motion controlled the low-temperature δ relaxation in polymers with an activation energy of $Q_\delta \approx Q_{\mathrm{libr}} \approx E_{\mathrm{coh}}/3$. Except for two specific cases, the common mechanism of the γ relaxation in flexible-chain polymers, such as the local torsional vibration including only two or three neighbouring monomer units, has been shown using FIR spectroscopy [34].

Meanwhile, the absorption band in the range $160–260\,\mathrm{cm}^{-1}$ turned out to be related to the skeletal torsional vibrations in chains and to the β relaxation process; it enabled us to confirm directly the above model of this transition [28, 32, 33, 46].

Hence for crosslinked systems with different concentrations of crosslinks, it was shown that at certain concentrations both the skeletal torsional vibrations band and the β relaxation peak in the mechanical loss spectrum simultaneously and sharply dropped in intensity. This suppression of the segmental motion occurred when the average distance between crosslinks became commensurable with or less than the Kuhn segment size S [34].

Further, for 15 flexible-chain polymers varying in structure the potential barriers of skeletal torsional vibrations Q_{sk}, estimated from the FIR spectra, appeared to be close to the activation energies Q_β (with an accuracy of 20%) whereas the estimated values of the torsional-vibrational segments coincided, to a first approximation, with the sizes of the statistical segment in the relevant polymers [32] (see Table 2).

TABLE 2

Experimental values of the motional segment sizes in flexible-chain polymers

Polymer	Temperature range or transition	Experimental technique	Monomer units		Ref.
			N	S	
Polyacrylonitrile	β Transition	FIR spectroscopy	7	9	28, 32
Polychlorostyrene	β Transition	FIR spectroscopy	6	8	28, 32
Poly(decyl methacrylate)	β Transition	FIR spectroscopy	5	7–8	28, 32
Poly(dimethyl siloxane)	$T \geq T_g$	NMR	5	5	84
Poly(ethyl acrylate)	$T_g \leq T < T_{ll}$	Photon correlation spectroscopy	4	6	85
Polyethylene	β Transition	FIR spectroscopy	7	8	28, 32
	β Transition	Thermostimulated current depolarization	8 ± 2	8	86
	$T > T_g$	Diffusion	7	8	37, 87
Poly(ethylene glycol)	$T > T_{ll}$	Paramagnetic probes	5	4–5	88
	β Transition	FIR spectroscopy	4	4–5	28, 32
Poly(ethylene oxide)	α Transition	Light scattering	6–7	4–5	89
Polyisoprene	$T_g \leq T \leq T_{ll}$	Paramagnetic probes	3–4	3–4	90
	$T_g < T \leq T_{ll}$	Fluorescence depolarization	4–5	3–4	91
Poly(methyl acrylate)	β Transition	FIR spectroscopy	4	6	28, 32
Poly(methyl methacrylate)	β Transition	FIR spectroscopy	5	6	28, 32
Polypropylene	β Transition	FIR spectroscopy	9–10	9	28, 32
Polystyrene	β Transition	Raman spectroscopy	>3	8	61
		FIR spectroscopy	7	8	28, 32
Poly(vinyl acetate)	β Transition	FIR spectroscopy	6	7	28, 32
Poly(vinyl chloride)	β Transition	FIR spectroscopy	6	12	28, 32
Poly(vinyl fluoride)	β Transition	FIR spectroscopy	10	11	28, 32

Here we draw special attention to the temperature dependence of FIR spectra which have given a direct answer to the question concerning the onset of conformational mobility in glassy polymers, i.e. the participation of T–G transitions in the β relaxation process [33].

Earlier, the possibility of a T–G transition at $T < T_g$ has been shown by combining a theoretical analysis with mid-IR spectroscopy data on the dynamics of intermolecular hydrogen bonds in glassy polymers [20]; that was also in agreement with the beginning of physical ageing, necessarily related to molecular rearrangements, just from the β relaxation region onwards [4, 58, 59]. Besides, the growth of density thermal fluctuations [60], the liquid-like movement of chain segments (shown by Raman spectroscopy) [61], and the noticeable decrease in energy of intermolecular interactions [62] have been observed experimentally, beginning from temperatures close to the low-frequency T_β temperature.

We discovered [33, 46] that the band contours for skeletal torsional vibrations in FIR spectra of several polymers were conformationally-sensitive and had a doublet structure; the ratio of $K_{\nu 1}/K_{\nu 2}$ of the absorptivities of the doublet components (for example, 185 and 195 cm^{-1} in PVC, 240 and 257 cm^{-1} in PAN, and 220 and 230 cm^{-1} in PMMA) changed with increase in temperature (see, for PVC, Fig. 10). As shown, these changes reflected a change of conformational equilibrium in the polymer, i.e. in the relative population of G- and T-conformers and their influence on the torsional skeletal vibrations in chains. Consequently, the change in the $K_{\nu 1}/K_{\nu 2}$ ratio is an indication of T–G transitions and conformational mobility occurring due to the anomalous excitations of torsional states.

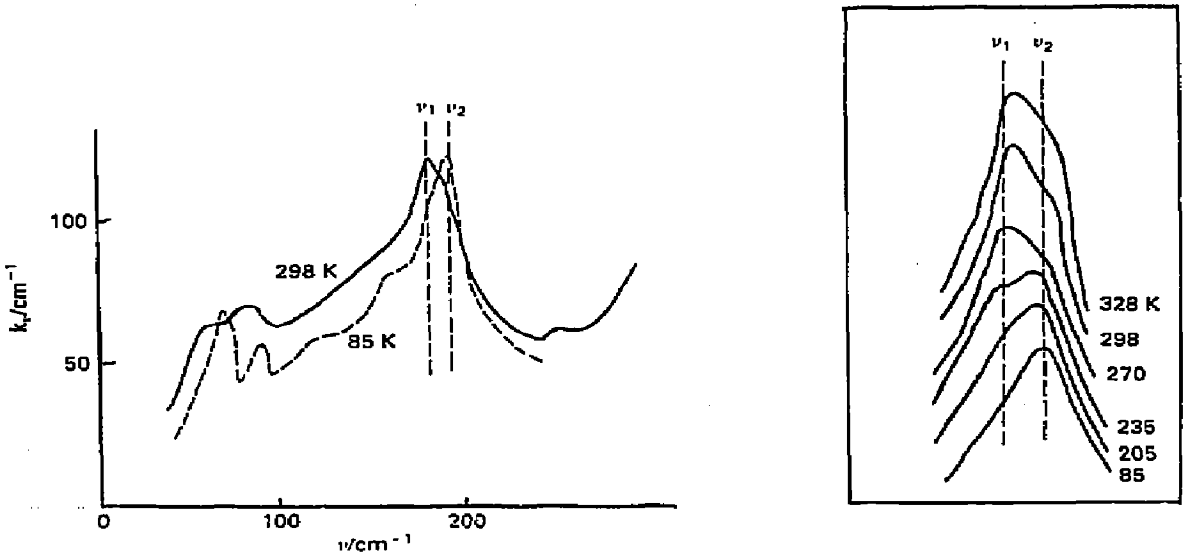

Fig. 10. Far infrared spectra of PVC at different temperatures [33, 46]. The changes in a doublet absorption band of torsional skeletal vibrations are shown on the right.

As seen in Fig. 11, the unfreezing of the conformational mobility starts from temperatures of T^* onwards that are equal to about 200 K in PVC, 250 K in PMMA, and 330 K in PAN and which are close to the temperatures of the low-frequency T_β temperature at $\nu \approx 10^{-2}$ Hz. This result directly confirms the participation of the T–G transition in the β relaxation event.

Finally, of considerable physical interest is the closeness or even approximate coincidence found of T^* and the low-frequency T_β with some well-known characteristic temperatures of glassy polymers, viz. the empirical constant of T_0 in the Fulcher–Fogel–Tammann and Williams–Landel–Ferry equations, and the temperature of T_2 in the Gibbs–DiMarzio thermodynamic glass transition theory [33]. Moreover, as was supposed for T_2 in refs. 63 and 64, all these temperatures were found to be proportional to the energy difference $\Delta E = E_G - E_T$ [33]. The origin of the unique conformity of the above temperatures is discussed in a review paper [46].

Thus, T^* is a quasi-thermodynamic temperature for the onset of the process when the correlated torsional oscillations in the chains become large enough in amplitude for a T–G transition to occur and for the local unfreezing of segmental motion, i.e. the manifestation of the β relaxation.

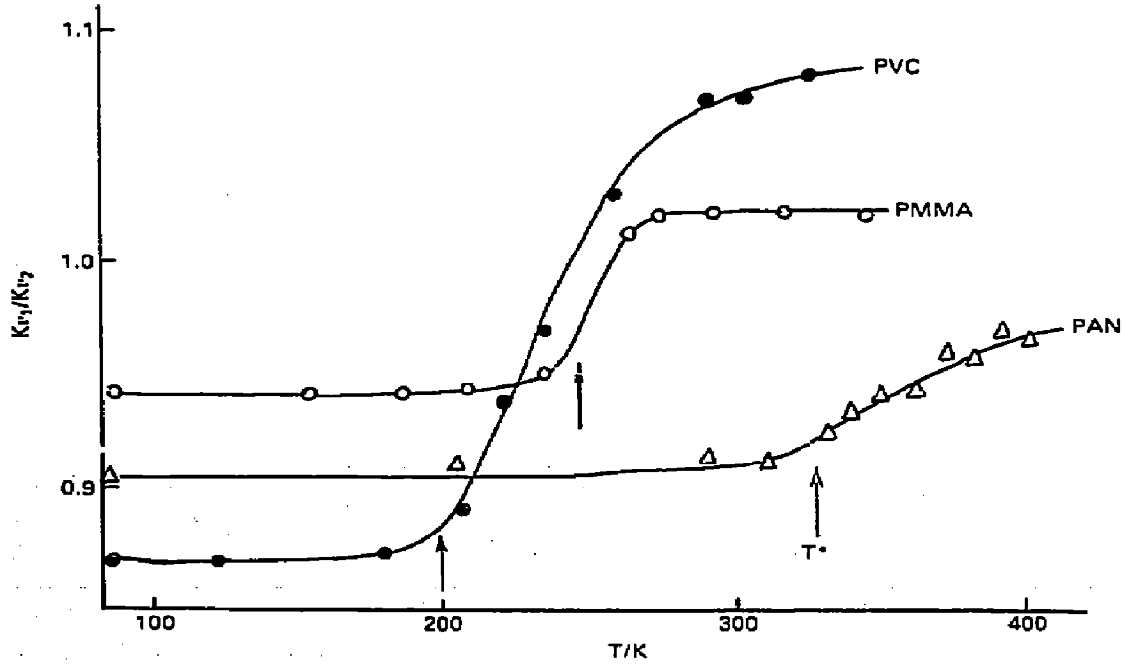

Fig. 11. The ratio of absorptivities of the components in a doublet band in the far infrared spectrum vs. temperature for PVC, PMMA and PAN [33, 46].

4. COOPERATIVE GLASS (α) TRANSITION AND ITS RELATION TO THE β TRANSITION

The significance of a β transition is that the β process is not only a feature of the glassy state at $T \ll T_g$, but that its inherent motional events, occurring quasi-independently or "collectively", control (as has turned out) the segmental mobility at all temperatures $T \gtrsim T_\beta$ including the temperature regions in the vicinity of T_g as well as the rubber-like state and the polymer melt. This was established experimentally, from the DSC analysis [17, 21, 22]. All the data obtained gave us a real idea of the size of the motional segments, the nature and degree of their cooperative motion in the α transition, and pointed out the fundamental "genetic" interrelationship of α, β and ll transitions, which will be briefly considered below.

The first principal result was that the undoubtedly sharp increase in the scale of the motional unit event of an α transition and in the magnitudes of its parameters in comparison with those for the β transition were not associated with increasing length of the intramolecular kinetic unit, as was frequently presumed (for instance, in refs. 6 and 10). Upon going from the β relaxation to the glass transition the length of the moving chain segment remains practically invariable, i.e. close to the Kuhn segment size. The following data support this statement.

Firstly, the T_g versus polymerization degree n and T_β versus n dependences have an absolutely identical shape (Fig. 12). Similarly, although the values of activation energies Q_α are much higher than Q_β, for linear polymers varying in structure, the Q_α versus n dependences are, virtually identical in shape to the Q_β versus n plots (Fig. 8); that is, both energies rise steeply, but only up to the critical chain length which is

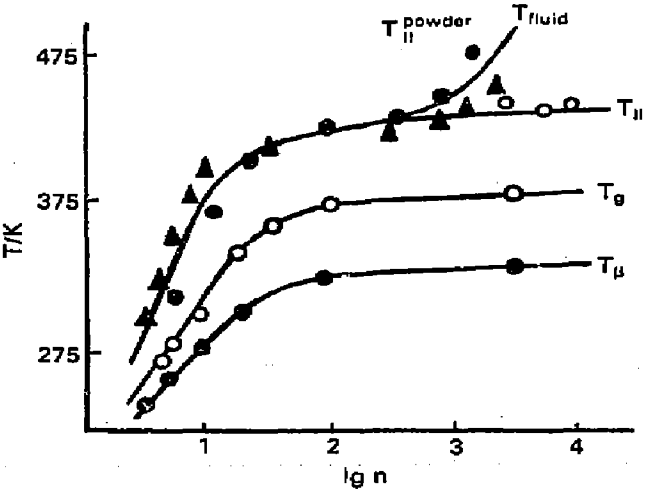

Fig. 12. The temperatures of T_β, T_g, T_{ll} and the fluidity point in PS vs. the average degree of polymerization. T_β and T_g values are DSC data [4, 22]; T_{ll} and T_{ll}^{powder} were obtained by DSC for films and powdered samples, respectively, in refs. 92 and 93, and the fluidity points T_{fluid} were taken from ref. 94.

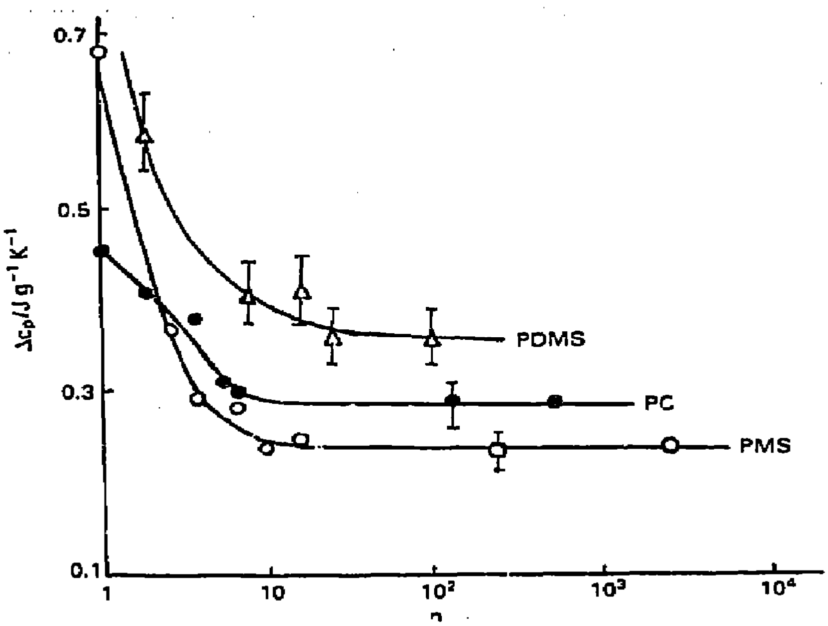

Fig. 13. Heat capacity step at T_g vs. the average polymerization degree for PDMS, PC and PMS [22].

approximately equal to S monomeric units (Kuhn segment) in the relevant polymers and then remain constant within the limits of the accuracy of their determination (±10%).

The relations for the heat capacity step $\Delta C_p = f(n)$ in the α transition were also specific, viz. when shortening of the polymer chains occurred the ΔC_p step increased substantially in magnitude beginning from the same "critical" values of $n \approx S$ (Fig. 13). The most obvious reason for this effect seems to be the change in the amplitudes and/or frequencies of the rotation-translational motion in the glass transition as a result of the transformation of segmental motion into the motion of the molecule as a whole.

For the question being considered, the DSC curves for the styrene–divinylbenzene (S–DVB) copolymers varying in the average crosslink concentration are also of interest; the control of the actual degree of crosslinking by infrared has been performed. As seen in Fig. 14, the suppression of the segmental motion in linear sections of the networks formed (viz. the sharp drop and vanishing of the ΔC_p step at T_g) and the disappearance of the possibilities for an exothermic reaction by post-polymerization in networks at $T > T_g$, was observed when the average distance between crosslinks $N_{cl} \leq S$; for PS $S \approx 8$ monomer units.

The above thermal analysis data are consistent with recent direct experimental estimates of the motional segment length N at temperatures of $T \gtrsim T_g$ carried out for different polymers by non-calorimetric techniques. As seen from Table 2, in all cases the values of N either coincided with

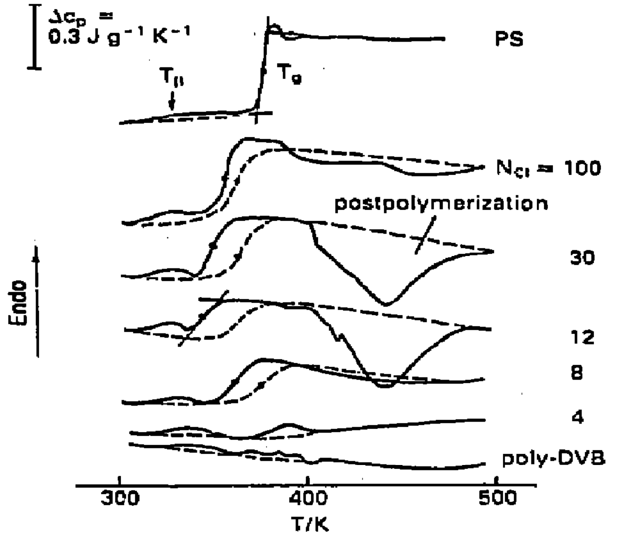

Fig. 14. DSC curves for PS, polydivinylbenzene and S/DVB copolymers [4]. The copolymers were prepared by polymerization at 353 K for 3 h, followed by cooling at 3 K min^{-1}. The average distance between cross-links in copolymers as a number of monomer units N_{cl} is indicated. ——, scan I; – – –, scan II. Heating rate $V = 20$ K min^{-1}.

those of a statistical segment S or were rather close to them, which means that the size of motional chain segment is, really, stable throughout a wide temperature range including T_β and T_g. This makes it possible to reject finally the assumptions encountered in the literature concerning the large changeability of the motional segment length in the vicinity of T_g.

All these results permitted us to consider the problem of the glass transition with more certainty. It was natural to assume that the "large-scale" nature of its unit event in polymers was determined by the cooperative (or correlated) motion, in an intermolecular way, of several neighbouring segments of approximately the same length, as in the β transition. Then, the anomalously high values of activation energies Q_α and activation volumes v_α of motion in the glass transition at low frequencies have to reflect this phenomenon, while the expected ratio $Z = Q_\alpha/Q_\beta \approx v_\alpha/v_\beta$ corresponds to the minimum and most probable parameter of the cooperativity of the segmental motion under these conditions.

For polymers at low frequencies Boyer's ratio between T_β and T_g (in kelvin) is well known [10]

$$T_\beta/T_g \approx 0.75 \pm 0.05 \tag{9}$$

although from our data [4], its limits were found to be somewhat broader

$$T_\beta/T_g \approx 0.75 \pm 0.1$$

The "genetic" connection between the α and β transitions was additionally confirmed by the relationship found between their kinetic parameters and also by DSC studies of the processes of mutual transformation of the α into the β transition and vice versa (see also Section 6).

We have found using DSC that for about two dozen flexible-chain polymers and four series of oligomers the ratio

$$Q_\alpha/Q_\beta \approx 4 \pm 1 \tag{10}$$

was observed [21, 22]. It is noteworthy that the values of energies changed over a wide range.

The activation volumes of the α transition were simultaneously estimated by DMA(τ_{sh}) [27] and DSC techniques [4], or more exactly, the shear activation volumes and the volumes v_{coop} characterizing the scale of cooperative motional unit event, respectively, were found. As seen from Table 1, both mechanical and calorimetric techniques gave to a first approximation close magnitudes of volumes v_α and v_{coop} at T_g. This result is notable because the physical content of the term "activation volume", as applied to relaxation and deformation processes, is still being discussed, although it is often associated with the real volume of the motional unit [65]. Therefore, the coincidence found testifies in favour of such an explanation for the term "shear activation volume of relaxation transition".

Of importance for understanding the common nature of α and β transitions is that a certain ratio of the v_α and v_β was also observed for different polymers ([27] and Table 1)

$$v_\alpha/v_\beta \approx 4 \pm 1 \tag{11a}$$

that is

$$Z = Q_\alpha/Q_\beta \approx v_\alpha/v_\beta \approx 4 \pm 1 \tag{11b}$$

This relation required a general interpretation and could be related to the expected parameter of motion cooperativity [4, 21, 22]. This statement is confirmed by theoretical data. Thus, in a number of theories [36, 63, 64, 66–72], the α transition event was considered as the collective mode of motion realized as the quasi-independent and localized event in the β transition, while a potential barrier Q_α was presumed to correspond to the correlated surmounting of several barriers Q_β. Of great interest is that the theoretical estimates [36, 48, 66, 69, 70] gave the same values for the most probable parameter of cooperativity $Z \approx 3$–5 as observed in our experiments. In these terms the "intermediate" relaxations should be responsible for the mixed, quasi-independent and cooperative, motion of segments. From this viewpoint, the continuous gradual transformation of the β into the α transition, as demonstrated by the $Q(T)$ curve in Fig. 4, is absolutely clear.

According to calculations [36], the parameter Z is not constant. Generally in the vicinity of ultrahigh frequency T_g (or at $T \geqslant T_{\text{ll}}$) $Z \to 1$, and at ultralow frequency glass transition temperatures $Z \rightarrow \infty$; however, in the normally employed low-frequency region of $\nu \approx 10^{-3}$–10^{3} Hz $Z \approx 3$–5 (see scheme in Fig. 1(b)). These estimates explain the fact of degeneration of the cooperative segmental motion ($\alpha \rightarrow \beta$ transition transformation) at $\nu \geqslant 10^{8}$ Hz (Fig. 1(b)).

Work should also be mentioned which considers the simultaneous appearance of α and β transitions in an amorphous solid proceeding from the distribution function of density fluctuations [8], quasi-punctual defects of enthalpy and entropy excess [73, 74], or from non-equilibrium thermodynamics [75], namely as a dissipative process of the formation of an amorphous structure consisting of low-energy regions of short-range order (blocks of more-or-less unidirectional segments, evidently, correspond to them) and of high-energy sites of loose packing of segments. Two relaxation modes ("rapid", β and "slow", α) could be separately observed in the vicinity of T_g from dielectric relaxation spectra [14], photon correlation spectroscopy [76, 77] or by a combination of different NMR techniques [3]; a law of their mutual compensation was observed, viz. a growth in the intensity of one process was attended by the relevant diminution of the intensity of the other [14]. This enabled the phenomenon of "motional heterogeneity" to be discussed [3].

The value of $Z \approx 3$–5 segments corresponds, actually, to the scale of short-range order regions and to the coordination number of chains arrangement in the first coordination sphere of an intermolecular "lattice".

Consequently, unlike the β relaxation, the cooperative segmental motion is mostly realized in regions having a closer packing, and the values of Q_{α}, obtained by DSC for the narrow temperature range at low frequencies, really have the meaning of potential barriers to the correlated motion of several neighbouring segments, virtually, the same ones as the motional units in the β transition.

Relations (7)–(11) provided new possibilities for an approximate prediction of T_g at $\nu \approx 10^{-2}$–10^{2} Hz proceeding from the molecular characteristics of flexible-chain polymer [4]

$$T_g \approx (1.6 \pm 0.4) E_{\mathrm{coh}} S + 5B \qquad (12)$$

Figure 15 shows the satisfactory accord between the predicted and experimental values of T_g obtained for 23 different flexible-chain polymers.

5. LIQUID–LIQUID (ll) TRANSITION

The approximate physical boundary between rubber-like and fluid states in polymers is known as the liquid–liquid (ll) transition [11]. Its origin and even its existence have been widely debated [5, 11]. However, apart from relaxation data, a number of experiments confirmed its existence beyond doubt: (1) the onset of a sharp drop in intermolecular interactions,

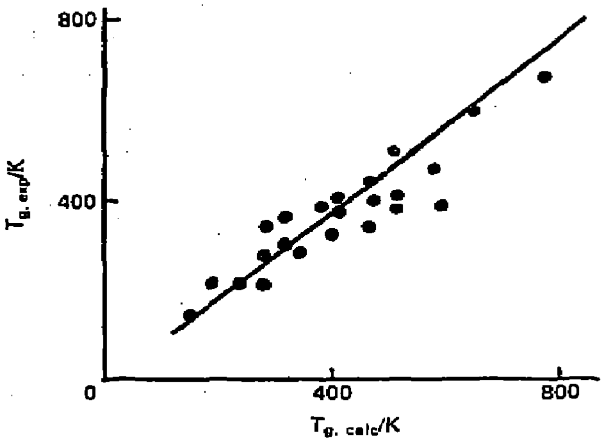

Fig. 15. Relation between the experimental ($\nu \approx 10^{-2}$–1 Hz) and predicted glass transition temperatures for different flexible-chain linear polymers (see table 2.4 in ref. 4). See the caption to Fig. 7.

apparent from differential mid-IR spectroscopy data [62], (2) a step increase in average interchain distance, determined by X-ray diffraction [78], (3) the critical change in behaviour of fluorescent additives in polymers, and (4) a cardinal change in the ESR spectrum (paramagnetic probe technique) [11] were observed at the T_{ll} temperature.

For understanding the nature of the ll transition we should also mention a break observed in the viscosity curves of $\lg \eta = f(1/T)$ [11] and the similarity between the manifestation of T_{ll} in non-crystallizing polymers and that of the temperature of maximum rate of crystallization in crystallizable polymers [4]. Moreover, the abovementioned degeneration of a cooperative α transition into the β transition at T_{ll} is of importance, i.e. the ll transition should be considered as an upper limit for T_g and possible manifestation of the cooperative motion of segments. An empirical relation of T_{ll} to T_g values measured at low frequencies of 10^{-2} to 10^3 Hz

$$T_{ll} \approx (1.20 \pm 0.05) T_g \qquad (13)$$

was established by Boyer [10, 11] and the deviations from it were rare and not great [79].

Extensive information on the ll transition in polymers has been obtained by Boyer and co-workers [5, 11] but our DSC study of this transition enabled us to find out, additionally, some of its peculiarities and to discuss the nature of the transition as a phenomenon "genetically" connected with two other main transitions, α and β [4, 23]. Without going into details, these peculiarities are the following.

When combining Boyer's and our data, it turns out that for uniform samples the T_{ll}, T_g or T_β versus polymerization degree curves are absolutely identical in shape (Fig. 12). As seen, the special behaviour for T_{ll} versus n is observed only when measuring powdery samples by DSC and was explained by the influence of the spreading process on the T_{ll} values (see the T_{fluid} versus n curve).

This accord and the proximity of Q_β to Q_η values measured at $T > T_{ll}$ (eqn. (6)), plus the direct estimates of the moving segment size below and above T_{ll} (Table 2) show the following: the above proofs concerning the motional segment length in a wide temperature range of $T \gtrsim T_\beta$ are also correct for ll transitions. According to eqns. (12) and (13)

$$T_{ll} \approx (1.9 \pm 0.5)E_{coh}S + 6B \tag{14}$$

i.e. the ll transition, like the α and β transitions, is mainly controlled by the thermodynamic rigidity of macromolecules (S) and the potential barriers of intermolecular interactions (E_{coh}), while the scale of the motional chain segment remains virtually constant below and above T_{ll}.

This result permitted us to reject the assumptions of both increasing the motional segment size in the vicinity of the ll transition [10] and of the "melting of segments" at T_{ll} with passage to monomer units as the kinetic units in a polymer melt [79].

Further, T_{ll} was found not to be a polymer constant; its value changed substantially with the annealing procedure in the rubber-like state (Fig. 16). As seen, in addition, the slope of the DSC curve at $T > T_{ll}$ may also rise, and a decrease in enthalpy (physical ageing) is observed under these treatments, for instance, in PVA. The latter effect, together with enthalpy relaxation manifesting itself in a drawn polymer within the range T_g to T_{ll} [4], brought us to the conclusion that it is not T_g but the T_{ll} temperature which corresponds to an upper limit for the possible existence of a polymer in the non-equilibrium state.

Finally, the quasi-thermodynamic nature of the ll transition was discovered in the experiments performed at various heating rates v [23]. Actually, as shown in Fig. 16(b) for low-polar PS, the displacement of T_{ll} with changing v was very small and the formal estimate of an activation energy for this transition using eqn. (2) gave an enormous value of $Q_{ll} \approx 800–900\ \mathrm{kJ\ mol^{-1}}$. Meanwhile, in the case of a high-polar polymer (PVA, Fig. 16(a)) the value of T_{ll} remained invariable when varying v by an order of magnitude. Moreover, a considerable discrepancy between T_{ll} values obtained on heating and cooling was observed (Fig. 16(a)), which is similar to the well known supercooling effect in crystallization–melting processes for crystallizable polymers [80].

The data considered enabled us to interpret the ll transition in terms of disintegration ("quasi-melting") on heating or, alternatively, formation on cooling the polymer melt of the long-living ("stable") associates of neighbouring segments [4] (The absence of a noticeable enthalpy jump at T_{ll}, that generally characterizes the phase transitions of the first kind, may be associated with the low "melting" enthalpy and low concentration of stable associates.); in some sense, this corresponds to an idea of T_{ll} as the

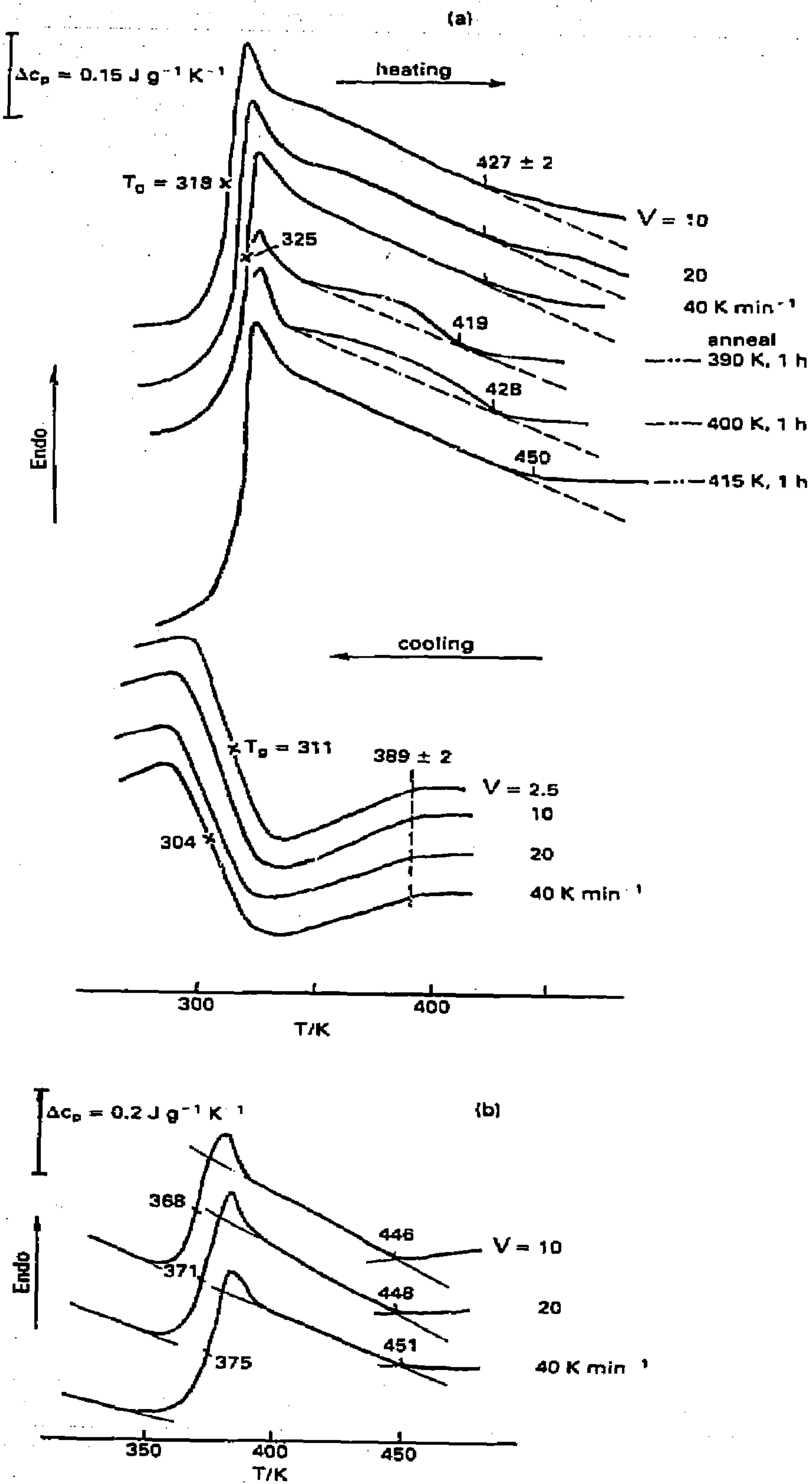

Fig. 16. DSC curves obtained (a) on heating and cooling PVA and (b) for heating PS at various rates as well as on PVA samples annealed differently in the rubber-like state [23]. $V = 20$ K min^{-1}.

temperature of a short-range order–disorder transition [71, 81]. Indeed, the ordering process caused by cooling of polymer melt includes, in general, three stages, (a) accumulation of conformationally-regular sequences of monomer units in chains (intramolecular ordering), (b) the occurrence of their associates similar to the most imperfect crystal nuclei (short-range order), and (c) the appearance of long-range order. While all these stages occur for crystallizable polymers, in non-crystallizing polymers this process stops (obviously) at the second stage corresponding to the ll transition manifestation on cooling of melt.

Thus, the general picture of segmental motion in flexible-chain polymers may be imagined as follows. At $T > T_{ll}$ a high hole concentration occurs and by the above mechanism the quasi-independent β process events play the main role in the motions. On cooling of the melt which decreases the free volume, the equilibrium between the competing processes of fluctuation disintegration and formation of segment associates gradually shifts to the side of the latter. As a result, at a certain temperature the centres of short-range order arise, viz. the crystalline nuclei for crystallizable polymers (at T_{cr}), or the relatively stable blocks of more-or-less parallel segments (associates) in the case of non-crystallizing polymers (at T_{ll}). Simultaneously, the relative contribution of cooperative segmental motions (i.e. of the α process) increases.

When T_g is reached, a dissipative structure, including regions of short-range order and less tightly packed sites in the polymer, arises. Below T_g the cooperative motions are gradually frozen-in, and at T_β the segmental motion is retained only as the liquid-like loosely packed "islets of mobility", i.e. localized events of β relaxation. Below T_β the conformational segmental mobility in chains vanishes completely and a chain becomes "dead" in this sense, with only small-scale low-amplitude processes of δ and γ relaxations remaining. Figure 1(c) shows schematically the temperature dependence of an effective activation energy Q for molecular motion throughout the range extending from 0 K to the polymer melt.

Thus, the statistical (Kuhn) segment plays a role of the basic "brick" in the molecular dynamics in flexible-chain polymers; its motion determines the basic transitions and the properties and processes controlled by molecular mobility.

6. THE PECULIARITIES OF THE MANIFESTATION OF THE GLASS TRANSITION IN MULTICOMPONENT POLYMERIC SYSTEMS AND A GENERAL APPROACH FOR THEIR PREDICTION

The diverse anomalies of T_g manifestation in such systems as block and graft copolymers, polymer blends, etc. are known and have been shown in detail in our DSC studies [4, 39–42, 45].

Hence, (a) the T_g of microphases formed by either flexible or rigid blocks may be higher than, equal to or lower than that for the relevant homopolymers; (b) the T_g of microphases may strongly depend on the preparation conditions and annealing history of samples; (c) more than two "T_gs" may be observed in two-component phase-separated materials; (d) the temperature range of the glass transition in multicomponent material may be very strongly broadened compared to that in homopolymers; (e) the T_g value may be invariant to the relative concentration of components in such samples, unlike the situation for a statistical copolymer; (f) the "abnormal" effect of rise in T_g with decrease in molecular mass can be observed for blocks in block copolymers, and (g) the transitions' activation energies in the materials in question may manifest anomalous behaviour.

The above concept of α and β transitions enabled us to offer a simple general approach to the explanation of these anomalies as well as to the plasticization effects in polymer–plasticizer systems. It was shown that both kinds of phenomena may be successfully quantitatively predicted, to a first approximation, proceeding from the molecular characteristics of the components of multicomponent systems [4, 39–45].

The analysis concerned two basic situations [4, 39].

(1) Good microphase separation. In this case the segment packing density may appreciably differ from that in the relevant homopolymers. The poorer packing, by a weakening of the intermolecular interactions, and the relevant appearance of an additional free volume, may occur as a result of the difference in the thermal expansion coefficients of the components, of the chemical binding of block ends producing the entropy hindrances to packing, etc.

This phenomenon results in more or less disassociated segmental motions, i.e. in the higher relative contribution to the latter of low-cooperative and, in the limit, of kinetically independent segmental motions. It means an increase in the role of the intermediate and β relaxations at the expense of the intensity of α processes which decrease. From this viewpoint, the displacement of the T_g position to the lower temperatures ($T_g \rightarrow T_i \rightarrow T_\beta$), a sharp drop in the value of activation energy ($Q_\alpha \rightarrow Q_i \rightarrow Q_\beta$), as well as the effects of broadening (up to a range of $T_\beta - T_g$) and manifestation of the "multiplicity" for glass transition could be expected. The values of T_β and Q_β in the relevant homopolymers should be considered as a limit for the displacement magnitude of the main relaxation transition under these conditions.

(2) Contact between heterogeneous segments because of the molecular mixing of components. Here we have in view not only the mixing of segments of different blocks, backbone and grafted chains, etc., but also the plasticized polymers.

If the α and β transitions in the components of polymeric systems are manifest in the distant temperature ranges, the breaking of intermolecular contacts between identical segments should result in the same situation as in the previous case, i.e. in the partial or complete disassociation of the motion of segments. In other words, if the mixing of heterogeneous segments or the plasticization process were sufficiently complete, the "$\alpha \rightarrow \beta$ transition transformation" should also take place, and the glass transition could be realized through the non-cooperative mechanism of β relaxation.

However, unlike the preceding case, the motion of segments of a given type occurs herein in the presence of "foreign" adjacent segments (or plasticizer molecules). Therefore, the limit values of T^* and Q^* parameters for a new "glass transition" have inevitably to depend on the chemical structure and molecular characteristics of these new "neighbours".

Actually, as a parameter of solubility $\delta = (E_{\mathrm{coh}}/V_{\mathrm{M}})^{1/2}$ where V_{M} is the molar volume, eqn. (7) can be rewritten as

$$Q_\beta \approx (0.30 \pm 0.05) V_{\mathrm{M}} \delta^2 S + B \tag{15}$$

Let us assume that the motion of the given segment in a polymer with parameter δ_1 is realized through the β transition mechanism, but in the neighbourhood of the segments of another component characterized by a parameter δ_2. Then, in the simplest case the activation energy of such a movement is

$$Q^* \approx (0.30 \pm 0.05)\left(\frac{\delta_1^2 + \delta_2^2}{2}\right) V_{\mathrm{M}} S + B \tag{16}$$

while the temperature of the new transition, according to eqn. (8) is

$$T^* \approx Q^*(0.250 - 0.019 \lg v)^{-1} \tag{17}$$

where T^* is in K and Q^* is in kJ mol^{-1}.

Finally, if the temperature T_β is known for the relevant homopolymer, the value of T^* can also be found by the equation

$$\frac{(0.25 - 0.019 \lg v) T^* - B}{(0.25 - 0.019 \lg v) T_\beta - B} = \frac{\delta_1^2 + \delta_2^2}{2\delta_1^2} \tag{18}$$

Consequently, as a result of the segmental motion disassociation in multicomponent polymeric system or plasticized polymer, one can expect that at $\delta_1 \approx \delta_2$ $T^* \approx T_\beta$ and $Q^* \approx Q_\beta$; at $\delta_2 < \delta_1$ $T^* < T_\beta$ and $Q^* \lesssim Q_\beta$, and at $\delta_2 > \delta_1$ $T^* > T_\beta$ and $Q^* \gtrsim Q_\beta$.

DSC curves of block and graft copolymers given in Fig. 17 demonstrate the examples of the peculiarities considered caused by the disassociation of segmental motion, namely, $\alpha \leftrightarrow \beta$ transition transformations.

Figure 17(a) shows the influence of the rigid block length in polydimethylsiloxane–polyphenylsilsesquioxane (PDMS–PPhSSO) block copolymers on the T_g of flexible PDMS blocks, upon the condition of a

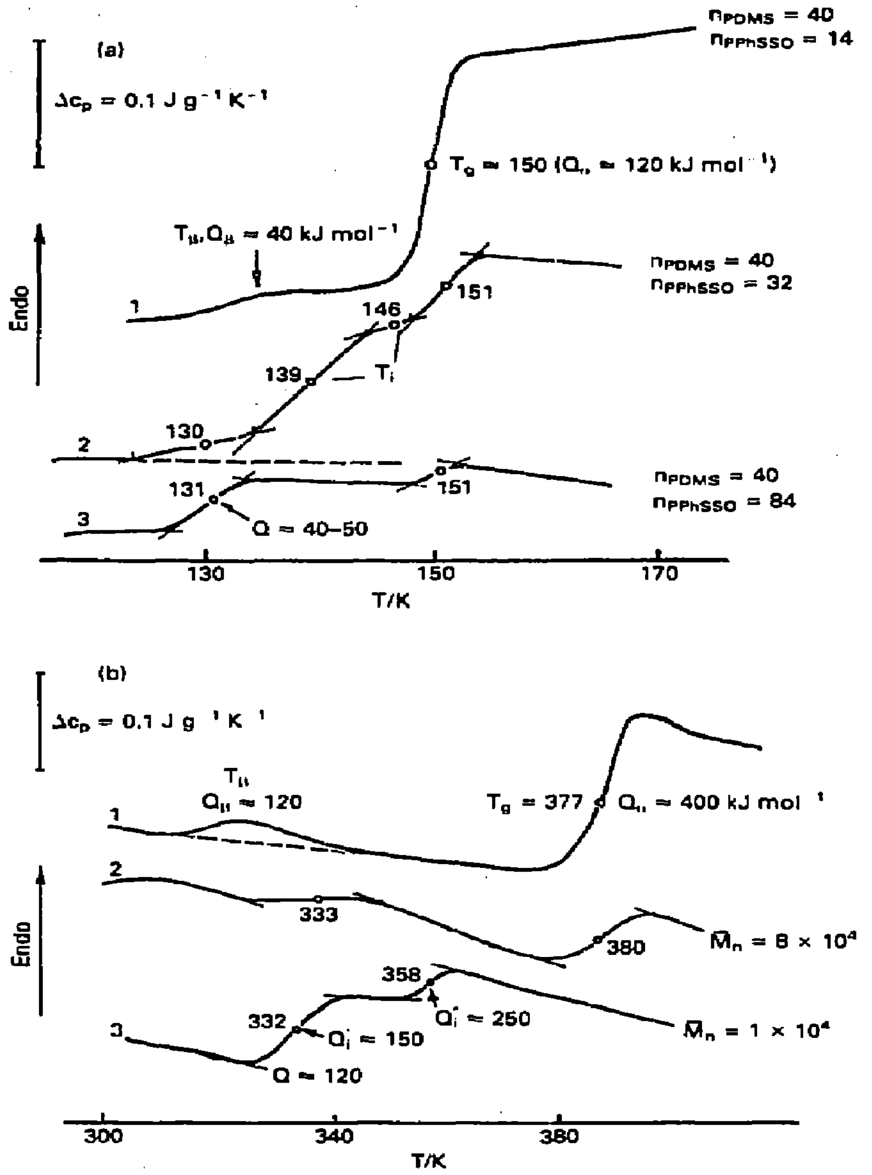

Fig. 17. DSC curves characterizing (a) PDMS blocks (curves 1–3) in PDMS–PPhSSO block copolymers [39], (b) PS (curve 1) and PS blocks in PS–PB diblock copolymers (curves 2, 3) [42], and (c) PS phase in PS/PB blend (curves 1) and PS/PB graft copolymer (curves 2) [41]. Heating rate $V = 20\,\mathrm{K\,min^{-1}}$. After scan I (——) the sample was cooled at $320\,\mathrm{K\,min^{-1}}$, followed by scan II (– – –).

distinct microphase separation [39]. As predicted, one can see the disassociation effects as the "game" between T_g, T_β, T_i temperatures for the main relaxation transition, which manifests itself in the strong broadening of the "glass transition" range extending from T_β to T_g, in the appearance of an abnormal four-stage ΔC_p step in this range, and in the dominant role of the β processes when increasing the rigid block content in the copolymer.

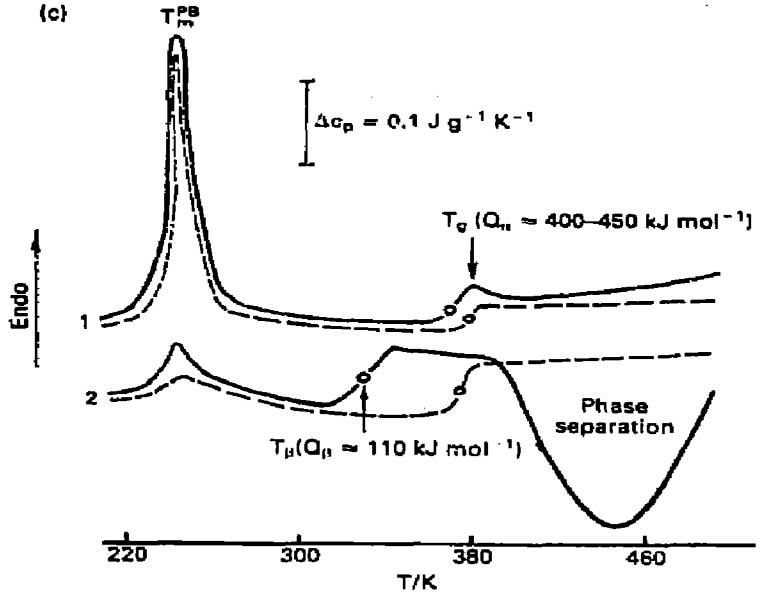

Fig. 17 (continued).

The latter disassociative effect is due to the hindrances created by rigid blocks for the optimal packing of flexible PDMS blocks.

A similar picture of a gradual $\alpha \longrightarrow \beta$ transition transformation can be observed for PS blocks in PS–PB diblock copolymers (Fig. 17(b)) [42] where $\delta_{PS} \approx \delta_{PB}$ and the mixing of different blocks occurs. As the molecular mass of the PS blocks decreased, the mixing degree rose and, simultaneously, the expected three-fold drop in the activation energy of motion was observed ($Q_\alpha \longrightarrow Q_\beta$).

Finally, Fig. 17(c) also allows us to compare the DSC curves for PS–PB blend and PS–PB graft copolymer with an identical ratio of components (11:89) [41]. The curve for the phase-separated blend shows the endothermic melting peak of PB crystallites and the ΔC_p step at $T_g^{PS} \approx 370$ K. Moreover, a high value of $Q_\alpha^{PS} \approx 400–450$ kJ mol^{-1} was observed. Meanwhile, the mixing of the components in the graft copolymer provided the suppression of the melting peak (decrease of PB crystallite content) and the manifestation of grafted PS glass transition at T_β and Q_β parameters (scan 1). A fact of interest is that the exothermic effect of microphase separation is observed at high temperatures. As a result scan 2 indicates a back transformation from the β transition to the cooperative α transition, viz. to the restoration of a "normal" position of T_g^{PS}.

It is a surprise that, despite the simplest starting principles, the above analysis has found experimental confirmation in studies of different block polymers [39, 40, 42], graft copolymers [41], comb-like [45] and plasticized polymers [43, 44]. As a matter of fact, all the above-mentioned anomalies of the glass transition have been observed by DSC. The data obtained for many multicomponent systems and polymer–plasticizer pairs [4] have shown a satisfactory agreement between the predicted and experimental values including also data obtained by other authors. It enabled us, in particular, to offer a general approach to the prediction of plasticization effects proceeding from the molecular characteristics of polymer and plasticizer [43, 44].

The data reviewed in this part can, undoubtedly, be considered as independent evidence of the correctness of the α and β transition concept in question.

7. CONCLUDING REMARKS

The studies considered, obtained by different techniques of thermal analysis, allowed us to gain more insight into the molecular nature of basic (α, β, ll) transitions in flexible-chain polymers as a common phenomenon.

It is of importance for polymer physics that correlations between kinetic properties, molecular mobility in the condensed state of polymers and thermodynamic characteristics have been established. The main finding is the experimental evidence that the statistical (Kuhn) segment acquires, as a quasi-molecule, the status of motional unit. Its quasi-independent or cooperative (in an intermolecular way) rotational–translational motion controls mobility at all temperatures $T \geqslant T_\beta$ in flexible-chain polymers. The T–G transition takes part in the motional events under these conditions although the activation barriers of the transitions in question are basically determined by the potential barriers of intermolecular interactions.

For the first time, the common relations of α, β and ll transition parameters to Kuhn segment size S, cohesion energy E_{coh} and internal rotation barrier B have been found. They enable not only many experimental facts to be explained but successful prediction of the characteristics of the transitions in homopolymers (including the highly crystalline [38] and ion-containing polymers [82, 83]), the anomalies of the manifestation of T_g in multicomponent polymeric systems, and plasticization effects.

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