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Local intramolecular mobility in linear polyesters simulating the structure of thermotropic polymers

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Abstract

Local intramolecular mobility in regular linear polyesters with flexible siloxane and more rigid ester aromatic fragments providing in some cases LC state was studied by dielectric spectroscopy. The dielectric transitions related to the local mobility in the ester aromatic fragment were observed. It was shown that two local relaxation processes (β' and β'') with different mechanisms of mobility took place in these systems. One of them, the β'' process, having the shortest relaxation times ($\tau \sim 10^{-7}$ s) is connected with the motion of ester groups and phenyl rings. It is determined only by intramolecular interactions. The second local process, β', reflects the motion of the polar ester group including the central part of the ester aromatic fragment ($\tau \sim 10^{-1}$–10^{-4} s). This motion can be realized at the beginning of flipping of the aromatic ring. Parameters of the β' process depend on intra- and intermolecular interactions. © 1999 Elsevier Science Ltd. All rights reserved.

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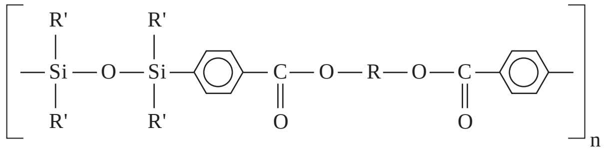
1. Introduction

Investigation of molecular mobility is a necessary step in considering ordering state problems in polymers [1, 2]. Of special interest is the investigation of local forms of molecular mobility which is probably the main source of information about the connection between the structure and mobility of different fragments of the polymer chain and the tendency to the ordering state formation. The investigation of kinetic properties of model heterogeneous polymers with different rigid parts is of significance because the regular alternation of rigid and flexible chains elements determines the existence of different types of intramolecular movement.

At present, polymers with rigid (rod or disc-like) fragments and flexible ones (spacers, joints) are well known [3, 4]. Such polymers are disposed to thermotropic mesophase formation.

In this work the molecular mobility of regular polyesters with flexible siloxane (Si–O–Si) and more rigid ester aromatic fragments providing in some cases LC state was studied by the dielectric method. Below, the chemical structure formula of these systems is given.



The structure of R and R$'$ fragments of investigated polymers are presented in Table 1. The synthesis, structure and some properties of these polymers are described in Ref. [5]. It may be seen that the siloxane fragment has methyl or ethyl groups at the Si-atom. The structure of ester aromatic fragments is also complicated by introducing the bulky or polar groups in its central part.

In contrast to siloxane containing LC polymers [2, 6], the systems investigated here have a shorter siloxane fragment and an ester aromatic fragment connected by a silarylene bond. The macrochain of these polymers consists of two polar parts: siloxane and ester aromatic. The variation of R and R$'$ enables us to establish the influence of different structural fragments on the molecular mobility and to analyze the mechanism of local motion in polymers of this structure.

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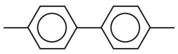
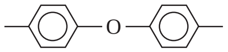
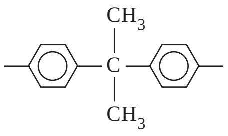
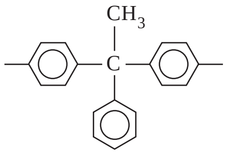
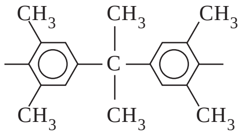
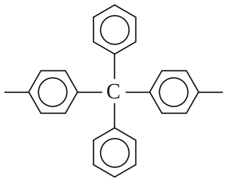
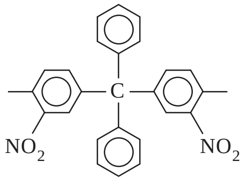
Table 1
The structure of R and R′ fragments

Polymer	R	R'
I		CH_3
II		CH_3
III		CH_3
III'		C_2H_5
IV		CH_3
V		CH_3
VI		CH_3
VI'		C_2H_5
VII		CH_3

2. Experimental

Dielectric measurements were carried out in the frequency range 10^2–10^7 Hz at a temperature of -150–$+250$°C. Relative precision was $\sim 2\%$ on tgδ. Films 30–50 μm thick and 20 mm in diameter were used as samples for measurements. The relaxation time and the activation energy were calculated from the Arrhenius equation: $\tau = \tau_0 \exp U/KT$, $\tau = 1/2\pi f_{\max}$, where $f_{\max}$ is the frequency of $tg\delta_{\max}$.

3. Results and discussion

Fig. 1 shows the temperature dependencies of tgδ for polymer III. Similar dependencies were obtained for all polymers in Table 1. It appears that over the investigated temperature region there are three dielectric transitions. One of them, above 100°C, is the α-process related to the segmental mobility because the glass transition temperatures of these polymers are about 100–140°C[5].

Below T_g there are two relaxation processes named β'' (at the lowest temperatures) and β' (at higher temperatures). For polymer III the β' process appears as an asymmetry of the tgδ(T) curves. For polymers V and VII, inverse ratio takes place: β' is more intensive, but β'' has a smaller height (Fig. 2 and Fig. 3).

To understand the mechanism of molecular mobility it is necessary to consider the influence of chemical structure of both chain fragments on the parameters of local processes β' and β''.

4. The influence of chain chemical structure on the parameters of the β'' process

Fig. 4 shows the reciprocal temperature dependencies of relaxation time of β' and β'' processes for polymers I–VII having the same siloxane fragments but different ester aromatic ones. These dependencies for β' (curves 1–4) and β'' (curve 5) are located in two different regions. In all cases, the Arrhenius relation was found to describe the results correctly. As can be seen from Fig. 4 the substitution of the linear joint of phenyl groups in R (polymers I and II) by the bulky groups (polymers III, IV and VI) has practically no influence on the relaxation times of β''. It indicates that the introduction of bulky groups in ester aromatic fragment has no influence on the mobility of kinetic units connected with the β'' process.

The influence of dipole–dipole interactions on the local mobility may be considered by comparing the results for polymers VI and VII—the latter has the strong polar group NO_2 in the ester aromatic fragment. Fig. 4 shows that introduction of the NO_2 group does not practically change the β'' process parameters. Thus, both the steric restriction and the changing of dipole–dipole interactions have no influence on the parameters of the lowest temperature β'' process.

Variation of the siloxane fragment leads to differences in relaxation properties, as can be seen from the temperature dependencies tgδ for polymers III, III′, VI and VI′ (Fig. 5) with different siloxane fragment R′ (CH_3 or C_2H_5). For these polymers the increasing of side substitution at the Si-atom influences the molecular mobility. As can be seen from Fig. 6, the relaxation time for the β'' process is increased if the CH_3 group in the siloxane fragment is substituted for C_2H_5 (curves 1, 1′). This fact may be explained by the participation of a silarylene bond loaded by the more massive C_2H_5 group in the movement connected with the β'' process.

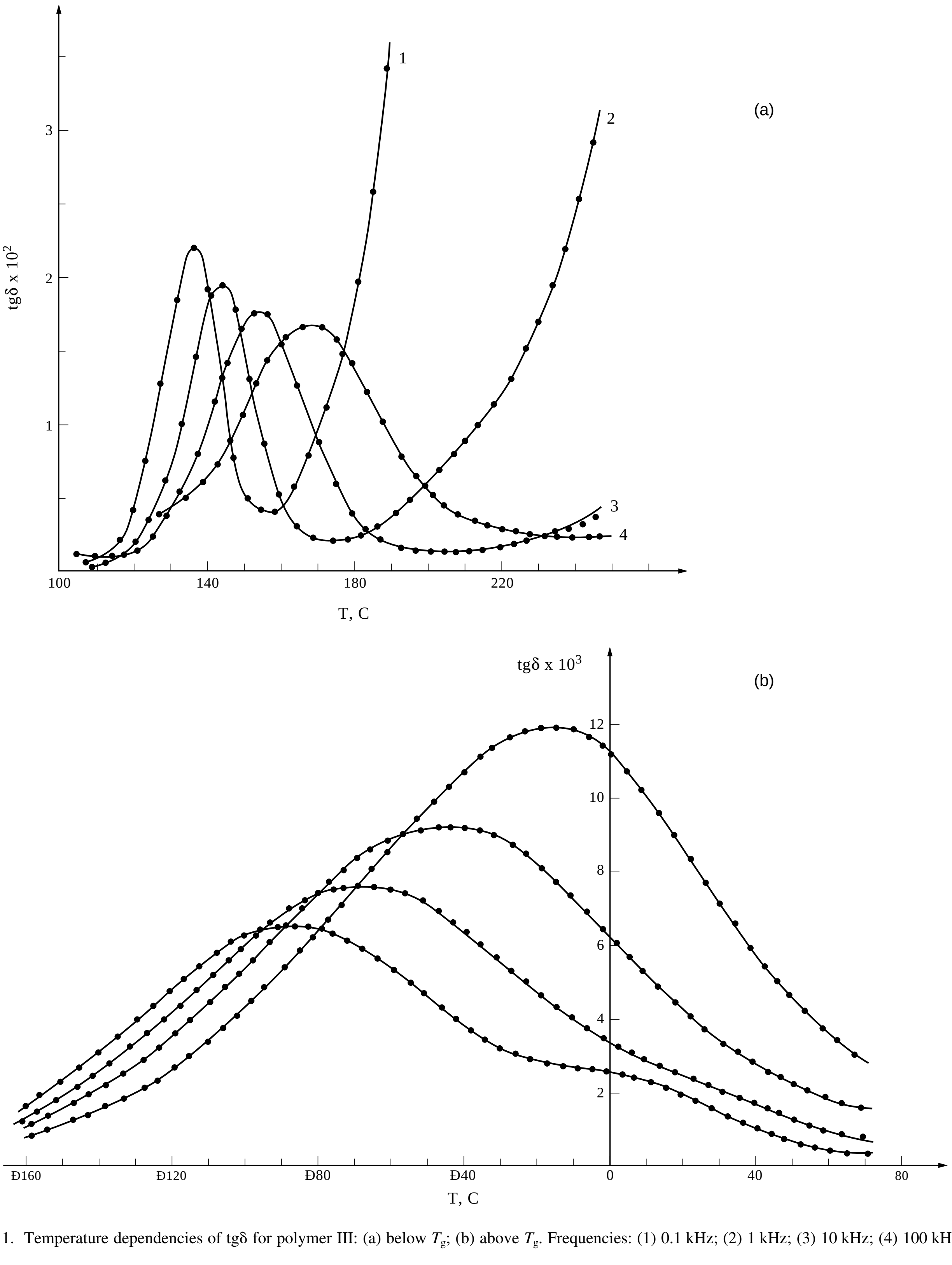


Fig. 1. Temperature dependencies of tgδ for polymer III: (a) below T_g; (b) above T_g. Frequencies: (1) 0.1 kHz; (2) 1 kHz; (3) 10 kHz; (4) 100 kHz.

5. Mechanism of the β'' process

Considering the relaxation phenomena at low temperatures it must be noted that a relaxation process with the same parameters ($\tau \sim 10^{-6}$–10^{-7} s at 20°C and activation energy about 8–12 kcal/mol) is observed for all linear polyesters with different spacers including alkyl and α-methylstyrene ones [6, 7] and for linear polyesters without spacers [8]. In

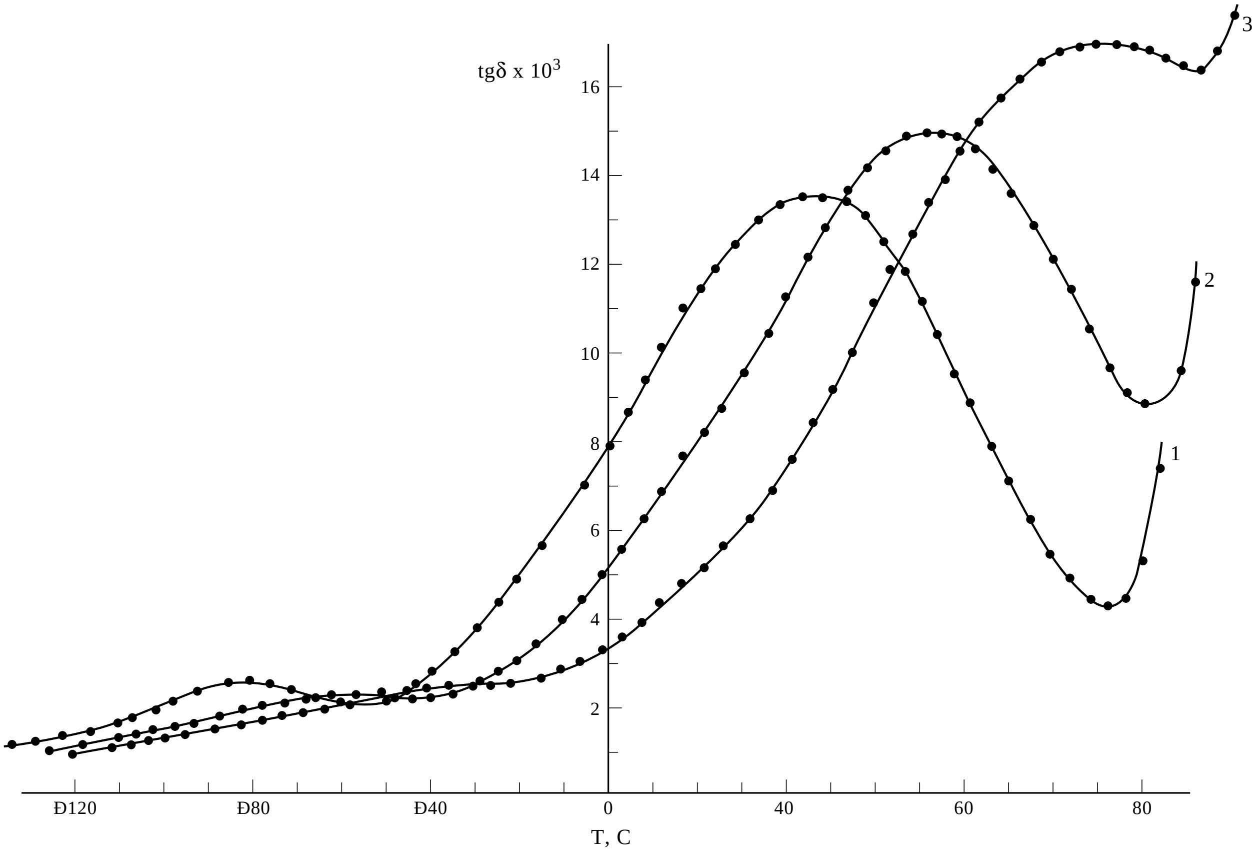


Fig. 2. Temperature dependencies of tgδ in the range of local dielectric transitions for polymer V: (1) 0.1 kHz; (2) 1 kHz; (3) 10 kHz.

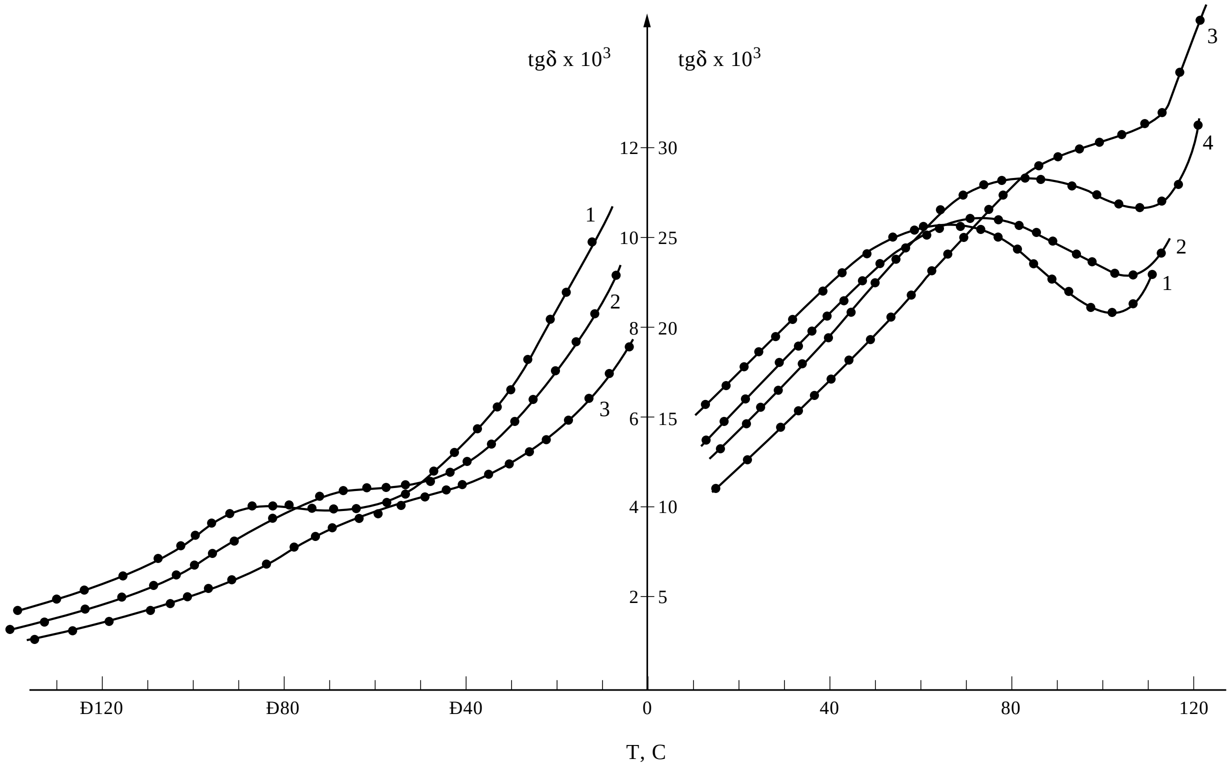


Fig. 3. Temperature dependencies of tgδ in the range of local dielectric transitions for polymer VII: (1) 0.03 kHz; (2) 0.1 kHz; (3) 1 kHz; (4) 0.3 kHz.

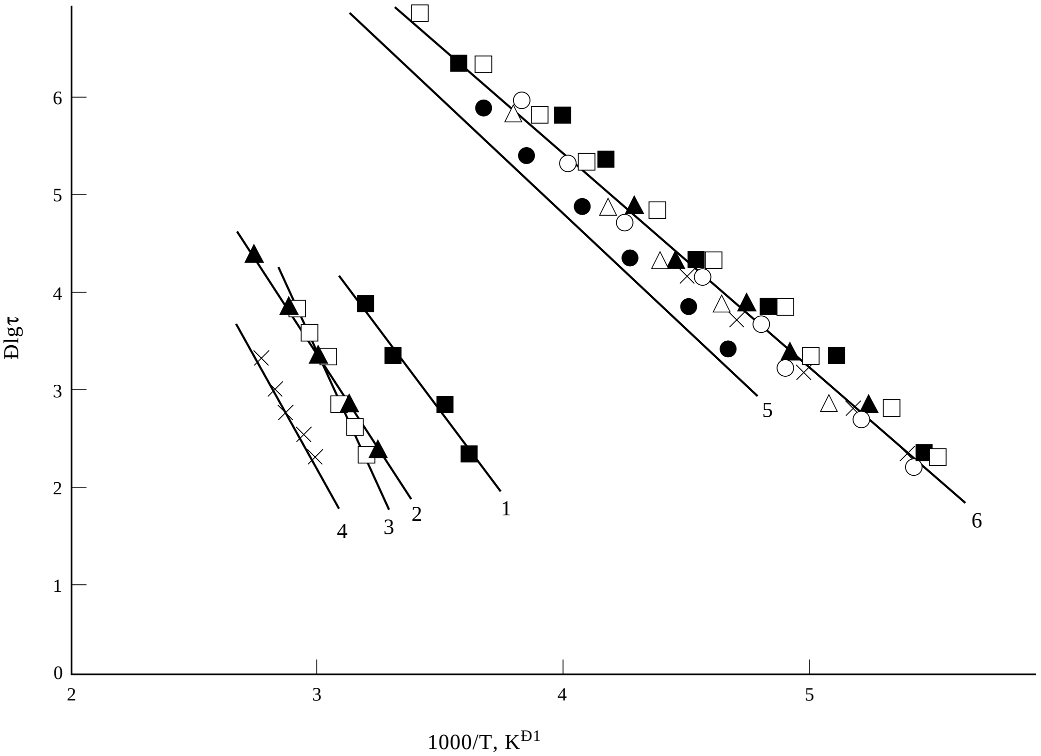


Fig. 4. Relaxation times vs reciprocal temperature for local dielectric transitions β′ (curves 1–4) and β″ (curve 5). Polymers: 1 (●), II (△), III (■), IV (0), V (▲), VI (□), VII (×) and curve 6-PDT [8].

this work polymer III contains the same ester aromatic fragment as polydiamonoterephtalate (PDT). The results for PDT, according to Ref. [8], are also given in Fig. 4 (curve 6). It can be seen that the low-temperature process for PDT has approximately the same activation parameters as the β″ process. Thus, it can be supposed that the β″ process is connected with the mobility of polar parts of the ester aromatic fragments. Fig. 4 demonstrates that the main pecu-

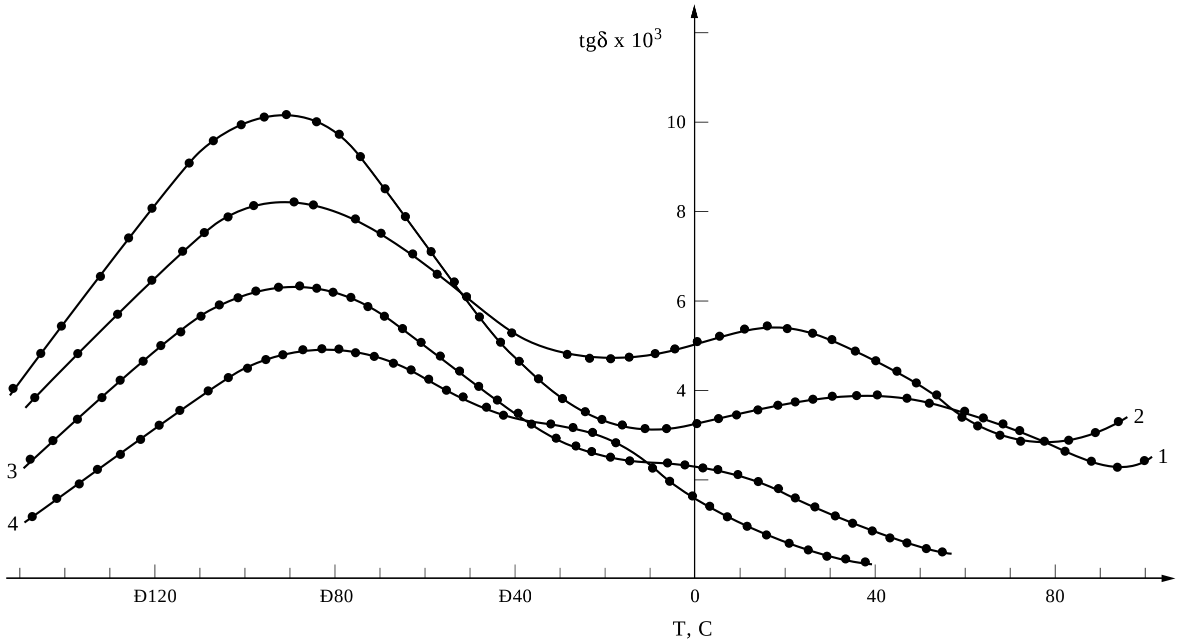


Fig. 5. Temperature dependencies of tgδ in the range of local dielectric transitions for polymers III, III′ (curves 1 and 2, frequency 30 Hz), VI and VI′ (curves 3 and 4, frequency 100 Hz).

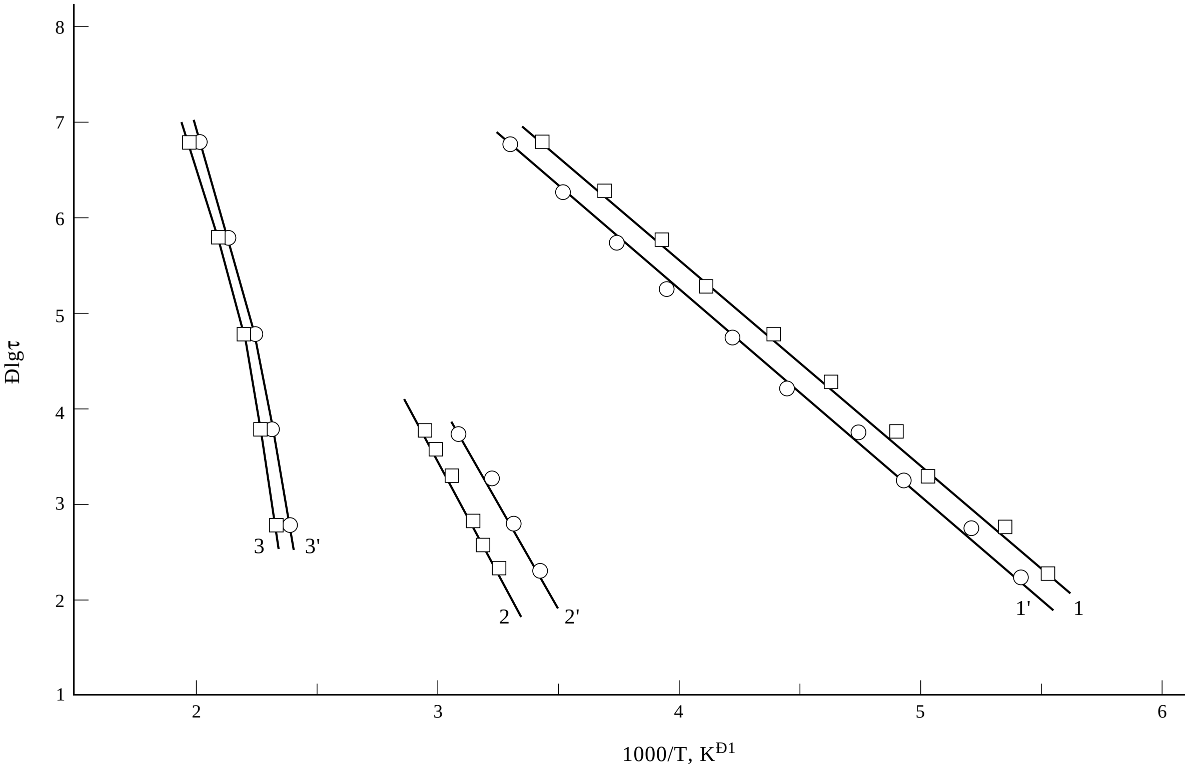


Fig. 6. Relaxation times vs reciprocal temperature for polymers VI (curves 1–3) and VI′ (curves 1′–3′). Curves: (1) 1′–β'', (2) 2′–β' and (3) 3′–α transitions.

liarity of the β'' process (curve 5) is a weak dependence of the relaxation times from any modification of the central part of the ester aromatic fragment. Small values of relaxation times and activation energies reflect the great localization of this process. It may be supposed that such a local process is connected with the mobility of COO groups conjugated with the phenyl ring. It is obvious that all linear polyesters, including LC polyesters with different spacers, must have the same low-temperature process as all these polymers have ester polar groups connected with phenyl rings [9–12]. Therefore, the β'' process reflects the mobility of kinetic units including the ester groups and phenyl rings. It is important to note that the relaxation times of the β'' process are very near to values observed in solution for these polymers and the difference of relaxation times is not more than one order of magnitude[12, 13]. This means that the local β'' process depends generally on intramolecular interactions.

6. The influence of chain chemical structure on the parameters of the β' process

Other peculiarities were observed for the second local β' process. In this case, any structural changes of the ester aromatic fragment providing a change of sterical or polar interactions influence β' parameters. Thus, Fig. 4 shows that the introduction of four CH_3 groups (polymer V) or NO_2 groups (polymer VII) or phenyl rings in the central fragment (polymer VI) leads to an increase in relaxation time for the β' process. The introduction of NO_2 groups changes both the polarity of central fragments and the sterical conditions. However, in contrast to the β'' process, the relaxation time of the β' process decreases if the CH_3 group in the siloxane fragment is replaced by the C_2H_5 one (6). It is well known that the lengthening of the side group acts as the inner plasticization leading to reductions in the glass transition temperature and intermolecular interactions. The temperature dependencies of the relaxation time of the α process show that τ is lower in polymer VI′ with the C_2H_5 group in the siloxane fragment (curve 3′) than in polymer VI with the CH_3 one (curve 3) and glass transition temperatures are 120°C and 130°C, correspondingly. Thus, the decrease in relaxation time in polymer VI′ is observed both for α and β' processes. It means that not only inter- but intramolecular interactions influence the parameters of the β' process.

It is important that the parameters for the β'' and β' processes are very different. Thus, the relaxation time at 20°C for β'' is $\sim 10^{-7}$ s, but for β' is 10^{-1}–10^{-4} s. The activation energy for β'' is about 10 kcal/mol and for β' 18–25 kcal/mol.

7. Mechanism of the β' process

Figs 2 and 3 show that the β' process intensity is sharply increased for polymers V and VII containing four CH_3 or two NO_2 groups in the aromatic ring. The bulky group introduction leads to the local loosening of polymer structure[14]. The structure loosening may promote the movement of larger kinetic units than in the case of the more localised β″ process. It is necessary to take into account that aromatic rings accomplish both the small amplitude oscillations at the lowest temperatures (β″ process) and the 180°-rotation transitions (π-flip) near room temperature [15–19]. In Henrichs et al. [15], for bisphenol A polycarbonate, whose structure is similar to the ester aromatic fragment of the polymers considered here, the connection of the π-flipping process with dielectric and mechanic relaxation has been analyzed. As the ring rotation on 180° is not dielectrically active, the authors suppose that there is a correlation of π-flipping with other processes connected with the dynamic mechanical relaxation phenomenon or the dielectric one. It follows from the above-mentioned work that local motions such as flipping processes depend on inter- and intramolecular interactions. Therefore, it may be proposed that the mechanism of β′ dielectric relaxation whose origin is the motion of polar groups, includes the correlated movement of phenyl-ester groups and central parts of ester aromatic fragment R (Table 1). Naturally, that intramolecular correlation is determined by the hindrance of internal rotation which depends on sterical restriction due to the presence of CH_3, NO_2 or phenyl rings in the central part of R. It may be supposed that the appearance of flipping provides the additive dipole orientation and leads to the appearance of the β′ dipole relaxation region. It provides a possible explanation for the β′ process mechanism. It is necessary to denote that the relaxation time of the β′ process is several orders higher than the relaxation time of other local processes for the same polymers in solution. For example, the relaxation time of polymer V for β′ process at 20°C in bulk and in solution is 2×10^{-2} s and 7×10^{-8} s, respectively [13]. This indicates the influence of intermolecular interaction on the parameters of the β′ process. The influence of intermolecular interactions on the β′ process may be explained by the necessity of local loosening of the structural lattice near the aromatic rings participating in the flipping.

8. Conclusions

Summarizing the results of this investigation, it may be affirmed that the linear polyesters with ester aromatic groups manifest in the glassy state as two local relaxation processes (β′, β″) having different motion mechanisms. For these polymers, low amplitude motion of the practically flat and rigid ester-phenyl group has been observed. The corresponding dipole relaxation process (β″) having the shortest relaxation times ($\tau \sim 10^{-7}$ s) is determined only by intramolecular interactions. The β′ process ($\tau \sim 10^{-1}$–10^{-4} s) reflects the motion of the same COO groups, but including the central part of the ester aromatic fragment. This motion is possible only at the beginning of aromatic ring flipping.

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