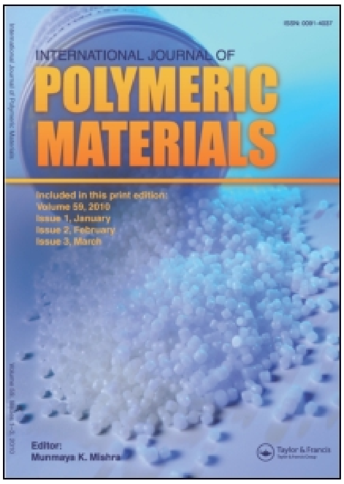

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Mechanical Relaxation in Solid-state Polymerized Poly(ethylene terephthalate)*

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The dynamic mechanical tensile properties, storage modulus E' and loss modulus E'', of the amorphous and semi-crystalline PET samples, ranging in molecular weight from 15,000 to 300,000 g/mol, were measured over temperature T range from $-150°C$ to $+250°C$ at four frequencies $\nu = 3.5$, 11, 35 and 110 Hz. The samples with molecular weight larger than 15,000 were produced by solid-state polymerization in high vacuum. An increase in the height of loss β-peak, at $T = -60 \cdots -30°C$, with an increase in molecular weight was found both in the amorphous and semi-crystalline PET. On the other hand, the height of loss β-peak for the amorphous samples appeared to be smaller in comparison with that for the semi-crystalline samples. By contrast, the height of loss α-peak, at $T = +90 \cdots +110°C$, for the amorphous samples was larger than for the semi-crystalline samples. An increase in the E' value with an increase in the molecular weight of the amorphous polymer was accompanied by an increase in the E'' value. This behavior was explained by the effective interpenetrated network of the high-molecular-weight polymer and better short-range ordering in the low-molecular-weight polymer. The intensity of the β-process was found to weaken with an increase in the chain ends concentration in both the amorphous and semi-crystalline samples. This result indicates that there is no contribution of the chain ends to the process of β-relaxation in PET.

Keywords: Poly(ethylene terephthalate); Molecular weight; Storage modulus; Loss modulus

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[*] On the occasion of the 60-th Birthday of Prof. S. Fakirov.

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INTRODUCTION

It is well known that an increase in molecular weight gives an opportunity to enhance the mechanical properties and thermostability of polymers. In the case of poly(ethylene terephthalate) (PET), the achievement of a high molecular weight of about 300 kg/mol is provided by solid-state [1] or swollen-state polymerization of the low-molecular-weight polymer [2]. For instance, an increase in molecular weight from 15 to 300 kg/mol led to a remarkable rise in the melting point T_m of solid-state polymerized PET, from 246 to 272°C [1]. Such an increase in the T_m value was explained by a large number of tie molecules between the neighboring lamella created by chemical reaction of the chain ends [3] (the contribution of the lamellae thickening to an increase of T_m is relatively small [3, 4]).

Chain ends, which are chemically active in PET, are located in the disordered interlamellar regions of a semi-crystalline polymer for the minimization of the free energy of the crystal [5]. For this reason, the molecular mobility in these regions becomes very important from the point of view of the "closure" of the chain ends with the release of an ethylene glycol molecule [6]. The evaluation of the potentials of solid-state polymerization of PET as a method to produce high-molecular-weight polymer was made in a previous paper [3] by studying its kinetics and morphology development. On the other hand, the information of the molecular mobility in the disordered regions is also important for this purpose. Besides, an investigation of the effect of molecular weight and of morphology of the disordered regions on the mechanical relaxation gives an opportunity of better understanding the molecular events, responsible for α- and β-relaxation in PET. For this goal, dynamic mechanical spectroscopic measurements have been followed for a number of amorphous and semi-crystalline PET samples, differing in molecular weight from 15 to 300 kg/mol.

EXPERIMENTAL

Samples

Two amorphous (viscosity-average molecular weight $M_\eta = 15$ and 76 kg/mol) and three semi-crystalline PET samples with crystallinity

$K = 0.28$ ($M_\eta = 15$ kg/mol), $K = 0.34$ ($M_\eta = 74$ kg/mol), and $K = 0.41$ ($M_\eta = 300$ kg/mol) were used in this study. The samples with molecular weight larger than 15 kg/mol were produced by solid-state polymerization in high vacuum (5×10^{-5} mm Hg) with a stepwise growth of the annealing temperature up to 245°C. At that temperature, the samples were annealed for up to 20 h. Those high-molecular-weight samples are hereafter abbreviated as HMW samples whereas the samples with a low molecular weight of 15 kg/mol are abbreviated as LMW samples. The amorphous samples were obtained by quenching the melt into ice-cold water.

Mechanical Measurements

Storage modulus E' and loss modulus E'' were measured on a Toyo Baldwin Rheovibron DDV-III-EP viscoelastometer over temperature range from -150 to $+250$°C at four frequencies $\nu = 3.5$, 11, 35 and 110 Hz and at a heating rate of 2°C/min. The vibration amplitude used and the distance between the clamps were 25 µm and 30 mm, respectively. More details about the samples preparation and dynamic mechanical measurements can be found elsewhere [3, 7, 8].

RESULTS

Figure 1 shows the values of storage modulus measured at a frequency of 3.5 Hz as a function of temperature. A sharper lessening in the E' value with a rise in temperature is observed for the amorphous samples (depicted as solid symbols) in comparison with that for the crystalline samples. In spite of the E' value for the amorphous sample with $M_\eta = 76$ kg/mol is the highest at $T < -100$°C, it becomes smaller than those for the crystalline samples at $T > -30$°C. The amorphous sample with $M_\eta = 15$ kg/mol has the lowest values of E' in the temperature range investigated. However, this sample demonstrates a plateau between -10 and $+70$°C where the E' value remains constant, in contrast to the other samples.

For the amorphous samples, a rubbery plateau is observed in the temperature range from 85 to 110°C and from 90 to 135°C for the LMW and HMW sample, respectively. The presence of the rubbery

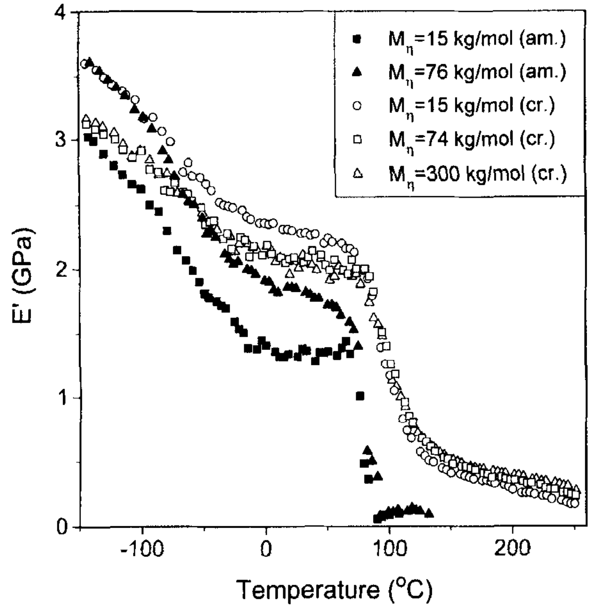

FIGURE 1 Storage modulus of PET as a function of temperature at a frequency of 3.5 Hz.

plateau in amorphous PET is sometimes explained by the onset of crystallization induced during the measurements at $T > T_\alpha$ [9, 10], where T_α is the α-transition temperature. Indeed, the validity of this assumption in Ref. [10] is in accordance with the recovery of the E' values at $T > T_\alpha$ almost to the E' values at $T < T_\alpha$. In addition, the sample shape was retained at least up to 180°C. All this is in disagreement with the data presented in Figure 1. Moreover, as follows from the shown in Figure 2 wide-angle X-ray diffraction photographs taken prior to and after the measurements of the HMW sample, the amorphous halo shape remained unchanged and no reflexes from the crystallites are observed in the photograph taken after the measurements (the same was found for the LMW sample). Therefore, the rubbery plateau in the amorphous samples in Figure 1 is not due to the onset of crystallization. The explanation of this observation will be proposed in the Discussion section.

In the crystalline samples, the E' value is larger for the sample with $M_\eta = 15$ kg/mol at $T < 80$°C, *i.e.*, below the glass or α-transition

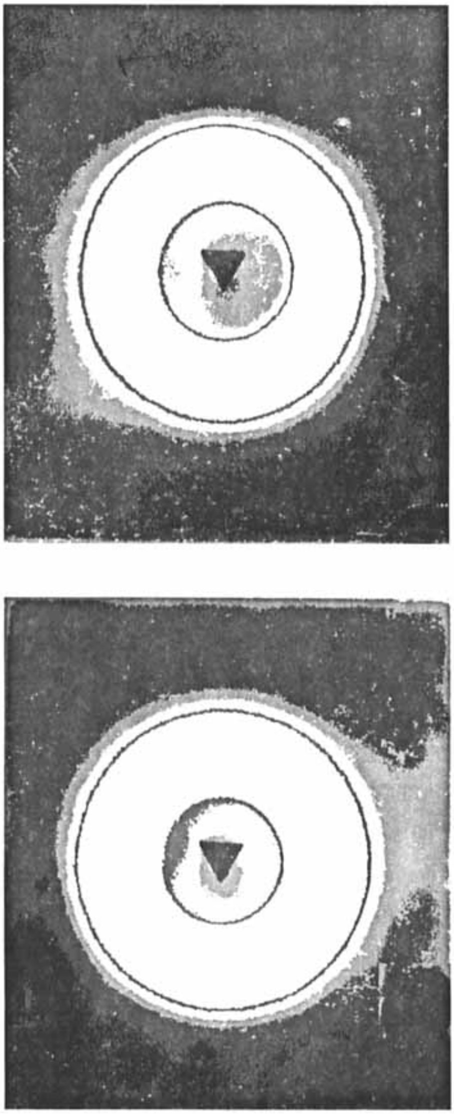

FIGURE 2 Wide-angle X-ray diffraction photographs for an amorphous PET with $M_\eta = 76\,\text{kg/mol}$. (a) prior to and (b) after the measurements up to 135°C.

[11, 12], whereas at $T > 150°\text{C}$ the value of E' increases with molecular weight. Below the glass transition temperature, the sample rigidity mainly depends on the rigidity of the disordered (amorphous)

interlamellar regions. Hence, the former observation may be explained by the larger fraction of the disordered regions $A = 1 - K$ in the LMW sample whereas the latter one correlates with the crystallinity growth and an increase in the number of tie molecules when molecular weight grows [3].

Figure 3 shows the values of loss modulus, measured at a frequency of 35 Hz, as a function of temperature. A distinct β-peak is observed at -50°C. Its position weakly depends on both crystallinity and molecular weight. The highest losses demonstrates the amorphous sample with $M_\eta = 76$ kg/mol. The peak is asymmetrical for all the samples investigated, in particular, for the two HMW semi-crysatlline samples (low-temperature shoulder), meaning that there is the contribution of several processes [7, 11]. In general, an increase in the E'' value with an increase in molecular weight is seen for both the amorphous and semi-crystalline samples. In the latter case, the value of E'' increases with crystallinity as well, *i.e.*, lessens with the fraction of disordered regions. This behavior is fairly unexpected since

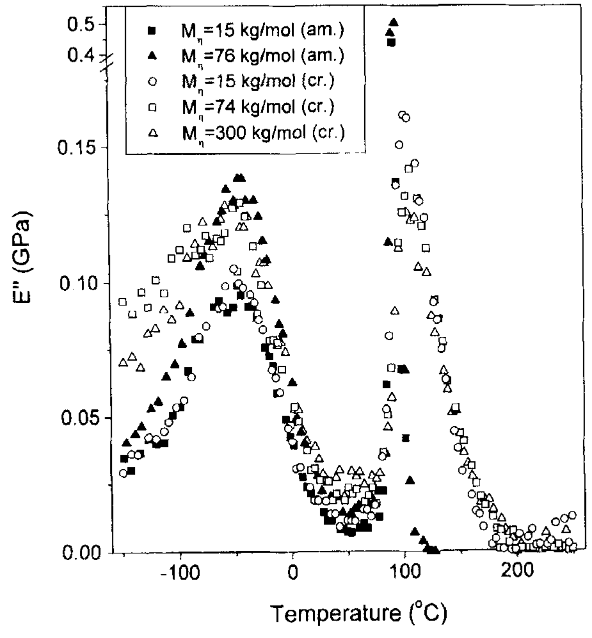

FIGURE 3 Loss modulus of PET as a function of temperature at a frequency of 35 Hz.

β-transition in PET is associated with segmental mobility in those regions, involving rotation of aliphatic groups [13].

In the α-relaxation region, the sharp peaks at 90°C are observed for the amorphous samples. For the crystalline samples, α-peaks have a higher temperature of 100°C; they are broader and have high-temperature shoulder. The mechanical losses in the amorphous samples are by a factor of 3 to 4 higher in comparison with those in the crystalline samples, in contrast to the β-relaxation region where the values of E'' for both the amorphous and crystalline samples fall into the same E'' range. The E'' values for the amorphous samples still grows with molecular weight. However, they become smaller for the crystalline samples with larger molecular weight and higher crystallinity. The latter is expected in the surrounding of the glass transition [11, 12]. Comparing the data in Figures 1 and 3 for the crystalline samples, it should be noticed that the sample with smaller E' value has larger E'' value, or *vice versa*, which is reasonable. By contrast, the amorphous (HMW) sample with larger E' value has larger E'' value as well. This observation will be discussed below.

Temperature dependencies of loss modulus at a frequency of 3.5 Hz are presented in Figure 4. It is seen that β-peak is less sharp than at a higher frequency of 35 Hz (Fig. 3). The values of E'' for the amorphous sample with $M_\eta = 76$ kg/mol are larger than those for the amorphous sample with $M_\eta = 15$ kg/mol by a factor of 2 and 4 in the β- and α-relaxation region, respectively. As far as the crystalline samples are concerned, the values of E'' for the HMW samples in the β-relaxation region are larger in comparison with those in the α-relaxation region.

Consider the intensity of the two relaxation processes. For this, the largest E'' values observed in the β- and α-relaxation regions (height of loss peaks) are plotted as a function of amorphous fraction A in Figures 5 and 6, respectively. It follows from Figure 5 that the heights of the loss β-peak of the HMW amorphous sample and of the HMW crystalline samples are almost the same at the each frequency investigated. In addition, the loss β-peaks of the HMW samples are, in general, higher in comparison with those of the LMW samples. For the two LMW samples, β-peaks have nearly the same height at higher frequencies. However, the β-peak for the crystalline sample is higher at $\nu \leq 11$ Hz, in particular, at $\nu = 3.5$ Hz. These observations mean that,

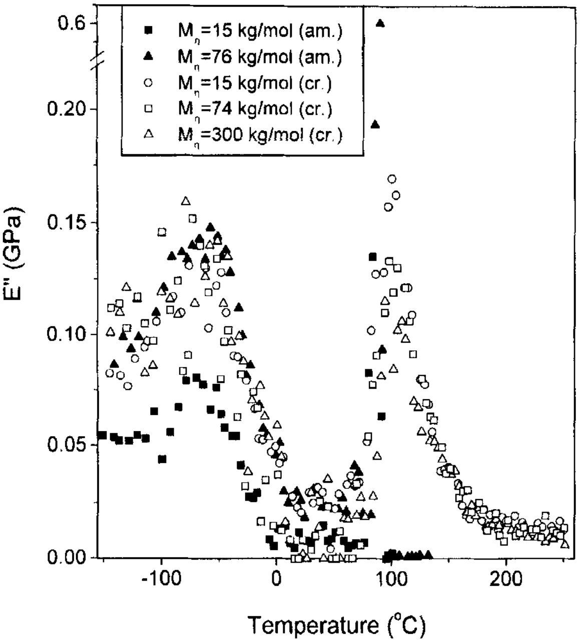

FIGURE 4 Loss modulus of PET as a function of temperature at a frequency of 3.5 Hz.

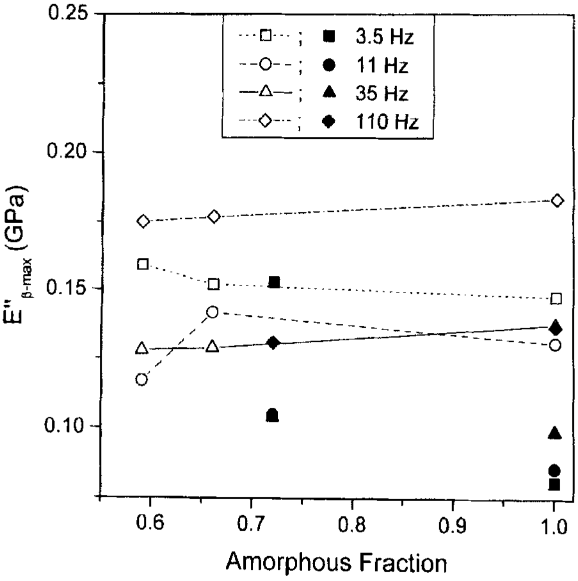

FIGURE 5 Height of loss β-peak of PET as a function of amorphous fraction. Solid and open symbols correspond to LMW and HMW samples, respectively.

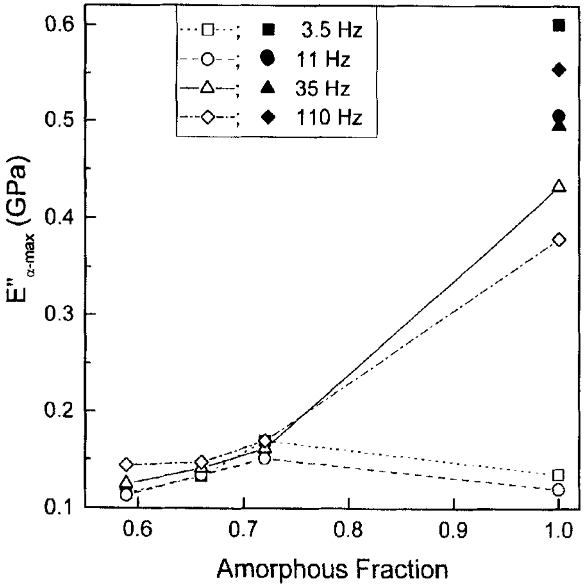

FIGURE 6 Height of loss α-peak of PET as a function of amorphous fraction. Solid symbols correspond to PET with $M_\eta = 76\,\text{kg/mol}$.

first, molecular mobility in the LMW PET is hampered and, second, the molecular chains in the disordered regions of the crystalline samples are more mobile than in the amorphous samples. In the α-relaxation region (Fig. 6), the height of the loss peak grows with an increase of amorphous fraction (with the exception of low frequencies for the LMW amorphous sample).

In order to follow the relaxation intensity as a function of molecular weight as well as to compare the energy dissipation per unit of volume of the amorphous fraction, the E'' values in Figures 5 and 6 were normalized by the amorphous fraction of the samples. These E''/A values are plotted in Figures 7 and 8 as a function of molecular weight for the β- and α-relaxation regions, respectively. The growth of the E''/A values with molecular weight is clearly seen for β-relaxation at the four frequencies investigated for both the crystalline (open symbols) and amorphous samples (solid symbols) (Fig. 7). Moreover, the energy losses per unit of volume are now demonstrated to be always higher in the crystalline samples. In the α-relaxation region (Fig. 8), the tendency of the growth of the E''/A values with an increase in molecular weight holds for the amorphous samples. By contrast, the

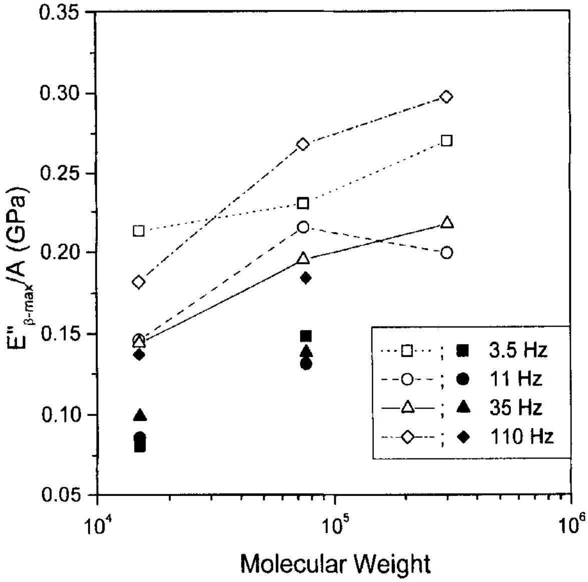

FIGURE 7 Height of loss β-peak of PET normalized by the amorphous fraction as a function of molecular weight. Solid and open symbols correspond to amorphous and crystalline samples, respectively.

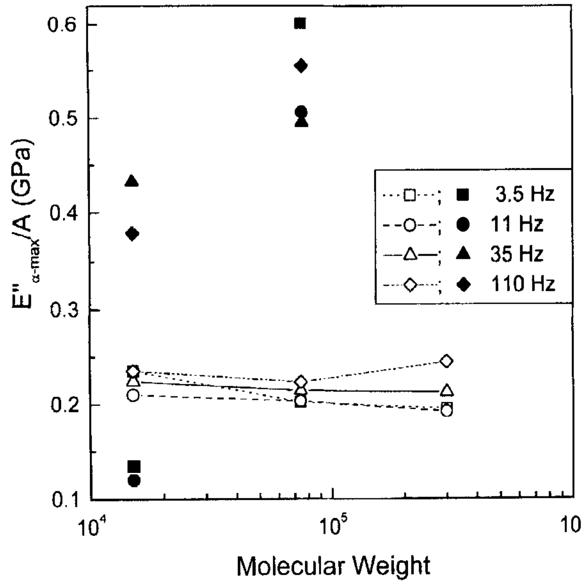

FIGURE 8 Height of loss α-peak of PET normalized by the amorphous fraction as a function of molecular weight. Solid and open symbols correspond to amorphous and crystalline samples, respectively.

normalized losses slightly decrease with molecular weight of the crystalline samples at the frequencies 3.5 and 11 Hz.

DISCUSSION

In an amorphous polymer, the radius of gyration of a molecular statistical coil R_g is related to molecular weight M as $R_g \sim M^{1/2}$ [14]. The ratio between the volume occupied by a molecule with $M = 76$ kg/mol and that of a molecule with $M = 15$ kg/mol, equal to $4/3\pi R_g^3$, is, hence, 11.4. Therefore, the expected entanglement density (the number of chains located in a unit of volume) in the HMW polymer is one order of magnitude larger since the densities of the two samples are roughly the same. Thus, the broad storage modulus rubbery plateau observed in Figure 1 for the HMW polymer may be explained by the presence of the effective interpenetrated network, which is resistant to higher temperatures than that of the LMW polymer. The more effective interpenetrated network in the amorphous HMW PET, on the other hand, might be also responsible for the higher mechanical losses observed for this polymer in Figures 3 and 4. Indeed, the neighboring segments in an amorphous polymer tend to locate in parallel with respect to each other inducing short-range order [15, 16]. In the case of PET, short-range order is mainly due to the coplanar coupling of benzene rings [17, 18]. The interpenetrated network of the HMW polymer serves as topological constraints for short-range ordering because of a large number of entanglements. By contrast, such ordering can proceed easier in the LMW polymer, first, due to the higher concentration of the mobile chain ends and, second, by the lesser entanglement density. Short-range order depletes molecular mobility and, hence, lessens the energy losses during cyclic deformation.

In part, the interpenetrated network of the HMW polymer also explains the fact that the E' values for the HMW polymer are by 20% larger in comparison with those for the LMW polymer (Fig. 1). In addition, the HMW polymer has the lower concentration of the chain ends, which are the defects in the network. Actually, assuming $M_\eta/M_n \approx 2$ [19–21], the degrees of polymerization $P_n = M_n/M_{ru}$, where M_{ru} is the repeat unit molecular weight of 192 g/mol, are 39 and 198 for the LMW and HMW polymer, respectively. The fractions of the chain ends monomers in the total number of the monomers per chain, equal to $2/P_n$, are, hence, 5% and 1% for the LMW and HMW polymer, respectively. This is in reasonable agreement with the contribution of this factor to the lesser E' values for the LMW polymer.

As was shown by nuclear magnetic resonance measurements [22], the rotational motion of aromatic rings in PET is possible only above T_α. For this reason, no changes in the (effective) short-range order of the LMW polymer may be expected to occur at $T < T_\alpha$. It might preserve the rigidity of a chain in a certain temperature range and be responsible for the storage modulus plateau observed between 0 and +70°C in the amorphous LMW polymer (Fig. 1).

The heightening of the intensity of β-relaxation with an increase in the molecular weight of the semi-crystalline samples (Figs. 5, 7) might be caused by the same reason as for the amorphous samples, *i.e.*, by more effective short-range order in the samples with lower molecular weight. In this case, the interlamellar tie molecules, created in the course of solid-state polymerization, play a role of topological constraints and hinder short-range ordering in the noncrystalline regions of the HMW samples. In addition, the defects are pushed out from the crystalline core of lamella during annealing (solid-state polymerization). The crystallite perfecting leads to the lengthening of the chain portions in the noncrystalline regions, thus, giving a rise in mechanical losses.

Comparing the $E''_{\beta\text{-max}}/A$ values for the amorphous and crystalline samples in Figure 7, one can conclude that the mobility of the relatively short segments in the amorphous samples is more hindered than in the noncrystalline regions of the crystalline samples. Therefore, the molecules of the amorphous PET are packed denser than the molecules in the disordered regions of the crystalline PET. However, higher values of T_α, smaller values of $E''_{\alpha-\max}/A$ and broader α-peak for the semi-crystalline samples in comparison with those for the amorphous samples indicate that the mobility of longer portions of chains, realized in the glass transition region, is more intensive in the amorphous polymer. It can be due to the location of a chain of a semi-crystalline polymer both in the rigid lamellae core and noncrystalline regions. For this reason, in contrast to the amorphous samples, the motion of the relatively long portions of the chains (loops, chain ends) in the interlamellar space of the crystalline PET is restricted (i) by small distance between the neighboring lamella of the order of 100 Å [4] ("structural restriction"), (ii) by the fact that one (for a chain end) or two ends of these portions (for loops) are firmly fixed inside the rigid lamellae core, and (iii) due to a large number of the extended tie molecules between neighboring lamella, in particular, in the HMW samples [3].

A small decrease in the $E''_{\alpha-\max}/A$ value with an increase in the molecular weight of the semi-crystalline samples can be detected at low frequencies (Fig. 8). This less intensive micro-Brownian mobility also agrees well with the growth of the number of intercrystalline tie molecules with molecular weight of PET [3].

An interesting observation of a drastic drop of mechanical losses by a factor of 3 with a decrease in frequency from 35 to 11 Hz was found for the LMW amorphous sample (Figs. 6 and 8). Moreover, the mechanical losses per unit of volume for this sample at the frequencies 3.5 and 11 Hz are smaller by a factor of 2 in comparison with those for the crystalline samples (Fig. 8). The phenomenon observed may indicate that the short-range order in the LMW amorphous sample can be partially recovered during the measurements at those frequencies, *i.e.*, for times ($=1/2\pi\nu$) of 0.014 s and longer.

In spite of the higher mobility in the aliphatic parts of the chains of the HMW crystalline samples (β-relaxation), the intensity of the translational segmental motion (α-relaxation) in the disordered regions of these samples weakens with molecular weight. The hindered translational segmental motion decreases the probability of the contact of chemically active chain ends and is a negative factor for the further growth of the molecular weight of PET.

Finally, our results did not reveal any contribution of the chain ends to the process of β-relaxation in both amorphous and semi-crystalline PET, as was suggested by Reddish [17] long ago. Moreover, the intensity of the β-process weakens with an increase in the chain ends concentration by a factor of 5 and over one order of magnitude in the case of the amorphous and semi-crystalline PET samples, respectively.

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