

Rupture of Macromolecules at Orientational Drawing of Crystalline Polymers

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The high-strength crystalline polymer samples can be obtained by polymer drawing at elevated temperature ^{1,2}. The draw ratio (λ) of polyethylene (PE), for example, and consequently strength linearly increases with increasing deformation temperature. In the case of polycapromide (PKA) the effective strengthening takes place at its drawing over 140°C ¹.

Strengthening is a result of molecular ordering in the amorphous regions of polymer ³.

On the other hand the fracture processes can also occur at drawing along with chains ordering. The mechanical fracture of the polymer can be considered according to of kinetic strength concept ³⁻⁵ as a process of destruction of stressed covalent chemical bonds by thermal fluctuations. The broken bonds are supposed to be the basis for the formation of submicrocracks and they begin the fracture processes ³. One can suppose that fracture processes are slowed at high temperature deformation and this enable to achieve greater value of draw ratio and hence to obtain the more strong samples.

The purpose of the present work was study of macromolecules rupture at oriental drawing of crystalline polymers at different temperatures in order to understand the molecular mechanism of deformation and orientational strengthen-

ing. Investigation was carried out using infra-red spectroscopy on the PE and PKA samples. The number of ruptured bonds was determined by the change in the intensity of characteristic absorption bands assigned to the different stable terminal groups. These groups are forming after chemical chains reaction which proceed follow bonds breakage. 3,6-8.

Results and Discussion

In Fig.1 the some infra-red absorption bands of the unoriented (a) and 8 fold drawn PE samples (b) are given. As it is seen from Fig. the absorption of bands connected with terminal groups increases after of sample elongation, i.e., the polymer drawing is accompanied by covalent bonds rupture. Fig.2 shows the change of a total number of terminal groups versus PE draw ratio for temperature 20 and 80°C and Fig.3 shows that (the C = O terminal groups concentration plotted in arbitrary units) for PKA at 20, 130 and 180°C. We can see from these Fig. that the bonds rupture begin takes place from a certain value of draw ratio and they are slowed remarkably with increasing of deformation temperature. Orientational drawing of PKA is accompanied at 180°C by far smaller number of bonds breakage than it at 20 or 130°C.

The described above results we explain as follows.

In the unoriented polymer the crystallites consist mainly of the folded chains. At polymer drawing these crystallites breakes and on their basis the oriented microfibrillar structure is forming^{9,10}. The initial crystalli-

ne blocks are reorganized by unfolding of polymer chains. This processes require the comparatively small efforts mainly to successive of the intermolecular bonds breakage. In this case the number chains rupture is negligible. After of microfibrillar structure formation further macromolecules orientation in the amorphous regions require either slip out of crystalline parts of the short chains or their rupture. Now the slip out of these chains will require the simultaneous breaking some intermolecular coupling. In last case the more considerable orientational loads will be required and the probability of stressed polymer chains rupture increases. The ordering processes lead to the rise of the coupling between the neighbouring straightend chains and the probability of macromolecules breakage increases further on. One can suppose that in order to a more oriented polymere to obtain, it is necessary, the coupling between moleculare chains to diminish and their mobility to rise. These phenomena take place probably in the case of high temperature drawing.

The splitting decrease of bands 720 and 730cm⁻¹ with increasing temperature about weakening of intermolecular bonds (of the van-der-Waals forces) in the polyethylene gives evidence^{11,12}. Macromolecules are coupled in the polykaproamide mainly by hydrogen bonds and the amid groups are the most rigid links in polyamid chains. The shift of band 3300cm⁻¹ connected with stretching vibration of NH groups¹³ to high frequents shows weakening of hydrogen bonds in the polykaproamide (see Fig.4). The rapid shift of this band over 190° due to the melting of

crystallite. One can judge about the appearance of chain mobility by the exponential broadening of bands connected with skelet vibrations of molecular chains ^{14,15}. Such band for PKA is band 930cm^{-1} attributed mainly to skelet vibrations of amid groups in the crystalline regions ¹⁶. Experimental data have shown that the exponential broadening of this band begins at about 135°C for oriented polymer. For reasons given one can say that thermal motions appear with temperature 135° , i.e., mobility of polysaid chains in crystalline parts of polykaproamide with this temperature begins.

Thus the chain mutual translational slip out is relieved by weaking of intermoleculare couplings (van der Waals forces for PE and hydrogen bonds moreover for PKA) with the rise of temperature. In the case of polykaproamide it is facilitated above 135°C in addition to by thermal motion of amid groups in crystalline regions. These phenomena sloved the fracture processes enable one to obtain high oriented and hence high-strength crystalline polymer samples by drawing at elevated temperature.

Reference

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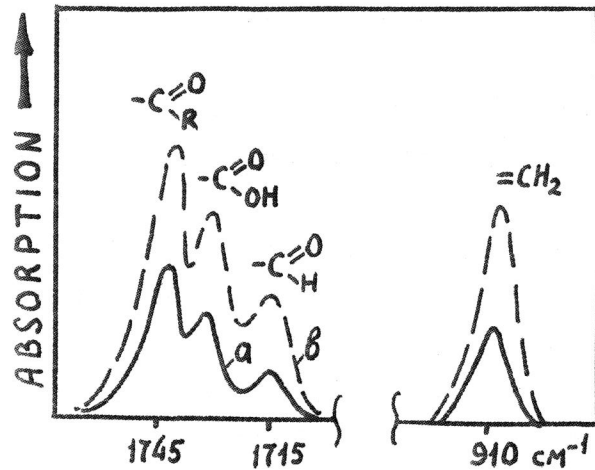


Fig.1 Infra-red absorption bands assigned to the different terminal groups; a-unoriented, b- 8 fold drawn polyethylen samples.

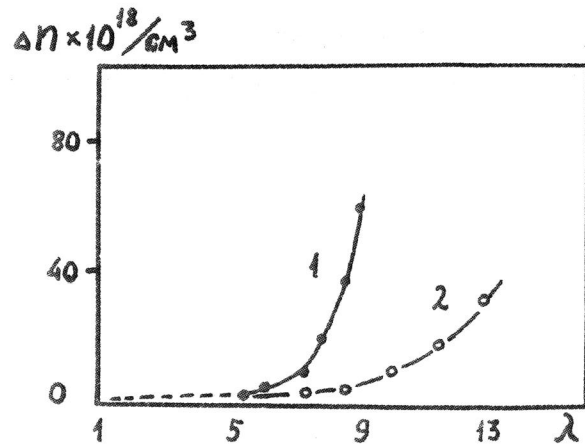


Fig.2 The change of a total number of terminal groups versus PE draw ratio for temperature: (1)- 20° and (2) - 80° C.

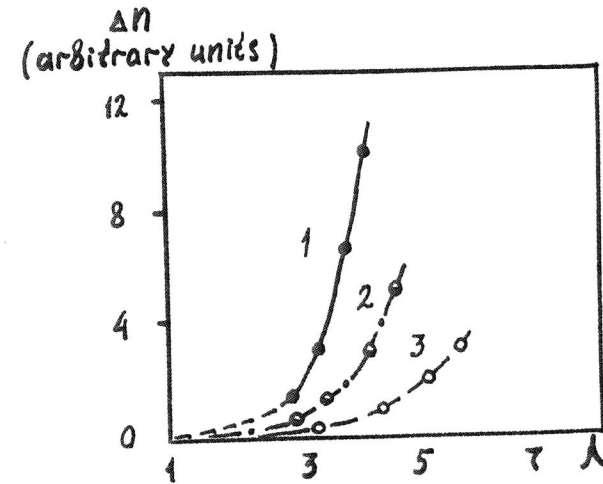


Fig.3 The change of a number terminal groups versus PKA draw ratio for temperature: (1)-20°, (2)- 130°, (3)- 180° C.

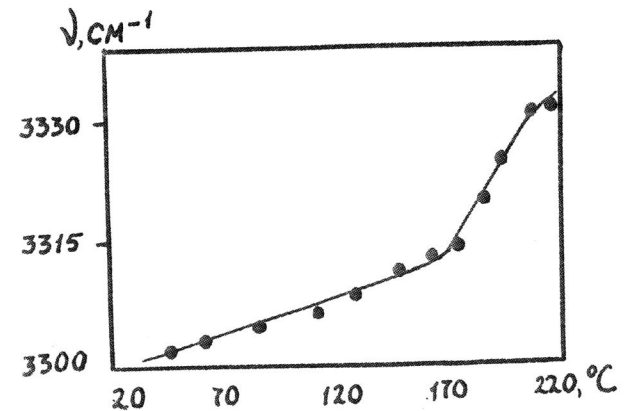


Fig.4 The shift of band $3300cm^{-1}$ connected with stretching vibration of NH groups in PKA with the increasing temperature.