

Mechano-Chemical Aspects of Fracture of Highly Oriented Semicrystalline Fibers

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It is well established that mechanical action on highly oriented polymers causes rupture of the most strained tie molecules in the amorphous regions of the material. The maximum number of radicals observed at sample failure is much larger than twice the number of tie molecules in the cross-section. The number also differs widely with the morphology of the specimen and from polymer to polymer. For these reasons the relation between individual chain scissions and macroscopic fracture initiations is not fully understood.

The small number of radicals obtained in polyamide-12 (PA-12), polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) fibers in comparison with PA-6 and PA-6,6 fibres has been explained by chain slip through the crystall lattice in the PA-12, PE, PP and PET group of polymers (1). This was deduced primarily from experiments where fibers irradiated with 1 MeV electrons were strained within the cavity of an ESR spectrometer. Recent numerical calculations of the tensile forces exerted by neighboring chains on a particular molecule in PA-6 and PE crystals have shown that these forces are indeed larger in the case of PA-6 (2). There is no influence of the long period of the crystalline regions in as much as the displacements of the particular chain atoms caused by maximum longitudinal chain tension at the boundary of a crystallite decrease below the level of the thermal vibrations within a distance of about 50 Å, which is much less than the corresponding long periods.

Another explanation of the differences in the number of radicals formed is the assumption that a radical chain reaction occurs in which each radical is responsible for the fracture of many macromolecules (3). This explanation was suggested by the appearance of more than one new end group per chain radical. A primary radical (formed by thermal activation after the energy of the C-C-bond is reduced by the action of the external force) is a very active chain-end radical which is assumed to react with a neighboring chain abstracting a hydrogen atom and thus forming a new stable end group and a chain radical. This is a likely explanation as the free chain ends have enough freedom to move. Now, it is argued (3) that the "mechanical strength" of a chain having a radical site is much lower than that of a normal chain ($\sim 1/3$), so that the radical chain is expected to break more readily under external forces thus propagating the reaction chain. Aside from the question whether the neighboring chain always is exposed to mechanical stress high enough to cause rupture, which will be discussed later, the basic assumption is open to discussion.

The backbone of a polyethylene macromolecule is formed by a planar zig-zag chain of C atoms. The eigenfunctions of the C-C bonds are so-called sp^3 -hybrides. Fig. 1a shows the sterical arrangement. If a C atom is converted into a radical by hydrogen abstraction, the bond eigenfunctions of this C-atom are now sp^2 -hybrides. The radical free electron is considered to be located in a completely separated π -eigenfunction which has no interaction with the σ -system. The geometry of this state is shown in Fig. 1b. The C atom under discussion may quite easily stay in this position and the distances to neighboring C atoms in the equilibrium state are more likely to expand rather than to contract the chain, thus favoring a little decrease in the mechanical tension. More important is the argument that (no other reactant regarded to be

Literature

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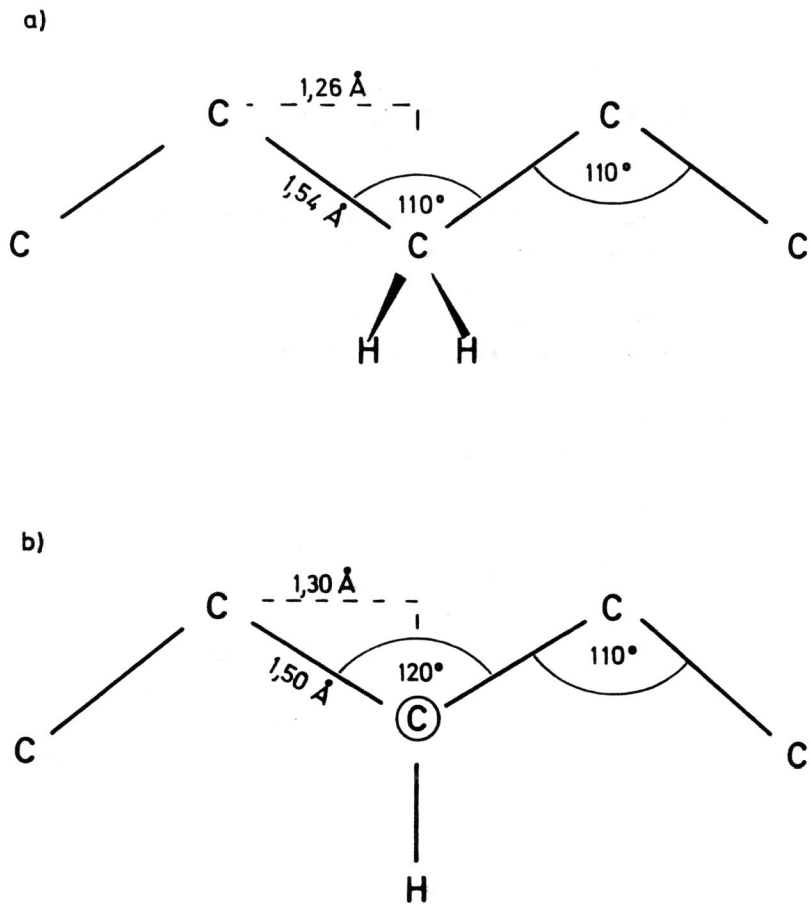


Fig.1: Conformation of a polyethylene-chain without (a) and with (b) a radical site