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Effect of Decoupling of Molecular Segments, Microscopic Stress-transfer, and Confinement of the Nanophases in Semicrystalline Polymers

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Semicrystalline polymers are globally metastable, multi-phase system with the possibility of locally reversible nanophases on the growth faces of its crystals. The crystals of macromolecules are of micrometer or nanometer dimensions, and the molecules, being usually longer than one micrometer, cross the boundaries and cause various degrees of coupling between the phases. Thermodynamically, the crystals can be characterized by their melting behavior, the noncrystalline part, by their glass transition. On weak coupling, the dynamics of the noncrystalline segments shows only a broadening of the glass transition range to higher temperature. This change is described by a decrease in activation energy and an increase of the preexponential factor, so that the beginning of the glass transition is little altered. On stronger coupling, a part or all of the noncrystalline material remains solid at the glass transition temperature of the bulk-amorphous phase, it forms a separate, rigid-amorphous phase, RAF. The RAF undergoes its glass transition at a higher temperature, either below, at, or even above the melting point. In the presence of RAF, the semicrystalline polymers are to be described as a system of at least three types of phases with the noncrystalline fraction possessing different relaxation effects due to the confinement between the crystals. On drawing of polymer films of fibers, the RAF can attain a certain degree of metastable orientation which only relaxes on melting of the crystals. This changed dynamics of the RAF can be studied by thermomechanical analysis as a shift of shrinking to higher temperature, by full-pattern X-ray diffraction (Rietvelt method) as a mesophase order, by thermal analysis as a residual, endothermic heat of disordering, and by solid-state NMR as an decreased molecular mobility of the partially ordered noncrystalline segments of the molecules. In copolymers with a lamellar superstructure, the crystal morphology, in turn, may be influenced by confinement between the glassy layers. Many of these aspects of the influence of the microscopic structure to the macroscopic properties have in the past been overlooked, but must be considered for modern, high-performance materials.