Nuclear magnetic resonance combined with extension of the specimens in the NMR spectrometer on the reversible deformation range has been used to study the cooperative modes of motion of the macromolecules in polymers, specifically poly(epsilon-caprolactam) and polyethylene terephthalate. For each of these polymers there are two temperatures near which the nature of the molecular motion changes sharply. At low temperatures there is a transition from independent hindered vibrations of the repeating units to correlated vibrations, as a result of which the chains in the amorphous regions acquire limited kinetic flexibility within the glassy state; at high temperatures there is a transition to segmental motion. The question of how changes in the modes of molecular motion are reflected in the macroscopic mechanical properties of polymers is examined.

For most linear polymers there are several temperatures near which the mechanical properties change sharply. One of these is the glass transition temperature \( T_g \). Below \( T_g \) polymers, as distinct from low-molecular glasses, may undergo considerable deformation without breaking. So-called "brittle fracture" occurs at temperatures lower than \( T_g \) [1]. The brittle point \( T_{br} \) is usually determined as the temperature below which the residual deformation of the specimens at fracture decreases sharply [2]. The temperature \( T_{br} \), like \( T_g \), cannot be established without a certain indeterminacy [3, 4]. Below the glass transition temperature a number of polymers have not one, but several characteristic temperatures, near which the deformability and strength properties change abruptly [5]. In these circumstances the physical meaning of the concept "brittleness" becomes indefinite. Sometimes the data of different authors relating to the characteristic temperatures are in conflict. Thus, according to [6] the glass transition temperature of Kapron is \(-65^\circ C\) and according to [7] \(+55^\circ C\). The arbitrariness can be eliminated and a strict physical meaning can be assigned to the characteristic temperatures if they can be related with certain microscopic processes taking place in the polymer. In [5, 8] it was shown that sharp changes in the deformability of polymers are correlated with changes in molecular mobility, but the molecular relaxation mechanisms responsible for these changes were not more precisely defined. It is now possible to inquire into the nature and scale of the relaxation processes controlling the various mechanical properties of polymers on different temperature intervals.

From the standpoint of polymer mechanics, we are primarily concerned with those coordinated (cooperative) modes of internal motion responsible for changes in the conformation of the elements of the macromolecules, i.e., for the kinetic flexibility of the chains. Motions of this type are specific for high-molecular compounds.

We have made an attempt to determine how the kinetic flexibility of the macromolecules of rigid polymers varies with temperature and how the changes in flexibility are reflected in the mechanical properties.
To observe the molecular mobility we employed the nuclear magnetic resonance (NMR) technique. This technique is sensitive to the rapid motions of nearest-neighbor nuclei (protons) [9]. In order to adapt NMR for observing the degree of coordination of the motion of the many units of a polymer chain, we employed mechanical inhibition of the molecular motion [10, 11]. In addition to varying the temperature, we also subjected the specimens to extension on the reversible deformation range directly in the NMR spectrometer. In analyzing the results we started out from the assumption [12] that when the macromolecules are stretched by an external load the molecular mobility is reduced if the motion is cooperative and the mobility of the individual elements depends on the relative position and motion of their neighbors. Stretching the chains reduces the set of possible conformations and hence the number of degrees of freedom. Reducing the conformation spectrum should not affect the uncoordinated vibrational motions of the units of the main chain. Thus, NMR combined with the extension of the specimens was used as a sort of "indicator of the cooperativeness" of molecular motion.

We selected for investigation the amorphous-crystalline polymers polycaprolactam (Kapron) and polyethylene terephthalate (PETP, Dacron). The macromolecules of these polymers have no side chains; they provide the means of observing the mobility of both fairly long (Kapron) and very short (Dacron) paraffin subchains. The specimens consisted of bundles of oriented fibers; it was technically more convenient to operate with oriented polymers. The specimens were stretched by an external load along the orientation axis, in a direction perpendicular to the magnetic field of the spectrometer, to various degrees of deformation short of fracture. In the case of measurements at elevated temperatures the specimens were deformed at the experimental temperature. In the case of experiments at lower temperatures the specimens were extended at room temperature and then cooled. The spectra were recorded in the form of the first derivative of the absorption line and in the original form by pulse modulation of the magnetic field [13]. The latter method gave a considerable increase in accuracy.

Kapron. It is possible to distinguish three temperature regions in which the temperature and deformation have qualitatively different effects on the NMR spectra.

1. At temperatures below -80°C the spectra are represented by a single line and are unaffected by deformation (Fig. 1a).

2. At temperatures from -80 to +70°C the spectra are likewise represented by a single line, but the spectra corresponding to the stretched state of the specimen are always broader than those corresponding to the starting specimen (Fig. 1b). The spectra broadened gradually as the deformation increased. The spectra obtained after unloading the specimen and allowing it to shorten to its original length coincided with the starting spectra.

3. At temperatures above +70°C the spectra consisted of two components - broad and sharp. The sharp component increased with increase in temperature [11], while stretching irreversibly reduced the amplitude of the sharp component (Fig. 1c).

These three regions are also detected on the temperature dependence of the mean square width of the spectrum (second moment, $\Delta H^2$) for the starting specimen and a specimen stretched at constant strain (I, II, and III in Fig. 2).

Dacron. Similar behavior was observed in the case of Dacron. Stretching affected the spectra only above -40°C. Above +110°C a sharp component appeared in the spectra. Its amplitude varied with deformation (Fig. 3) in qualitatively the same way as for Kapron.

In the temperature region -40-100°C changes more complex than in the case of Kapron, which could not be reduced to simple line broadening, developed in the spectra (see Fig. 3a). The starting spectrum of PETP is a superposition of two lines of equal area - associated with the protons of the aromatic rings and the protons of the methylene groups. The contribution of the former is a sharper line, located nearer to the center of the spectrum, since the magnetic interaction of the protons in the rings is weaker than in the