Using the NMR method the authors have investigated thermal molecular movement in polymers under the conditions of fatigue tests. They have found that the increase in molecular mobility under cyclic loading (cycle frequency 1-10 Hz) is due only to general self-heating of the polymer. Heating of the specimens as a result of hysteresis heat release takes place uniformly throughout the volume.

To investigate the mechanical properties of polymers under cyclic loading we must employ not only phenomenological, but also direct physical methods [1]. Knovov et al. [2] were among the first authors to follow this procedure.

We have investigated the variation of molecular mobility in polymers during fatigue tests. We used the nuclear magnetic resonance (NMR) method, which enables high-frequency vibrations of polymer groups to be monitored [3].

Self-heating of the material is regarded as one of the causes of reduced life during fatigue tests. The character of molecular movement enables one to assess the degree of uniformity of heating of a specimen. If throughout the polymer (not merely in the vicinity of fatigue cracks) we observe regions locally superheated in comparison with the overall temperature of the specimen, mobility of the macromolecules must be heightened in these regions. Nuclear magnetic resonance enables us to record this from the appearance in the spectrum center of an additional narrow component, absent when the polymer is uniformly heated. It is also known [4] that the various different changes in the mechanical characteristics of polymers, including the coefficient $\gamma$ of the durability equation (see [1]), may be due to a change in molecular mobility. This explains the interest in research on thermal molecular movement in polymers under cyclic tests.

The experiments were performed on highly oriented fibers (fishing lines) of Kapron and low-pressure polyethylene. Selection of these materials was dictated by the fact that they exhibit a marked dependence of the width of the NMR spectrum on temperature. The specimens were bundles of fibers uniformly laid and glued in clamps (see [5]), the overall cross section being 5 mm$^2$ and the length 75 mm. The fibers were washed to remove any lubricant and then dried in hot nitrogen. Furthermore, we tested a series of "moist" Kapron fibers which had been kept for about a month under atmospheric (room) conditions at an atmospheric humidity of 30-40%.

The specimens were placed in the measuring coil of an NMR spectrometer and subjected to cyclic elongation during recording of the spectrum at a frequency of 1, 5, or 10 Hz. The maximum stress amplitude ($\sigma_0$) was 30 kg/mm$^2$. Most of the measurements were performed at a given deformation amplitude ($\varepsilon_0$). Our scheme enabled the spectra of statically loaded specimens to be recorded in a wide temperature range. The specimens were heated up to the fatigue tests. Their "overall" temperature was measured by thermocouples (copper-constantan, wire diameter 0.05 mm) attached to individual fibers, both on the surface and within the bundle. The surface temperature was 8-12% lower than the temperature within the body of the specimens.

Fig. 1. NMR spectra of dried Kapron specimens: a) unloaded specimen, 20°C; b) in cyclic tests, 10 Hz, \( \varepsilon_0 = 6\% \), \( \sigma_0 = 20 \text{ kg/mm}^2 \), heating up to 135°C.

Fig. 2. Spectra of moist Kapron specimens: a) initial specimen, 20°C; b-e) 3, 12, 30, and 180 min, respectively, after beginning of cyclic tests, 10 Hz, \( \varepsilon_0 = 6\% \).

The principal experimental difficulty was the avoidance of noise due to vibrations of the coil and other components of the high-frequency channel of the spectrometer during cyclic tests. To reduce vibration, the specimen was placed in the center of the coil without coming into contact with its loops. Periodic loading was obtained by means of an electric motor via a reducing gear. All the load-carrying components of the elongating device rested on the stand of the spectrometer magnet and did not come into direct mechanical contact with the autodyne and other electronic units. Exact centering of the specimen in the measuring coil enabled us to eliminate virtually all additional noise in the fatigue tests. Control experiments revealed that the spectra were not distorted as a result of periodic displacement of the specimen in the coil during recording of the spectrum.

Figure 1 gives the results of experiments on dried Kapron specimens tested at 10 Hz at a constant deformation amplitude \( \varepsilon_0 = 6\% \) (\( \sigma_0 \) was about 20 \text{ kg/mm}^2); Fig. 1a shows the spectrum recorded at room temperature before loading began, and Fig. 1b shows the spectrum 3 min after the onset of fatigue tests. The form of the spectrum then remained constant during the tests. The overall temperature of the spectrum, recorded by thermocouples, increased sharply in the first few minutes (cf. [6]), and then remained constant at 135°C. Narrowing of the NMR spectra, indicating intensification of molecular movement, took place symbolically with the increase in the overall temperature of the specimen.

Figure 2 shows the spectra of moist Kapron specimens tested at 1 Hz (\( \varepsilon_0 = 6\% \), \( \sigma_0 = 19 \text{ kg/mm}^2 \)). In the initial state at room temperature the spectrum had a narrow component due to sorbed moisture (a). In the first few minutes of the fatigue tests this component increased sharply (b), but then fell slowly (c-e) approximately by an exponential law with time constant 45 min. The overall temperature of the specimen rose to 60°C.

To determine whether part of the molecular movements is due to cyclic loading, we must compare the spectra recorded in fatigue tests with those obtained under static conditions at the same overall specimen temperature. It is known [7] that molecular segmental movement is retarded and the narrow component decreases when a polymer is subjected to static elastic elongation. If the maximum deformation in cyclic tests is \( \varepsilon_0 \), the mean for the deformation cycle is \( \varepsilon_\sigma / 2 \). It is by specifically this value that the specimen must be extended under static conditions in order to correctly compare the molecular mobilities under static and cyclic tests. Figure 1b shows the spectrum (points) of a specimen heated in a thermostat to 135°C at a static elastic deformation of 3%. The coincidence of the spectra denotes that the molecular mobility in the polymer under cyclic and static loading is the same if the specimen temperature and the mean deformation are the same. Similar results were obtained for Kapron under other fatigue test conditions and for polyethylene. The spectrum of the cyclically loaded specimen did not display the additional narrow component. However, before we can definitely refute the possibility of existence of local superheatings in the polymer body in fatigue tests, we must take account of the potentialities of the NMR method. Let us assume that centers of local superheating exist within the body of the specimen and that the proportion of macromolecules confined in them is \( C \). Let \( T \) be the loading period, and \( \tau \) the time for which the temperature of the specimen superheated as a result of hysteresis heat release exceeds that of the surrounding material. The propor-