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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE EFFECT OF TENSILE STRESS ON MOLECULAR MOBILITY IN ORIENTED POLYMERS

The study of molecular mobility in polymers and of their structure is of undoubted interest for understanding the nature of the strength and deformability of high-molecular-weight materials.

It is known that the thermal motion of macromolecules in polymers causes narrowing of the absorption lines of nuclear magnetic resonance, NMR [1–3]. In the presence of intense segmental motion the NMR spectrum becomes very narrow—close to the spectrum of liquids. If a polymer is heterophase

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and the different phases are characterized by different mobility, then the spectrum may be a superposition of two or more [4] components differing in width. The areas of these components are proportional to the number of resonating nuclei in the corresponding phases. The spectra of crystallizing polymers in a certain temperature interval usually consist of two components: a broad and a narrow one. As follows from the investigations carried out to date, the first may be associated with the crystalline regions and the more densely packed part of the amorphous phase; the second, with the most "loose" amorphous regions and crystal defects. The NMR method makes it possible to study the influence of various external factors on the molecular mobility of polymers. Most of the work performed has been devoted to studying the effect of temperature on the motion of polymer chains and individual groups. Attempts have also been made to determine the dependence of the NMR spectrum on mechanical actions on polymers: it has been shown that both all-round compression (polyisobutylene [5]) and uniaxial stretching (rubber [6]) lead to broadening of the NMR lines.

Figure 2

Figure 2: Figure 2

In the present work, the NMR method was used to study the influence of mechanical stresses arising in a specimen when tensile stresses are applied to it ...

load, on molecular mobility in highly oriented fibers of polycaprolactam (capron) and polyethylene terephthalate (lavsan). The spectra of the materials studied, within a certain temperature interval, consist of two components: a broad one and a narrow one. This made it possible to trace separately the influence of load on the "rigid" and "mobile" regions. In this connection, the study of the dependence of NMR spectra on temperature was also of definite interest to us.

The measurements were carried out on a spectrometer with an autodyne detector made in the laboratory. The spectra (in the form of the first derivative) were recorded in a magnetic field of 7000 oersteds, with a modulation amplitude of 0.25-0.5 Oe. The specimen tested, in the form of a bundle of fibers with a total cross section of about 7 mm^2, was positioned so that the fibers were parallel to the axis of the spectrometer coil. The specimen was thermostated with an accuracy of up to 1° in the range 20-210°. A special device made it possible to apply a tensile force to the specimen directly during recording of the spectrum. Before measurement, the fibers were thoroughly washed free of impurities and dried.

Fig. 2. Temperature dependence of the intensity of the narrow component of the capron spectrum (referred to the total intensity of the NMR line)

Figure 1 shows the temperature changes in the spectra of unloaded capron fibers. At a temperature close to room temperature, the spectra, as can be seen, have no clearly expressed structure and consist of one broad line. With increasing temperature, beginning at 90-100°, the spectrum becomes more complex: together with the broad component there appears a very narrow one, which may be associated with the onset of intensive segmental motion. The ratio (D) of the area of the narrow component to the total area of the spectrum proved to increase practically linearly with increasing temperature (Fig. 2). In this case the spectrum remains composed of two components up to temperatures close to the melting temperature of capron crystals (215°). It should be noted that the general form of the temperature dependences of the line width and of the second moment for capron agrees with the data for other polyamides ([7,8]).

Next, the influence of tensile forces on the shape of the NMR spectrum was traced. During recording of the absorption line, the stress in the specimens was kept constant with an accuracy of $±$5%. The maximum loads in a number of experiments were close to the breaking loads and, consequently, the spectra recorded in these cases corresponded to the pre-rupture state of the polymer.

Fig. 3. Influence of tensile stress on NMR spectra of oriented capron fibers

Figure 3: Fig. 3. Influence of tensile stress on NMR spectra of oriented capron fibers

The spectra of capron fibers under various loads were recorded in the temperature range from 20 to 180°. In Fig. 3, by way of example, data are given for two temperatures: 130°, when a narrow component is present in the spectrum, and 27°, when the absorption line is devoid of structure. At the elevated temperature, the tensile load causes a considerable decrease in the intensity of the narrow component and a simultaneous increase in the intensity of the broad one (Fig. 3, *a*). This redistribution of intensities between the components is the stronger, the greater the tensile force.

At lower temperatures, the effect of mechanical load on the NMR spectra also occurs (Fig. 3*b*), although the effect is smaller in magnitude. From the change in the spectra with load it may be concluded that the tensile force creates additional obstacles to molecular motion in the polymer and, in this sense, stretching is equivalent to cooling of the specimen (cf. Figs. 1 and 3). The observed effect is reversible: after removal of the load the spectrum was practically restored. The small irreversible phenomena are undoubtedly connected with the residual deformation of the material.

Analogous results were obtained upon application of tensile

forces to lavsan fibers (Fig. 4), but in this case the measurements were carried out only at elevated temperatures, at which the spectrum consists of two components.

The experimental data described make it possible to draw some conclusions about the influence of mechanical loading on the mobility of chain macromolecules. The presence of two components in the absorption spectrum of the material indicates the heterogeneity of its structure. The monotonic increase of the narrow component at the expense of the broad one in the capron spectrum with increasing temperature indicates that the polymer may be regarded as a set of

Fig. 3. Influence of tensile stress (σ, kg/mm^2) on the NMR spectra of oriented capron fibers:
a –at 130°: 1 –$\sigma = 0$ (before loading); 2 –$\sigma = 5.9$; 3 –$\sigma = 16.8$; 4 –$\sigma = 36.0$; 5 –$\sigma = 0$ (after removal of the load);
b –at 27°: 1 –$\sigma = 0$; 2 –$\sigma = 28.8$; 3 –$\sigma = 57.6$

regions whose molecules possess different degrees of hindrance to motion. As follows from Fig. 2, in the least "fixed" regions segmental motion arises at 80-100°, whereas in the most "rigid"regions it is absent even at temperatures close to the melting temperature of capron. Thus, at 210° the regions not encompassed by intensive segmental motion amount to about 35%. It is possible that these

Fig. 4

Figure 4: Fig. 4

most "fixed" regions are the crystalline phase. This assumption is all the more probable because the value of 35% corresponds to the degree of crystallinity of capron fibers determined by other methods. It may be expected that intensive thermal motion of macromolecules first arises in the most "loose" regions and then, as the temperature rises, spreads to increasingly densely packed sections. These conclusions agree with data ([9]) on the presence in polyamides of an entire set of molecular structures with different degrees of ordering.

In studying the influence of mechanical loading on the NMR spectra of a polymer, the heterogeneity of its structure should be taken into account, since macromolecules belonging to regions with different degrees of ordering may respond differently to an external load. It is evident from Figs. 3 and 4 that the greatest changes under stretching were undergone by the spectral components corresponding to the most "mobile" sections of the macromolecules. At present we do not have a sufficient amount of data for a detailed discussion of the mechanisms of the action of stress on molecular mobility, but it may be assumed that one of the mechanisms, at least at elevated temperature, is the following. According to configurational statistics ([10], [11]), the segmental motion of a section of a polymeric

the chain can be regarded as the realization of various possible configurations of this segment, occurring with a certain frequency. (In our case, with a frequency sufficient for a significant narrowing of the NMR line.) Stretching leads to a decrease in the number of possible configurations, and from this the chain becomes more "rigid." Such a process is, naturally, reversible: if no bonds arise that hinder contraction of the chain, then after removal of the load the intensity of thermal motion is restored.

Taking this mechanism as an explanation of the mechanical effect observed by us in the NMR spectrum, one may assert that only a small fraction of the stress borne by the "rigid" molecules in a loaded specimen falls on those portions of the molecules that undergo intense segmental motion. In other words, the "mobile" chains make an insignificant contribution to the mechanical strength of the material. A polymer in whose NMR spectrum narrow and broad components are present may be conventionally regarded as a "structure" consisting of "rigid" (bearing the principal load) and "mobile" (unloaded) elements. The redistribution of the intensities of the narrow and broad components may be interpreted as a redistribution of stresses in such a "structure."

Fig. 4. Effect of tensile stress (σ, kg/mm^2) on the NMR spectra of oriented lavsan fibers at 162°: 1 $-\sigma = 0$ (before loading); 2 $-\sigma = 15.4$; 3 $-\sigma = 0$ (after unloading)

The fact that the narrow component in the spectrum of capron does not dis-

appear completely even under loads close to breaking loads (Fig. 3a, spectrum 4) indicates a nonuniform distribution of stress between the macromolecules of this polymer.

Of course, this explanation of the influence of load on the NMR spectrum is highly schematic. However, we hope that further application of the NMR method will make it possible to understand more deeply the cause of the deterioration of molecular mobility in polymers under load and to obtain data on the distribution of stresses between polymer chains.

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Note: Figure translations are in progress. See original paper for figures.