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## Abstract

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# THE INFLUENCE OF THE RIGIDITY OF POLYMER MACROMOLECULES ON TRANSITION TEMPERATURES AND THE MORPHOLOGY OF CRYSTALLINE STRUCTURES

*(Presented by Academician V. A. Kargin on 31 VII 1963)*

In light of modern ideas about the essential role of supramolecular formations in the formation of the properties of polymers and in the course of crystallization processes in them, it was of interest to return again to the study of these characteristics and processes for natural and synthetic polymers, which constitute an extensive class of high-molecular compounds.

Tri-substituted ethylcellulose* was used as the object, possessing the greatest molecular rigidity of all simple cellulose ethers. The asymmetry of the shape of the static coils of polymer molecules in dilute solutions is a criterion of their kinetic rigidity. According to optical studies of ethylcellulose solutions in ethyl acetate and bromoform, the asymmetry of the shape of its chains is 20 times greater than the asymmetry of a "normal"Gaussian coil (^1), which characterizes the rather high rigidity of the molecules of this polymer. At the same time, it is known that precisely rigid-chain polymers are most prone to the formation of highly ordered supramolecular structures, which determine the emergence of the specific properties of such polymers. Thus, for example, the study of certain complex cellulose ethers upon the introduction of small amounts of specially selected low-molecular substances revealed the manifestation of mobility of the supramolecular structures of such polymers. This led to a substantial lowering of the glass-transition point of the substance, although no segmental mobility of the polymer chains could occur in these cases (^2). Consequently, with such an expanded interpretation of the glass-transition temperature of rigid-chain polymers, there arises the need, as Bartenev (^3) rightly considers, to separate this transition point into the temperature of structural and mechanical glass transition. The first is determined by the onset of mobility of supramolecular structural formations, the second by the segmental mobility of the chains.

The emergence of supramolecular formations typical of rigid-chain polymers should apparently have a substantial effect on the morphology of crystalline structures. Using triethylcellulose as an example, it was of interest to study this influence. Triethylcellulose was subjected to thorough purification by repeated reprecipitation with water from dilute solutions in a mixture of glacial acetic acid and methanol (9 : 1), followed by drying in vacuum at 20°. The molecular weight of the product was 82,000. In completely substituted triethylcellulose the theoretical content of elements is: $C = 58.53\%$, $H = 8.34\%$. According to microanalysis, in the specimen studied the elemental content was as follows: $C = 58.40\%$, $H = 5.05\%$. The reduced hydrogen content apparently indicates the presence of peroxide groups in the specimen.

The results of thermomechanical tests of triethylcellulose are given in Fig. 1. The rate of temperature increase in these tests was 1° per min., the periodic load was 30 kg/cm$^2$, and the time of load action

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**Fig. 2.** X-ray diffraction patterns of triethylcellulose: **a** —initial amorphous; **b** —crystallized

**Fig. 3.** Electron-microscopic photographs of structural elements of triethylcellulose from solution in xylene: **a** —$c = 0.001$, **b** —$c = 0.015\%$. Shadowed with tungsten oxide.

10 sec. As can be seen from Fig. 1, in a twofold test of one and the same specimen (curve *1*—first test, curve *2*—repeated test), in the region of 90° there is a small but well reproducible maximum in deformability. A further increase in temperature does not essentially change the deformability of the specimens up to the temperature region 160–180°, in which the deformability increases sharply. Finally, a further increase in temperature in the course of thermomechanical tests leads to a certain decrease in the deformability of the specimen, with the appearance, consequently, of a second maximum, and to the subsequent transition of cellulose ether into a viscous-flow state with simultaneous chemical decomposition of the product.

An increase in deformability in the region of 90° is apparently associated with the appearance of mobility of secondary supramolecular structures. The appearance of some mobility of supramolecular formations enables them to carry out denser packing, as a result of which, upon a further increase in temperature, a slight but strictly reproducible hardening of the substance occurs. The foregoing is well confirmed by X-ray diffraction patterns taken from triethylcellulose at temperature points of 100 and 120°, i.e., above the glass-transition temperature of the structural elements but below the temperature at which segmental mobility arises. On the X-ray diffraction patterns the same two diffuse rings were found as for the initial triethylcellulose, differing, as the heating temperature was raised, by increased sharpness and reduced thickness. The absence of new additional rings on the X-ray diffraction patterns, which usually prove the

Fig. 1

Figure 1: Fig. 1

appearance of new planes of symmetry, indicates the absence of crystallization processes in the products. Upon reaching a temperature of 160-180°, which apparently is the region of glass transition of the chain molecules of triethylcellulose themselves, their segmental mobility is realized, providing the possibility of crystallization processes, recorded by a decrease in deformability and characterized by the appearance of new rings on the X-ray diffraction pattern of the product. Fig. 2 shows X-ray diffraction patterns of the initial and crystallized product. Raising the temperature to 200-210°, accompanied by thermal decomposition of the product, disrupts the order attained earlier. On the X-ray diffraction patterns of the ether heated in this temperature region, the sharp rings are observed to disappear; they become blurred, i.e., destruction of the crystalline structures occurs.

**Fig. 1.** Dependence of deformation on temperature for triethylcellulose. *1*—first test, *2*—repeated test

Crystallization, as is typical for rigid-chain polymers, proceeds extremely slowly and does not attain high degrees of structural transformations. Fig. 3 presents electron-microscopic photographs of structural elements of triethylcellulose arising upon evaporation of its solutions in xylene. At low weight concentrations of the product (0.001%) in the initial solution, the photographs show distinct rodlike formations with transverse dimensions of about 250 Å (Fig. 3*a*). Increasing the concentration (to 0.01-0.1%) leads to packing of these rodlike elements into bundle-like formations without changing the original form of the primary elements (Fig. 3*b*). The indicated bundle-like formations become nuclei of growing spherulites. The spherulites themselves, visible in the optical microscope (Fig. 4), were obtained by slow evaporation of triethylcellulose solutions in a mixture of acetic acid and methanol (9 : 1). From the presen-

···from the photograph obtained it follows that the spherulites of triethylcellulose belong to the radial morphological type (Fig. 4a), which is very clearly seen in Fig. 4b, where the initial stage of spherulite growth is recorded. As is known from works (4, 5), the appearance of radial and ring morphological types of spherulites is determined by the kinetic conditions of their growth. By regulating the rate of the process, it is possible to obtain one or another type of spherulitic structure. However, broad use of these possibilities in our experiments with triethylcellulose always led to the formation of spherulites of only one, radial type. It follows from this that for rigid-chain polymers, apparently, formation of the radial form of the spherulitic structure is preferred, and that the ring form of the structure is kinetically unlikely. This is well illustrated by the nature of the structural elements of triethylcellulose, which consist of rodlike formations whose packing into spherulitic structures is most convenient in the formation of spherulites of the radial type.

Fig. 4

Figure 2: Fig. 4

**Fig. 4.** Radial spherulites of triethylcellulose from a solution of an acetic acid –methanol mixture (9 : 1):
*a* –spherulites of the radial type, *b* –dendritic growth of a spherulite, polarized light

Thus, for rigid-chain crystallizing polymers the appearance of two glass-transition points is characteristic, and these are reproduced quite convincingly on one and the same thermomechanical curve. One of them determines the appearance of mobility of supramolecular rigid formations, the other the appearance of segmental mobility of chain molecules. After the maximum deformability is reached at these points, a certain decrease in deformability is observed with further increase in temperature. In the first case this is associated with densification of highly ordered supramolecular structural formations, without a phase transition; in the second case, crystallization of the polymer leads to stiffening of the material. During crystallization of such rigid-chain polymers, the packing of the structural elements of the polymer leads to the appearance of the radial form of spherulitic structures, while the crystallization process itself is kinetically very difficult for such polymers.

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