

RHEOLOGY AND ENERGY PROPERTIES OF SPONTANEOUS SIZE CHANGES OF ACETATE FIBERS IN DIMETHYLSULFOXIDE VAPOR

N.O. Gegel

SGU, department of polymers, Saratov, Russia

gegelno@yandex.ru

The paper considers the phenomenon of spontaneous change of the linear sizes (elongation–contraction) of diacetate and triacetate fibers in the vapor of dimethylsulfoxide (DMSO) as a specific solvent where cellulose acetates form a lyotropic liquid-crystal (LC) phase.

Swelling of acetate fibers in DMSO vapor was found to be accompanied by 50–70% changes of the linear size of an anisometric sample. This process proceeds most intensely at room temperature (T) and around it. Any increase in T reduces the maximum value of elongation, and the process becomes shorter. Kinetic reversibility is a peculiarity of the effect of spontaneous fiber elongation in DMSO vapor. Having achieved its maximum elongation value, the fiber sample starts reducing its size under the same conditions (i.e. in the same vapor medium). The reduction of the elongated sample proceeds with an approximately half rate in comparison with its elongation. However, the fiber does not resume its initial size and remains elongated (sagging) for ~3 months.

Using the strain–time curves recorded at applying a small external load σ to the fiber (Fig. 1), we found the dependences of the external stress σ_k developed in the elongating sample and the “negative” longitudinal viscosity λ of the system on the elongation value (Fig. 2). The work of self-deformation ΔA_D , calculated from the $\sigma_k=f(\gamma)$ curve, has appeared to be 0.3 mJ/cm^3 . Such a low value of specific heat is typical of isotropic-to-LC transitions and confirms once more that this spontaneous change of the linear sizes of a polymeric body is caused by orientational macrochain ordering and phase transition to an LC state rather than by crystallization.

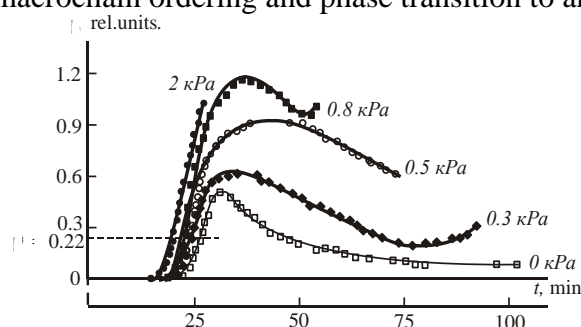


Figure 1. Kinetics of relative strain (elongation-contraction) of a diacetate fiber in DMSO vapor at 25°C for several σ .

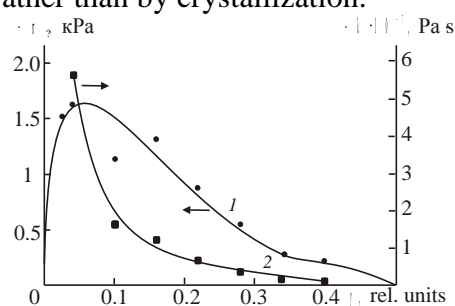


Figure 2. Internal stress σ_k (1) and longitudinal viscosity λ (2) as functions of the relative strain of an acetate fiber in DMSO vapor.

A mechanism of interactions of cellulosic esters with DMSO is proposed to explain the reverse (to self-elongation) process, namely, spontaneous contraction of an anisometric sample having elongated in vapor. The elongation-contraction phenomenon has been established to be due to specific interaction of the polymeric segments with the solvent, resulting, at a molecular level, in conformation transformations of the polymeric molecules and, at a supramolecular one, in the appearance of LC ordered chiral structures. The phenomenon of spontaneous elongation–contraction of acetate fibers in DMSO vapor is interpreted as a result of time- and space-distributed self-assembling of supramolecular structures in the process of their attaining an energetically favorable LC state and equilibrium conformations.