ON THE THEORY OF BIAXIAL ORIENTATION OF AMORPHOUS POLYMERS

G. M. Bartenev, A. A. Valishin, B. V. Perov, and E. S. Osikina

UDC 678.01:539.22

The macromolecule orientation distribution function for biaxial orientation is calculated on the basis of a network model of a linear amorphous polymer. The dependence of the distribution function on the biaxial stretch ratio, orientation temperature, and certain other factors is investigated. A relation is established between the distribution function and the experimentally observed birefringence. The birefringence of biaxially oriented polymethyl methacrylate is measured in relation to the degree of deformation. The experimental data are compared with theory.

One of the principal methods of improving the mechanical properties of polymers is to orient them, usually by stretching in the high-elastic state. In the high-elastic state polymers are capable of large reversible deformations associated with the rotation of the macromolecules and changes in their conformations. Deformation is also accompanied by the destruction of the starting supermolecular structure and the formation of a new one typical of the oriented state. As a result of stretching the macromolecules are oriented in the direction of action of the external load, which leads to considerable anisotropy of the polymer properties. The orientation obtained by stretching is fixed by cooling the polymer to temperatures below the glass transition point [1, 2].

Exhaustive information on the orientation of the macromolecules is given by the distribution function. It is necessary to know the distribution function in order to calculate a variety of orientation-dependent physical effects: elasticity, strength, birefringence, infrared dichroism, scattering of light, x-ray diffraction, propagation of sound, etc. We shall derive the macromolecular orientation distribution function for an amorphous polymer in biaxial tension. Our derivation is based on the results of [3], where the distribution function for uniaxial tension was obtained. Having derived the distribution function, we shall use it to calculate the birefringence in biaxial tension.

MODEL OF AMORPHOUS POLYMER

Linear amorphous polymers are quite generally regarded as network polymers, in which the molecular network is formed by strong local intermolecular bonds as well as by entanglements at individual points. This view of the structure of linear amorphous polymers is held by many scientists within the Soviet Union and abroad [4, 5]. For example, according to Shishkin and Milagin [6], in polymethyl methacrylate the molecular network is formed by strong intermolecular bonds between COOCH₃ radicals.

In what follows we employ the same network model as in [3]. This model is based on the following assumptions:

a) each chain of the network, i.e., each portion of a polymer molecule bounded by two successive network points, consists of N freely articulated statistical segments;
b) the distance \( r_0 \) between chain ends in the unstretched state is equal to the mean square distance for the free chain, i.e.,

\[
\begin{align*}
\frac{r_0}{N_0} = & I,
\end{align*}
\]

where \( I \) is the length of the statistical segment;

c) under deformation the vectors between chain ends (network vectors) experience an affine transformation;

d) deformation does not affect the volume of the polymer.

**DERIVATION OF THE SEGMENT ORIENTATION DISTRIBUTION FUNCTION**

The commonest types of orientation are uniaxial and biaxial. In uniaxial tension the statistical segments of the macromolecules are predominantly oriented in the direction of action of the tensile load. Biaxial orientation stretches the polymer in two mutually perpendicular directions. In this case the segments tend to be oriented parallel to the stretching plane. The principal stretch ratios in uniaxial and biaxial orientation are respectively equal to \[ \lambda_1 = \lambda; \quad \lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}}; \quad \lambda_4 = \lambda_5 = \lambda; \quad \lambda_6 = \frac{1}{\lambda^2}. \] (2a, b)

We characterize the orientation of an individual statistical segment in biaxial tension by the angle \( \chi \) (or \( \xi = \cos \chi \)) between the segment and the normal to the stretching plane. In ideal biaxial orientation all the segments are arranged parallel to the stretching plane, so that \( \chi = \pi/2 \) (or \( \xi = 0 \)). The direction in space of an arbitrary network vector \( \mathbf{r} \) is determined by the angle \( \theta \) between the normal to the stretching plane and the vector \( \mathbf{r} \). The orientation of a statistical segment belonging to some network chain relative to the network vector of that chain is determined by the polar angles \( \varphi \) and \( \psi \) (for the determination of these angles see [3]). It required to find the distribution function of the angle \( \chi \) (or \( \xi = \cos \chi \)). We denote it by \( w(\xi) \).

In what follows we shall need the network-vector orientation distribution function \( g(\theta; \lambda) \) and the distribution function of the orientation of the segments of a single chain relative to the network vector \( \mathbf{r} \) of that chain at a fixed value of the chain length \( r \): \( f(\xi, \varphi) \). The former is easily derived from the affine deformation condition:

\[
g(\cos \theta; \lambda) = \frac{1}{2} \frac{\lambda^3}{1 + (\lambda^2 - 1) \cos^2 \theta}. \tag{3}
\]

This function has a maximum at \( \cos \theta = 0 \), the height of the maximum increasing with increase in stretch ratio. The latter function was derived in [8].

\[
f(\xi, \varphi) = \frac{1}{4 \pi} \frac{\beta}{\sinh \beta} e^{\beta \xi}. \tag{4}
\]

Here, \( \xi = \cos \psi; \quad \beta = L^{-1} \left( \frac{r}{N_0} \right); \quad L^{-1} \) is the inverse of the Langevin function.

We will consider the joint distribution function \( \rho(\xi, \theta, \xi, \varphi) \) of the parameters \( \xi, \theta, \xi, \varphi \). The required function \( w(\xi) \) is obtained from this function by integration with respect to \( \theta, \xi, \) and \( \varphi \). Twice applying the probability multiplication theorem, we represent the function \( \rho(\xi, \theta, \xi, \varphi) \) in the form

\[
\rho(\xi, \theta, \xi, \varphi) = \rho(\theta, \xi, \varphi) \rho(\xi|\theta, \xi, \varphi) = \rho(\xi|\theta) \rho(\xi, \varphi|\theta) \rho(\xi|\theta, \xi, \varphi). \tag{5}
\]

The distribution function of the parameter \( \theta \) is nothing other than the distribution function of the network-vector orientations \( g(\theta; \lambda) \) (3). The conditional distribution function of the parameters \( \xi \) and \( \varphi \) for fixed \( \theta = \rho(\xi, \varphi|\theta) - \) is the Kuhn–Gr"{u}n function \( f(\xi, \varphi) \) (4). The parameters \( \xi, \theta, \xi \) and \( \varphi \) are not independent, but related by the expression

\[
\xi = \cos \psi \cos \theta + \sin \psi \sin \theta \cos \varphi. \tag{6}
\]

Accordingly,

\[
\rho(\xi|\theta, \xi, \varphi) = \delta[\xi - \xi(\theta, \xi, \varphi)]. \tag{7}
\]

Thus, integrating (5), we obtain the required distribution function

\[
w(\xi) = \int_{0}^{\pi} \int_{-1}^{1} \int_{0}^{2\pi} g(\theta; \lambda) f(\xi, \varphi) \delta[\xi - \xi(\theta, \xi, \varphi)] d\xi d\varphi d\theta. \tag{8}
\]