In the entire field of liquid-crystal polymers, an important place has been assigned to the analysis of the molecular structure of polymers capable of exhibiting lyotropic or thermotropic mesomorphism. The study of the conformation of the macromolecules, the features of their structure determined by the structure of the monomeric unit and the molecular weight, and the degree of flexibility of the polymer molecule showed that the nature of polymeric mesomorphism is determined on the molecular level [1, 2].

The first theories of the liquid-crystalline state of polymers [3, 4] were based on the concept that the equilibrium rigidity of the macromolecule was the determining factor. Notions concerning absolutely rigid rod-shaped macromolecules were the most common. Subsequent studies showed the difference of these views from the experimental data on phase transitions and the phase diagrams of liquid-crystal polymers [1]. The concepts of “flexible” and “ semiflexible” chains subsequently began to be widely used in studying liquid-crystalline order in polymers, but with no quantitative experimental determination of the flexibility of the polymer molecule in many cases [2]. The characteristics of the macromolecule important in elaborating concepts of polymeric mesomorphism which are a function of the structure of the monomeric unit of the molecule—its equilibrium and kinetic rigidity—are quantitatively determined in studying the hydrodynamic, optical, and electrooptical properties of polymer molecules on the molecular level [1, 5].

3.1. CONFORMATIONAL CHARACTERISTICS OF THE MACROMOLECULES

The number of polymers which form structures intermediate between a three-dimensionally ordered crystalline phase and a disordered isotropic phase is
now large and their chemical structure is very different. Lyotropic liquid-crystal polymers, i.e., polymers which undergo a phase transition with a change in the concentration in solutions, were studied in sufficient detail before the others. It should be noted that the conformational parameters of some of these polymers, for example, poly-γ-benzyl glutamate, polyalkyl isocyanates, and p-aromatic polyamides [1, 5], were studied even before their mesomorphism had been discovered and investigated [6, 7]. These studies were later stimulated by the great practical significance of solutions of lyotropic liquid-crystal polymers from which ultrahigh-strength, high-modulus polyamide fibers were prepared [1, 8].

The study of the molecular organization of lyotropic and some thermotropic comb-shaped polymers was of primary importance in understanding the mechanism of formation of intramolecular orientational order [9]; these concepts subsequently served as the basis for notions on ordering of liquid-crystal polymers on the molecular level.

Thermotropic liquid-crystal polymers with mesogenic groups in the main chain only began to be intensely studied in recent years due to their limited solubility and relative infusibility.

The presence of orientational long-range order which results in the appearance of macroscopic anisotropy of the substance with respect to a number of physical properties—optical, hydrodynamic, electrical, and magnetic—in a low-molecular-weight liquid crystal is the determining feature of the liquid-crystalline state of a substance. Ordering of the structure of the molecule of a linear polymer is confirmed by the rigidity of the intramolecular valence bonds and the constancy of the valence angles between them. This should also have caused mutual ordering in the arrangement of both the neighboring molecules and the elements of the macromolecule in the amorphous state. However, due to the flexibility of the chain, the correlation in the mutual orientations of the successive units rapidly decreases in moving from one to the next along the chain.

The length of the Kuhn segment $A$ in Gaussian chain theory [10] or persistence length $a = A/2$ in the persistence chain theory can be a measure of the distance at which this correlation persists and a significant characteristic of the molecular conformation. In modern polymer physics, the values of $A$ or $a$ are used as a quantitative measure of the equilibrium rigidity (or flexibility) of the main chain of the molecule, characterizing the “average” conformation of the chain of a molecule in an equilibrium state in a dilute solution. These values characterize the degree of convolution of the macromolecule and the orientational order in it.

Quantitative data on the equilibrium and kinetic [1, 5, 10] rigidity of macromolecules can be obtained by the well-tested methods of complex investigation of the hydrodynamic, optical, and electrooptical properties of macromolecules in dilute solutions [10].