EFFECT OF FORCE FIELDS ON A THERMOTROPIC LIQUID-CRYSTALLINE COPOLYMER OF HYDROXYBENZOIC ACID AND ETHYLENE TEREPHTHALATE. 1. CREATION OF ORIENTED COPOLYMER STRUCTURE IN A UNIFORM MAGNETIC FIELD

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A melt of a copolymer of 60% hydroxybenzoic acid and 40% ethylene terephthalate was subjected to a uniform magnetic field with $B = 0.65$ T at $300^\circ$C. The structure and thermal expansion of the material was studied by x-ray diffraction and dilatometry. The magnetic field produced a highly oriented structure. Dilatometry revealed previously unreported relaxation transitions in this material.

Composites derived from high-molecular-weight fibers have found common use in industry, especially when high specific material parameters are required. Most of such fibers have been obtained from lyotropic liquid-crystalline polymers. These polymers cannot be treated by the methods common for thermoplastics. As a consequence of the high rigidity of the molecular chain, the temperature for their transition to the mesomorphic state exceeds the decomposition temperature. Thus, the fibers are spun from their anisotropic solutions, in which various highly concentrated acids are often used as the solvent. This gives rise to some technological difficulties. In order to reduce the transition temperature, polymers were synthesized, which were capable of forming the meso phase upon heating to temperatures much less than those, at which thermal decomposition begins. Such materials may be used directly for manufacturing large items, eliminating the steps involving fiber preparation, impregnation by the binder, winding, and hardening. In most cases, these are copolymers featuring mesogenic blocks in the main chain, which are connected to each other by flexible links termed spacers. The copolymer of hydroxybenzoic acid (HB) and ethylene terephthalate (ET) is such a material.

In the first communication on the synthesis of such a copolymer, Jackson and Kuhfuss [1] noted that the best mechanical indices and lowest viscosity of the melt are found for the copolymer, in which the mesogenic hydroxybenzoic acid blocks comprise 60 mole %. The melt of this copolymer separates into two phases upon formation of the liquid crystal state: one phase is enriched in HB sequences, while the other is enriched in ET sequences [2-5]. The compositions of the isotropic and anisotropic phases at $280^\circ$C contain 35 and 80% HB, respectively [6].

The two-phase nature of the copolymer is also indicated by the finding of two glassy temperature regions. The first glassy range, as indicated in many studies, extends from 52 to $87^\circ$C, while the second extends from 149 to $168^\circ$C [1-3, 5, 7-16]. The greatest width of the first glass region, according to the reported data, does not exceed $10^\circ$C, while the greatest width of the second region does not exceed $5^\circ$C. The difference in the positions of the regions on the temperature scale reported by different workers is related, in our view, to the methods employed for measurement and sample preparation, and the prior thermal and mechanical history of the samples.

In addition to the two glass regions, this copolymer has, in the opinion of some authors, melting points at 190-195°C [7, 8, 13, 16, 17], 220-236°C [1, 5, 9, 12, 14], and 247-273°C [2, 3, 7, 10-13]. The scatter of these results is probably also a consequence of the reasons indicated above. The first melting point has been related to melting of polyethylene terephthalate crystallites in regions enriched with ET, while the third has been related to melting of crystallites in the phase enriched with HB. However, Shiwaku et al. [5] proposed that the melting point of HB crystallites is the transition temperature, which these
authors found at 233°C (second region). They did not find a transition at 247-273°C. These authors obtained samples of a previously filtered solution of the copolymer. The solution prior to filtration was turbid, which these authors attributed to the presence of undissolved polyhydroxybenzoic acid crystallites (about 1 mass %) formed during synthesis of the copolymer. The solution became transparent after filtration. In our opinion, the polyhydroxybenzoic acid crystallites present in the copolymer, which have high affinity for the HB units, may serve as sites for nucleation and growth of HB crystallites by a mechanism involving epitaxy. The melting point of such crystallites is somewhat higher than for crystallites formed only by HB units, which leads to two melting points.

The copolymer melt decomposes above the melting point of HB crystals, as shown above, into an isotropic phase enriched in ET units and an anisotropic phase, in which HB sequences predominate. The anisotropic phase consists of domains, in each of which there is a predominant orientation of the copolymer macromolecules. However, there is no macroscopic orientation of the melt due to the random orientation of the domains. Such a melt is rather readily converted to the oriented state. In order to study the structure and properties of the copolymer in the oriented state, some authors prepared extrudates by means of drawing the melt through a capillary [4, 7, 18-22], varying some of the extrusion process parameters, while others spun fibers from the melt by extrusion with subsequent stretching [9, 12-14, 23], also varying the spinning conditions. Scanning electron microscopy was used by some workers [4, 14, 20] to show that the extent of orientation in the central part of the extrudates and fibers is much lower than on the surface, i.e., their structure is extremely nonuniform. The mechanical properties of the fibers obtained are quite good but depend significantly on the formation conditions. The maximum tensile strength and elasticity modulus values are 438 MPa and 37 GPa, respectively [14].

In the present work, we studied the possibility of obtaining a uniform orientation of the macromolecules over the entire bulk of the copolymer of 60% hydroxybenzoic acid and 40% ethylene terephthalate by the action of a constant uniform magnetic field and investigated the structure and properties of this material. The stimulus for this study was the report of a change in the structure of polymers in a magnetic field resulting from anisotropy of the diamagnetic susceptibility of the macromolecules, their fragments, and aggregates [24]. In the first part of this work, which is the subject of the present communication, the possibility of obtaining an oriented structure in this copolymer in a magnetic field was demonstrated in principle. In the second part, results are given for a detailed investigation of the effect of the forming conditions on the structure and properties of the copolymer.

Prior to preparation of the samples, the copolymer granules were dried in vacuum at 110°C for 20 h and then placed into a flat-bottomed Teflon crucible and heated in a thermostat at 280°C, at which the copolymer is in a molten state. The melt was thoroughly stirred, maintained at this temperature for 1 h, and cooled together with the thermostat. The temperature was lowered from 280 to 190°C over about 2.5 h. The samples thereby prepared were isotropic, as shown by x-ray diffraction analysis. After cooling, a plate of the copolymer with thickness of about 2 mm was cut into samples 20 mm in length and 3 mm in width, which were stored in vacuum.

The sample was placed into a Teflon form for magnetic treatment. The form was a half-cylinder cut parallel to the generatrix with a groove having dimensions 20 × 3 × 2 mm. The form with the sample was placed into the channel of a cylindrical furnace 6 mm in diameter. The furnace was placed between the pole ends of a constant electromagnet. The distance between the ends was 21 mm. The sample was heated to 300°C and maintained at this temperature for 1.5 h. The electromagnet was then switched on and magnetic treatment was carried out in a field with induction \( B = 0.65 \, \text{T} \) over 45 min. The furnace was then turned off and the cooling sample was maintained in the magnetic field for an additional 13 min. The electromagnet was then switched off. The temperature of the sample over this period had dropped to 40°C.

Oriented copolymer samples were also prepared by pressure-die casting according to the method described by Maksimov [25]. This was carried out to elucidate the effect of different methods of orientation on the structure of this material.

The study of the structure and properties of the oriented copolymer was carried out by wide-angle x-ray diffraction on a DRON-3M diffractometer using transillumination with NiKα radiation and by dilatometry on a UIP-70M instrument for the thermomechanical study of polymers.

Two types of diffraction patterns were taken on the diffractometer in the study of the oriented samples. The first type displayed a dependence of the x-ray scattering intensity on the Bragg angle of the sample in the direction perpendicular to the force lines of the magnetic field in the copolymer upon magnetic treatment, while the second displayed scattering along the direction of the force lines. Survey diffraction patterns were obtained with scanning step \( 2\theta = 1^\circ \). Scanning of the angular range with step 0.05° and pulse collection time at each step 30 sec was carried out to determine the angular positions of the diffraction maxima. In each exposure method, the error in determining the apex of the maximum did not exceed 0.025°, while the error in determining the intensity did not exceed 0.1%. A diffraction pattern of an isotropic sample was obtained using the