The study of heat-resistant fibers obtained from a melt of thermoplastic crystallizable polyimide

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Abstract. The homologous series of thermoplastic polyetherimide based on resorcinol dianhydride R (1,3-bis-(3,3’,4,4’-dicarboxyphenoxy)benzene) and tetranuclear diamine BAPB (4,4’-bis(4”-aminophenoxy) biphenyl) (R-BAPB) were synthesized in powder form. Fibers were obtained by melt spinning of this polyimide. It was analyzed, how changes in the molecular weight of polyimide can affect the ability to form fibers through the melt. The influence of the degree of orientation high-temperature drawing on the thermal mechanical properties and the change in the morphology of the polymer was studied. An increase in draw ration (DR) from 1 to 4 led to a substantial increase in tensile strength and Young's modulus of polyimide fibers.

1. Introduction
Aromatic polyimides are known for their outstanding heat resistance, excellent mechanical and electrical properties, as well as chemical resistance. These properties make them attractive for use in high-tech industries (aerospace, mechanical engineering, chemical engineering, electronics, etc.). Polyimides (PI) found their application for the manufacture of various kinds of materials: films, coatings, binders for composite materials [1,2]. A number of polymers of this class have the ability to form fibers with good technological and operational properties. However, the structural rigidity of the polymer backbone leads to the fact that most aromatic polyimides are insoluble and cannot be processed by the melt technology. Thus, the main method for obtaining PI fibers consists in molding through a solution in high boiling solvents that leads to significant difficulties in their production of technological and environmental nature [3]. Therefore, the development of melt-processable thermoplastic PI fibers is of particular interest.

Nowadays, most commercial thermoplastic polyimides are amorphous. Their operating temperatures are limited by glass transition temperatures (Tg), which usually do not exceed 220-250°C [6,7]. The creation of crystallizable PIs increases the limiting temperature of their operation, which in this case will be determined not by the glass transition temperature (as in amorphous polyimides), but by the melting temperature being much higher.

One of the prominent representatives of polyimides capable of melt recrystallization is the polyimide based on R (1,3-bis-(3,3’,4,4’-dicarboxyphenoxy) benzene resorbite dianhydride) and BAPB (4,4”) tetrahdral diamine. bis (4”-aminophenoxy) biphenyl) [8, 9]. A feature of this thermoplastic polyimide R-BAPB is its ability to controlled crystallization and recrystallization, which was repeatedly shown in [10, 11, 12] using films, coatings and binders for composite materials, as an example. R-BAPB fibers were obtained only through a polyamide acid solution [13]. Thus, the aim of the present work was to obtain and to study heat-resistant fibers formed from a melt of thermoplastic crystallizable polyimide.
2. The experimental part

2.1. Materials and methods

The following monomers were used to synthesize polyimide: 1,3-bis (3', 4-dicarboxyphenoxy) benzene dianhydride (R dianhydride), $T_m=163-165^\circ C$, (OOO TechHimProm, Yaroslavl, Russia), diamine 4,4'-bis(aminophenoxy) diphenyl (BAPB), $T_m=198-199^\circ C$, manufacturer VWR International. Phthalic anhydride was chosen as the chain growth limiter during polycondensation. $T_m=131-134^\circ C$, Sigma-Aldrich Co. LLC.

Molecular weight of the obtained R-BAPB polyimide was determined by the intrinsic viscosity of the synthesized polyamide acid. The intrinsic viscosity was measured by a viscometric method using an Ubbelode viscometer. The molecular weight of the polymer ($M_w$) was calculated from the Mark Kuhn Houwink equation [14,15].

The melt viscosity of the polymer was studied on a Physica MCR301 rheometer (Anton Paar, Netherlands) in a CP25-2 cone-plane measuring unit (diameter 25 mm, angle 2°, gap between the cone and plane 0.05 mm) at the temperature of 360°C. The test was carried out in shear mode at shear rates of 1 to 0.01 s$^{-1}$.

Polyimide fibers were obtained by the melt technology from R-BAPB using a twin-screw microextruder (DSM Xplore, Netherlands) with a special installation for producing fibers. Fiber extrusion was carried out at the temperature of 360°C. The choice of technological parameters for obtaining samples was related to the study of the rheological, thermophysical and structural properties of these fibers. In order to increase the mechanical properties, polyimide fibers were subjected to orientational thermal drawing using a device developed at the IMC RAS. The orientation of the R-BAPB polyimide fibers was carried out stepwise in the temperature range from 208°C to 215°C.

Mechanical tensile tests were carried out using an INSTRON 5943 universal tensile testing machine. The test speed was 10 mm/min. For each fiber type, 10 samples having a base length of 30 mm were tested. The values of tensile strength, Young's modulus and deformation at break were calculated from the obtained stress-strain curves.

The structure of the PI fiber was studied with the help of SUPRA-55VP scanning electron microscope (Carl Zeiss, Germany) using a secondary electron detector. Chipped fibers made at liquid nitrogen temperature were examined.

The thermal properties of the samples were investigated by differential scanning calorimetry method (DSC) on a NETZSCH instrument (Germany) DSC 204 F1. The tests were carried out in the temperature range from 30 to 400°C at a heating rate of 10°C/min in an inert atmosphere (argon). NETZSCH Proteus® software was used to determine the glass transition temperature $T_g$, the melting temperature $T_m$ as well as crystallization temperature $T_{cr}$.

2.2. Results and discussions

The synthesis of semi-crystalline R-BAPB polyimide was carried out on the basis of the resorcinol dianhydride R (1,3-bis- (3,3', 4,4'-dicarboxyphenoxy) benzene) and the tetranuclear diamine BAPB (4,4'-bis (4") -aminophenoxy) diphenyl) by chemical imidization according to the procedure described in [8]. The molecular weight of each prepolymer obtained was regulated by violating the stoichiometric ratio of the starting monomers during the formation of the polyamide acid. Moreover, the closer the molar ratio of dianhydride to diamine, the higher the molecular weight. The ratio of dianhydride to diamine was changed from 0.8 to 1. As a result, finely dispersed R-BAPB polyimide powder was obtained.
The most important condition for the molding process is the viscosity of the melts. At very high viscosities, outflow discontinuities with the appearance of melt jet breaks are possible. In the case of obtaining polymer fibers through a melt, the viscosity can be varied by changing the molecular weight of the synthesized polymer (Figure 1). By varying the ratio of monomers and, consequently, by changing the molecular weight, it was determined that the optimal ratio of dianhydride to diamine should not exceed 0.95. Namely this ratio is necessary to achieve the viscosity, which allows obtaining a defect-free fiber.

![Figure 1. The dependence of the viscosity of the R-BAPB melt on molecular weight (dianhydride/diamine ratio).](image)

Figure 2 shows DSC curves of R-BAPB polyimide fibers with varying degrees of orientation drawing. An increase in the degree of orientation drawing (draw ratio - DR) leads to the appearance of highly diffused crystallization peaks and a melting peak. Moreover, in comparison with non-oriented samples, these peaks have 2 maxima (see Table 1). In addition, an increase of draw ratio leads to shift of the crystallization onset toward lower temperatures (Figure 2). This gives us extremely important information about the temperatures, at what the next stage of sample preparation should be carried out, namely, thermal annealing resulting in the crystallization of the polymer matrix.

Crystallized oriented fibers based on R-BAPB were studied by SEM before (DR=1) and after orientational drawing (DR=4). Crystallization of the fibers was carried out by special thermal annealing at a temperature of 250°C for 1 hour. To visualize the internal structure, such fibers were subjected to selective chemical etching using a solution of KMnO₄ in H₃PO₄ acid.
Figure 2. DSC curves of polyimide R-BAPB fibers at various degrees of orientation drawing.

Table 1. Glass transition, crystallization and melting temperatures of fibers based on R-BAPB with different molecular weights.

| Draw ratio | T_g (°C) | T_cr (°C) | T_m (°C) |
|------------|----------|-----------|----------|
| DR=1       | 197      | 300.1     | 325.4    |
| DR=3       | 197      | 256.7     | 323.0    |
| DR=4       | 195      | 252.6     | 320.2    |
|            |          | 275.0     | 339.4    |

where, T_g – glass transition temperature; T_cr – crystallization temperature; T_m, – melting temperature.

Figure 3. SEM images of the surface of crystallized fibers based on R-BAPB polyimide before (DR=1) and after orientation drawing (DR=4). The arrows indicate the direction of the fiber orientation.

Analysis of SEM microphotographs allows one to conclude that, prior to orientational drawing, the crystallized R-BAPB fiber consists of radially oriented lamellas forming the so-called degenerate spherulites. At the same time, after passing the stage of high-temperature orientation drawing, partially crystalline lamellas are oriented perpendicular to the fiber axis (and, accordingly, normal to the drawing direction) (Figure 3).

Oriented high-temperature drawing of fibers leads to a change in the deformational behaviour (Figure 4). After fiber drawing by DR=2.25, the material is deformed without the formation of a neck. Looking at by the deformation curves, one can assume the dominant deformation mechanism to be forced high
elastic deformation. During deformation, orientational hardening of the samples is observed, the intensity of which increases with increasing the degree of drawing. Due to the further orientational thermal drawing, it is possible to increase the mechanical properties of polyimide fibers (strength and Young’s modulus) by almost 4 times. It should be noted that the deformation of the fibers practically does not change from that at DR=2.25 and remains at a sufficiently high level.

![Deformation curves of PI fibers with various draw ratios.](image)

**Figure 4.** Deformation curves of PI fibers with various draw ratios.

### 3. Conclusions
In the present work, the heat-resistant fibers based on the synthesized thermoplastic polyimide R-BAPB by melt-technology were obtained. The study of the rheological properties of polyimide melts with different molecular weights showed that the optimal ratio of dianhydride to diamine in the synthesis of R-BAPB polyimide is 0.95.

High-temperature drawing leads to significant changes in the thermal and mechanical properties and the morphology of the polymer matrix. Due to the orientation thermal drawing, it is possible to increase the strength and the Young’s modulus by stretching polyimide fibers by almost 4 times. When drawing, several peaks of melting and crystallization appear.

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