

Influence of temperature and imidization method on the structure and properties of polyimide fibers prepared by wet spinning

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A polyamic acid (PAA) based on 4,4'-bis(4-aminophenoxy)diphenyldiamine and 1,3-bis(3',4'-dicarboxyphenoxy)benzene dianhydride was synthesized. PAA fibers were prepared by wet spinning. Subsequent cyclization of PAA units was achieved using chemical or thermal imidization. The influence of the imidization method and process conditions on the chemical structure, porosity, morphology, thermal and mechanical properties of polyimide (PI) fibers was studied. Thermal imidization was carried out in the temperature range from 60 to 300 °C at different process durations. The degree of imidization of PI fibers was studied by IR spectroscopy. The structure and properties of PI fibers were studied by scanning electron microscopy, thermal analysis, and by measuring the stress-strain properties.

Key words: wet spinning, polyamic acid, partially crystalline polyimide, thermal and chemical imidization, porous structure, mechanical properties of fibers.

Aromatic polyimides (PI) combine imide rings and aromatic moieties in the repeating unit and possess unique mechanical properties, a relatively high thermal stability, excellent chemical stability, high radiation resistance, and good dielectric properties.^{1–5} This gives PI fibers significant advances over other advanced polymer fibers (especially, when using under severe conditions and in aggressive media) and opens great prospects for application in microelectronics, mechanical engineering, aerospace industry, and aviation.⁴ The use of PI fibers for wet and dry filtration under high temperatures in the presence of aggressive reactants seems to be one more specific application field of these materials. Among the filter media, of particular interest are porous hollow-fiber membranes for gas separation and filtration.^{5,6}

Polyimide fibers are prepared by wet and dry-jet wet spinning,⁷ melt spinning,⁸ and electrospinning.⁹ Among them, two-step wet spinning, or coagulation method, is most widely used. It involves fiber spinning from a polyamic acid (PAA) solution followed by thermal or chemical imidization affording PI. Thermal imidization is usually carried out at temperatures below 300 °C while chemical imidization is performed at room temperature using a cyclization agent, *i.e.*, a mixture containing an aliphatic carboxylic acid anhydride and a tertiary amine.^{10–14} For instance, we used a PAA solution and a solution of acetic anhydride and triethylamine in benzene to obtain fully imidized PI powders.¹¹

Generation of water is a salient feature of the imidization process. When PI fibers are prepared by two-step wet spinning, the formation of a porous structure during both the fiber spinning step and subsequent removal of water from the fibers during cyclization yielding PI is highly probable. On the one hand, porosity has an undoubted negative effect on the mechanical properties of PI fibers.^{15–17} On the other hand, it can provide some benefits for solving certain practical problems, *e.g.*, production of filters in the form of hollow-fiber gas separation membranes. In this case, filtration requires that fibers have a particular porous structure.^{18–22} However, there are only a few studies on the influence of the PAA imidization method and process conditions on the porosity and properties of PI fibers based on partially crystallizable PI. The aim of this work is to bridge this gap.

Experimental

Materials. A partially crystalline polyimide based on 1,3-bis(3',4'-dicarboxyphenoxy)benzene (dianhydride **R**, **1**) and 4,4'-bis(4''-aminophenoxy)biphenyl (diamine BABP, **2**), was used. Dianhydride **R** (OOO TekhKhimProm, Yaroslavl, Russia) was dried in vacuo at 140 °C, m.p. = 163–165 °C. Diamine BABP (VWR International) was dried in vacuo at 140 °C, m.p. = 198–199 °C. *N*-Methyl-2-pyrrolidone (*N*-MP) used as solvent was dried over CaH₂ and distilled, b.p. = 202 °C, density $d_4^{20} = 1.024 \text{ g cm}^{-3}$, refractive index $n_D^{20} = 1.4684$.

Preparation of fibers. Fibers were formed by wet spinning on a PIFV-01 installation (Institute of Macromolecular Compounds, Russian Academy of Sciences) from the R-BABP (**1**) PAA solution using a coagulation bath based on an ethylene glycol–ethanol mixture (1 : 1 v/v). The single fibers were formed by drawing through a die 150 μm in diameter. Then, the PAA fibers were washed in distilled water and dried at 50 $^{\circ}\text{C}$ for 10 min. The fibers thus prepared were converted to PI fibers using thermal or chemical imidization.

The chemical structure of PAA (**I**) and PI (**II**) was confirmed by IR spectroscopy using an IRAffinity-1S FT IR spectrometer (Shimadzu, Japan) equipped with a MIRacle attenuated total reflectance (ATR) microaccessory (PIKE Technologies, USA). The spectra were recorded in the region of 4000–600 cm^{-1} .

The glass transition temperatures and the melting points were determined by differential scanning calorimetry on a NETZSCH DSC 204 F1 instrument (Germany) in the temperature range from 30 to 400 $^{\circ}\text{C}$ at a heating rate of 10 deg min^{-1} in inert medium (argon). The weight of samples was 4 to 5 mg. In addition, the enthalpy of melting was determined using the NETZSCH Proteus® software.

Thermogravimetric analysis traces were obtained using a NETZSCH TG 209 F1 thermobalance (Germany) in the temperature range from 30 to 800 $^{\circ}\text{C}$ at a heating rate of 10 deg min^{-1} in inert medium (argon). The weight of samples was 2 to 3 mg.

The fiber structure was studied using a SUPRA 55VP scanning electron microscope (Carl Zeiss, Germany). Prior to placing the samples inside the microscope chamber, a thin platinum layer was sputtered on their surface. The accelerating voltage was 5 kV. The pore size was analyzed using the ImageJ image processing program.

Mechanical properties of PI fibers were determined using an INSTRON 5943 universal tensile testing machine at room temperature. The test speed was 10 mm min^{-1} and the fiber samples were 30 mm long.

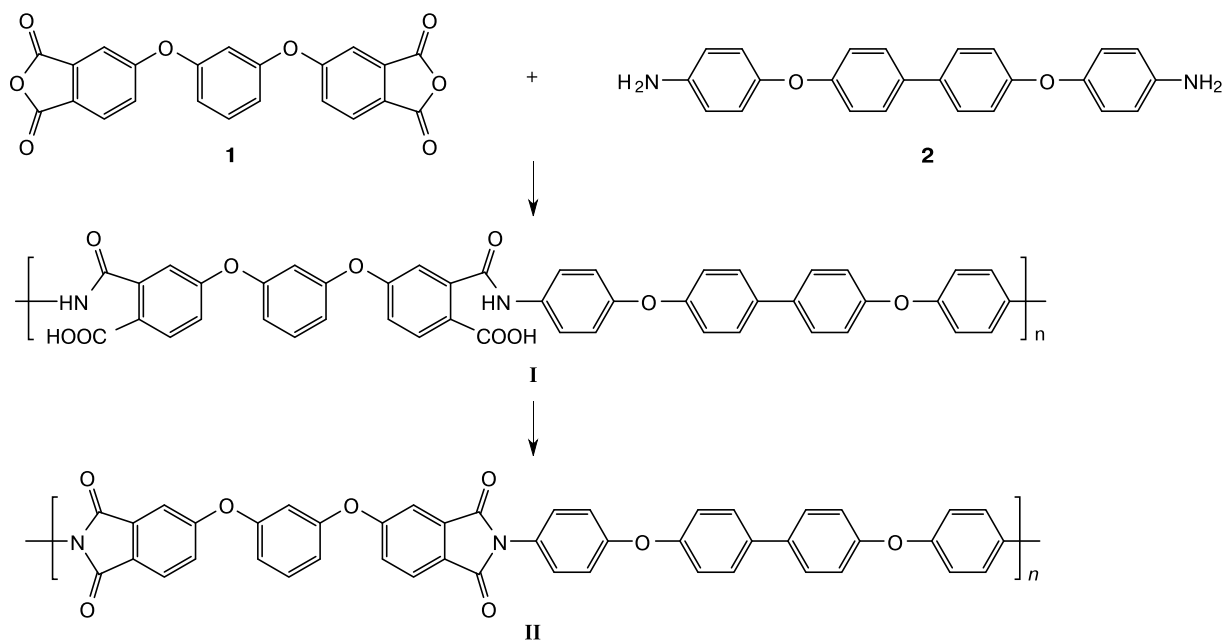
Results and Discussion

Polyamic acid was synthesized by polycondensation of dianhydride **R (1)** with BABP (**2**) in an *N*-methylpyrrolidone (*N*-MP) solution following a published procedure⁷ (see Scheme 1).

The equimolar ratio of the reactants was strictly maintained during the synthesis. The PAA solutions thus prepared were filtered and evacuated. The concentration of the PAA solution was 20%. To reduce the solution viscosity for wet spinning of fibers, the PAA concentration was decreased to 16% by adding *N*-MP. The intrinsic viscosity of the synthesized PAA measured using an Ubbelohde viscometer was 2.1. The molecular weight of PAA calculated from the Mark–Kuhn–Houwink equation with the constants $K = 1.1 \cdot 10^{-4}$ and $\alpha = 0.91$ (see Refs 23 and 24) was ~ 86 kDa.

We studied how the method for imidization of PAA fibers and the process conditions influence the chemical structure, porosity, morphology, as well as the thermal and mechanical properties of PI fibers. Thermal imidization of PAA fibers was carried out in the temperature range from 60 to 300 $^{\circ}\text{C}$. Chemical imidization was performed by placing PAA fibers in a bath filled with a two-component solution containing equimolar amounts of propionic anhydride and triethylamine taken in a 30-fold excess with respect to the amount (in moles) necessary for cyclization of PAA fibers to PI fibers. Imidization in the cyclization agent solution was carried out at 25 $^{\circ}\text{C}$ over a period of 12 h. Then, the fibers were washed with diethyl ether and ethanol and dried at 50 $^{\circ}\text{C}$ for 12 h.

Scheme 1



The influence of the imidization method and temperature was studied by IR spectroscopy using a series of the R-BABP (I) PAA samples prepared by different imidization techniques at different temperatures. The spectra of polymer samples exhibit a set of characteristic bands of medium and strong intensity in the range of $1850\text{--}700\text{ cm}^{-1}$ (Fig. 1). These are two bands at 1780 and 1720 cm^{-1} corresponding to the imide ring C=O stretching vibrations, a band at 1660 cm^{-1} corresponding to the stretching vibrations of the C=O bonds in the residual PAA groups, a band at 1594 cm^{-1} corresponding to the aromatic ring C=C stretching vibrations, a band at 1380 cm^{-1} corresponding to the imide ring C–N stretching vibrations, and a band at 1545 cm^{-1} corresponding to the N–H deformation vibrations in the residual groups at the PAA units. The degree of imidization of the forpolymer can be assessed from the increase in the relative intensity of the band corresponding to the imide ring C=O stretching vibrations (1720 cm^{-1}) and from the decrease in the relative intensity of the band corresponding to the stretching vibrations of the C=O bonds in the PAA groups (1660 cm^{-1}).

In the case of thermal imidization an increase in both the heat treatment time and the heating temperature from 60 to $300\text{ }^{\circ}\text{C}$ (see Figs 1 and 2) causes noticeable changes in the IR spectra. This mainly concerns the region of

vibrational fingerprints of C=O groups. The longer the heat treatment time the larger the proportion of imide units in the PAA fiber. This manifests itself as changes in the intensities of corresponding spectral bands (see Fig. 1). In particular, the intensity of the imide ring C=O stretching band at 1720 cm^{-1} increases considerably (see Figs 1 and 2) while the relative intensity of the band at 1660 cm^{-1} corresponding to the stretching vibrations of the C=O bonds in the PAA groups decreases. Besides, noteworthy is a proportional decrease in the intensity of other bands of the PAA units, *viz.*, $\nu(\text{N–H})$, $\delta(\text{N–H})$, and $\delta(\text{O–H})$. However, the spectra demonstrate the residual C=O stretching bands of the PAA group at 1660 cm^{-1} even after 36 h of heat treatment at $140\text{ }^{\circ}\text{C}$, which is indicative of incomplete imidization of the PAA fiber (see Figs 1 and 2).

To determine the optimum heat treatment temperature at which the degree of imidization is maximum, we studied the vibrational spectra of the polymers heat treated in the temperature range of $60\text{--}300\text{ }^{\circ}\text{C}$ (see Figs 1 and 2). The degree of imidization was quantified from IR spectroscopy data using the strong imide ring C=O stretching band at 1720 cm^{-1} and the aromatic ring C=C stretching band at 1594 cm^{-1} as a reference (internal standard). Our analysis of the spectra of the thermally and chemically imidized polymer fibers revealed the maximum degree of

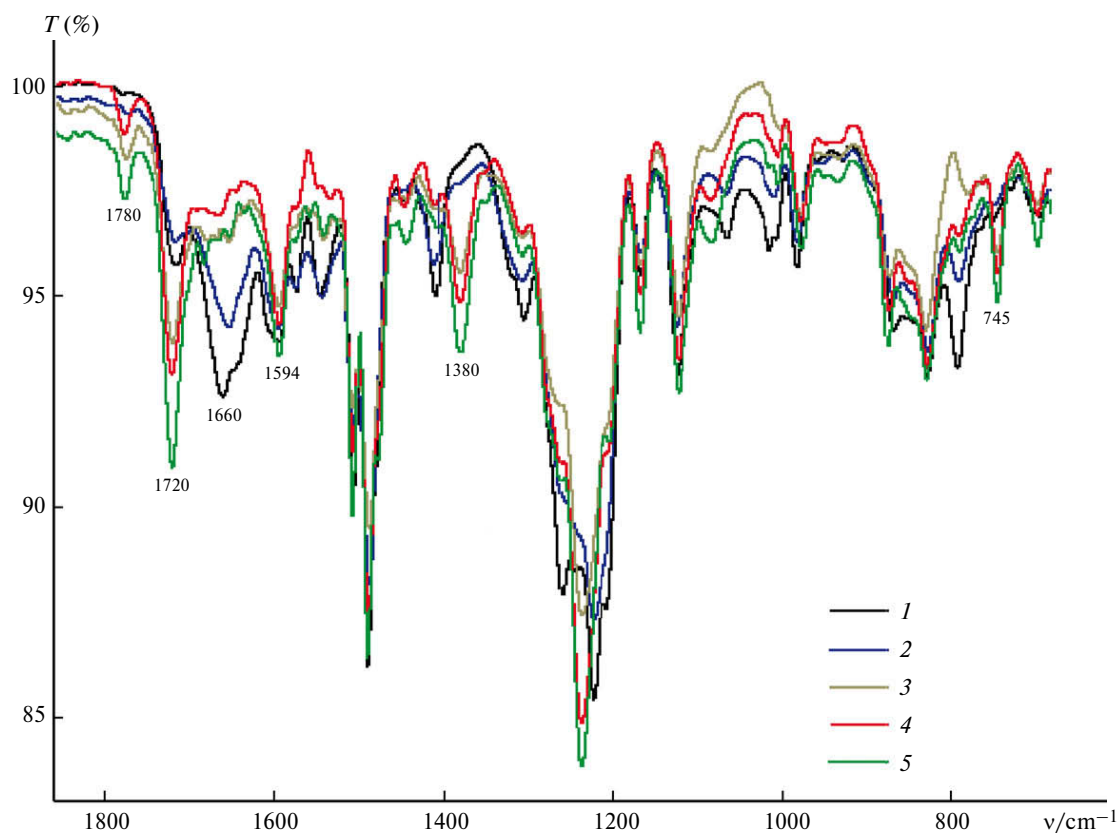


Fig. 1. Fragments of the IR spectra of R-BABP PAA thermally imidized at $60\text{ }^{\circ}\text{C}$ for 30 h (1), at $80\text{ }^{\circ}\text{C}$ for 30 h (2), and at $140\text{ }^{\circ}\text{C}$ for 4 (3), 10 (4), and 24 h (5).

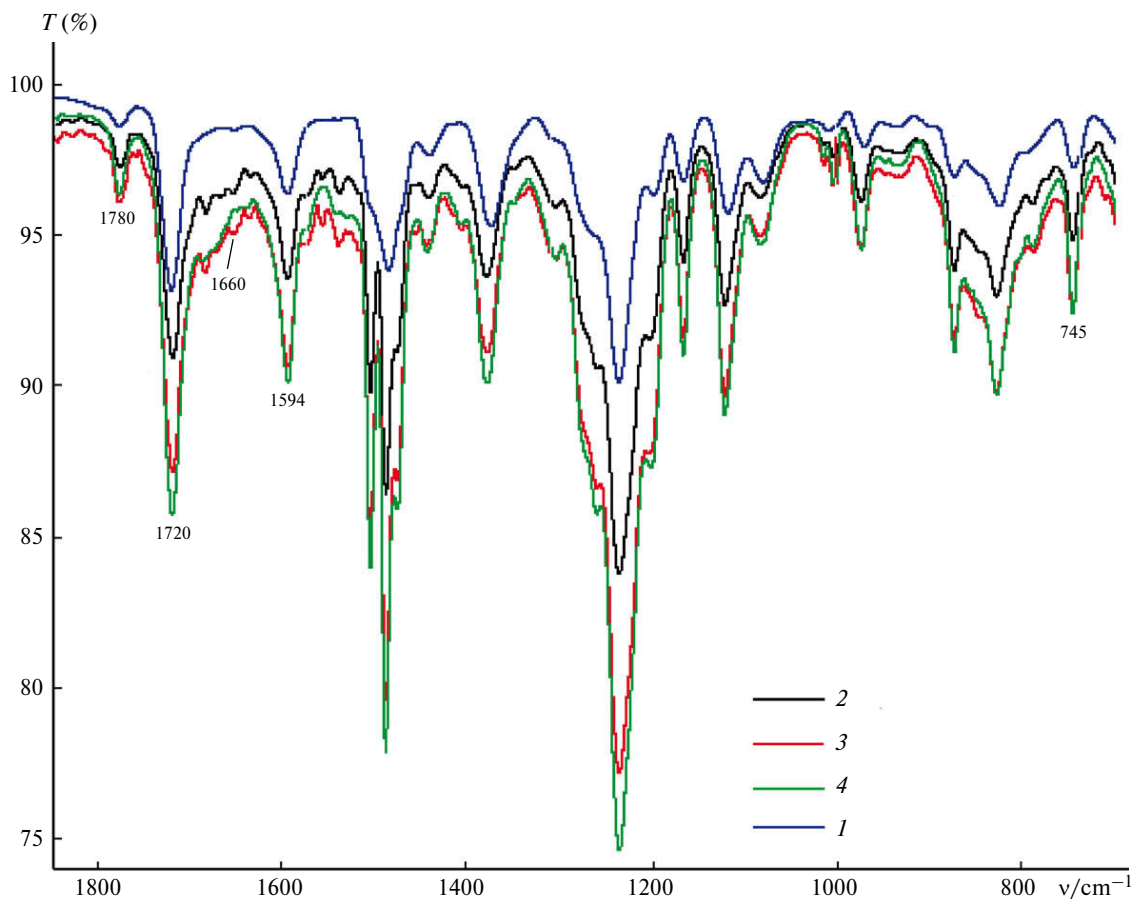


Fig. 2. Fragments of IR spectra. Chemically imidized R-BABP PAA (1) and thermally imidized R-BABP PAA: at 140 °C for 36 h (2), at 240 °C for 1 h (3), and at 300 °C for 1 h (4).

imidization (100%) in the latter. Indeed, the spectra of the chemically imidized polymer fibers exhibit no C=O stretching bands of the PAA group at 1660 cm^{-1} while the relative intensity of the imide ring C=O stretching band is maximum (see Fig. 2). The degree of imidization of thermally imidized polymer fibers is only slightly lower than that of chemically imidized fibers. The thermally imidized fiber heat treated at 300 °C has a degree of imidization of 98% (*cf.* 90–92% for the fiber heat treated at 140 °C for 36 h). The PAA fiber heat treated at 60–80 °C contains only a small amount of imide units since the imide ring vibrational bands at 1720, 1380, and 745 cm^{-1} are very weak. Noteworthy is the strong C=O stretching band of PAA units at 1660 cm^{-1} .

A SEM analysis of the structure of the PI fiber showed that the PAA fiber has a porous structure with micropores from 0.1 to 0.6 μm in size (Fig. 3, *a*). The porous structure is retained after thermal imidization at temperatures of up to 240 °C (Fig. 3, *b*, *c*). At 300 °C, the internal structure of the fiber becomes rather dense and no pores are visible (see Fig. 3, *d*), *i.e.*, the pores in the PAA fiber become closed at this temperature. No pore closure was observed in the chemically imidized PAA fiber. The proportion of

large pores decreases and the porosity maximum is shifted toward the smaller pore size region, and the pore size is varied from 0.1 to 0.3 μm (see Fig. 3, *e*).

The PI fibers are characterized by endothermic melting peaks (T_m) in the range from 316 to 319 °C, which suggests the presence of a crystalline phase. However, the enthalpy of melting of the PI fiber prepared by chemical imidization is much lower (Table 1). This can be due to the fact that thermal imidization is accompanied by accelerated crystallization owing to higher treatment temperatures. The degree of crystallinity of PI fibers was assessed from the enthalpy of melting H_m calculated in our previous study¹⁷ for R-BABP with a degree of crystallinity of 100%, which was equal to 90 J g^{-1} . This suggests that degree of crystallinity of the PI fibers prepared by thermal imidization is about 34% (*cf.* nearly 7% for the chemically imidized fibers, see Table 1). The glass transition temperature of the PI fibers prepared by chemical imidization lies in the range of about 208–210 °C, being slightly higher than that of the thermally imidized fibers (see Table 1). The temperature of 5% weight loss of the PI fibers prepared by chemical imidization is 16 degrees higher than that of the thermally imidized sample (see

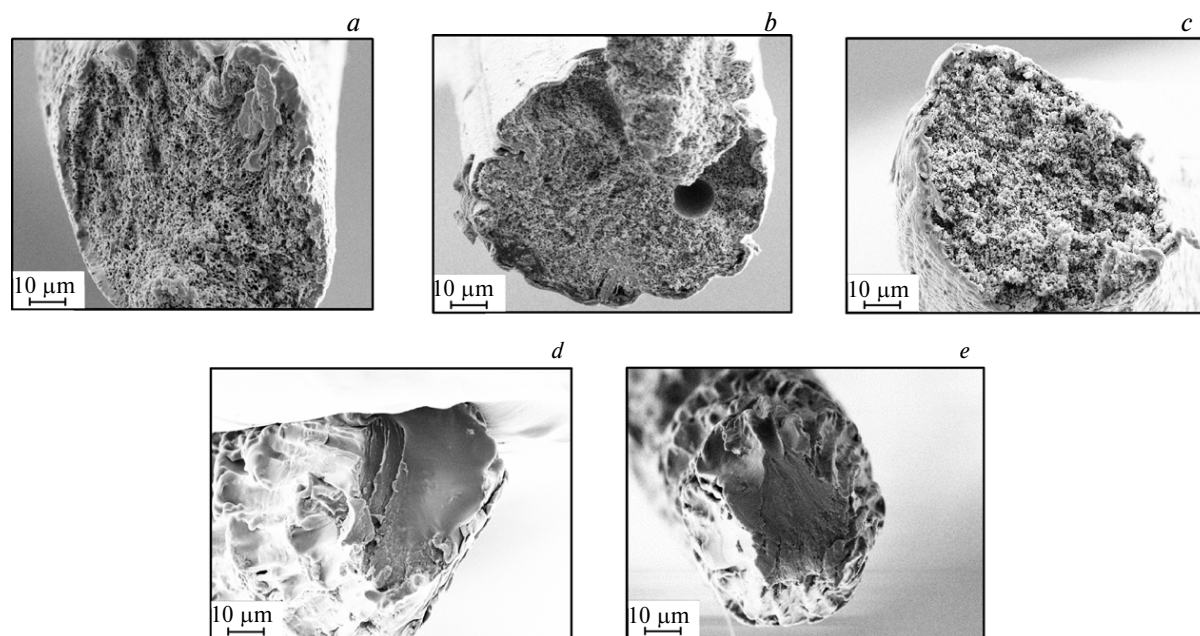


Fig. 3. SEM images of PAA fibers: untreated (*a*); heat treated at 140 °C for 36 h (*b*); heat treated at 240 °C for 1 h (*c*); heat treated at 300 °C for 1 h (*d*); and chemically imidized (*e*).

Table 1). This seems to be due to more complete cyclization of PAA units in the case of chemical imidization.

Data on the influence of the imidization method and the process temperature on the stress-strain properties of the fibers are collected in Table 2. An analysis of the mechanical properties of PI fibers revealed their dependence on the heat treatment regime of the PAA fibers. As the treatment temperature of the PAA fibers increases, the tensile strength increases from ~60 MPa for the untreated PAA fiber to 118 MPa at 300 °C for the imidized one. The increase in the tensile strength with the treatment tem-

perature of PAA fibers is consistent with the porosity data described above. Due to their porous structure (see Fig. 3) PI fibers prepared by chemical imidization possess poorer stress-strain properties and are characterized by lower strain-to-fracture compared to the thermally imidized fibers (Table 2).

Summing up, the maximum degree of imidization of fibers can be obtained upon heat treatment at temperatures below 300 °C or using a cyclization agent. Thermal imidization involving heat treatment at 300 °C affords PI fibers with dense poreless internal structure. Chemically

Table 1. Thermal characteristics of R-BABP polyimide fibers

Imidization method	T_c °C	T_m °C	ΔH /J g ⁻¹	Degree of crystallinity (%)	Temperature of 5% weight loss /°C
Chemical	210	319	6.1	7	514
Thermal	208	316	31.3	34	498

Table 2. Mechanical properties of R-BABP fibers

Fiber sample	Treatment regime	σ /MPa	E /MPa	ε (%)
R-BABP PAA	—	58.1±5.6	2013±328	68.1±15.3
ThermImide PI	140 °C, 36 h	68.9±4.3	2463±158	7.6±1.4
ThermImide PI	100 °C, 200 °C, 240 °C, 1 h	102.8±14.9	2521±178	90.6±24.4
ThermImide PI	100 °C, 200 °C, 300 °C, 1 h	118.2±6.0	3116±110	82.4±14.2
ChemImide PI	Cyclization agent	97.8±4.5	2824±87	47.7±9.9

Note: σ is the tensile stress, E is the elastic modulus, and ε is the tensile strain.

imidized fibers contain pores 0.1 to 0.3 μm in size. The imidization method influences the degree of crystallinity of PI fibers. Thermally imidized fibers are characterized by a higher degree of crystallinity than chemically imidized ones. The best stress-strain properties were demonstrated by the thermally imidized fibers heat treated at 240 or 300 $^{\circ}\text{C}$.

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