ISSN 1560-0904, Polymer Science, Series B, 2020, Vol. 62, No. 1, pp. 39–46. © Pleiades Publishing, Ltd., 2020.
Russian Text © The Author(s), 2020, published in Vysokomolekulyarnye Soedineniya, Seriya B, 2020, Vol. 62, No. 1, pp. 44–52.

FUNCTIONAL POLYMERS

Synthesis of Organosoluble Polyimides and Optical Fiber Protective Coatings on Their Basis

D. A. Sapozhnikov[a,*], **B. A. Bayminov**[a], **A. V. Chuchalov**[b], **S. L. Semenov**[c],
A. F. Kosolapov[c], **O. N. Zabegaeva**[a], **and Ya. S. Vygodskii**[a,*]

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*
[b] *Mendeleev University of Chemical Technology of Russia, Moscow, 125047 Russia*
[c] *Fiber Optics Research Center, Russian Academy of Sciences, Moscow, 119333 Russia*
**e-mail: ssddaa@inbox.ru*

Received August 20, 2019; revised September 17, 2019; accepted September 24, 2019

1 **Abstract**—Homo- and copolyimides containing F, Cl, or Si atoms and COOH, OH, and cardo groups are synthesized by one-step high-temperature polycyclocondensation. It is shown that the structure of the polymer affects its solubility, thermal, mechanical, and optical properties and use as a coating. The resulting polymers with η_{in} = 0.3–1.3 dL/g are characterized by high heat resistance and thermal stability (240°C $\le T_g \le$ 375°C, 440°C $\le T_{10\%} \le$ 58°C) and also form high-strength films (55 MPa $\le \sigma \le$ 140 MPa; 1.1 GPa $\le E \le$ 2.8 GPa). The developed polyimides are promising as new highly thermostable protective coatings, in particular, of optical fibers, whose mechanical properties do not change after prolonged exposure at 300°C.

DOI: 10.1134/S1560090420010078

Despite significant advances in the synthesis of polyimides and their versatile practical application in a number of high technologies, they still remain in demand and relevant, mainly for the manufacture of materials with a set of requirements: highly heat-resistant protective coatings [1–4], optically transparent films with low coefficient of thermal expansion [5–8], gas separation membranes [9, 10], foams, and other materials [1, 10–12].

A significant drawback of most industrial polyimides is their poor solubility in organic solvents, making them difficult to process. The introduction of various fragments into the polymer structure, for example, cardo 1 groups [13, 14] and fluorinated or aliphatic ones [5–8, 11, 15, 16], allows ~~one~~ to synthesize organosoluble polymers and to significantly simplify the technology of manufacturing materials with variable characteristics.

In the review [17], the effect of introducing different side and functional groups into the PI structure was examined in detail and it was shown that the nature of side fragments significantly affects the solubility of polymers, their heat resistance, thermal stability, optical properties, gas separation efficiency, and proton conductivity. New properties of such polyimides predetermine their use in various high technologies.

Earlier, we demonstrated that organosoluble polyimides [18–20], polyamides [21], and some copolymers can be used for creating highly thermally stable protective coatings of optical fibers. It should be noted that the traditional method of manufacturing highly heat-resistant polyimide coatings of optical fibers is based on the use of PAA solutions and has a number of significant drawbacks [3, 4, 22, 23]. The authors of [20] synthesized and tested fluorinated copolyimide PI-1 with a set of valuable properties: high thermal, mechanical, and optical characteristics and excellent solubility in many organic solvents, including volatile ones, which makes it possible to produce coatings at different temperatures. However, monomers with perfluoroalkylene moieties are expensive. Using the much more commercially available PI-2 as an example, the most favorable viscosity characteristics of polymer solutions, as well as the parameters and conditions for drawing an optical fiber and forming a polyimide coating, were ascertained [18].

The purpose of this work is the synthesis of homo- and ~~(co)~~polyimides containing F, Cl, or Si atoms and COOH, OH, and cardo groups, the study of the effect 1 of these atoms on polymer properties, the manufacturability of optical fiber coatings based on them, and the comparison of the operational characteristics of optical fibers with new protective coatings.

EXPERIMENTAL

Initial Compounds

3,5-Diaminobenzoic acid (T_m = 236–237/234–235°C (hereinafter in the denominator the values of T_m are given according to the Aldrich catalog), 9.9-bis(*p*-aminophenyl)fluorene (T_m = 236–237/234–

235°C), 4,4'-diaminodiphenyl-1,1,1,3,3,3-hexafluoropropane-2 (T_m = 194–196/195–198°C), 2-chloro-1,4-diaminobenzene (T_m = 65–67/62–66°C), 2,5-dichloro-1,4-diaminobenzene (T_m = 169–170/164–166°C), 3,3'-dihydroxybenzidine (T_m = 240/238°C), 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (T_m = 244–245/244–247°C), and 3,3',4,4'-tetracarboxydiphenyl oxide dianhydride (T_m = 229–230/225–229°C) were purified by sublimation in vacuum (20 Pa) at a temperature close to their melting point. The experimentally measured melting temperatures of the monomers corresponded to the published data. 1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane was purified by vacuum distillation in a flow of argon ($T_b \approx$ 133°C/3 mmHg).

m-Cresol was distilled in vacuum ($T_b \approx$ 100°C/10 mmHg), *N*-methyl-2-pyrrolidone (**MP**) was distilled over CaH_2 in vacuum, and DMF and chloroform were used without preliminary purification.

Synthesis of Polyimides

Polyimides were obtained in a quantitative yield by the one-step high-temperature polycondensation in *m*-cresol or MP in the presence of benzoic acid as a catalyst or without it [13, 14].

The IR spectra of all the obtained polymers show absorption bands characteristic of imide cycles [13, 14].

Production of Films and Coatings

Polymer films based on PI-1–PI-4 were obtained by casting their solutions in chloroform on a Cellophane substrate, and films based on PI-5–PI-7 were cast from their MP solutions on a glass substrate under heating at ~50–70°C. Samples ~20–30 μm thick were dried in vacuum at 70–150°C.

Polyimide coatings of optical fibers were formed from 20% polymer solutions in MP on a 9 m stack [18, 20]. Coatings based on PI-1–PI-5 were made with the addition of 2 wt % 3-aminopropyltriethoxysilane as a dressing. Coatings based on PI-6 and PI-7 were prepared in situ from the obtained polymer solution without an adhesion promoter.

Analytical Methods

~~Logarithmic~~ viscosities η~~$_{\ln}$~~ of polymer (0.05 g) solutions in 10 mL of MP were determined in an Ostwald viscometer at 25°C.

IR spectra were recorded on a Tensor 37 spectrometer (Bruker); samples were pressed with KBr.

~~The heat resistance~~ of the polymers was characterized by dynamic thermogravimetric analysis in air at a heating rate of 5°C/min on a Q1500 derivatograph (MOM, Hungary) using samples weighing ~15 mg.

The thermomechanical curves were recorded on a TA Instruments TMA Q400 instrument with a probe diameter of 2.54 mm, a loading force of 1 N (100 g), and a heating rate of 5°C/min.

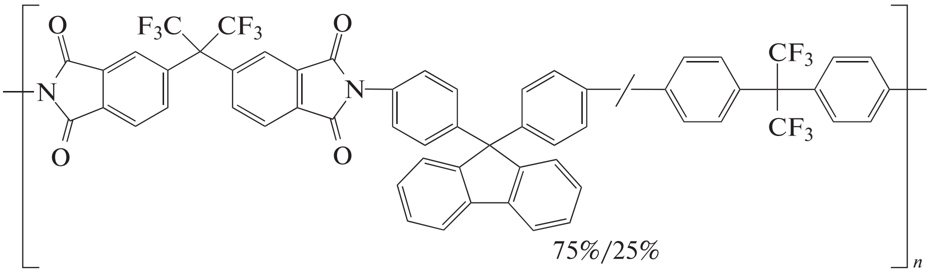
Physicomechanical tests of the films were carried out on a Polyany-type dynamometer.

The optical transmittance of the films was measured on a PerkinElmer Lambda 900 spectrophotometer.

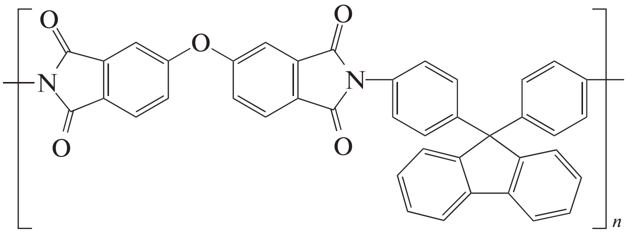
RESULTS AND DISCUSSION

Synthesis and Properties of Polyimides

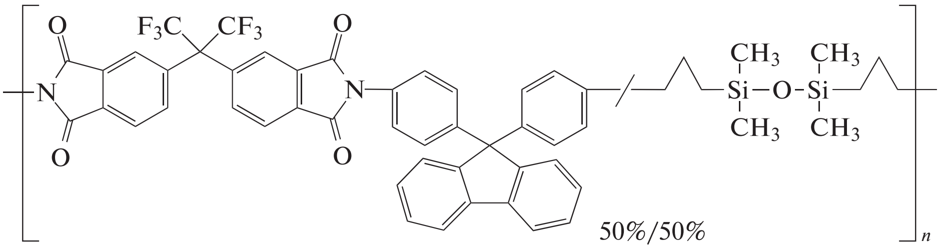
In order to study the effect of the structure of PIs on the properties of coatings of optical fibers, one-step high-temperature polycondensation in solution was used for the synthesis of the following (co)polyimides.



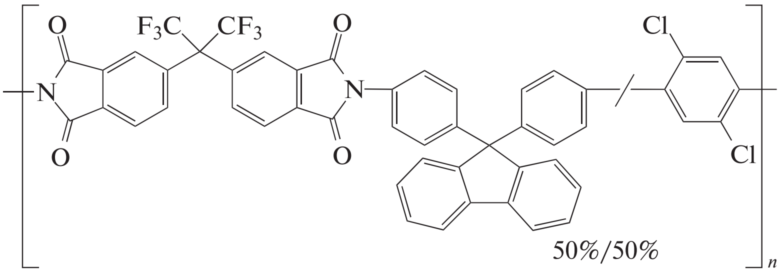
PI-1



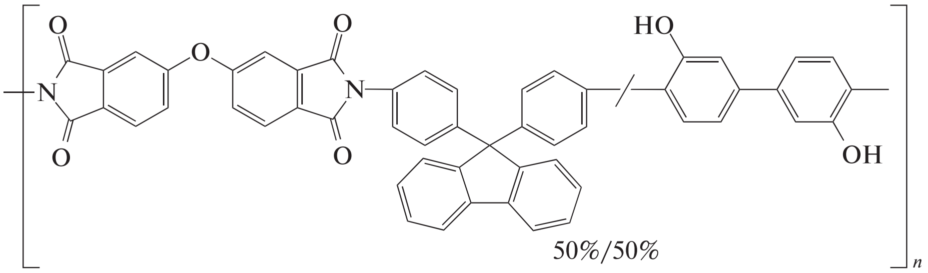
PI-2



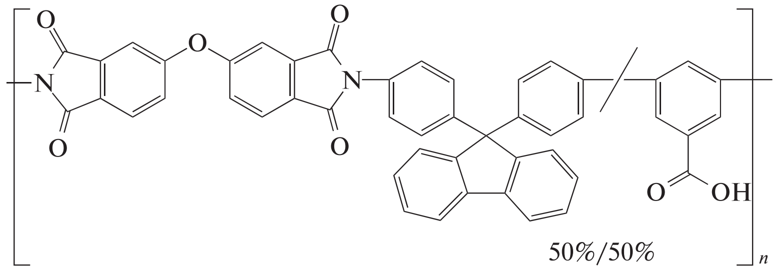
PI-3



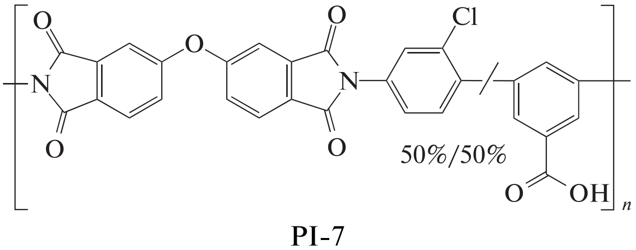
PI-4



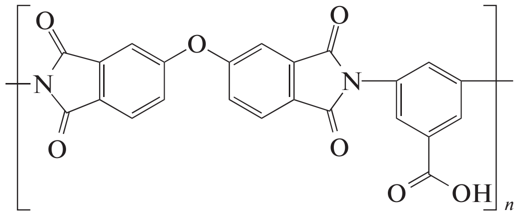
PI-5



PI-6



PI-7



PI-8

Table 1. Synthesis conditions and properties of (co)polyimides

Polymer	Solvent	Benzoic acid	Reaction time, h	η_{inh}, dL/g	Solubility		
					MP	DMF	chloroform
PI-1	*m*-Cresol	+	5	1.3	+	+	+
PI-2	*m*-Cresol	+	4	1.2	+	+	+
PI-2	MP	–	8	0.4	+	+	+
PI-3	*m*-Cresol	+	9	0.3	+	+	+
PI-4	*m*-Cresol	+	17	0.4	+	+	+
PI-5	*m*-Cresol	+	4	0.6	+	+	–
PI-6	*m*-Cresol	+	5	1.0	+	+	–
PI-6	MP	–	5	1.3	+	+	–
PI-7	MP	–	11	0.5	+	±	–
PI-8	MP	–	3	0.7	±	–	–

Plus means soluble at room temperature, plus-minus means soluble under heating, and minus means insoluble.

As was shown earlier, organosoluble PI-1 [20] and PI-2 [18] form highly heat-resistant protective coatings of optical fibers that can withstand heating at 300°C for 24 h and for a short time (30 s) at 430°C without the critical loss of strength by the optical fiber. However, to achieve satisfactory adhesion of such coatings to the fiber, a dressing is required. This complicates the process of coating manufacturing and significantly reduces the lifetime of solution. Silicon- and chlorine-containing diamines can be an alternative to fluorinated monomers when creating optically transparent polyimide films [24–31]. It was assumed that the introduction of dimethylsiloxane fragments into the PI chain would also contribute to an increase in the affinity of the polyimide coating for the surface of the quartz optical fiber [24, 32, 33].

As initial monomers, 1,3-bis(3-aminopropyl)tetramethyldisiloxane and 2,5-dichloro-*p*-phenylenediamine were selected. The introduction of flexible dimethylsiloxane fragments into the structure of the PI-3 copolymer leads to a decrease in various polymer characteristics: $\eta_{inh} = 0.3$ dL/g, $T_g = 240°C$, and $T_{10\%} = 440°C$; the tensile strength of the films decreases by almost 2 times compared with that of the PI-1 and PI-2 films (Table 1).

It should be noted that PI-4 based on 2,5-dichloro-*p*-phenylenediamine with $\eta_{inh} = 0.4$ dL/g is formed after a long reaction time (17 h). Its thermal and mechanical parameters are comparable with those of PI-1 and PI-2: $T_g = 350°C$ and $T_{10\%} = 530°C$; for the film, $\sigma = 90$ MPa, $E = 2.4$ GPa, and $\varepsilon = 5\%$ (Table 1).

PI-3 and PI-4 are soluble in MP, DMF, chloroform, and other solvents. It was found that coatings based on PI-3 and PI-4 exhibit insufficient adhesion to the optical fiber. The use of 3-aminopropyltriethoxysilane (2 wt % in terms of the polymer) eliminates this disadvantage.

To improve the adhesion of coatings to the optical fiber without adding a dressing, PI-5 and PI-6 containing HO and HOOC groups were synthesized. Both copolyimides obtained in *m*-cresol in the presence of the catalyst have a high MW ($\eta_{inh} = 0.6–1.0$ dL/g) and good heat resistance and thermal stability ($T_g = 345–360°C$, $T_{10\%} = 520–540°C$). They are soluble at room temperature in DMF and MP. Transparent colorless films with a tensile strength of 135–140 MPa were cast from MP solutions. Most likely, the increase in strength characteristics in comparison with the previously described polymers is associated with the formation of hydrogen bonds. Note that PI-5 forms a colored film.

3,5-Diaminobenzoic acid is a known monomer in the two-step synthesis of polyimides [32–34]. It was of interest to study the possibility of using DABA simultaneously in the role of monomer and catalyst in the one-step synthesis of PI. In addition, the synthesis of PI in a solvent such as MP will make it possible to use the resulting solution directly in the manufacture of coatings, without isolation and purification of the polymer. As can be seen from Table 1, high molecular weight PI-6 ($\eta_{inh} = 1.3$ dL/g) was synthesized in the MP medium for 5 h without additional catalyst. At the same time, for comparison, using the example of PI-2, it was shown that, in the absence of the catalyst, a high molecular weight polymer does not form even after 8 h of synthesis (Table 1). The properties of PI-6 obtained in *N*-methyl-2-pyrrolidone are similar to those of the polymer synthesized in *m*-cresol in the presence of the catalyst.

It was found that the presence of side hydroxyl groups in PI-5 does not provide the necessary adhesion of the coating to the fiber, while the carboxyl-containing PI-6 forms a high-strength coating. Further, for the thermal testing of optical fibers with the coating based on PI-5, a dressing was used.

Table 2. Thermal and mechanical properties of (co)polyimides

Polymer	T_g, °C	$T_{10\%}$, °C	Film		
			σ, MPa	*E*, GPa	ε, %
PI-1	355	530	95	1.1	25
PI-2	375	580	90	1.2	10
PI-3	240	440	55	1.3	7
PI-4	350	530	90	2.4	5
PI-5	360	520	140	2.8	8
PI-6	345	540	135	1.2	15
PI-7	315	515	120	1.5	10
PI-8	330	520	140	1.2	15

Here, σ is the tensile strength, *E* is Young's modulus, and ε is elongation at break.

Replacing anilinfluorene in PI-6 with the more commercially available 2-chloro-1,4-diaminobenzene made it possible to synthesize PI-7 in *N*-methyl-2-pyrrolidone (Table 1) with comparable parameters of heat resistance and thermal stability (Table 2). The copolymer is soluble in MP at room temperature and forms high-strength films (Table 2) with satisfactory adhesion to the fiber.

In the medium of MP, the organosoluble polyimide PI-8 based on 3,3',4,4'-tetracarboxydiphenyl oxide dianhydride and 3,5-diaminobenzoic acid was synthesized. According to thermal and other physicochemical properties, PI-8 is an analog of other carboxylated polyimides (PI-6 and PI-7); after isolation, it is soluble in MP under heating.

The traditional method of manufacturing fiber Bragg gratings with the use of UV radiation involves the preliminary removal of the polyimide shell absorbing in this region and its subsequent restoration. The creation of PI coatings of optical fibers with optical transparency in the near UV region will greatly simplify the technology for producing Bragg gratings. Figure 1 shows the transmission curves of the films cast from the synthesized PIs. The optical transmission of PI-1, PI-2, PI-3, PI-4, PI-5, and PI-6 films with a thickness of 20–30 μm and PI-7 with a thickness of ≈100 μm at a wavelength of 400 nm is 48, 40, 62, 67, 53, 32, and 28%, respectively. As can be seen, the films of copolyimides based on 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride and 9,9-bis(*p*-aminophenyl)fluorene with silicon- and chlorine-containing comonomers (PI-3 and PI-4, respectively) exhibit the highest optical transparency in the near UV region.

Optical Fiber Polyimide Coatings

Polyimide coatings of optical fibers are used to maintain the strength properties of the latter at 300°C or above. The traditional method for assessing the quality of an optical fiber coating is a point-to-point bending method [35]. Figure 2 shows the measured values of the strength of optical fibers with new coat-

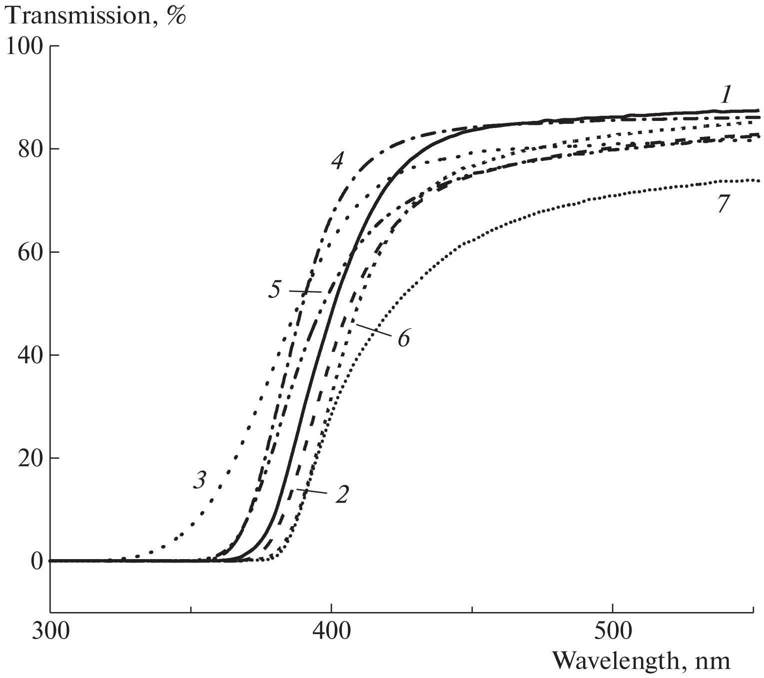


Fig. 1. Dependence of the optical transmission of (*1*) PI-1, (*2*) PI-2, (*3*) PI-3, (*4*) PI-4, (*5*) PI-5, (*6*) PI-6, and (*7*) PI-7 films on wavelength.

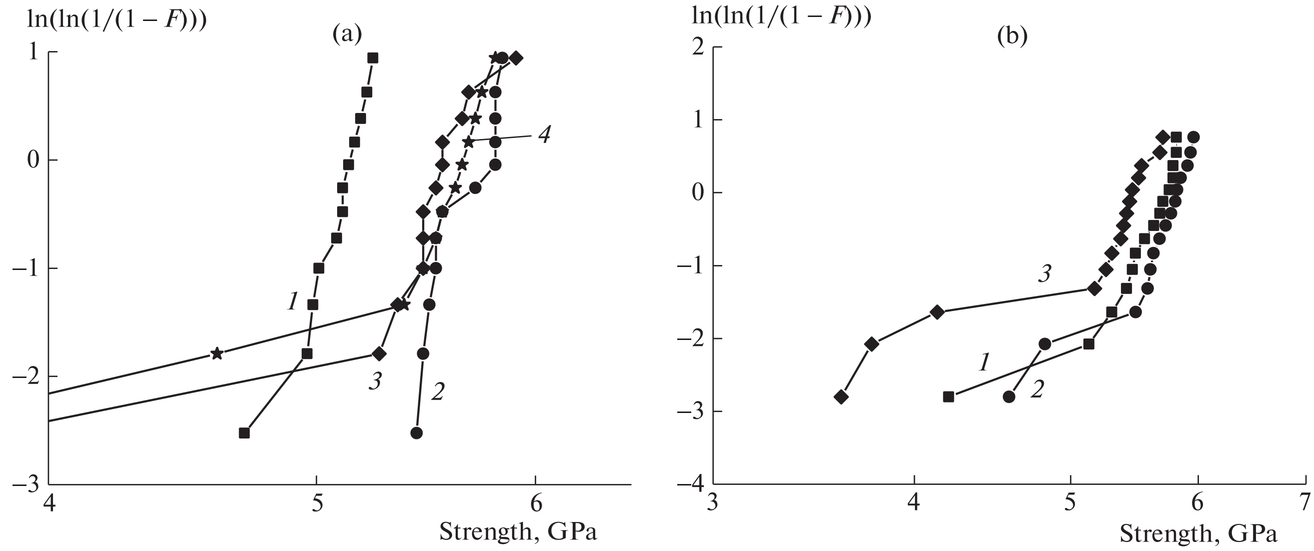


Fig. 2. Strength of optical fibers with coatings based on (a) PI-3 and (b) PI-4 (*1*) before and after annealing for (*2*) 1, (*3*) 24, and (*4*) 72 h at 300°C presented as the Weibull function (*F* is the cumulative probability of destruction of the fiber).

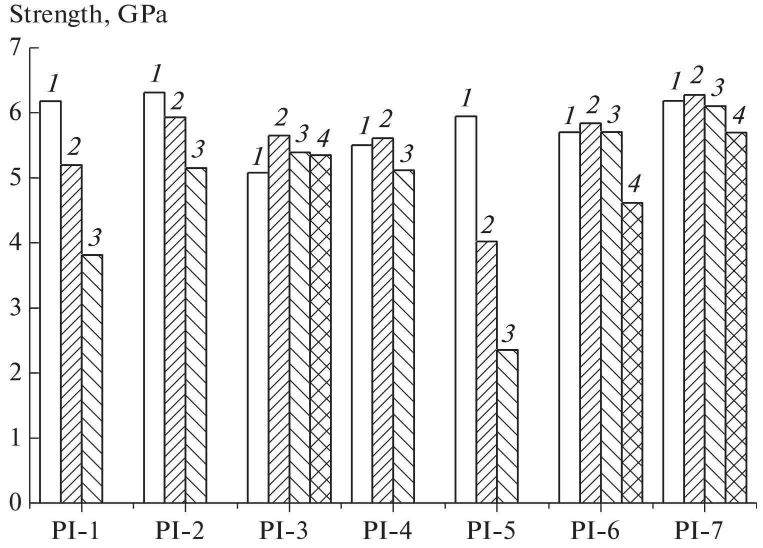


Fig. 3. Strength of optical fibers with coatings based on PI-1—PI-7 (*1*) before and after annealing for (*2*) 1, (*3*) 24, and (*4*) 72 h at 300°C.

ings based on PI-3 and PI-4 before and after annealing at 300°C. The data are presented in the form of Weibull curves. The initial strength of the optical fiber coated with PI-3 is 5.1 GPa. With holding at 300°C for 1 h, a slight increase in strength to 5.7 GPa was observed, which is not surprising and is related to the removal of small residual amounts of the solvent from the coating. A longer heat treatment is a consequence of the appearance of the so-called "fox tail," when the strength of a significant number of samples remains the same and decreases only for one or two optical fibers (Fig. 2a).

Optical fibers with the coating based on PI-4 initially had heterogeneity in strength, as indicated by a significant angle of inclination of the curve in Fig. 2b. After annealing, the spread in the strength of the fiber became even more noticeable.

Coatings based on PI-1—PI-4 are characterized by a low adhesion to the optical fiber, like many commercial analogs, which leads to the need to add a dressing to the polymer solution before application. To improve the adhesion of the coating, hydroxyl- (PI-5) and carboxyl-containing (PI-6) comonomers were used in the synthesis of PI. It was found that hydroxyl

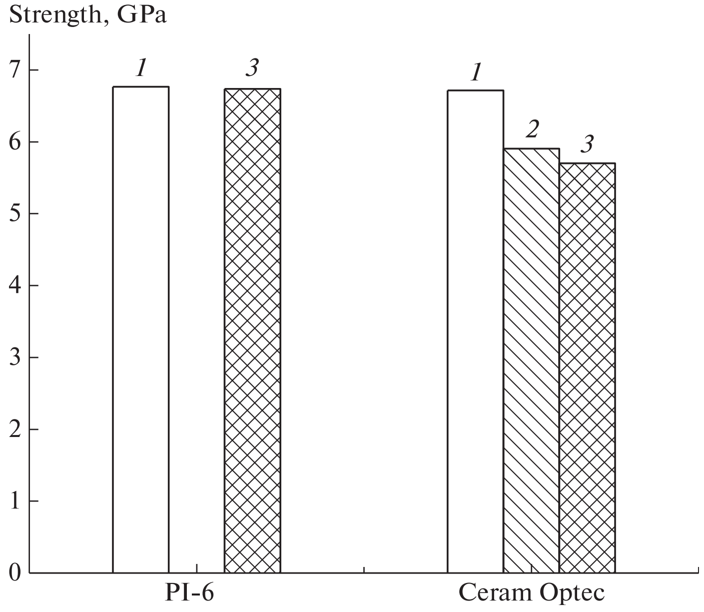


Fig. 4. Strength of the fiber with the PI-6 coating and of the Ceram Optec commercial fiber with the PI coating (*1*) before and after exposure for (*2*) 24 and (*3*) 72 h in water.

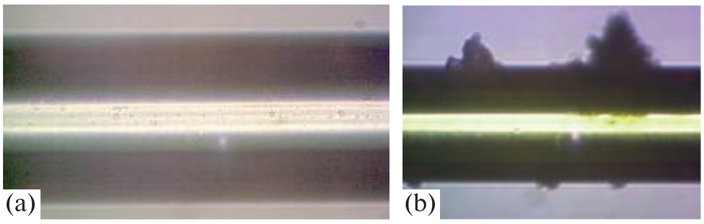


Fig. 5. (Color online) Photographs of (a) PI-6 coated optical fibers and (b) the Ceram Optec commercial optical fiber with the PI coating after holding for 72 h in water.

groups do not provide the necessary adhesion of the coating to the fiber, while carboxylated PI-6 forms a high-strength coating on the surface of the optical fiber. This allows one to avoid addition of the dressing agent to the solution. Moreover, it was shown that the solution of PI-6 in MP can be used immediately after its synthesis. Similarly, a PI-7 solution in MP was obtained and used.

According to the data presented in Fig. 3, two groups of optical fibers with newly developed polyimide coatings can be distinguished. The first group includes optical fibers with coatings based on PI-1, PI-2, and PI-5, the strength of which decreases by 16, 6, and 32%, respectively, even only after 1 h of exposure at 300°C. With an increase in the duration of annealing to 24 h, the strength of the optical fibers decreases even more. In this case, the optical fiber with the coating based on PI-2 retains about 83% of the initial value.

The second group is formed by optical fibers with coatings based on PI-3, PI-4, PI-6, and PI-7, the strength of which remains unchanged or increases after 1 h of annealing at 300°C (Fig. 3). Heat treatment at this temperature for 24 h causes a decrease in the strength of the fibers with the coatings based on fluorine- and chlorine-containing PI-4. It should be noted that coatings based on silicon-containing PI-3 and carboxylated PI-7 exhibit the greatest thermal stability. The strength of such optical fibers hardly decreases after 3 days of exposure at 300°C.

One of the important requirements for optical fiber coating is moisture inertness. Our studies demonstrated that the coatings possess hydrolytic stability for 3 days. As an example, Fig. 4 presents the test results of the optical fiber with the PI-6 coating. For comparison, a commercial optical fiber manufactured by Ceram Optec (Latvia) loses about 15% of its strength after 24 h of exposure. As can be seen in Fig. 5, unlike the developed coatings, the commercial product is partially destroyed after hydrolytic stability testing. This observation is most likely related to the nonquantitative imidization of poly(amic acid) used in the manufacture of commercial PI coatings.

ACKNOWLEDGMENTS

We are grateful to E.L. Vulakh for providing the chlorinated monomers, M.I. Buzin for the thermogravimetric studies of polymers, E.N. Afanasyev for the thermomechanical testing of polymers, and E.M. Chaika for the mechanical testing of films.

FUNDING

The study was supported by the Russian Foundation for Basic Research (project no. 18-29-17035 mk). The studies of polymer properties were supported by the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

1. M. Abadie, *High Performance Polymers-Polyimides Based: From Chemistry to Applications* (InTech, Rijeka, 2012).
2. D. A. Scola, US Patent No. 4056651 (1977).
3. A. K. Dikshit, Int. J. Plast. Technol **20**, 401 (2016).
4. A. A. Stolov, B. E. Slyman, D. A. Simoff, A. S. Hokansson, R. S. Allen, and J. P. Earnhardt, Int. Soc. Opt. Photonics, 82150 (2012).
5. M.-C. Choi, Y. Kim, and C.-S. Ha, Prog. Polym. Sci. **33**, 581 (2008).
6. M. Hasegawa, Polymers (Basel, Switz.) **9**, 520 (2017).
7. J.-G. Liu, H.-J. Ni, Z.-H. Wang, S.-Y. Yang, and W.-F., in Optoelectronics. Materials and Devices, Ed. by S. Pyshkin (IntechOpen, London, 2015), p. 57.
8. H.-J. Ni, J.-G. Liu, Z.-H. Wang, and S.-Y. Yang, J. Ind. Eng. Chem. **28**, 16 (2015).
9. H. Sanaeepur, A. Ebadi Amooghin, S. Bandehali, A. Moghadassi, T. Matsuura, and B. Van der Bruggen, Prog. Polym. Sci. **91**, 80 (2019).
10. C. Sroog, Prog. Polym. Sci. **16**, 561 (1991).
11. D.-J. Liaw, K.-L. Wang, Y.-C. Huang, K.-R. Lee, J.-Y. Lai, and C.-S. Ha, Prog. Polym. Sci. **37**, 907 (2012).
12. Y. N. Sazanov, Russ. J. Appl. Chem. **74**, 1253 (2001).
13. V. V. Korshak, S. V. Vinogradova, and Y. S. Vygodskii, J. Macromol. Sci., Rev. Macromol. Chem. **11**, 45 (1974).
14. S. V. Vinogradova, V. A. Vasnev, and Y. S. Vygodskii, Russ. Chem. Rev. **65**, 249 (1996).
15. M. G. Dhara and S. Banerjee, Prog. Polym. Sci. **35**, 1022 (2010).
16. Y. Zhuang, J. G. Seong, and Y. M. Lee, Prog. Polym. Sci. **92**, 35 (2019).
17. L. Yi, W. Huang, and D. Yan, J. Polym. Sci., Part A: Polym. Chem. **55**, 533 (2017).
18. A. Kosolapov, E. Plastinin, S. Semjonov, B. Bayminov, D. Sapozhnikov, D. Alekseeva, and Y. S. Vygodskii, Bull. Lebedev Phys. Inst. **44**, 159 (2017).
19. D. A. Sapozhnikov, B. A. Bayminov, O. N. Zabegaeva, D. D. Alexeeva, S. L. Semjonov, A. F. Kosolapov, E. A. Plastinin, M. I. Buzin, and Y. S. Vygodskii, High Perform. Polym. **29**, 663 (2017).
20. S. Semjonov, D. A. Sapozhnikov, D. Y. Erin, O. N. Zabegaeva, I. A. Kushtavkina, K. N. Nishchev, Y. S. Vygodskii, and E. M. Dianov, Quantum Electron. **45**, 330 (2015).
21. D. A. Sapozhnikov, B. A. Bayminov, N. A. Popova, O. N. Zabegaeva, D. D. Alekseyeva, S. L. Semjonov, A. F. Kosolapov, E. A. Plastinin, and Y. S. Vygodskii, Macromol. Symp. **375**, article ID 1700028 (2017).
22. A. A. Stolov, D. A. Simoff, and J. Li, J. Lightwave Technol. **26**, 3443 (2008).
23. B. J. Overton, F. Gooijer, and G. Krabshuis, in *Proceedings of 61 International Wire and Cable Symposium “An Optical Fiber with Advanced Polyimide Coating”, Rhode Island, USA, 2012* (Rhode Island, 2012), p. 321.
24. Y. Chen and J. O. Iroh, Chem. Mater. **11**, 1218 (1999).
25. M. C. Choi, J. C. Hwang, C. Kim, S. Ando, C. S. Ha, J. Polym. Sci., Part A: Polym. Chem. **48**, 1806 (2010).
26. M.-C. Choi, J. Wakita, C.-S. Ha, and S. Ando, Macromolecules **42**, 5112 (2009).
27. K. Han, K. You, W. H. Jang, and T. H. Rhee, Macromol. Chem. Phys. **201**, 747 (2000).
28. L. Li, Y. Xu, J. Che, X. Su, C. Song, and M. Xiuping, Macromol. Res. **25**, 1076 (2017).
29. M. B. H. Othman, M. R. Ramli, L. Y. Tyng, Z. Ahmad, and H. M. Akil, Mater. Des. **32**, 3173 (2011).
30. M.-H. Tsai, P.-C. Chiang, W.-T. Whang, C.-J. Ko, and S.-L. Huang, Surf. Coat. Technol. **200**, 3297 (2006).
31. B. Oktay, R. D. Toker, and N. Kayaman-Apohan, Polym. Bull. **72**, 2831 (2015).
32. E. Hamciuc, C. Hamciuc, and I. A. Ronova, Rev. Roum. Chim. **57**, 407 (2012).
33. D. H. Wang, R. N. McKenzie, P. R. Buskohl, R. A. Vaia, and L.-S. Tan, Macromolecules **49**, 3286 (2016).
34. J. D. Wind, C. Staudt-Bickel, D. R. Paul, and W. J. Koros, Macromolecules **36**, 1882 (2003).
35. M. J. Matthewson, C. R. Kurkjian, and S. T. Gulati, J. Am. Ceram. Soc. **69**, 815 (1986).

SPELL: 1. cardo