

Current trends in the synthesis of soluble and hot-melt polyimides

A. S. Kuleznev^{1*}, I. P. Storozhuk¹, V. A. Zhukova¹, A. N. Zarubina¹, and A. N. Ivankin¹

¹Bauman Moscow Technical University, 2-ya Baumanskaya ul., d.5, str.1, 105005 Moscow, Russia

Abstract. The work is devoted to a review of works published in recent years on the development of the chemical structure of soluble and hot-melt copolyimides, including a brief description of their synthesis and properties.

1 Introduction

In connection with the high rates of development of modern science and technology, heat-resistant structural and super-structural thermoplastics are becoming increasingly important for practical application, which are necessary, among other things, for the creation of various composite materials [1–9]. One of the most promising materials for these purposes are polyimides (PI), a large class of heterochain structural heat-resistant polymers containing imide rings and aromatic nuclei linked by heteroatoms or a carbon atom, as well as aliphatic or kard groups in their macrochains [10–13].

As practice shows, the problem in creating an assortment of practically demanded polyimides is their processing into products from solutions or melt, since these polymers are rigid-chain and have strong intermolecular interactions of polar groups. It is known that in order to process a polymer from a melt, its molecular weight should not be too high, and in order to maintain the necessary properties of the material, it should not seriously decrease during processing. Therefore, the development of optimal chemical structures of polyimides using new starting compounds that would satisfy a number of requirements remains an urgent task. In particular, they should have good solubility in organic solvents, a relatively low melting point compared to hard-chain polyimides that are difficult to process, melt flow, and high thermal and oxidative stability upon prolonged heating. Such polyimides can be used to produce high-strength and heat-resistant structural casting and extrusion parts, filtration membranes, films, fibers, electrical insulating coatings and shells. Currently, there are several trademarks of industrial solvent-soluble and fusible PIs, such as Ultem, Aurum, P84, and some others, among which a significant part refers to copolyimides [13].

* Corresponding author: storozhuk-ip@inbox.ru

1.1 Soluble and thermofusible copolyimides.

Copolyimides (CPI) usually have an irregular statistical distribution of units of different chemical nature, which gives the copolymers an amorphous structure and a low processing temperature, and the presence of various branches, aliphatic or aromatic "suspensions", the presence of hinge groups in the structure of the starting substances, for example, an ether bond or carbonyl group, increases the mobility of its macromolecules and makes polyimide soluble [10–13].

In the synthesis of polyimides and copolyimides with improved technological properties and, due to this, promising for industrial application, the main trends in recent years are the use of tetracarboxylic acid dianhydrides and diamines containing bulk groups and hinge groups presented in Table 1 [14].

It should be noted that, for example, card polyimides are readily soluble in organic solvents: dimethylformamide, dimethylacetamide, N-methylpyrrolidone, dimethyl sulfoxide, hexafluoroisopropanol, sulfolane, chloroform, methylene chloride, tetrachloroethane, phenol, m-cresol, nitrobenzene, etc., and some polyimides are soluble in dioxane and cyclohexanone. The solubility of such polyimides is affected by the content of kard groups in both the dianhydride and diamine components; such polyimides are more soluble than polyimides containing only one such group in the elementary unit; it is they that acquire solubility in cyclohexanone [15].

Table 1. Hinge groups and substituents in the starting materials for the synthesis of copolyimides

Grouping that improves the processability of PI from solutions and melt	Monomer fragment	
	dianhydride	Diamin
Card grouping	+	+
Carboxy suspension	–	+
Aliphatic suspension	+	+
Trifluoromethyl	+	+
Hexafluoroisopropylidene	+	+
cabronyl	+	+
simple ether connection	+	+
-Cl/-Br in the aromatic nucleus	+	+
Hydroxyl group	–	+
Alicyclic group	+	+

Recently, kard diamines have been actively used for the synthesis of copolyimides of various chemical structures. For example, through the use of fluorene card diamine, increased solubility of adamantane-containing copolyimides is obtained. According to thermogravimetric analysis (TGA), the temperature of 5% weight loss of melts of such polymers is at the level of 400–500 °C [16].

Another way to synthesize copolyimides is to use a mixture of tetracarboxylic acid dianhydrides, one of which contains a kard group, and the other may not have a solubility enhancing group at all. Additionally, in the synthesis of such copolyimides, a diamine containing aliphatic suspensions is used. The glass transition temperature of SPI is in the range of 346–353 °C, and the temperature of loss of 5% of the mass of polymer melts is about 400–450 °C [17]. The reaction equation for the synthesis of such copolyimides is shown in Figure 1.

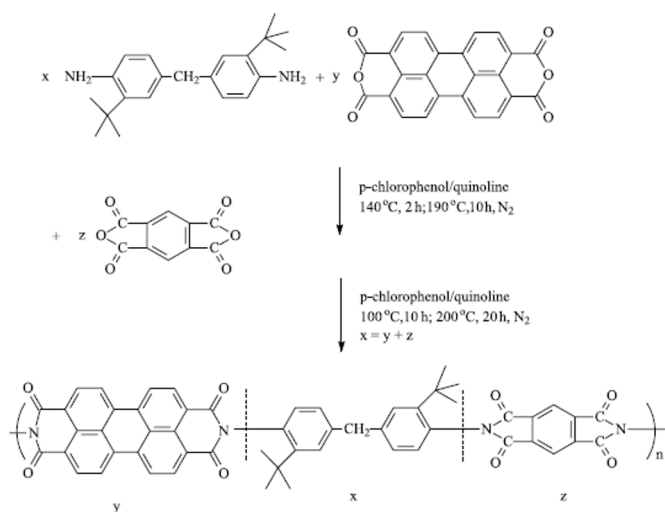


Fig. 1. Synthesis of copolyimides with carded groups and aliphatic hydrocarbon pendants

It is also worth mentioning polyimides and copolyimides, which can be modified due to the presence of reactive groups in the polymer chain in order to increase solubility and significantly increase the number of possible solvents [18]. Their glass transition temperatures are in the range of 285-343 °C, and temperatures of 5% melt mass loss at 365-430 °C. The reaction scheme for obtaining such copolymers is shown in Figure 2.

In the work of Sapozhnikov D.A. et al., devoted to the synthesis of solvent-soluble polyimides and copolyimides intended for coating optical fibers, studied polymers of various structures containing the groups indicated in Table 1. Most of the polymers obtained had good solubility in N-methylpyrrolidone, dimethylformamide, and or hydroxyl groups in the chain of copolymers did not allow them to dissolve in chloroform. The resulting polymers are characterized by high heat and heat resistance: T_c from 240 to 375 °C, temperature of 5% weight loss from 440 to 580 °C, and also form high-strength films from solutions in DMF with σ_p from 55 to 140 MPa and elastic modulus E from 1.1 to 2.8 GPa [19].

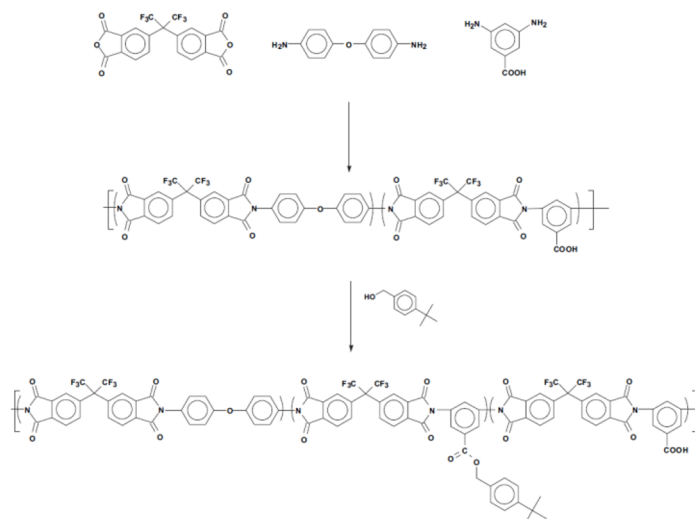


Fig. 2. Synthesis of copolyimides and their chemical modification

Another option for obtaining soluble polyimides is the use of alicyclic tetracarboxylic acid dianhydrides, while an increase in the solubility of PI is achieved due to an increased asymmetry of the macrochain and a decrease in its rigidity [20]. In addition, additional introduction of aliphatic diamines is also possible [21]. The scheme for obtaining such polymers is shown in the figure below.

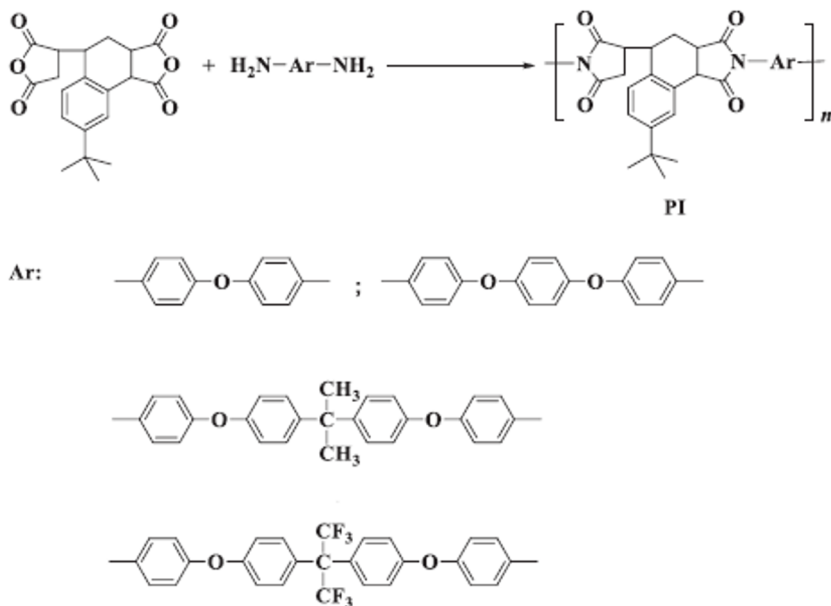


Fig. 3. Synthesis of polyimides based on alicyclic tetracarboxylic dianhydrides

In recent years, 4,4'-(4,4'-Isopropylidene diphenoxy) bis(phthalic anhydride), the structural formula of which is shown in Figure 4, has been widely used for the synthesis of solvent-soluble and hot melt PIs. This dianhydride, in particular, is used in the production of a group of injection and extruded polyimides under the Ultem trademark [22].

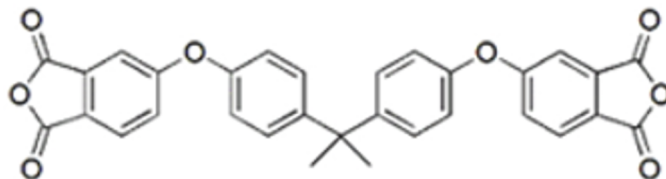


Fig. 4. 4,4'-(4,4'-Isopropylidenediphenoxy)bis(phthalic anhydride)

An increase in the solubility of copolyimides can also be achieved by introducing heterocyclic diamines into the polymer chain, which has a positive effect on the fabrication of fibers from concentrated solutions of such polymers [23, 24].

As regards melt-processable hot-melt polyimides containing hinged oxygen atoms, active research in this direction was carried out as early as the late 1990s, in particular, monomers of the following structure were used:

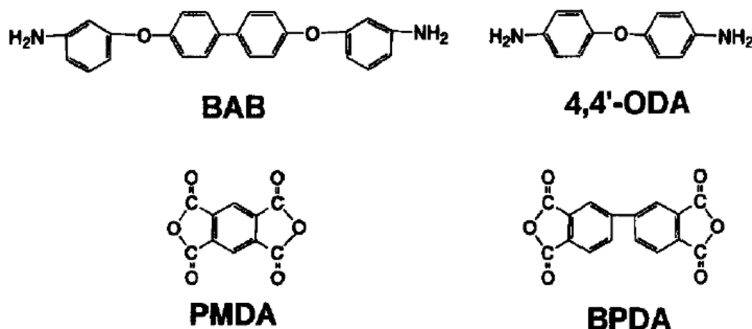


Fig. 5. Diamines and dianhydrides for the synthesis of hot-melt copolyimides

The synthesis of copolymers with different ratios of monomers was carried out for 4 hours at 150°C in m-cresol in the presence of a catalyst [25]. The properties of the obtained thermoplastics are presented in table 2.

Table 2. Composition and properties of copolyimides based on the starting materials presented in Figure 5 [25]

№	BAB content, mol, %	Content of 4,4'-ODA, mol, %	PMDA content, mol, %	BPDA content, mol, %	η , dl/g	T_c , °C	$T_{5\%}$, °C	Melt viscosity, Pa*s at T, °C		
								380	400	420
1	100	0	100	0	0.48	250	517	X	760	430
2	98	2	100	0	0.50	248	515	X	870	460
3	95	5	100	0	0.51	248	501	1910	810	470
4	90	10	100	0	0.50	252	508	1320	720	470
5	87	13	100	0	0.51	253	510	1900	910	510
6	70	30	100	0	0.50	249	514	X	10200	2670

7	100	0	90	10	0.47	246	503	-	-	410
8	100	0	80	20	0.47	239	514	-	-	390
9	100	0	50	50	0.52	232	527	-	-	350
10	100	0	20	80	0.53	229	529	-	-	360
11	100	0	0	100	0.50	225	536	-	-	350

Where: X - the melt was not formed

In recent years, interest in melt-processable polyimides and copolyimides has increased, as evidenced by the work of Chinese scientists. For example, copolymers based on isomers of hydroquinone diphthalic anhydride (HQDPA) have been synthesized by varying the ratio of diamines. Copolyimides based on 3,3'-HQDPA were obtained by changing the ratio of rigid 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and flexible 4,4'-oxydianiline (ODA). The obtained copolyimides showed good properties such as: excellent solubility in organic solvents, high T_c in the range of 328 to 354°C, good thermal stability of the melts (5% mass loss temperature was 502-514°C) and low melt viscosity in the range of 291 -935 Pa s. Copolymers based on 4,4'-HQDPA showed high T_c in the range of 315–330°C, T5% of 502–543°C, and minimal melt viscosity in the range of 291–479 Pa s. All samples formed strong and flexible films with high tensile strength (93–116 MPa) and moduli from 3.7 to 4.7 GPa [26].

Separately, it is worth highlighting an important modern direction of the targeted synthesis of polyimides and copolyimides for the production of highly selective gas separation membranes, since these rigid-chain glassy polymers are among the most suitable for membrane technologies due to their high selectivity in gas separation, mechanical strength, chemical and thermal stability. Heat-resistant polyimide membranes can be used at elevated temperatures for long periods of time and their high film-forming ability makes them an excellent material.

for the manufacture of asymmetric membranes in the form of hollow fibers or sheets. A wide variety of dianhydrides and diamines of tetracarboxylic acids creates the prerequisites to obtain polyimide membranes with various gas transport characteristics [27].

The most promising methods for modifying polyimides for their use as gas separation membranes are the introduction of non-coplanar fragments into macromolecules, such as spiro and cardo groups, the use of fragments that lead to the appearance of bends in the polymer chain, and the inclusion of side substituents, for example, -CF₃, and also other bulk groups of atoms [28-30]. For these purposes, often, various available, in comparison with dianhydrides, diamines are used.

A series of organically soluble homo- and copolyimides containing various side groups, such as -CF₃, -COOH, Cl- and fluorene, and certain combinations of them [29] was synthesized using single-stage high-temperature polycyclocondensation. The synthesized polymers with a reduced viscosity of 0.41–0.76 dl/g are characterized by a high glass transition temperature (from 230°C to 380°C) and form strong (σ_p from 60 to 140 MPa) and high modulus (E_p from 0.9 to 1, 6 GPa) films. It is shown that, depending on the nature of the side groups, the polyimides under consideration

demonstrate different gas transport behavior. For example, one of the copolyimides has a successful combination of high selectivity for He/CH₄ separation of 315 and good He permeability (permeability coefficient of 9.5 Barrer), another promising polymer has a selectivity coefficient for CO₂/CH₄ separation of 34 with a CO₂ permeability coefficient of 37,3 Barrera). For cross-linked polyimide films, which are more resistant to carbon dioxide plasticization and high gas pressure, the He/CH₄ separation selectivity is as high as 125 at He 19.7 brr, and the selectivity for CO₂/CH₄ separation is 43 at CO₂ 7.0 barr.

A group of researchers from Saudi Arabia obtained polyimides and copolyimides according to the reaction shown in Figure 6. Synthesis was carried out in m-cresol at

180°C. The properties of polymers and membrane films based on them are given in Table 3 [31]. As can be seen from the table, the polymers have a high permeability for such gases as He and CO₂, however, the selectivity in the separation of He/CH₄ and CO₂/CH₄ is low. This once again proves the need to continue the search for the creation of optimal polyimide structures that would provide the optimal (for industrial implementation) combination of membrane properties such as high selectivity and permeability to the target gas, resistance to gas plasticization, and stability of gas separation and mechanical properties.

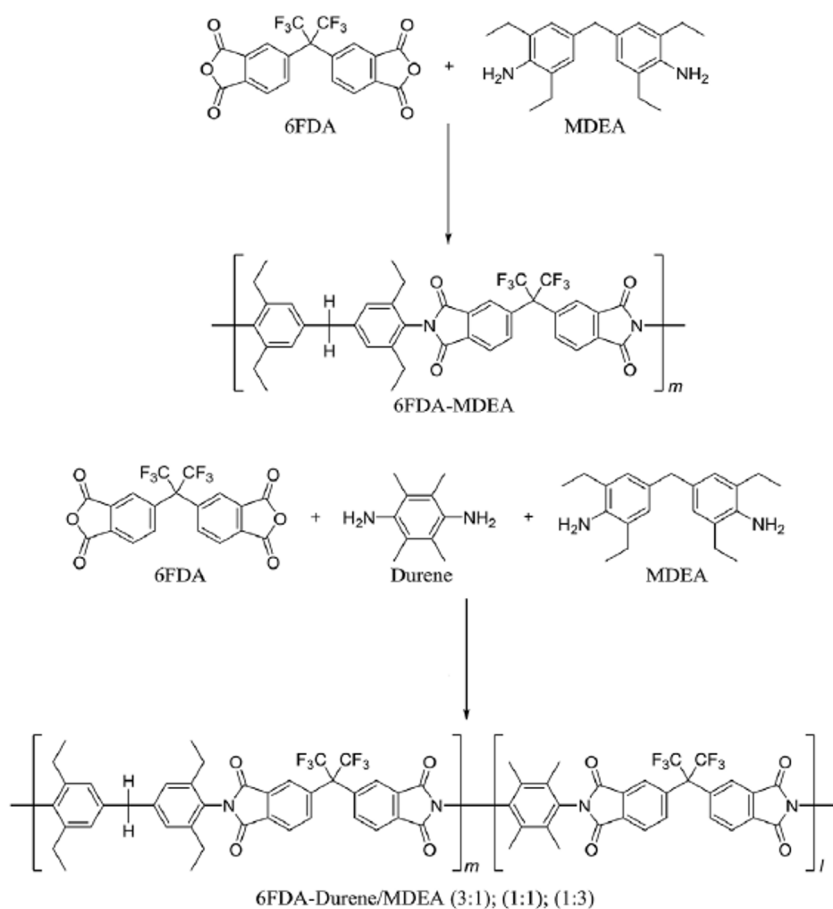


Fig. 6. Synthesis of copolyimides from a mixture of diamines

Table 3. Gas separation properties of copolyimides [31]

Starting materials	d, g/cm ³	T _{5%} , °C	T _{10%} , °C	T _c , °C	Permeability, Barrer*				Selectivity		
					He	N ₂	CH ₄	CO ₂	N ₂ /CH ₄	He/CH ₄	CO ₂ /CH ₄
6FDA-Durene	1,2929	510	527	426	450,5	55,9	46,1	739,5	9,77	1,21	16,0
6FDA-MDEA	1,2434	483	515	271	79,3	45,1	4,5	73,7	1,01	17,6	16,4
6FDA-Durene/MDEA (3:1)	1,2789	503	523	377	184,7	16,4	13,1	233,7	1,25	14,1	17,8
6FDA-	1,2687	500	523	345	118,3	12,0	8,5	158,3	1,41	13,9	18,6

Durene/ MDEA (1:1)											
6FDA- Durene/ MDEA (1:3)	1,2511	505	523	324	99,3	8,1	6,4	126,2	1,27	15,5	19,7

*The gas separation properties of film membranes were determined at a pressure drop of 690 kPa and 22°C.

Thus, at present, the synthesis of new structures and the improvement of technologies for the production of soluble and hot-melt copolyimides are still relevant and are at the stage of active development, work is underway to optimize technological parameters and select raw materials of the appropriate structure, since polyimides are used in various industries industry and the requirements for their basic and special functional properties are quite diverse.

2 Acknowledgements

This work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (Center NTI "Digital Materials Science: New Materials and Substances" on the basis of the Bauman Moscow State Technical University).

References

1. K.-U. Byuller, *Teplo- i termostoykiye polimery*; Per. s nem., Moscow, Khimiya, 1056 (1984)
2. YU. A. Mikhaylin, *Termoustoychivyye polimery i polimernyye materialy*, Saint-Petersburg, TSOP Professiya, 480 (2013)
3. YU. A. Mikhaylin, *Teplo, termo i ognestoykost' polimernykh materialov*. Saint-Petersburg, Izdatel'stvo: Nauchnyye osnovy i tekhnologii, 416 (2011)
4. YU. A. Mikhaylin, *Voloknistyye polimernyye kompozitsionnyye materialy v tekhnike*. Saint-Petersburg, Izdatel'stvo: Nauchnyye osnovy i tekhnologii, 752 (2013)
5. YU. A. Mikhaylin, *Spetsial'nyye polimernyye kompozitsionnyye materialy*. Saint-Petersburg.: NOT, 664 (2009)
6. YU. A. Mikhaylin, *Konstruksionnyye polimernyye kompozitsionnyye materialy*. Saint-Petersburg, NOT, 822 (2015)
7. M. L. Kerber, i dr., pod red. akademika A.A. Berlina, *Polimernyye kompozitsionnyye materialy: struktura, svoystva, tekhnologiya*, Saint-Petersburg, TSOP Professiya, 640 (2018)
8. M. L. Kerber, A. M. Bukanov, S. I. Vol'fson, I. YU. Gorbunova, L. B. Kandyrin, A. G. Sirota, M. A. Sheryshev, *Fizicheskiye i khimicheskiye protsessy pri pererabotke polimerov*, Saint-Petersburg, Izdatel'stvo: Nauchnyye osnovy i tekhnologii, 320 (2013)
9. A. S. Borodulin, A. N. Kalinnikov, at all., *New Polymeric Binders for the Production of Composit. – Materials Today: Procttdings*, **11**, 139–143 (2019)
10. M. I. Bessonov, M. M. Koton, V.V. Kudryavtsev, L. A. Layus, *Poliimidy - klass termostoykikh polimerov*, Nauka, 328 (1983)

11. J. M. Sonnett, T. P. Gannett, *Chemistry and Kinetics of Polyimide Formation. in Polyimides: Fundamentals and Applications*, New York: Marcel Dekker, 151 (1996)
12. A. S. Borodulin, A. N. Kalinnikov, A. G. Tereshkov, S. S. Musica, Polyetherimides for the creation of heat-resistant polymer composite materials with high physical and mechanical properties. *Vestnik BGTU im. V.G. Shukhov*, **11**, 94–100 (2019)
13. I. P. Storozhuk, N. G. Pavlukovich, A. S. Borodulin, A. N. Kalinnikov, V. M. Alekseev, *Thermoplastic Polyetherimides and Copolyimides for Heat-Resistant Composite Materials*, AIP Conference Proceedings, **2503**. 060011 (2022) DOI: 10.1063/5.0119920
14. R. Giesa, H.-W. Schmidt, Soluble Polyimides, *Encyclopedia of Materials: Science and Technology*, 8750-8752 (2001)
15. S. V. Vinogradova, V. A. Vasnev, YA. S. Vygodskiy, Kardovyye poligeteroarileny. Sintez, svoystva i svoeobraziye / *Uspekhi khimii*, **65(3)**, 266–295 (1996)
16. I. A. Novakov, B. S. Orlinson, R. V. Brunilin, Ye. A. Potayenkova, Zayavl Pat. RF 2409599, MPK C08G 73/10. Poliimidy i sopoliimidy, prednaznachennyye dlya izgotovleniya gidroliticheski ustoychivyykh poliimidnykh materialov, 27.04.09, **2** (2017)
17. H. Wei, Y. Deyue, L. Qinghua, H. Yue, Synthesis and characterization of highly soluble fluorescent main chain copolyimides containing perylene units, *European Polymer Journal*, **39**, 1099–1104 (2003)
18. E. M. Maya, A. E. Lozano, J. de Abajo, J. G. de la Campa, Chemical modification of copolyimides with bulky pendent groups: effect of modification on solubility and thermal stability, *Polymer Degradation and Stability*, **92**, 2294–2299 (2007)
19. D. A. Sapozhnikov, B. A. Bayminova, A. V. Chuchalova, S. L. Semenov, A. F. Kosolapov, O. N. Zabegayeva, YA. S. Vygodskiy, Sintez organorastvorimyykh poliimidov i zashchitnyye pokrytiya svetovodov na ikh osnove, *Vysokomolekulyarnyye soyedineniya*, **62(1)**, 44–52 (2020)
20. G. Yuan-Zheng, S. Deng-xiong, N. Hong-jiang, L. Jin-gang, Y. Shi-yong, Organosoluble semi-alicyclic polyimides derived from 3,4-dicarboxy-1,2,3,4-tetrahydro-6-tert-butyl-1-naphthalene succinic dianhydride and aromatic diamines: Synthesis, characterization and thermal degradation investigation, *Progress in Organic Coatings*, **76**, 768–777 (2013)
21. E. Schab-Balcerzak, D. Sek, A. Volozhin, T. Chamenko, B. Jarzazbek, Synthesis and characterization of organosoluble aliphatic–aromatic copolyimides based on cycloaliphatic dianhydride, *European Polymer Journal*, **38**, 423–430 (2002)
22. J. Lee, S. Yoo, D. Kim, Y. H. Kim, S. Park, N. K. Park, Y. So, Intrinsic low-dielectric constant and low-dielectric loss aliphatic-aromatic copolyimides: The effect of chemical structure / *Materials Today Communications*, **33**, 104479 (2022)
23. S. Xu, M. Yang, Synthesis and optical properties of two series of soluble acridine-containing copolyimides, *Polymer*, **48**, 2241–2249 (2007)
24. Q. Zhang, X. Li, J. Dong, X. Zhao, Chapter 6: High-performance polyimide fibers, *Advanced Industrial and Engineering Polymer Research*, **5**, 107–116 (2022)
25. S. Tamai, H. Oikawa, M. Ohta, A. Yamaguchi, Melt processable copolyimides based on 4,4'-bis(3-aminophenoxy)biphenyl, *Polymer*, **39(10)**, 1945-1949 (1998)
26. L. R. Sidra, G. Chen, N. Mushtaq, L. Xu, High Tg, melt processable copolyimides based on isomeric 3,3' and 4,4'-hydroquinone diphthalic anhydride (HQDPA) *Polymer* (2018) doi: 10.1016/j.polymer.2017.12.060.

27. H. Ohya, V. V. Kudryavtsev, S. I. Semenova, Polyimide Membranes: Applications, Fabrications, and Properties. Tokyo: Kodansha Ltd, 328 (1997)
doi.org/10.1201/9780203742969
28. N. N. Fateev, V. I. Solomakhin, B. A. Baiminov, A. V. Chuchalov, D. A. Sapozhnikov, Ya. S. Vygodskii, Gas-Transport Properties of Polyimides with Various Side Groups, Polymer Science, Series C, **62**, 266–272 (2020)
29. D.-J. Liaw, K.-L. Wang, Y.-C. Huang, K.-R. Lee, J.-Y. Lai, C.-S. Ha, Advanced polyimide materials: Syntheses, physical properties and applications. Progress in Polymer Science, **37(7)**, 907–974 (2012) doi:10.1016/j.progpolymsci.2012.02.005
30. Yi-Ch. Wang, S.-H. Huang, C.-C. Hu, C.-L. Li, K.-R. Lee, D.-J. Liaw, J.-Y. Lai, Sorption and transport properties of gases in aromatic polyimide membranes. J. Membr. Sci., **248(1–2)**, 15–25 (2005) doi.org/10.1016/j.memsci.2004.09.01
31. A. Hayek, G. O. Yahaya, A. Alsamah, A. A. Alghannam, Pure - and sour mixed-gas transport properties of 4,4'-methylenebis(2,6-diethylaniline)-based copolyimide membranes, Polymer, **166**, 184–195 (2019) doi.org/10.1016/j.polymer.2019.01.056.
32. I. P. Storozhuk, V. M. Alekseev, N. G. Pavlukovich, A. S. Borodulin, A. N. Kalinnikov, A. V. Polezhaev, Thermoplastic polyether sulfones for composite materials reinforced with fabrics, Journal of physics: conference series, 1990 (2021) 012038. DOI 10.1088/1742-6596/1990/1/012038
33. I. P. Storozhuk, A. N. Kallinnikov, A. S. Borodulin, N. G. Pavlukovich, V. M. Alekseev, Polyarylene ether ketone copolymers and their primary properties. Journal of physics: conference series, **1990**, 012033 (2021) DOI 10.1088/1742-6596/1990/1/012033
34. I. P. Storozhuk, V. M. Alekseev, A. N. Kalinnikov, A. S. Borodulin, Chemically modified polysulfones and their properties. Polymer Science - Series D., **14(4)**, 580-587 (2021)
35. A. S. Borodulin, A. N. Kalinnikov, A. M. Kharaev, at all., *Aromatic polysulfone to create polymer materials with high resistance to frost*, IOP Conf. Series: Earth and Environmental Science, **302**, 1-5 (2019)