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SYNTHESIS AND INVESTIGATION OF POLYIMIDOBENZIMIDAZOLES
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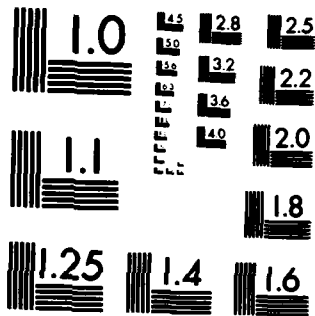
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SYNTHESIS AND INVESTIGATION OF POLYIMIDOBENZIMIDAZOLES

by

N. P. Lyubchenko, B. A. Zhubanov



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EDITED TRANSLATION

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ě in Russian, transliterate as yě or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh ⁻¹
cos	cos	ch	cosh	arc ch	cosh ⁻¹
tg	tan	th	tanh	arc th	tanh ⁻¹
ctg	cot	cth	coth	arc cth	coth ⁻¹
sec	sec	sch	sech	arc sch	sech ⁻¹
cosec	csc	csch	csch	arc csch	csch ⁻¹

Russian English

rot curl
lg log

GRAPHICS DISCLAIMER

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SYNTHESIS AND INVESTIGATION OF POLYIMIDOBENZIMIDAZOLES

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Submitted 6 Dec 1971

Among the polyheteroarylenes, to the synthesis and investigation of properties of which a great deal of attention is being given at the present time, the polybenzimidazoles represent a large group of polymers which possess increased thermal stability [1]. The only data found in the literature pertain to the use of diphenyl ethers of dicarboxylic acids and free acids for the synthesis of polymers of this class [2, 3].

In the present work for the synthesis of polybenzimidazoles bifunctional compounds were used which contain imide cycles (imido- and diimidodicarboxylic acids on a base of the anhydride of trimellitic acid and different amino acids or diamines) in a molecule, which made it possible to obtain polymers of regular structure with a specific alternation of the benzimidazole and imide groups. Together with this the possibility appears for the modification of the properties of the polymers as a result of a change of structure of the initial monomer.

Experimental Section

Initial substances. Different imido- and diimidodicarboxylic acids were synthesized using a method described earlier [4] by the interaction of trimellitic anhydride with amino acids or diamide in a solution of

m-cresol at a temperature of 160° for 4-5 hours. The acids obtained in this manner were identified by means of the melting point:

4-carboxy-(hexyl- ω -carboxy)-phthalimide, t_{m} - 166-167° (in the literature - 165°); 4-carboxy-N(decyl)-carboxy-phthalimide, t_{m} - 154-155° (in the literature - 155°); 4-carboxy-N(phenyl-n-carboxy)-phthalimide, t_{m} - 360-361° (in the literature - 351°); N,N-hexamethylene-bis-(trimellitimido acid), t_{m} - 314-315° (in the literature 310-311°); N,N-diphenyloxide-bis-(trimellitimido acid), t_{m} - 368-370° (in the literature - 369-370°).

Synthesis of dichloroanhydride of N,N-diphenyloxide-bis-(trimellitimido) acid. 0.01 moles of diimidocarboxylic acid, 0.02 moles of phosphorous pentachloride, and 0.02 moles of phosphorous oxychloride were heated at 160° for 5-6 hours (until HCl was no longer released). Upon completion of the reaction the phosphorous oxychloride was distilled off. The remaining product was treated in sequence with benzene, petroleum ether, and carbon tetrachloride, after which it was recrystallized from dry m-xylene. The dichloroanhydride obtained in this manner had t_{m} - 235-236° (in the literature - 236-237.5°).

The 3,3',4,4'-tetraaminophenyl ether, twice recrystallized from water, had a melting point of 149-150° and an equivalent of neutralization of 115.0 (calculated 115.0).

Obtaining polyphosphoric acid. 100 g of phosphoric anhydride was placed in a three-necked flask, equipped with a mixer, an inlet for nitrogen and a dropping funnel. The flask was cooled on an ice bath in a current of nitrogen and 40 ml of distilled water was added slowly. At the end of the reaction the temperature was raised gradually to 120° and heating was continued for 24 hours. The viscous product formed was almost colorless and contained up to 84% phosphoric anhydride.

The polyimidobenzimidazoles were synthesized by the generally accepted methods in a solution, in a melt, and on the phase interface.

Results and Discussion of Them

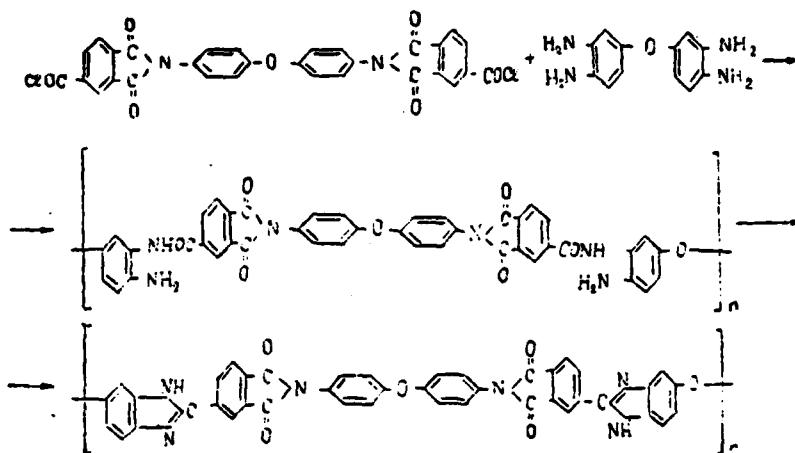
Depending on the properties of the imido- and diimidocarboxylic acids obtained (melting point, solubility), different methods of polycondensation in a melt, in solution, and on the phase interface were

used. In the case of polycondensation in a melt (initially the reaction mixture is found in a melted state, then hardens and subsequently the process flows in the solid phase) of the aliphatic imidodicarboxylic acids with the tetraamines the duration and temperature of the reaction have considerable influence on the products which are formed. With an increase of rate and temperature of the reaction, on the one hand there is a considerable increase in the yield of insoluble products, and on the other - the viscosity of the polyimidobenzimidazoles increases noticeably. Thus in the case of polycondensation of 4-carboxy-N-(hexyl- ω -carboxy)-phthalimide with 3,3',4,4'-tetraaminodiphenyl ether at 150° after two hours the reduced viscosity of the 0.5% solution of polymer comprises 0.15 dl/g, and after 10 hours it reaches 0.27 dl/g. With an increase of temperature from 180 to 200° the value of the reduced viscosity increases from 0.27 to 0.35 dl/g (table).

The most widespread methods of synthesis of polybenzimidazoles are polycondensation in a melt with the use of ethers of dicarboxylic acids and the carrying out of polycondensation in a solution of polyphosphoric acid with the use of free dicarboxylic acids. In the first case it is possible to obtain polybenzimidazole of high molecular weight, with a high degree of cyclization. In the case of conducting the reaction in polyphosphoric acid it is not possible to achieve a high degree of cyclization, but the use of tetrahydrochlorides of aromatic tetraamines and free dicarboxylic acids which are more stable to oxidation simplifies the process [2]. However, in our case polycondensation in polyphosphoric acid did not lead to the desired results, since the imido- and diimidodicarboxylic acids used were insoluble in polyphosphoric acid. Heating them for 17 hours at 200° with diaminobenzidine tetrahydrochloride leads to the formation of products of a black color which are insoluble in sulfuric and formic acid.

Imido acids on a base of trimellitic anhydride and aminobenzoic acid, hexamethylenediamine and 4,4'-diaminodiphenyl ether possess high melting points (310-370°) and poor solubility in organic solvents, which hampers their use for obtaining polymers in a melt and in solution. Therefore for obtaining polyimidobenzimidazoles the dichloroanhydrides of these acids were used. The polyimidobenzimidazoles were synthesized by two-stage polycondensation of dichloroanhydride of N,N-diphenyloxide-bis-(trimellitimidido) acid and 3,3',4,4'-tetraaminodiphenyl ether. The first stage was conducted in a medium of dry

N-methylpyrrolidone at room temperature and reaction duration of 3-4 hours.



Under these conditions along with the soluble prepolymer, the reduced viscosity of which is 0.10-0.12 dl/g (0.5% solution in dimethylformamide), an insoluble product is formed, apparently as a result of the formation of transverse amide bonds [5]. Carrying out of the reaction in dimethylacetamide leads to the formation of gel-like products.

By the method of interphase polycondensation (on the phase interface water:chloroform) it was possible to obtain polyimidoamidoamine with a reduced viscosity of the soluble portion of the polymer of 0.5 dl/g (0.2% solution in dimethylformamide).

The thermal stability of the synthesized polyimidobenzimidazoles was determined based on the data of thermogravimetric analysis. All the polyimidobenzimidazoles were stable in air up to 300°, The addition of an aromatic component to the macromolecule increased the thermal stability of the polymer from 320° in the case of hexamethylenediamine to 480° for polymers with 4,4'-diaminodiphenyl ether.

Thus in the case of the interaction of 3,3',4,4'-tetraaminodiphenyl ether with 4-carboxy-(hexyl- ω -carboxy)-phthalimide, 4-carboxy-N-(decyl-carboxy)-phthalimide, 4-carboxy-N-(phenyl-n-carboxy)-phthalimide, N,N-hexamethylene-bis-(trimellitimido) acid and N,N-diphenyloxide-bis-(trimellitimido) acid, polybenzimidazoles, modified by the imide fragments, were obtained which were stable up to 320-480°.

Properties of polyimidobenzimidazoles on a base of imido- and diimido-dicarboxylic acids and 3,3',4,4'-tetraaminodiphenyl ether.

Кислота (1)	Условия проведения реакции (2)	η_{sp} (dl/g) 0,5 %-ного раствора ПААК в H ₂ SO ₄ (3)	Температура начала разложения, °C (4)
	155°, 5ч 155°, 9ч 180°, 2ч 180°, 10ч 200°, 2ч 30 мин	0,09 0,12 0,15 0,27 0,35 ⁴	320
	155°, 5ч 155°, 9ч 155°, 10ч 180°, 2ч	0,06 0,09 0,10 0,12	390
	175°, 1ч 175°, 2ч 180°, 1ч 200°, 2ч 30 мин	0,05 0,07 0,10 0,15 ²	340
	160-180°, 2ч 180-210°, 1ч 210-290°, 3ч	0,21 0,22 — ³	405
	220-230°, 15 мин	0,35 ⁴	480

Key: (1) Acid; (2) Conditions for conducting reaction, time in hours and minutes; (3) η_{sp} (dl/g) of 0.5% solution of PAAK in H₂SO₄; (4) Temperature of onset of breakdown, °C.

Note. Samples were heated at 300° for three hours. 1 - reduced viscosity of 0.17% solution; 2 - of 0.40% solution; 3 - polymer not soluble in H₂SO₄; 4 - reduced viscosity of 0.30% solution.

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