Chemistry of Heterocyclic Compounds, Vol. 34, No. 4, 1998

2-AMINOPYRIDINIUM DI(*o*-PHENYLENEDIOXY)BORATE: A THERMAL STABILIZER AND PLASTICIZER FOR POLYAMIDE MEMBRANES

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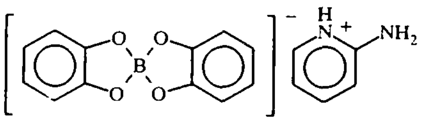
*We have synthesized 2-aminopyridinium di(*o*-phenylenedioxy)borate by reaction of boric acid with pyrocatechol and 2-aminopyridine, and we have investigated this compound as a thermal stabilizer and plasticizer for polyamide membranes.*

In previous research, we have shown that esters of boric acid exhibit high fungicidal activity [1, 2] and are good thermal stabilizers for polymer materials [3, 4]. Complex compounds of boron exhibiting good fungicidal properties [5] have not been studied for thermostabilizing activity. In this work, we have obtained a new complex compound of boron: 2-aminopyridinium di(*o*-phenylenedioxy)borate, and we have investigated it as a stabilizer and plasticizer of polyamide membranes.



The complex boron compound was obtained by reaction of boric acid, pyrocatechol, and 2-aminopyridine in an aqueous solution with heating. The composition and structure of the synthesized compound were confirmed by elemental analysis and spectral data.

In the IR spectrum of the complex compound, we see bands characterizing the symmetric and asymmetric vibrations of B–O in the 1040 cm^{-1} and 1345 cm^{-1} region, while in the 1090 cm^{-1} and 1240 cm^{-1} region we see bands for the symmetric and asymmetric vibrations of the C–O group. The bands corresponding to the pyridine ring are present in the 1580, 1570, and 1465 cm^{-1} region; i.e., they are slightly shifted toward the low-frequency region compared with absorption of 2-aminopyridine itself. Changes in the nature of the absorption indicate that a definite rearrangement of the electronic structure of the ligand occurs during complex formation. The peak in the 994 cm^{-1} region shows that in this compound, boron has coordination number four [6].

In the mass spectrum of the complex, the intensity of the ion peak $[M\text{-}H]^+$, m/z 321 is 46%. The most intense peaks in the spectrum (60-100%) are the peaks for the dipyrocatecholborate ion $[C_{12}H_8O_4B]^+$, m/z 227 and the fragmentary ion formed as a result of breaking of the C—O bond and cleavage of one benzene ring $[C_6H_4O_4B]^+$, m/z 151. Furthermore, the following low-intensity (10-18%) peaks are present: $[C_6H_4O_3B]^+$, m/z 135; $[C_6H_4O_2]^+$, m/z 108; $[C_6H_4O]^+$ m/z 92; $[C_5H_4N]^+$, m/z 68; and $[C_5H_5]^+$, m/z 65.

The synthesized 2-aminopyridinium di(*o*-phenylenedioxy)borate was introduced as 0.10-0.30 mass % into a polyamide (AK 60/40 grade) solution in a mixture of formic acid and glycerin. The solution was stirred and membranes were formed. The membranes obtained were dried in air, and then annealed at a temperature of 110°C. The comparative characteristics of the membranes (modified and control) are presented in Table 1. From Table 1 it follows that introduction of the complex does not change the basic structural and filtration properties of the membranes: the filtration capacity (Q) and the bubble point (P) are not substantially different from these parameters in the control sample. The basic physicomechanical characteristics of the

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TABLE 1. Characteristics of Modified Membranes

Membrane	Complex, mass %	Q, ml/min·cm^2	P, atm	σ, MPa	ε, %	ΔH*, cal/g	χ, %	T_{mp}, °C	T_5, °C	T_{10}, °C
1	0,10	21,5	2,20	9,9	54,3	16,3	33,4	194	280	360
2	0,15	21,8	2,18	9,9	73,0	15,9	32,7	200	355	398
3	0,20	21,9	2,16	10,0	82,6	15,6	31,8	205	360	400
4	0,25	22,6	2,12	10,3	91,0	15,0	30,9	208	360	400
5	0,30	24,6	2,11	9,8	88,0	15,6	29,6	198	355	396
6		21,5	2,20	9,2	43,1	17,3	37,6	180	210	340

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*Heat of melting.

TABLE 2. Physicomechanical Properties of Modified Membranes

σ_0, MPa	ε_0, %	Thermal aging (100°C, 24 h)				Exposure to radiation (2.5 Mrad, 30°C)			
		σ	$K\sigma$*	ε	$K\varepsilon$*	σ	$K\sigma$	ε	$K\varepsilon$
9,9	54,3	4,0	0,41	13,6	0,25	9,4	0,95	27,2	0,50
9,9	73,0	7,8	0,79	27,0	0,37	9,7	0,98	57,7	0,79
10,0	82,6	8,8	0,88	36,3	0,44	9,6	0,96	68,6	0,83
10,3	91,0	9,1	0,88	43,7	0,48	9.9	0,96	77,3	0,85
9,8	88,0	7,9	0,81	37,8	0,43	9,6	0,98	73,9	0,84
9,2	43,3	1,1	0,12	6,5	0,15	9,0	0,97	26,1	0,60

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*$K\sigma = \sigma/\sigma_0$, $K\varepsilon = \varepsilon/\varepsilon_0$.

membranes (breaking strength (σ) and elongation at break (ε)) of the modified membranes are higher than for the control membrane. Thus the strength increases by 7-11%, while the elongation increases by a factor of 1.25 to 2.1. The increase in elasticity is accompanied by a decrease in the degree of crystallinity of the membranes (χ). The degree of crystallinity decreases as the amount of complex compound in the membrane increases.

The DTA curves for the modified membranes show (Fig. 1) that at 180°C, for the control membrane there is an endothermic peak, suggesting melting of the polymer. The section of the curve between this peak and the exothermic peak at 360°C characterizes the initial stage of oxidation of the polymer. Comparing the DTA data for the control and modified samples, we can conclude that the curve from the melting peak to the exothermic peak for the modified membranes runs more smoothly, and an exothermic peak is observed at a temperature of 380°C. The melting point of the modified membranes increases by 20-28°C, the temperature for 5% mass loss increases by 145-150°C, and the temperature for 10% mass loss increases by 58-60°C.

The membranes were subjected to artificial aging in an oven at 100°C for 24 h. After aging, we determined their physicomechanical indices. Comparison of the data presented in Tables 1 and 2 shows that the strength and elasticity of the modified membranes changes less than for the control membrane. Thus when 0.1 mass % modifier is introduced, the strength changes by 29% while the elasticity is 10% less than for the control membrane. With an increase in the amount of complex compound up to 0.15-0.25 mass %, the strength changes by a factor of 4-6, while the elasticity is 14-33% less.

The investigations showed that 2-aminopyridinium di(*o*-phenylenedioxy)borate is a plasticizer and thermal stabilizer for polyamide membranes. The thermostabilizing effect of the complex compound is due first of all to the presence of boron atoms, which may block radicals because of their high tendency toward addition of groups possessing free electrons [7]; secondly, to the presence of nitrogen atoms, which can terminate chains [8]. The plasticizing effect of the modifier is explained by its insertion between macromolecules of the polymer chain, which leads to breaking of the intermolecular hydrogen bonds of the macrochains. In this case, chemical addition of the complex compound to the polyamide macromolecules (certainly chemical addition, since the water-soluble complex would be "swept out" by water during membrane fabrication) leads to branching of the polymer chain, which disrupts the regular structure of the chain and becomes a factor hindering crystallization of the polymer.

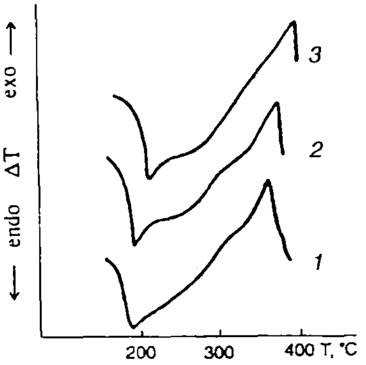

Fig. 1. DTA curves for the membranes: *1*) control membrane; *2*) membrane containing 1% modifier; *3*) membrane containing 2.5% modifier.

Application of microfiltration membranes in medicine, pharmacology, and the food industry requires that they be sterilized. One sterilization method is γ-irradiation at a dose of 2.5 Mrad. Investigations of the modified membranes after radiation sterilization showed (Table 2) that upon introduction of the modifier, the elasticity of the membranes changes 2.5 to 3 times less than for the control membrane, while retaining strength. Repeated sterilization of the modified membranes by γ-irradiation seems possible.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 in KBr pellets. The mass spectra were obtained on a Varian MAT-311 spectrometer with direct injection of the material into the ion source, for ionizing radiation energy 70 eV. The thermooxidative stability of the membranes was estimated on an MOM derivatograph (Hungary) with linear temperature rise at a rate of 5°C/min in an air medium. The sample mass was 100 mg. The physicomechanical characteristics of the membranes were determined by standard procedures on a UMIV-3 tester. The membrane samples were sterilized by γ-irradiation at a dose of 2.5 Mrad on an RKhM-20 apparatus, dose rate 300 rad/sec; ^{60}Co was the radiation source.

2-Aminopyridinium Di(*o*-phenylenedioxy)borate. Boric acid (3.1 g, 0.05 mole), 16.5 g (0.15 mole) pyrocatechol, and 4.7 g (0.05 mole) 2-aminopyridine were dissolved in 150 ml hot water. The mixture was heated up to 70°C and held for 1 h with stirring. Upon cooling, first an oily liquid fell out of solution, crystallizing when chilled. The crystalline material was separated, dried, and recrystallized from a mixture of ethanol–ether–hexane, 2:1:1. Obtained: white crystals of 2-aminopyridinium di(*o*-phenylenedioxy)borate. Yield, 11.4 g (71%). T_{mp} 205-206°C. Found, %: C 63.64; H 4.42; B 3.39; N 8.72. $C_{17}H_{15}BN_2O_4$. Calculated, %: C 63.42; H 4.65; B 3.35; N 8.70.

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