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MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Heat Resistance and Electrophysical Characteristics of Polyheteroarylenes and Ferroelectric–Polymer Film Composites Based on Them

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Abstract—Structurally related poly(amido-*o*-hydroxy amides) derived from 5,5-methylenebis(2-aminophenol) with tetramethylsiloxane and heteroaromatic (benzoxazole and benzotriazole) fragments incorporated in the second amine component or formed by polyheterocyclization of the corresponding prepolymers were prepared. The effect of modifying fragments introduced into the base poly(*o*-hydroxy amide) on the heat resistance of powders and films and of films of photosensitive compounds based on the synthesized polymers with the naphthoquinone diazide component was analyzed. The electrophysical parameters of the polymer films and film composites with a nanodispersed ferroelectric filler, (PZT: ceramic powder with the composition $Pb_{0.81}Sr_{0.04}Na_{0.075}Bi_{0.075}(Zr_{0.58}\ Ti_{0.42})O_3$, Russian brand PZT-1), prepared on the basis of modified polymer binders, were determined. Introduction of 20 mol % sulfur-containing fragments into the polymer binder ensures a 50–65°C increase in the heat resistance for all types of films without increasing the level of the dielectric loss for the composite coatings.

Keywords: poly(*o*-hydroxy amide), poly(benzoxazole), poly(benzothiazole), nanocomposite, ferroelectric, heat resistance, dielectric permittivity, dielectric loss tangent

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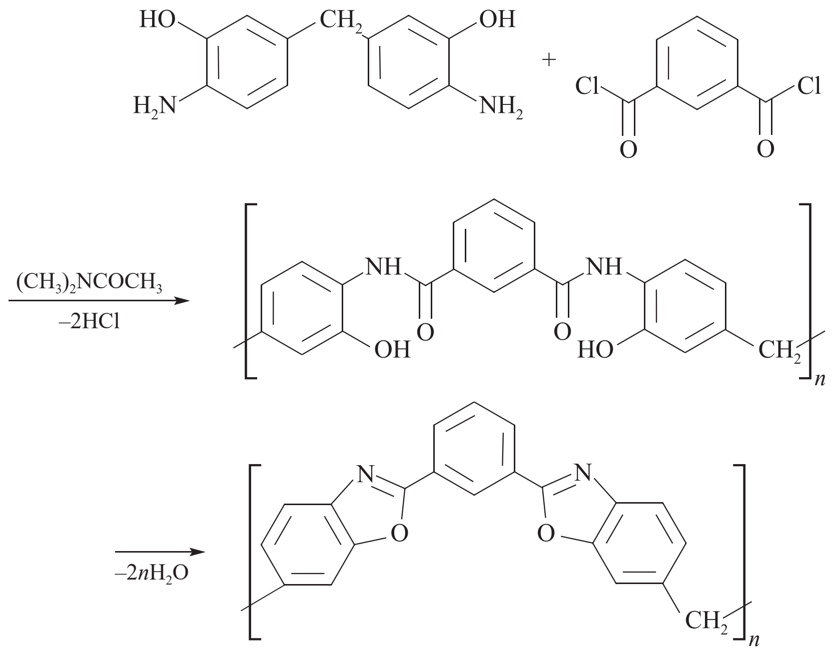
Searching for new polymer composites with ferroelectric fillers and studying their properties remain topical, because such materials are demanded in such branches of engineering as radio-, opto-, and acoustoelectronics and nonlinear optics [1–4].

In the development of film capacitor structures, the main goal is preparation of a heat-resistant composite (ferroelectric/polymer) film dielectric with increased values of the dielectric permittivity and electric strength and decreased dielectric loss tangent (tan δ). Depending on the production technology and concentration of the ferroelectric filler, the reached values of the dielectric permittivity ε' in ferroelectric/polymer composites range from 40 to 200, and those of tan δ, from 0.04 to 0.08, with no more than 30 vol % loading of the polymer with the filler [5–10]. An increase in the degree of loading the composite with the filler to 40–45 vol % allows ε' to be increased to 430, but in so doing, as expected, tan δ increases to 0.1 and higher values. So, there is some inner contradiction in the practice to manufacture the composites with low dielectric losses and enlarged dielectric permittivity by increasing the filler loading degree.

One of the ways to reduce the dielectric loss in the ferroelectric/polymer composite is using a dielectric polymer matrix with high insulation properties: low dielectric permittivity and low dielectric loss, e.g., polyamido acid (PAA) or poly(*o*-hydroxy amide) (POA), with POA being preferable because of its lower tendency to hydrolysis [11–14].

It is important that the parameters and functional destination of heterophase nanocomposites being developed can be varied in a wide range by varying the struc-

Scheme 1.



ture and properties of the polymer matrix. Specifically the polymer matrix is responsible for the heat resistance of the composite coating, adhesion to supports of different chemical nature, and formation of the polymer matrix–filler grain interface.

This paper continues the studies on modification of the base polymer matrix, POA I [15], and deals with synthesis of structurally related poly(*o*-hydroxy amides) and poly(amido-*o*-hydroxy amides) and comprehensive study of the properties of polymer matrices and polymer/ferroelectric composites based on them.

POA I is formed by polycondensation of 5,5-methylenebis-(2-aminophenol) with isophthaloyl dichloride (IPC) [16], followed by heat treatment leading to cyclodehydration with the formation of hydrophobic poly(benzoxazole) (PBO), which exhibits high heat resistance (up to 400°C), high chemical durability, and low moisture capacity. This fact predetermined its use as a material for protective layers in various multilevel electronic circuits [17], humidity sensors, and other electronic devices (Scheme 1).

To bring these results to the process practice, it was necessary to find polymer binders exhibiting, compared to POA I, increased levels of adhesion to supports of different chemical nature and of heat resistance.

The goals of this work were synthesis and study of a series of new polymers, poly(amido-*o*-hydroxy amides) prepared by introducing silicon- and sulfur-containing fragments into the macromolecule of base POA I; development of photosensitive formulations and ferroelectric/polymer dielectric composites based on them; and analysis of the influence of the polymer matrix composition on the properties of the formed films (heat resistance, adhesion, and electrophysical parameters).

The presence of $–(CH_3)_2SiOSi(CH_3)_2–$ fragments in the polymer molecule should enhance the adhesion to silicon-containing supports, and benzothiazole rings formed by thermal cyclodehydration of *o*-mercapto amides should enhance the heat resistance compared to POA I [18].

One of the most important conditions in preparation of copolymers is the choice of the ratio of diamines introduced into the reaction. The macromolecules should contain a sufficient amount of alkali-soluble fragments with hydroxy groups, which would allow the development of photosensitive formulations with a naphthoquinone diazide component, Posylux 2402, based on them, ensuring the formation of a highly heat-resistant microrelief in films using photolithographic operations with alkaline development.

EXPERIMENTAL

Isophthaloyl dichloride (IPC) (Sigma–Aldrich, CAS 99-63-8) and 3,3′-(1,1,3,3-tetramethyldisiloxane-1,3-

diyl)bis(propan-1-amine) were used without preliminary purification. 2-(Chloromethyl)oxirane (EPC) (Sigma–Aldrich, 99%, CAS 106-89-8) was distilled before use. Posylux 2402 (LLC FRAST-M, Moscow, Russia) was used without preliminary purification.

Devices and measurement methods. The IR spectra of solid substances were taken from KBr pellets with a Shimadzu FTIR-8400 S spectrometer in the interval 600–4000 cm^{-1}. The ^{1}H NMR spectra were recorded with a Bruker AC-400 spectrometer using tetramethylsilane (TMS) as internal reference. The chemical shifts are given in the δ scale relative to TMS.

The kinematic viscosity of polymers was measured with a VPZh-1 glass capillary viscometer.

The heat resistance of powdered polymer samples was evaluated by thermal gravimetric analysis (TGA), performed with a DTG-60 combined thermal analysis installation (Shimadzu, Japan) using 10-mg samples. The samples were placed in open corundum crucibles and heated in the self-generated air atmosphere at a rate of 5 deg min^{-1}. From the experiment results, we determined the heat resistance parameters τ_5 and τ_{10}: temperatures corresponding to the polymer weight loss of 5 and 10% after the removal of residual solvents, low-volatile components, and water due to thermal cyclodehydration of POA to PBO and poly(*o*-mercapto amide) (PMA) to poly(benzothiazole) (PBT).

5,5-Methylenebis(2-aminophenol) was synthesized by condensation of *o*-aminophenol with formalin in the presence of sulfuric acid and sodium sulfite [19]. The sulfur-containing diamine, 6-((2-aminobenzo[*d*]thiazol-5-yl)methyl)benzo[*d*]thiazol-2-amine, was prepared by thiocyanation of 4,4’-diphenylmethane in the presence of bromine [20], and 2,4-diaminobenzenethiol, by reduction of 2,4-dinitrochlorobenzene with $Na_2S\cdot9H_2O$ by analogy with [21]. The above-described compounds were prepared by these procedures for the first time. The structure of the diamines was confirmed by IR (KBr) and ^{1}H NMR (DMSO-d_6) spectroscopy. 5,5-Methylenebis(2-aminophenol): ν, cm^{-1}: 3378.09, 3305.76 (NH_2), (OH), 3024.18 (CH_{Ar}), 2910.38, 2924.56 (CH_2), 1598.88 (NH_2), 1213.14 (OH); δ, ppm: 3.49 (2H, CH_2), 4.29 (4H, $2NH_2$), 6.36, 6.38, 6.47 (6H, C_6H_4), 8.85 (2H, OH). 6-((2-Aminobenzo[*d*]thazol-5-yl)methyl)benzo[*d*]thazol-2-amine: ν, cm^{-1}: 3430 and 3376 (NH_2), 1621 (NH_2), 2932 (CH_2), 1535 (C=N); δ, ppm: 3.92 (2H, CH_2), 7.06, 7.08 (2H, C_6H_4), 7.19, 7.21 (2H, C_6H_4), 7.35 (4H, $2NH_2$), 7,45 (2H, C_6H_4). 2,4-Diaminobenzenethiol: ν, cm^{-1}: 3461 and 3433 (NH_2), 1692 (NH_2); δ, ppm: 4.02 (H, SH), 5,30 (4H, $2NH_2$), 6.01, 6.07, 7,04 (3H, C_6H_3).

Synthesis of POA I. 46 g of 5,5-methylenebis(2-aminophenol) was dissolved in 180 mL of DMAA containing no more than 0.035% moisture at room temperature. The solution was cooled to –5...0°C, and a solution of 40.6 g of IPC in 30 mL of DMAA was added to the cooled solution with stirring at a rate allowing self-heating of the reaction mixture over 40°C to be avoided. After adding the whole amount of IPC, the cooling was stopped, and the reaction mixture was allowed to stand at room temperature for 2 h and again was cooled to –5...0°C. Then, 31.5 mL of freshly distilled EPC was added dropwise over a period of 15–20 min, after which the solution was stirred at room temperature for 60 min. Copolymers II–IV were prepared by analogy with POA I by the reaction of IPC with a mixture of diamines taken in a definite molar ratio: 5,5-methylenebis(2-aminophenol) : 3,3′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(propan-1-amine) = 3 : 2 (II), 5,5-methylenebis(2-aminophenol) : 6-((2-aminobenzo[*d*]thiazol-5-yl) methyl)benzo[*d*]thiazol-2-amine = 4 : 1 (III), and 5,5-methylebebis(2-aminophenol) : 2,4-diaminobenzenethiol = 4 : 1 (IV).

Preparation of powdered samples of POA I–IV. A 10-mL portion of the reaction solution of the polymer was diluted with 20 mL of DMAA and added dropwise to 500 mL of an isopropanol : chloroform mixture (1 : 5 by volume) cooled to –5÷0°C. The precipitate was filtered off, washed with two portions of the precipitating mixture and then with isopropanol and acetone, and dried at 70°C for 5 h and then at 40°C in a vacuum oven for 3 h. Yield 80–90%.

The reduced viscosity (η, dL g^{-1}) for polymer I was 0.89 (0.5% solution in H_2SO_4), and for 0.5 g dL^{-1} solutions in DMAA it was 0.359 for II, 0.178 for III, and 0.162 for IV.

Preparation of I–IV:Posylux 2402 photosensitive formulations. Photosensitive formulations based on I–IV were prepared by mixing the reaction solution of the polymer binder with a solution of Posylux 2402 in DMAA at the component weight ratio of 5 : 1 (in terms of the dry polymer weight).

Procedure for forming the microphotorelief in photoresist films. Films on silicon supports were formed by centrifugation followed by drying in a thermostat at 95 ± 5°C. The coating thickness after drying was determined with an MII-4 interference microscope. The microrelief in films was created by photolithography using an EM 576 exposure installation, followed by the development in an aqueous KOH solution. The solution concentration and time of the latent image development were chosen experimentally for each photoresist. The film development time for the photoresists based on polymers I–IV was 45 s (0.3% KOH), 40 s (0.6% KOH), 25 s (0.45% KOH), and 2 min (0.2% KOH), respectively. The heat treatment of photoresist films with the relief image was performed by stepwise heating at 150–350°C (heating step 50°C with keeping at each temperature for 15 min).

Procedure for preparing polymer/ferroelectric film composites. Polymer/ferroelectric film composites were prepared by the procedure described in [16, 22], except the operation of ultrasonic dispersion of the ferroelectric filler in a polymer solution. In this study, to obtain a more homogeneous suspension, coarse particles of the ferroelectric filler powder were allowed to sediment from the solvent (DMAA), after which the remaining suspension was used for forming coatings.

Sample preparation for electrophysical studies. Film coatings of polymers I–IV and based on them composites were formed on two types of supports: Si–SiO_2–Pt and Al foil of A99 grade, GOST (State Standard) 11069–2001, 80 ± 5 μm thick. To form capacitor structures on plates of single-crystalline silicon of (100) orientation, lower platinum electrodes 80 nm thick were deposited onto the whole surface of the Si support by ion-plasma sputtering. A three-electrode ion-plasma sputtering installation was used; the support temperature in the course of the film deposition was 450°C. After forming a dielectric coating on the support surface, drying, and heat treatment, a system of upper electrodes was deposited onto this coating by ion-plasma sputtering through a shadow mask. The composite coating thickness was varied from 3 to 100 μm. The thickness of the upper platinum electrodes was 100 nm and the size varied from 1 to 6.75 mm^2. To increase the degree of filler loading in preparation of a composite coating, we chose the method of filler sedimentation in a suspension of the ferroelectric nanodispersed filler in the polymer solution. The composite coating thickness was varied from 3 to 100 μm.

Procedure for measuring electrophysical parameters. To evaluate the electrophysical properties of film coatings, we measured the capacitance (C) and dielectric loss tangent ($\tan \delta$) of the formed capacitor structures at a frequency of 200 kHz at room temperature.

The polymer and composite coatings deposited on supports were heat-treated in air in an SUOL-0.25.1/12.5-I1 muffle furnace in the stepwise mode: polymer coatings, at temperatures from 150 to 350°C with 50°C step and keeping for 15 min at each temperature; composite coatings, at temperatures from 150 to 350°C with 50°C step and keeping for 30 min at each temperature. The furnace temperature was monitored with a chromel–alumel thermocouple. The heat treatment of the coatings consisted of the following steps: heating at a rate of 10 deg min^{-1}, keeping for the preset time at preset temperature, and, after the annealing completion, slow cooling of the specimens with the furnace.

The capacitance and dielectric loss tangent of the capacitor structures were measured at room temperature at a frequency of 200 kHz with an E7-20 LCR meter.

RESULTS AND DISCUSSION

The synthesized polymers can be described by Scheme 2.

The fragment ratio m/k in the copolymer structure was chosen taking into account the fact that the films formed should exhibit high adhesion to various kinds of supports and ensure the formation of a highly heat-resistant microrelief using photolithographic operations.

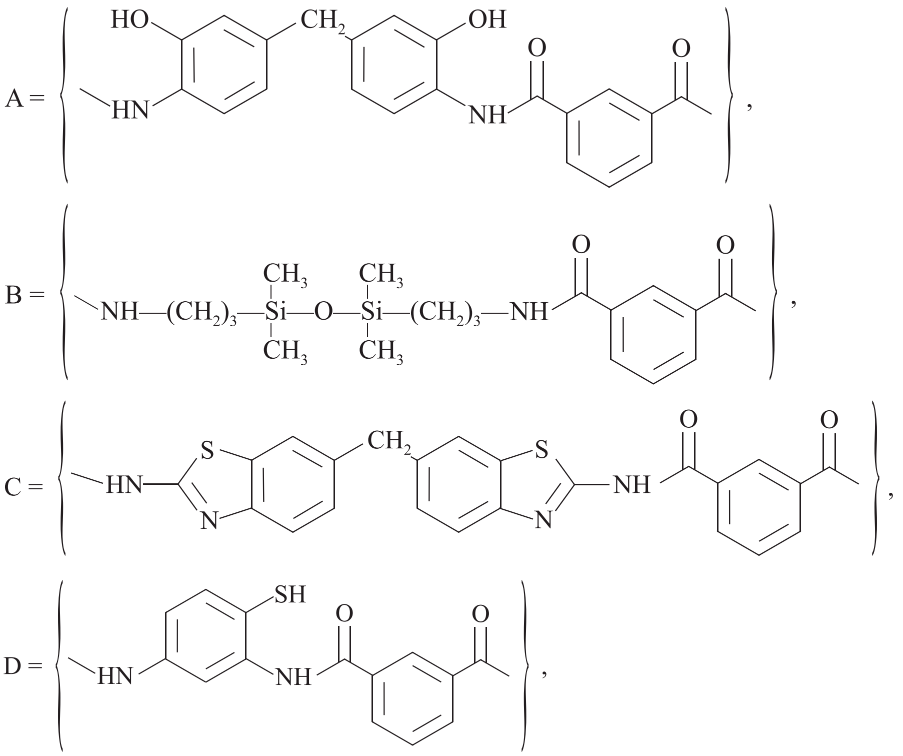
Previously [23] we studied the adhesion of films of photoresists based on silicon-containing poly(amido-*o*-hydroxy amides) with different content of $–(CH_3)_2SiOSi(CH_3)_2–$ fragments to supports of different chemical nature. The POA-Si copolymer II with the fragment ratio $m : k = 0.6 : 0.4$ showed the best properties.

Data on the adhesion of films of photoresists based on POA I and POA-Si II, formed on different supports, are given in Table 1. The adhesion of photoresist films was evaluated by the number of squares with the microrelief, peeled of onto SP 3007 adhesive tape, in accordance with ISO 2409 standard (GOST 31149–2014: Paint-and-Varnish Materials. Determination of the Adhesion by Cross-Cut Test).

For the photoresist based on copolymer II, we observed virtually no peel-off of fragments of the formed photorelief onto the adhesive tape from all types of supports; therefore, such polymer can be recommended for making microrelief layers both on

Scheme 1.

I = A_n; II = $(A_mB_k)_n$; III = $(A_mC_k)_n$; IV = $(A_mD_k)_n$, where



$m = 0.6$ (II); 0.8 (III, IV); $k = 1 - m$.

Table 1. Adhesion of films of photoresists based on POA I and POA-Si II, formed on supports of different chemical nature

Polymer binder of photoresist	Support type	Number of peeled-off squares of the photorelief formed in the film[a]
I	Si	28/100
I	SiO_2	46/100
I	Si_3N_4	40/100
I	Al	5/100
II	Si	0/100
II	SiO_2	0/100
II	Si_3N_4	2/100
II	Al	5/100

[a] Developer: 0.3% aqueous KOH for the photoresist based on polymer binder I and 0.6% aqueous KOH for the photoresist based on polymer binder II.

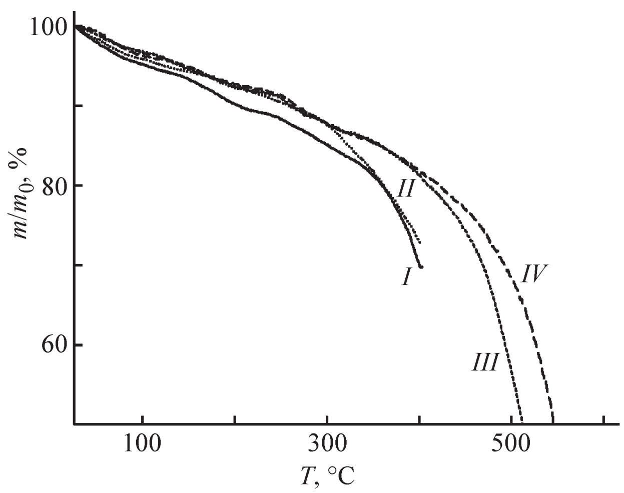


Fig. 1. Curves of thermal gravimetric analysis of powdered samples of POA I–IV.

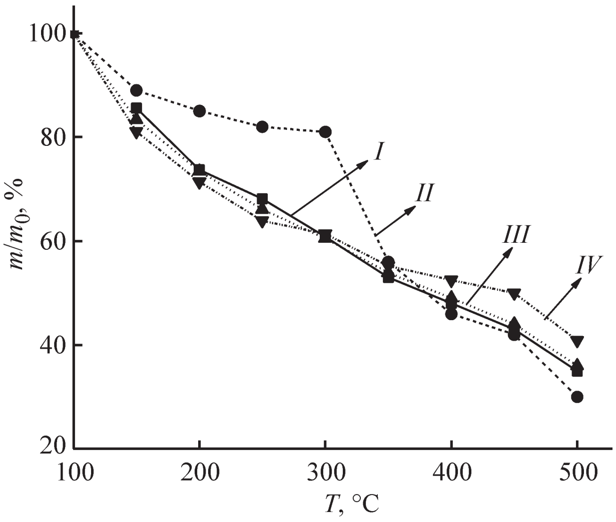


Fig. 2. Weight loss of films of polymers I–IV, formed from reaction solutions on a Si substrate under the conditions of stepwise heating to 500°C with a step of 50°C and keeping for 15 min at each temperature.

the above-mentioned types of supports and on silicon substrates with metal routing.

We studied the heat resistance of powders prepared by precipitation of the synthesized polymers from reaction lacquers; of films formed from reaction solutions of polymers I–IV on Si supports; and of photoresist films based on them (Figs. 1–3).

The lowest weight loss in the course of heating up to the onset of degradation is observed for copolymers II–IV, and the highest weight loss, for base polymer I (Fig. 1), in agreement with the content of units capable of cyclodehydration. The temperatures τ_5 and τ_{10}, corresponding to the 5 and 10% weight loss, respectively, relative to the initial polymer weight after the removal of water, solvents, and low-volatile components are, respectively, 366 and 385°C for I, 327 and 360°C for II, 397 and 437°C for III, and 406 and 450°C for IV. Lower values of these temperatures for copolymer II can be attributed to thermal instability of the –Si–C– bond [24]. According to [18], the presence of benzothiazole fragments should enhance the heat resistance of the copolymers. Our studies confirmed this assumption. The presence of even 20% benzothiazole fragments, along with benzoxazole units, in the base matrix I after the cyclodehydration enhances the heat resistance of the polymers formed by 50–65°C (copolymers III and IV).

In the course of stepwise heating to 250°C, the weight loss of the films formed from the reaction solutions of polymers I–IV is associated with the degradation of the residual low-molecular-mass fractions, and it is higher than that for the corresponding powdered samples (Figs. 1, 2). The polyheterocyclization of POA and PMA with the formation of benzoxazole and benzothiazole rings occurs at 300–350°C and is accompanied by ~20% weight loss. The lowest weight loss is observed for copolymer II, and this result, as for the powdered samples, correlates with the content of units capable of cyclodehydration.

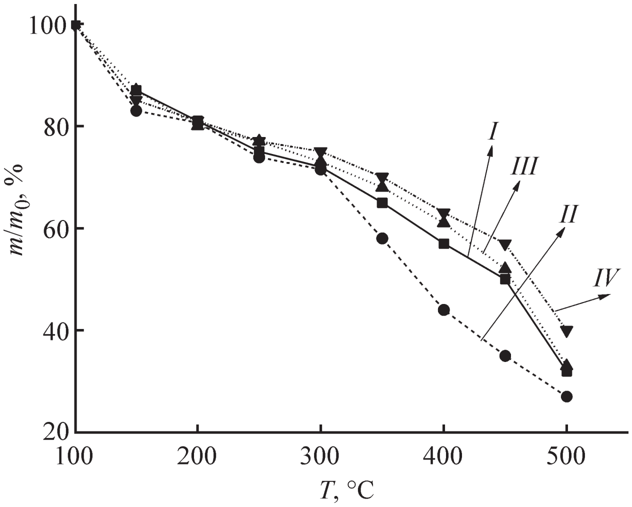


Fig. 3. Weight loss of films of photoresists I–IV, formed on a Si substrate under the conditions of stepwise heating to 500°C with a step of 50°C and keeping for 15 min at each temperature.

Table 2. Dielectric parameters of polymer and composite coatings

Polymer binder/support	Filler	ε′	tan δ
(I)/Si/Pt	–	3.4	0.02
(II)/Si/Pt	–	3.5	0.01
(III)/Si/Pt	–	3.7	0.03
(IV)/Si/Pt	–	8.0	0.02
(I)/Si/Pt	PZT-1-1	23–185[a]	0.04–0.08[a]
(II)/Si/Pt	PZT-1-1	10.0	0.04
(III)/Al foil	PZT-1-1	15.0	0.03
(IV)/Al foil	PZT-1-1	38.0	0.1

[a] Data for a series of specimens with different film thickness, range 3–15 μm.

It should be noted that the thermal curing of the polymer films was not accompanied by their peel-off, and there were no flaws and cracks in the films.

Data on the heat resistance show that introduction of 40% Si-containing units as modifying fragments into the base polymer molecule (copolymer II) leads to an approximately 30°C decrease in the heat resistance, whereas introduction of even 20% sulfur-containing fragments considerably enhances the heat resistance: For films of IV, it is higher by 40–60°C.

The characteristic features of the curves and the relationships of the thermal degradation of photoresist films are similar to the relationships of the weight loss of the films formed from reaction polymer solutions (Fig. 3).

The results of measuring the electrophysical parameters of the polymer and composite coatings are given in Table 2. For all the polymer matrices, the values of tan δ were in the interval 0.01–0.03. The lowest value of tan δ was observed for polymer II. Modification of the initial polymer I with benzothiazole rings did not lead to a noticeable increase in tan δ, but for the most heat-resistant copolymer IV the dielectric permittivity ε′ considerably exceeded that of the initial polymer I (Table 2). Such an increase in the dielectric permittivity can be attributed to increased polarity of the structure of copolymer IV, caused by the asymmetric structure of the polymer unit. In combination with the resistance to temperatures of up to 480°C, this fact allows copolymer IV to be recommended as the most promising for the use as a polymer matrix for dielectric composites with increased dielectric permittivity.

Introduction of PZT-1 filler, as expected, increases both ε′ and tan δ. The reached values of ε′, depending on the degree of loading with the ferroelectric filler, are in the range 10–185, and the maximal values of tan δ do not exceed 0.1. Such value of tan δ in the composite based on copolymer IV is most likely due to an increase in the degree of loading with the ferroelectric filler, rather than to parameters of the polymer matrix.

The minimal value of tan δ = 0.03 was observed for composite coatings based on polymer matrix III. As shown in [22], owing to specific process features of preparing composite coatings, ε increases with the coating thickness, because the degree of filling of the composite with the ferroelectric filler increases also. The corresponding dependences for the POA I/PZT-1 composite are given in [22]. The maximal value of ε = 185 in the experimental samples of the composite coatings corresponds to no more than 35 vol % filling with the ferroelectric filler. It should be noted that the structure and hence the dielectric parameters of the composite coating can depend on the material and on the state of the surface of the support used. However, in this case for the coatings of equal thickness prepared on Si/Pt supports and Al foil we observed no differences in the dielectric parameters exceeding the uncertainty of their determination (±10% for ε and ±0.01 for tan δ).

As shown in [22], the composite coatings consisting of polymer matrix I and PZT-1 as a filler are characterized by the stability of ε′ (temperature stability up to 300°C and frequency stability up to 10^7 Hz) and, correspondingly, of the capacitance of the capacitor structures. Because the temperature stability ε′ of the composite with a ceramic ferroelectric filler is largely ensured by the characteristics of the polymer matrix, enhanced (up to 480°C) heat resistance of sulfur-containing polymer matrices allows us to expect wider range of the temperature stability of ε′ for the ferroelectric composites based on this polymer.

The electrophysical parameters, heat resistance, film formation ability, and adhesion characteristics allow copolymers II–IV to be recommended for use in multilevel integrated circuits both as high-heat-resistance organic dielectrics and protective coatings and as promising polymer binders in composite film dielectrics for heat-resistant capacitor structures with high specific capacitance and low loss.

CONCLUSIONS

(1) Structurally related high-heat-resistance poly(amido-*o*-hydroxy amides) with tetramethylsiloxane and heteroaromatic (benzoxazole, benzothiazole) fragments incorporated in one of the amine components or formed by the polyheterocyclization of the prepolymers were prepared, and a comparative study of their heat resistance and electrophysical parameters was made.

(2) Incorporation of the tetramethylsiloxane fragment into poly(*o*-hydroxy amide) considerably enhances the adhesion of the films of the resulting polymer to Si-containing supports but decreases the heat resistance of the cyclized polymer and its films by 30–40°C relative to the base poly(benzoxazole). The heat resistance of the sulfur-containing cyclized polymers exceeds that of poly(benzoxazole) by 40–60°C.

(3) Polymer/PZT-1 ferroelectric film composites with increased dielectric permittivity, based on the polymer binders obtained, were investigated. The examined ways of modification of the polymer matrix do not lead to an increase in the dielectric loss in the composite films.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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