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Preparation of films based on β-diketophosphazene and different amines and study their properties

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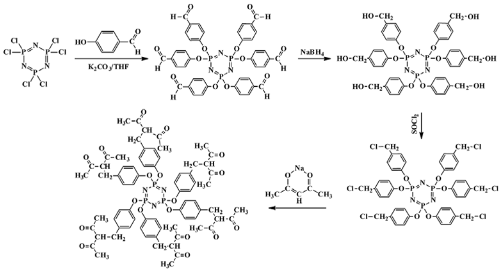
HIGHLIGHTS

- Cyclophosphazene, containing beta-diketo groups in organic radicals, were synthesized and study.
- The polymers based on these compounds and various amines were received.
- Obtained polymers are polyimines (Schiff base polymers).
- Polymers were tested for water repellency, heat resistance and adhesion to the glass.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of the work was to prepare the films on base of β-diketophosphazene and amines and to study their properties. The diketo-function-containing aryloxycyclotriphosphazene was synthesized by reaction of hexakis (4-chloromethylphenoxy)cyclotriphosphazene with sodium acetylacetonate. It has been established that the optimal solvent for this reaction is dimethylformamide. The chemical structure of the synthesized diketophosphazene was characterized by Fourier transform infrared spectroscopy (FTIR), ^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance (NMR) and MALDI-TOF mass-spectrometry. The synthesized diketophosphazene was used to obtain polymers, which were characterized by infrared spectroscopy. In addition, all these polymers were used for films preparing, which were tested for hydrophobicity, heat resistance (TGA) and adhesion to glass. It was found that the obtained film, which were made using diketophosphazene and α,ω-bis(3-aminopropyl)oligodimethylsiloxane, demonstrates the best operational properties. This film is quite flexible, its decomposition temperature is 320 °C, adhesion value to glass is 1 by ISO 2409: 2007, and the contact angle is 101°. The obtained films can be used in the form of metal complexes in the OLED technology.

1. Introduction

Phosphazene compounds represent a significant scientific and practical interest, especially for obtaining and modification of polymers. Introduction of phosphazene fragments into polymer structures is able to enhance their useful properties. Thus, addition of appropriate phosphazenes to epoxy resin [1–3], polylactides [4], poly(oxyalkylene) monoamines [5], polyethyleneterephtalate [6], polymethylmethacrylate [7], cotton [8] increases heat setting and decreases combustibility of the obtained polymers. However, the properties of phosphazenes is highly dependent on side substituents of the phosphorus atoms. For example, fluorinated phosphazenes are excellent

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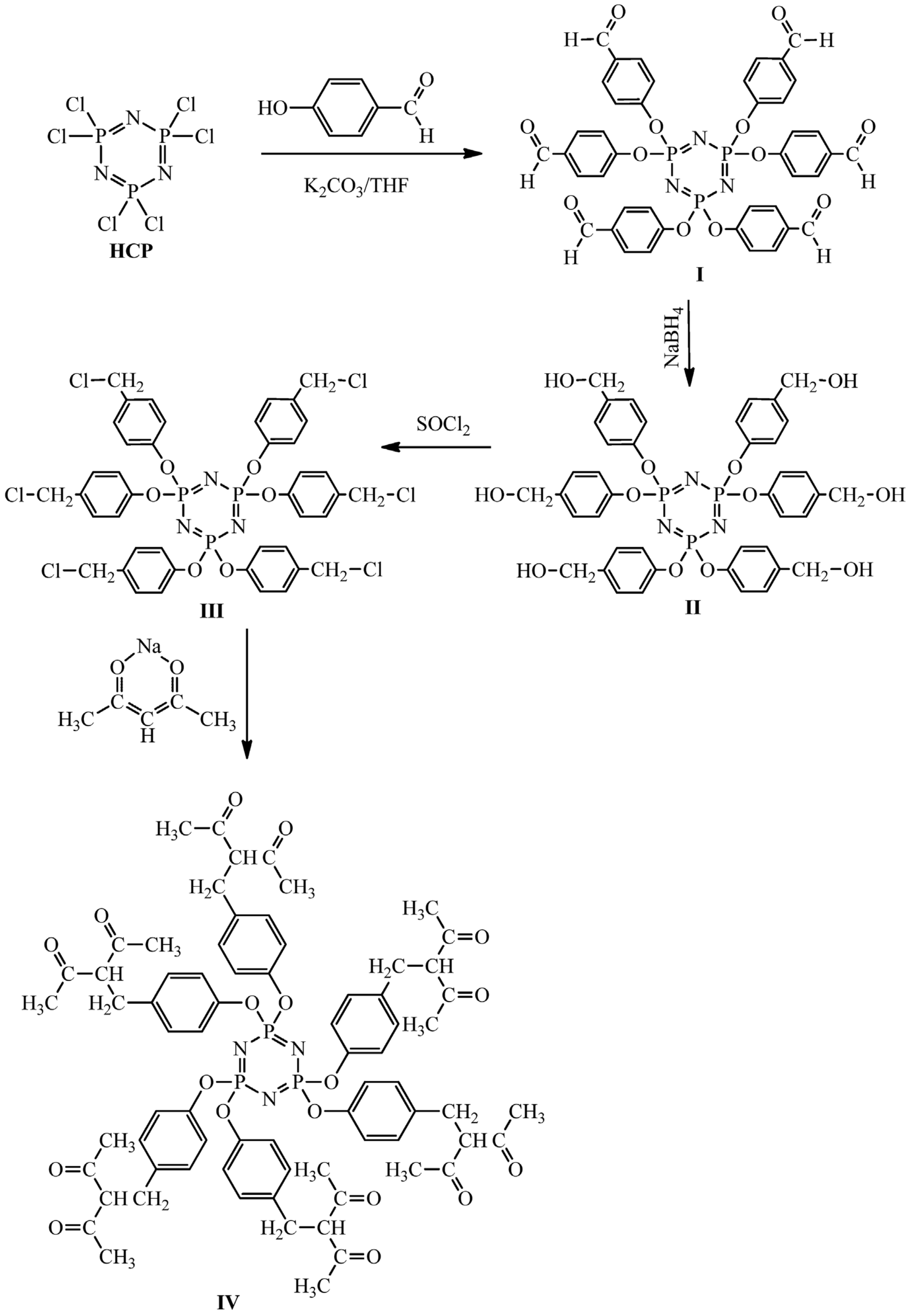


Scheme 1. Synthesis of diketophosphazene.

lubricants, but they are hydrolytically unstable [9], and cyclophosphazenes included to polylactides undergo rapid biodegradation [10]. Meanwhile, carboxyl-function-containing phosphazenes are able to improve mechanical properties and adhesion of stomatological materials to dental tissue and metals [11,12]. Phenoxyphosphazenes based dendrimers increase heat resistance and luminescence properties [13]. However, it's impossible to regulate the intensity and wavelength in this case. Regulation of fluorescence in phosphazene compounds can be provided by addition of different kinds of metals if there is a ligand in the structure that may form complexes. It is more efficient to use β-diketones as this kind of ligand that may form chelate complexes [14–16] with almost all metals. The introduction of diketo groups into the phosphazene ring will produce a polydentate chelating ligand. It is known that europium complexes with such kind of ligands have higher quantum fluorescence yields [17]. Introduction this complexes into polymer will expand the scope of their application. Wherein, it's needed

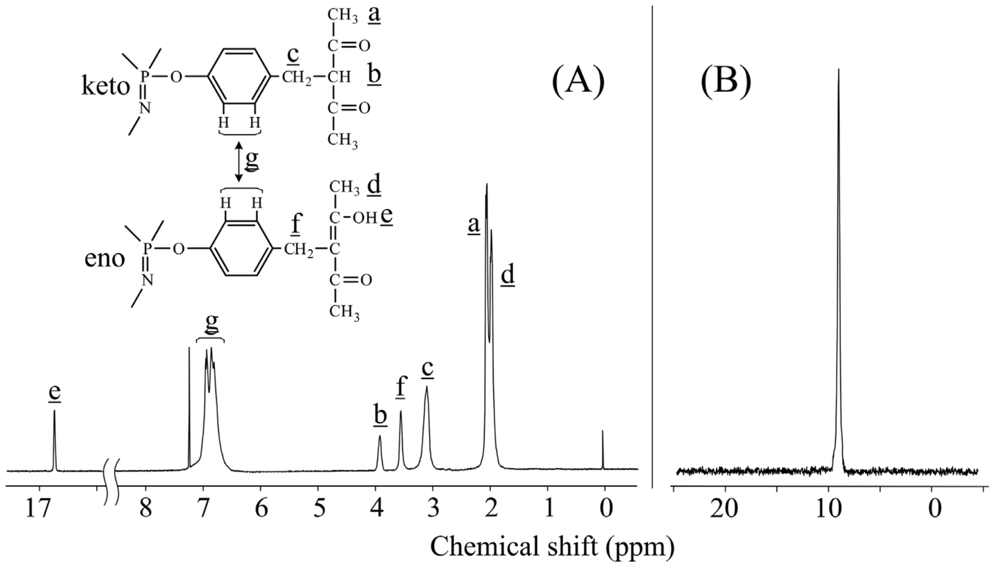


Fig. 1. ^1H (A) and ^{31}P (B) NMR spectrum of compound **IV**.

that complex or ligand formed a homogeneous structure with a polymer for stability of composition and to improve properties. For this purposes we can use ligand or complex as a monomer. It is well-known, that β-diketones are able to react with amines to form polymers [18]. The resulting ketoamino groups are also capable of complexing, i.e the functionality of a polydentante ligand based on β-diketo groups does not change after the reaction with amines. The aim of this study was the synthesis of β-diketo phosphazene, its reaction with various amines and the study of the properties of the resulting polymers.

2. Experimental

2.1. Materials

4-hydroxybenzaldehyde, 1,6-hexanediamine, acetylacetone, m-phenylenediamine, sodium iodide and thionyl chloride were purchased from Acros Organics. Sodium borohydride was purchased from Sigma-Aldrich Corporation. α,ω-bis(3-aminopropyl)oligodimethylsiloxane (DAS) and 3-aminopropyltriethoxysilane (APTES) were purchased from Penta 91. Tetrahydrofuran (THF), dimethylsulfoxide (DMSO) and chloroform were purified by distillation and dried with molecular sieves type 10Å before use. Ethanol was dried with aluminium amalgam. Hexachlorocyclotriphosphazene (HCP) was prepared as described in literature [19] and purified by recrystallization from dry hexane.

2.2. Measurements

^{31}P and ^1H NMR spectra were obtained on a Bruker AV400 NMR spectrometer using $CDCl_3$ as the solvent. MALDI mass spectra were recorded using Bruker autoflex speed instrument operated in the positive reflectron mode. The analyte (2 mg/mL, THF) was mixed with matrix solution (2,5-dihydroxybenzoic acid; 20 mg/mL, THF) in 1:2 v/v ratio. The mixture was dripped on a steel target (MTP 384 ground steel; Bruker Daltonics Inc., Germany) and air dried. The IR spectra were recorded on a FTIR spectrometer Nicolet 380 with the FTIR prefix spectrometer in the transmission mode in the range 4000–400 cm^{-1}. The thermogravimetric studies were conducted on a Derivatograph_C instrument (MOM, Hungary) in argon with the use of ~10 mg samples. The heating rate was 10 °C/min. Differential scanning calorimetry measurements were made using a DSC-822e calorimeter (Mettler-Toledo, Switzerland) (20 °C/min). Adhesion was measured in accordance with GOST R 54563–2011 (ISO 2409:2007). Water contact angles were measured using the Goniometer LK-1and «Drop Shape» software.

2.3. Synthesis of compounds I-III

Compounds I and II was prepared as described in Ref. [20]. Compound III was prepared as described in literature [21].

2.4. Synthesis of diketophosphazene (IV)

Sodium acetylacetonate (7.32 g, 0.06 mol) and sodium iodide (0.1 g) was dissolved in DMF (100 mL). Then the solution of hexakis(4-chloromethylphenoxy)cyclotriphosphazene (**III**) (4.92 g, 0.005 mol) in DMF (50 mL) was added to the first solution at room temperature. The reaction mixture was stirred with magnetic stirrer for 24 h at room temperature. Then solution was poured into 500 mL of water with vigorously stirring. The precipitate was filtered and purified by recrystallization from chloroform-ethanol mixture. Final product was dried under vacuum for 2 h at 50 °C.

Yield: 70%. ^{31}P NMR δ 9.1 (s). MS (MALDI-TOF) *m/z* 1366 $[M + H]^+$; 1388 $[M + Na]^+$ (calc. *m/z* 1365). Found % C 63.12; H 5.84; P 6.92; N 3.01 (calc. % C 63.30; H 5.71; P 6.81; N 3.03).

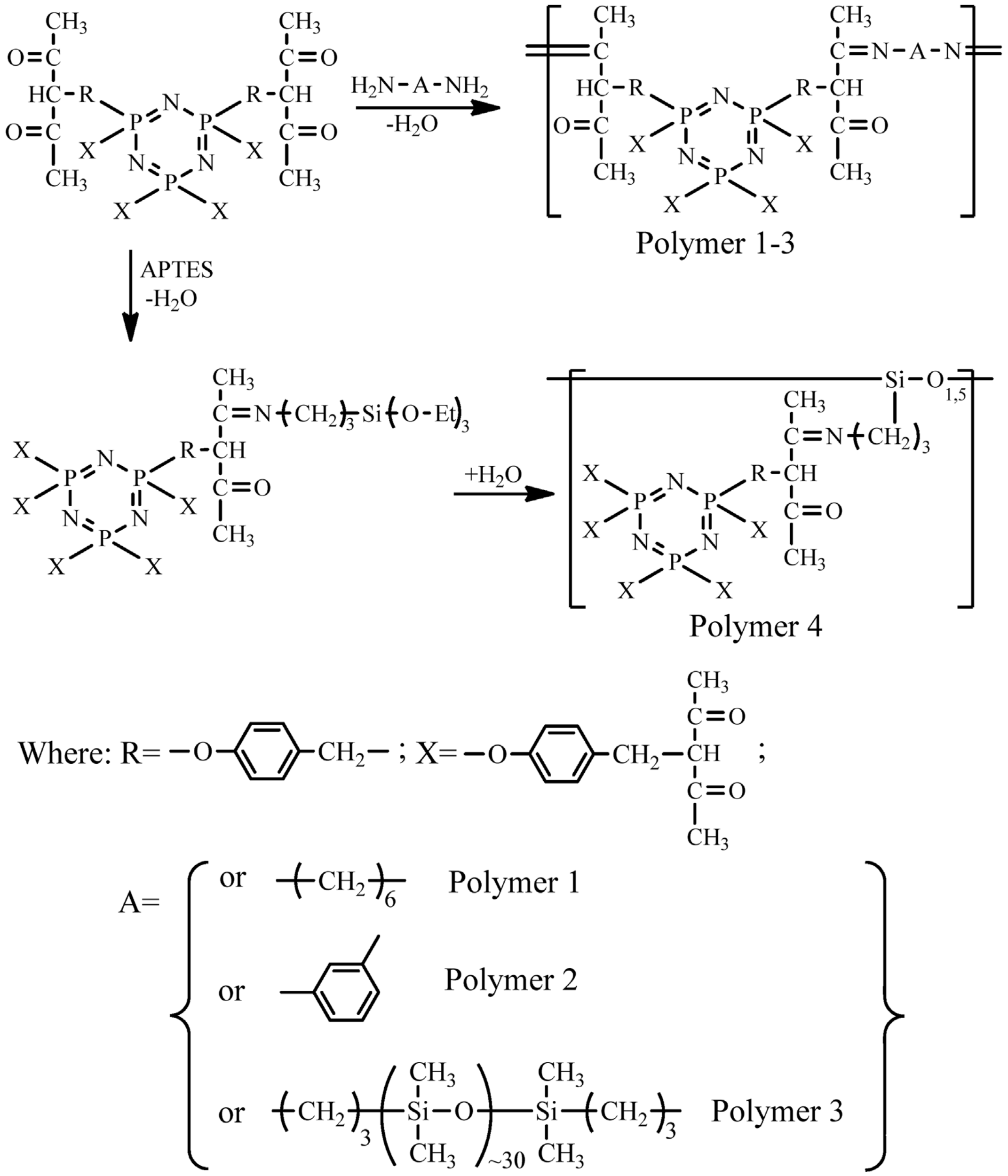
2.5. Preparation of solutions for the production of films based on amines

(**IV**) (0.5 g, 0.366 mmol) and 0.366 mmol amine (0.0425 g 1,6-hexanediamine or 0.0395 g m-phenylenediamine or 0.838 g DAS or 0.243 g APTES) were dissolved in chloroform (5 mL) and then 0.1 g $MgSO_4$ was added. The reaction mixture was stirred at room temperature for 12 h.

2.6. Film preparation

Two types of films were prepared. For the study of films on the hydrophobicity and adhesion the solutions, which were obtained in paragraphs 2.5, pre-separating from the desiccant. The reaction mixture was poured on a glass surface (Polymer 4) or glass surface coated by APTES (Polymers 1–3). Chloroform was evaporated at room temperature, and the sample was then heated in a muffle oven at 50 °C to constant weight. The thickness of the obtained film varied from 45 to 125 μm (determined by ISO2808).

To determine the glass transition temperature and heat resistance of polymers, filtered solutions (described in paragraphs 2.5) poured on



Scheme 2. Synthesis of polymers based on the **IV** and various amines.

cellophane film, dried in a muffle oven at 50 °C to constant weight. Then the film was separated from cellophane and carried out TGA and DSC analysis.

3. Results and discussion

The direct attachment of β-diketones to the phosphazene ring lead to O-acylation and the resulting ester is not capable of forming complexes [22]. Therefore, the more efficient method to obtain diketo-function-containing cyclotriphosphazene could be provided through organic fragment in several stages as shown on Scheme 1.

The attachment of diketones to a carbon atom may occur in case of using an alkyl halides in aprotonic media. However, the introduction of alkyl halides into phosphazenes in one step is impossible due to side reactions. At the first stage it was decided to substitute chlorine atoms in the HCP for 4-formylphenoxy group. The 4-hydroxybenzaldehyde was used because the aldehyde group is inert to HCP, also in that case p-position is sterically available. Furthermore, aryloxy radical is thermally stable and not prone to phosphazene-phosphazane rearrangement. The second step was the reduction of the aldehyde group to alcohol group. The reaction was carried out with sodium borohydride that is well known reduction agent.

Then, the compound **II** was treated with thionyl chloride, thus obtaining a benzyl chloride group capable of reacting with diketones by a carbon atom to form **IV**.

Sodium acetylacetonate, obtained from the reaction of sodium metal with a slight excess of acetylacetone in ethanol, was used for C-alkylation. The excess of acetylacetone could be easily removed by evaporation with ethanol.

The reaction between **III** and a large excess of Na acetylacetonate (AcAcNa) was provided at room temperature (to avoid the side reaction of O-alkylation) in DMF. A small amount of sodium iodide was used as a catalyst. The substitution of chlorine atoms in compound **III** was provided completely and without any side reactions, which can be confirmed by ^{1}H NMR spectrum (Fig. 1A). Due to keto-enol tautomerism in the spectrum are observed two forms: keto-form and eno-form.

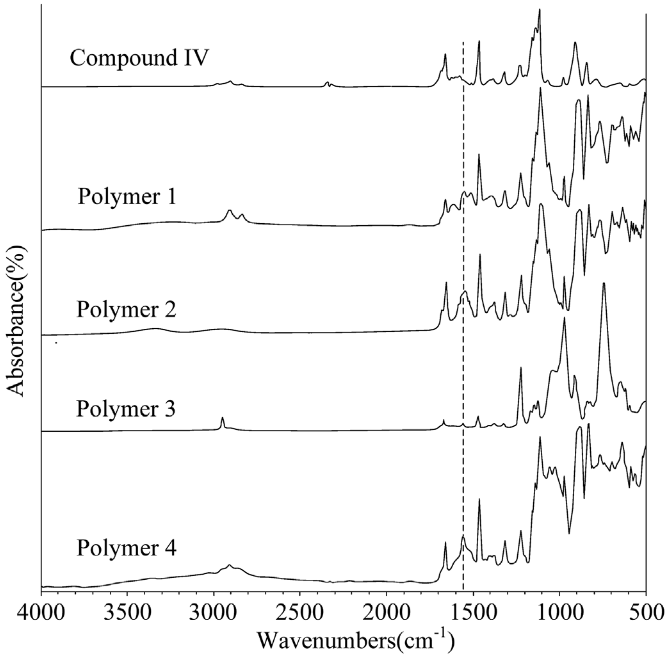


Fig. 2. FTIR spectra of the synthesized polymers.

Table 1
Content of gel fraction, water contact angles and adhesion to glass for synthesized films.

	Polymer 1	Polymer 2	Polymer 3	Polymer 4
Gel fraction, % mass	93	93	94	98
Contact angle, deg.	70	67	101	99
Adhesion	2	3	1	0

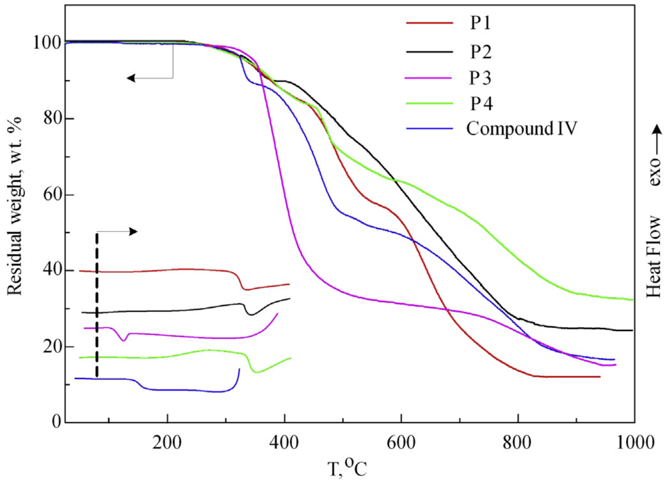


Fig. 3. TGA and DSC curves of compound **IV** and synthesized polymers.

Tautomerism makes a significant difference in the chemical shifts of the protons signals methyl and methylene groups. Also for the enol form, the presence of the proton signal of the OH group in the weak field area of 16.7 ppm is characteristic.

In ^{31}P NMR spectrum (Fig. 1B) is a singlet in the area 9.8 ppm. It indicates that the reaction between compound III and AcAcNa proceeds without affecting the phosphazene cycle.

Since diketones are capable of forming a Schiff base, we have selected several amines to obtain the polymers. In order to achieve a broader variety of properties of the resulting polymers we used amines of different types. The organic-aliphatic (hexamethylenediamine for polymer 1 preparation) and the aromatic amines (m-phenylendiamine for polymer 2 preparation) were used. Also we used silicones with low molecular weight (APTES for polymer 4 preparation) and with high molecular weight (DAS for polymer 3 preparation). The formation of the respective polymers proceeded according to Scheme 2.

The reaction between amines and **IV** was carried out in chloroform using magnesium sulfate to get rid of released water. Films were cast from the resulting solution. IR spectra of the obtained polymers are shown in Fig. 2. The presence of the stretching vibrations of C = N bonds in 1560 cm^{-1} confirms that azomethine groups were formed while in the original compound this type of vibration is absent.

The obtained polymers have cross-linked structure. The content of gel fraction was determined by extraction, the data are listed in Table 1.

Films of polymers 1, 2 and 4 were brittle, and the film of polymer 3 turned out to be flexible. This fact is consistent to DSC measurements (Fig. 3) – glass transition temperature for polymers 1, 2 and 4 is 320, 335 and 340 °C respectively. In while, polymer 3 has glass transition temperature equal 115 °C. The only explanation of this fact is a the siloxane long chain flexibility of polymer 3. In other cases, polymers were formed from short sterically obstructed links.

The decomposition of compound **IV** in air proceeds in several stages. The first decomposition stage is occurs in the area of 350 °C (Fig. 3). The sample loses up to 10% of its initial weight at this step. Then, the weight remains unchanged, up to 420 °C. The rise in the temperature leads to the development of further destructive processes which ends near 1000 °C. According to TGA, the temperature of the synthesized polymers decomposition is practically the same and lies in the region of 400 °C, which is slightly higher than the temperature of initial stage of diketophosphazenes **IV** destruction. It should be noted that the weight loss for polymer 3 at this decomposition step is close to 70%, while polymers 1, 2 and 4 lose only about 10 wt%. The last three samples are characterized by a plateau at higher temperatures on the TGA curves, in a manner analogous to that for the compound **IV**. The presence of a plateau suggests the occurrence of diketo groups condensation, accompanied by the release of water. Such reactions is described in Ref. [23]. High condensation temperature for polymers 1, 2 and 4 compared to compound **IV** is due to the rigidity of their chains, which makes it more difficult for diketo groups to access each other. In the case of polymer 3, the plateau is absent and as noted above, weight loss at this stage of decomposition reaches 70%. As a result, degradation of polymer 3 occurs with the formation of volatile cyclosiloxanes, which leads to a rapid loss of sample mass. The thermal transformations in the investigated polymers end in the region of 800–1000°C and the mass of the solid residue lies in the row 4 > 2 > 3 > 1.

As can be seen from Table 1, polymer 4 demonstrates the best adhesion to glass. High adhesion is probably observed due to the interaction between the silanol groups existing on the glass and polymer 4 surfaces. Also, polymer 3 has high adhesion, which is supposedly achieved due to the high flexibility of the polymer chains (internal plasticization), and hence easy access of diketo group of polymer to the amino groups of the coating deposited on a glass surface. The dried films of polymers 1 and 2 are partially cracked and deformed, thus it have poor adhesion.

Measurement of the water contact angles of the films showed (Fig. 4) that polymers 3 and 4 demonstrate the highest hydrophobicity. This fact can be explained by the high water-repellent ability of long fragments of dimethylsiloxane (polymer 3) and nonpolar silsesquioxane structure of polymer 4. Short aliphatic and aromatic chains in polymers 1 and 2 are not capable of giving films with water repellency properties, so hydrophobicity of these polymers is relatively low.

4. Conclusion

The diketo-function-containing aryloxycyclotriphosphazene **IV** was synthesized for the first time, it was characterized by ^{1}H and ^{31}P NMR

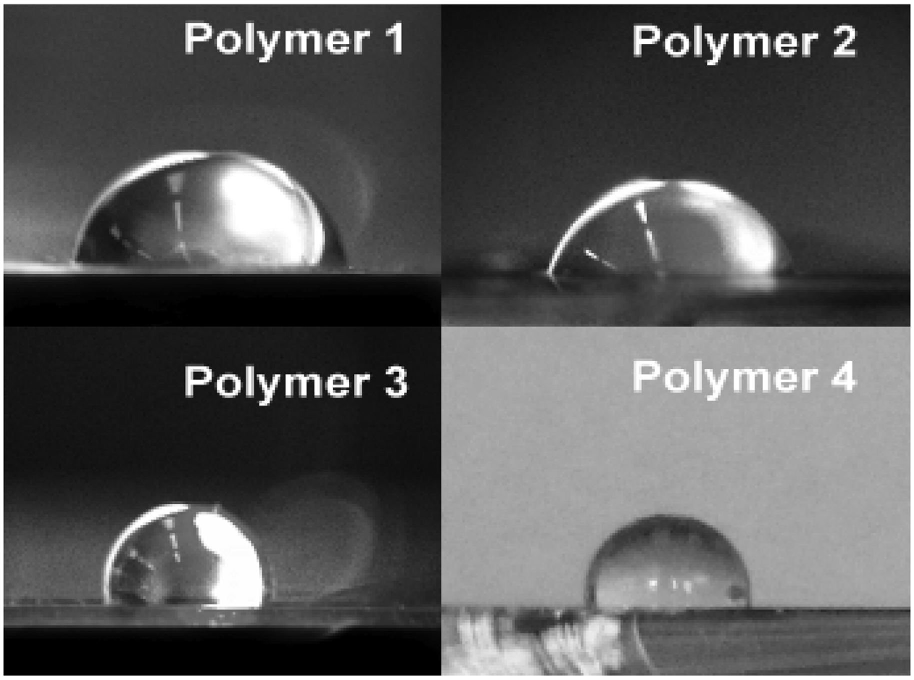


Fig. 4. Photos of water droplets deposited on films of synthesized polymers.

and IR spectroscopy. Polymer films were obtained by interaction of **IV** with various amines. It is determined that polymer based on **IV** and (3-aminopropyl) triethoxysilane has the best adhesion to glass, but its heat resistance is slightly less than that of other synthesized polymers. Polymer 3 ranks below polymer 4 in adhesive characteristic, but insignificantly surpasses it and other polymers in hydrophobic properties and heat resistance. Hence, polymer 3 has the most appropriate exploitative properties, that can be used under quite extreme conditions. On the basis of this polymer, metal-containing films can be produced by forming complexes of diketo groups with metals. These metal complexes can be applied in OLED technology [24–26] as luminesensitive, moisture-resistant and heat-resistant materials [27].

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matchemphys.2018.11.008.

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