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INORGANIC-ORGANIC HYBRIDS BASED ON CYCLOTETRAPHOSPHAZENES

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Organic cyclic and oligoaminoacid derivatives of cyclotetraphosphazenes were synthesized and characterized. WAXS and DSC methods were applied to the bulk and LB-films study, being different crystalline structures are shown both for initial cyclotetraphosphazenes and for their organic hybrids.

Keywords: cyclotetraphosphazenes; oligoaminoacids; crystalline structure

INTRODUCTION

Cyclophosphazenes and their derivatives are attractive subjects for current chemical, physical and biological study. Structures of the unique polymers, such as dendrimers and arborols can be obtained on the cyclophosphazene basis [1]. On the other hand, the unusual low molecular compounds (f. ex. adamantane and triptamines derivatives) were prepared by chlorine atoms substitution in cyclophosphazenes [2,3]. These Research permit to investigate different properties, thermal and oxidative stability, lipophilicity, bioactivity and biocompability. Taking in account great amount of papers concerning cyclotriphosphazene modification, we concentrated attention

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on octachlorocyclotetraphosphazene (OCTP) transformation. It was necessary to prepare pure crystalline OCTP and substituted CTP as initial reagents. We described as well 5-methoxytryptamine containing cyclotetraphosphazene, olygoalanyl- and olygoglutamyl- derivatives of cyclotetraphosphazene. WAXS data shown discotic-like structures for few compounds, the loss of crystalinity is noticed for olygomeric forms of CTP, although their LB-films can contain some crystalline domains.

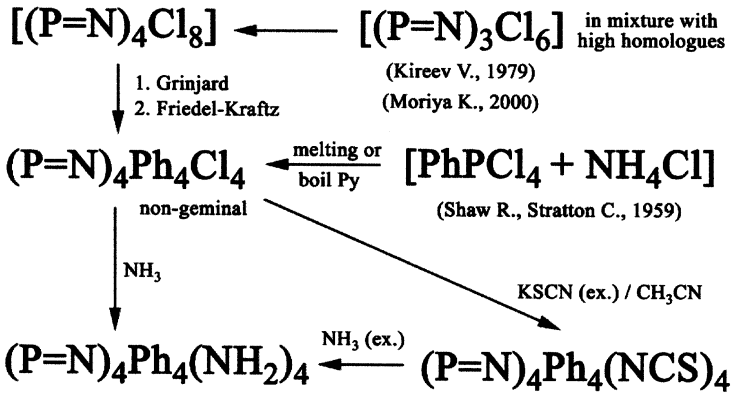
SUBSTITUTION IN OCTACHLOROCYCLOTETRA-PHOSPHAZENE BY LOW MOLECULAR COMPOUNDS

General conversion of cyclotetraphosphazenes and synthesis of inorganic low molecular synthons are represented by Scheme 1.

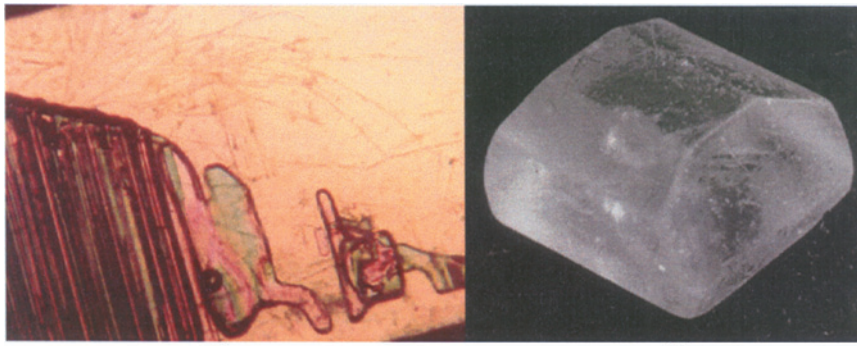
We could use two ways at least for our purposes: the substitution of chlorine atoms in OCTP directly or in defined non-geminal intermediate compounds for variant isomers decreasing.

Early we have described OCTP preparation by cyclo-widening reaction in fusion [4]. The yield of tetramer is depended upon purity and ideal crystallinity of initial cyclophosphazenes (mixture of tri- and tetra-) strongly. Analysis of publications and own results on morphological and optical investigations confirmed symmetry of OCTP as tetragonic syngony, trimer possess rhombic syngony, both compounds relate to planexial type with D_{4R} (4/mmm). Optical constants are different, being OCTP has bright interference, Figure 1.

Using of non-geminal tetraphenyltetrachlorocyclotetraphosphazene (TPTCP) is more suitable, than OCTP, so we can carry out easy two next



SCHEME 1 Conversion of cyclotetraphosphazenes. Synthons preparation.



1a 1b

FIGURE 1 1a. Microphotography of crystalline piece of hexachlorocyclotriphosphazene with octochlorocyclotetraphosphazene inclusion (500x increasing polarization microscope). 1b. Ideal monocrystal of high-pure hexachlorocyclotriphosphazene.

reactions: tetraamine - and tetrraisocyanate - functional cyclophosphazene preparation, Scheme 1, Table 1.

Aminolysis of TPTCP by 5-methoxytriptamine and 1-pyrenylbutirylhydrazide result to di- and tetrasubstituted tetraphenylcyclotetraphosphazene, Figure 2.

OLIGOAMINOACID DERIVATIVES OF CYCLOTETRAPHOSPHAZENE

N-Carboxyanhydrides of γ-methylglutamate (γ-Me-Gly-NCA) and Alanine were polymerizated by action with tetraphenyltetraaminocyclotetrapho-

TABLE 1 Properties of Synthesized Synthons

	Yield, %	M.p., °C	IR, cm^{-1}	^{31}P NMR	^{1}H NMR
$(P{=}N)_4Ph_4(NCS)_4$	85–90	154	1990–2000 (NCS) 1440 (P-Ph) 1300 (P=N)	−12.1 (singl.)	8.2 (Ph)
$(P{=}N)_4Ph_4(NH_2)_4$	30–50	225	3400 (NH_2) 3380 (NH_2) 1440 (P-Ph) 1300 (P=N)	−3 (singl.)	8.8 (NH_2) 6.5–7.1 (Ph)

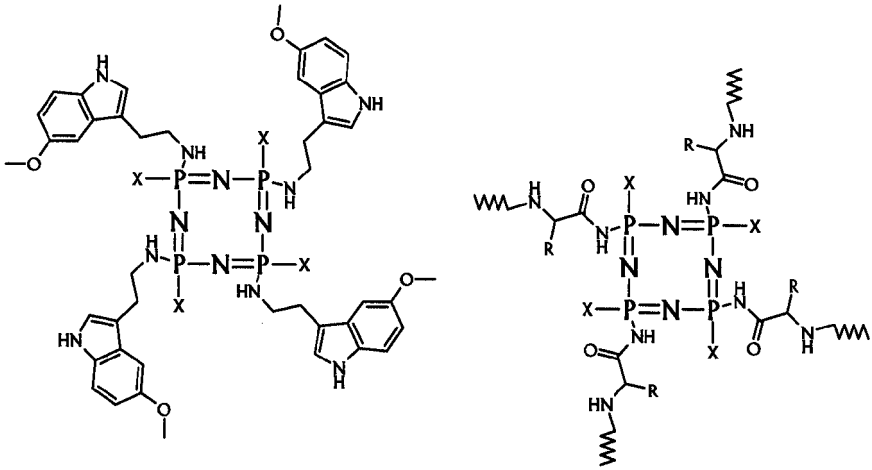


FIGURE 2 Chemical structures of the cyclotetraphosphazenes.

sphazene (TATP) as initiator, Figure 2. Reaction is existed in dimethylformamide at room temperature under an atmosphere of dry argon and at different molar rations of NCA/TATP. The molecular weight of olygomers calculated from the NMR-^{1}H data and gel-permittion chromatography measurement, n = 40, MM = 6000, n = 20, MM = 3100. Symmetric replacement of olygoaminoacid chains on the inorganic plate could result to induction of α-helical conformation (4-helix bundle) that was noticed for porphirine and pyridine – functionalized templates [5]. This event is achieved when metallocompounds taked place inside cycliophosphazene.

STRUCTURAL PROPERTIES

We compared initial tetrasubstituted and olygoaminoacid derivatives of cyclotetraphosphazene. As it was shown by X-ray method the synthesized species are crystalline with different degree of crystallinity. Aminosubstituted cyclotetraphosphazene is powder with large grain morphology. Its WAXS pattern contains up to 18 reflection, Figure 3, Table 2.

Isocyanate derivatives is rather crystalline also (about 7 distinct reflections). Olygoaminoacid derivatives (polymerization degree ≤ 40) have broad diffuse reflections, that is in accordance with loss of crystallinity. The ratio of d-spacing is approximately 1:2:3:4 pointing to the layered structure. The layer width is 7.8Å which is conistent with voluemn

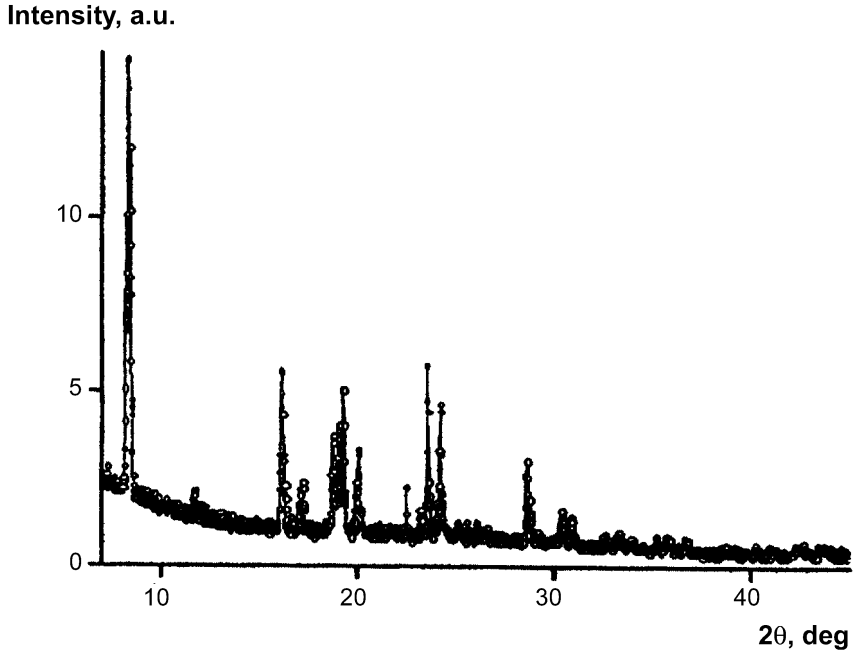


FIGURE 3 The scattering profile of $(P{=}N)_4Ph_4(NH_2)_4$.

of cyclic tetraphosphazene fragment. It was proposed the discotic shape of cyclotetraphosphazene derivatives.

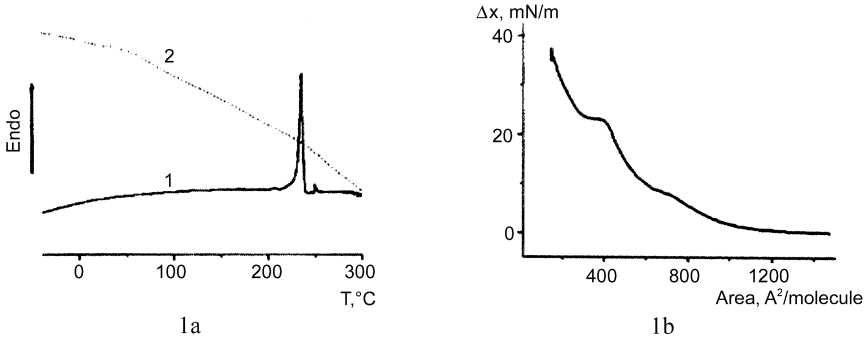
DSC study is agreed with X-ray data. On the DSC curve of the most crystalline NH_2-substituted there are three endothermic peaks at 208, 236, 250°C. Polyaminoacid chains ($n \leq 40$) lead to the less of crystallinity there is one very weak peak only, at 55°C, Figure 4.

Polyalanylderivatives have bad solubility in common solvents, however form monolayers. Polyglutamylcyclotetraphosphazene form stable monolayers and LB-films (∼40 monolayers). Character π/A isotherm is not simple, Figure 4b. Perhaps, it demonstrates crystallization domains on the surface [6], that was noticed for polyglutamic derivatives [7].

TABLE 2 D-Spacing, A

$-NH_2$	10.5	7.6	5.5	5.2	4.6	4.4	3.7	3.4	3.1	2.9	2.7	2.5	2.3	2.2	2.1	2.0	1.9
–NCS	7.8	4.9	4.6	4.2	3.9												
–n-Ala	7.5	5.3	4.5	3.7													

D8Advance Bruker, expose 4–5 h.



1a 1b

FIGURE 4 1a. DSC Data: 1 - NH_2-derivative has 3 endothermic peaks at 208, 236 and 250°C. 2 - n-Ala (n = 20) has 1 very weak peak at 55°C. Mettler 1000, Scan rate of 20°C/min at of (−50) −300°C. 1b. Langmuir isotherm of $(P{=}N)_4Ph_4(Glu)_n$, n = 20; 40.

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