Synthesis and characterization of linear multi-functional phosphazene structures for polymer cross-linking

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Abstract. Phosphazenes are a well-studied class of organometallic compounds with perspective characteristics, already tested in various applications. However, until now, three-dimensionally crosslinked structures based on them are primarily obtained by irradiation (that is UV and Cobalt-60). It is generally accepted that such processes proceed via the mechanism of the cleavage of C-H bonds present in the organic substituents, which clearly indicates the lack of selectivity and the impossibility to control the crosslinking degree and distribution. Within this article, multifunctional organosubstituted structures based on the short-chain penta-functional trichlorophosphazodichlorophosphonyl with eugenol and methacrylic fragments were obtained. All products were characterized by $^1$H and $^{31}$P NMR spectroscopy and MALDI-TOF mass spectrometry. The tendency of compounds with linear methacrylic substituents to undergo the phosphazene-phosphazene rearrangement, so that the dominant reaction product turns to the tetrasubstituted derivative, has been shown. All the obtained compounds can be used as the independent monomers to obtain rigid hybrid organo-inorganic matrices, as well as polyfunctional crosslinking agents for various polymers.

1. Introduction

Phosphazene materials have found a wide range of applications in various fields of science [1, 2]. They possess such unique and diverse properties as high thermal and chemical stability, good biocompatibility and the ease of derivatization, which makes them promising starting materials for elastomers [3, 4], polyelectrolytes [5-7], dentistry [8, 9], polymer modification [10], adsorption and extraction processes [11-13], catalysis [14], and, thanks to the discovery of chain length precise control via $\text{Cl}_3\text{P}=$NSiMe$_3$ synthesis and polymerization [15-17], drug delivery [18, 19]. However, most of these applications demand the formation of relatively hard three-dimensional polymeric matrixes with the possibility for tuning and control of cross-linking degree [20, 21]. For example, in case of polyelectrolytes the cross-linking not only improves the dimensional stability of the final material [22] but also prevents the formation of undesired dendrites [23]. As well, considering catalysts, the cross-linked ones can be recycled in comparison with non-cross-linked [24, 25]. The traditionally exploited methods for cross-linking of phosphazene chains, such as UV-irradiation, in some cases are not quite appropriate, since they can lead to chemical bond cleavages [26] and usually do not provide sufficient control of final product hardness. On the other hand, the chemical routes are more effective because the amount and the
distribution of linkable functional groups can be regulated and so the cross-linking degree can be well tuned, excluding the existence of the side processes. Hence, the investigation of novel phosphazene structures capable for further cross-linking and methods to obtain them is still of utmost importance. In this work we synthesized low-molecular-weight model multi-functional compounds on the basis of trichlorophosphazodichlorophosphonyl, which can be both monomers for three dimensional phosphonitrilic matrixes and cross-linking agents for other functional polymeric systems. These compounds contain methacrylic and eugenol groups and are promising for cross-linking by such reactions as hydrosilylation, thiol-ene reaction and radical polymerization.

2. Experimental part

2.1. Materials

Unless otherwise noted, all the reagents and solvents were purchased from commercial suppliers and used without further purification. Trichlorophosphazodichlorophosphonyl Cl₃P=N-P(O)Cl₂ (TCDP) was synthesized according to reported method [27]. After vacuum distillation white crystals (Tₘ = 32–35°C) were obtained with the 74% yield. ^{31}P NMR, CDCl₃: –3 – 4 ppm (d, Cl₃P=N–), –11 – 12 ppm (d, –P(=O)Cl₂).

All the solvents were purified by standard methods and were used freshly distilled.

2.2. Characterization methods

^31P and ^1H NMR spectra were recorded by Bruker CXP-200 spectrometer at 81 and 200 MHz respectively. MALDI-TOF mass-spectra were recorded by Bruker Auto Flex II spectrometer.

2.3. Synthesis of eugenol derivative of TCDP (TCDP-Eug)

7.22 g (0.044 mol) of eugenol and 20 mL of dioxane were charged in the three-necked flask, equipped with a magnetic stirrer and reflux condenser. Then 1.36 g (0.0444 mol) of sodium were added gradually in the form of thin plates. After the full dissolution of sodium, the solvent was totally removed. Then 30 mL of toluene was introduced, followed by the dropwise addition of 2 g (0.0074 mol) of TCDP in 5 mL of toluene solution. Reaction was carried out at room temperature for 14 h, washed with water and dried with MgSO₄. Afterwards solvent was evaporated and the product was dried under vacuum. ^31P NMR, CDCl₃: –15 – 17 ppm (d, (EugO)₃P=N–), –22 – 23 ppm (d, (–P(=O)(OEug)₂)), –10 – 12 ppm (d, Cl(EugO)₂P=N–), –22 – 23 ppm (d, (–P(=O)(OEug)₂)). The product was obtained with a 80% yield.

2.4. Synthesis of methacrylic derivatives of TCDP (TCDP-2-HEM)

TCDP-2-HEM-1: 86.83 g (0.668 mol) of 2-hydroxyethylmethacrylate (2-HEM), 377.66 g (424.72 mL) of THF and 30 g (0.111 mol) of TCDP were charged in the three-necked flask. Then 52.76 g (0.667 mol) of pyridine were added to the reaction mixture. Reaction was stirred for 6 h at room temperature. Then the mixture was poured into the solution of HCl and the precipitated product was dissolved in chloroform and washed with water. The organic layer was dried with MgSO₄ and then the solvent was rotary evaporated, yielded the desired product with a 73% yield.

TCDP-2-HEM-2: The synthesis was carried out according to the same procedure with the use of toluene as a solvent. The product was obtained with a 78% yield.

Both methacrylic products represent transparent yellowish viscous liquids.

3. Results and discussion

Synthesis of eugenol derivative TCDP-Eug was performed via two step method (Figure 1) with preliminary sodium eugenolate preparation and its further reaction with TCDP in toluene medium at room temperature. For the preparation of arylxoy derivative with the maximum substitution degree the excess of eugenolate was used and molar ratio TCDP:EugONa was 1:6. However, the final product along with the desired pentaeugenxyphosphazaphosphonyl (characteristic doublets for (EugO)₅P=N– group at –15 – 17 ppm and doublets for –P(=O)(OEug)₂ group at –22 – 23 ppm) also include some
amount of tetrasubstituted compound (doublets at $-10 \div -12$ ppm for Cl(EugO)$_2$P=N– group and $-22 \div -23$ ppm for $-P(=O)(OEug)_2$), which cannot be purified by recrystallization.

**Figure. 1** Synthesis of TCDP-Eug.

$^1$H NMR spectra of the obtained product includes the signals of the aromatic protons at 6.5 – 7.4 ppm, methoxy groups signals at 3.7 ppm and peaks at 6.0 (m, -CH$_2$-CH=CH$_2$), 5.0 (d, -CH$_2$-CH=CH$_2$) and 3.2 ppm (d, -CH$_2$-CH=CH$_2$), corresponding to allyl group protons. From the splitted character of aromatic and methoxy group signals we can conclude that these protons are not equal for eugenol substituents at phosphazenyl and phosphonyl phosphorus atoms in pentaeugenoxo- and tetraeugenoxochlorophosphazophosphonyl.

**Figure. 2** $^{31}$P (a) and $^1$H (b) NMR spectra of TCDP-Eug.

The presence of both penta- and tetrasubstituted TCDP was additionally confirmed by MALDI-TOF analysis (Figure 3).

**Figure. 3** MALDI-TOF spectrum of TCDP-Eug.
A low-intensity signal of tetrasubstituted compound (m/z = 779) is observed as well as the signals of the targeted pentasubstituted derivative (m/z = 908, 930, 946). Tetrasubstituted product formation even in the presence of sodium eugenolate excess most probably might be explained by existing steric hindrances due to the eugenol structure.

It should be noted that if the reaction of sodium eugenolate with TCDP is carried out at reflux, the side product bis(dieugenoylphosphonyl)amine can be formed by the reaction of phosphazene-phosphazane rearrangement (Figure 4) [28].

This product exhibits one singlet at –6 ppm in the $^{31}$P NMR spectrum and two signals at m/z = 762 and 785 in the MALDI-TOF spectrum (Figure 5).

Synthesis of methacrylate derivatives was conducted by the following scheme (Figure 6) with the use of THF and toluene as solvents:

Analysis of the obtained compounds has shown that the final products, regardless of the solvent used, also consist of tetra- and pentasubstituted derivatives, despite the fact that nucleophilic 2-HEM was taken in excess. There are two singlets at +0.3 and –2.5 ppm in the $^{31}$P NMR spectra (Figure 7) of the product, corresponding for tetra- and pentasubstituted derivatives, respectively.
Unlike the eugenol derivatives, the singlet character of these peaks indicates that phosphazene-phosphazane rearrangement proceeds quantitatively with the formation of the more stable phosphazane structure. The yields of the products, obtained in THF are 62 and 73%, whereas in toluene medium – 70 and 83% when calculated over penta and tetrasubstituted derivatives respectively.

4. Conclusions
In conclusion, the functional eugenol and methacrylate derivatives of trichlorophosphazophospholyl were synthesized and characterized. It was shown that, regardless of the structure of substituent, both tetra- and pentasubstituted products are formed. Moreover, for methacrylic derivative, due to its aliphatic structure, the phosphazene-phosphazane rearrangement process takes place. The obtained products, due to the presence of the functional groups, in further, are promising agents for the preparation of phosphazene-based cross-linked polymeric materials.

5. References
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