The product of interaction of elemental sulfur and dimethylphosphate 1,3-dimethylimidazolium is a new green initiator of formaldehyde polymerization

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ABSTRACT

Interaction of 1,3-dimethylimidazolium dimethylphosphate and elemental sulfur synthesized a new initiator of polymerization of formaldehyde, opening the possibility of its implementation in accordance with the principles of Green chemistry. The possibility of fast oligomerization of formaldehyde in an aqueous medium with the formation of insoluble products, the structure of which is determined by FTIR, MALDI-TOF, 1H NMR, 13C NMR, HSQC and HMBC spectroscopy, is shown. It was found that (phosphonooxy-)oligosulfanide anion initiates formaldehyde oligomerization by anionic mechanism with chain termination due to interaction with water. It was shown that the synthesized formaldehyde oligomers retain resistance to degradation up to a temperature of 443 K, and then slowly thermally decompose to a temperature of 513 K, above which the rate of thermal degradation increases significantly.

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Introduction

Polyformaldehyde is a large-capacity commercially produced structural thermoplastics, the volume of production of which is constantly increasing (1). Therefore, the development of new approaches to the synthesis of polyformaldehyde is a task that must be solved in accordance with the principles of green chemistry (2). This paper describes a new system that initiates the polymerization of formaldehyde at a high rate at room temperature, which allows to achieve absolute atomic economy, does not create a load on the environment, and uses sulfur, which is common in nature, and the ionic liquid 1,3-dimethylimidazolium dimethylphosphate, as the starting materials. This approach is promising for initiating the polymerization of not only formaldehyde but also a number of other electron-deficient monomers, especially in cases where the synthesis of polymers creates a significant load on the environment. Elemental sulfur occurs in nature, but recently the volume of its production by the oil refining industry exceeds demand and leads to the accumulation of sulfur dumps (3, 4). Therefore, the development of new approaches to include elemental sulfur in technologies and processes is of interest for increasing possibilities of chemical synthetic methods with ecological and economic benefits (4).

In contrast, ionic liquids are traditionally considered to be green solvents (5, 6). However, there are indications, in some cases, that they are potential environmental hazards (7). Nevertheless, ionic liquids should be considered as green solvents because many are non-toxic, non-flammable, and potentially safe for the
environment (8). Apparently, some phosphates, such as dimethylphosphate-1,3-dimethylimidazolium, meet the requirements for green compounds (9), while showing reactivity with elemental sulfur (10–12). The latter fact was used by us to develop a method for green initiation of formaldehyde polymerization.

Materials and methods

The initiating system was obtained by dispersing 1.46 g (5.7×10⁻³ mol) of S₈ and 1 mL (5.7×10⁻³ mol) of 1,3-dimethylimidazolium dimethylphosphate in 50 mL of benzene at a temperature of 298 K and stirring for 1 h. All reagents were produced by Sigma-Aldrich. The dark-brown product of the interaction of the ionic liquid and elemental sulfur accumulates in the lower layer as a result of phase separation, so that its quantitative isolation, accompanied by complete regeneration of benzene, was possible with the help of a dividing funnel. Benzene can be replaced with p-cymene, as a green alternative. It is assumed that the formation of the initiating system is accompanied by the opening of the S₈ ring as a result of a nucleophilic attack by a dimethylphosphate anion (Scheme 1). At least, ionic liquids that do not contain a dimethylphosphate anion (and its homologs) did not interact with S₈, and the opening of the S₈ ring when interacting with dimethylphosphate-containing ionic liquids was confirmed earlier by high-resolution mass spectroscopy data and the appearance of an additional oxygen atom signal in the ¹⁷O NMR spectra (10–12).

Initiation of polymerization of formaldehyde in the medium of aprotic organic solvents allows to obtain high-molecular polyoxymethylene, however, to establish the features of initiation, the reaction is convenient to carry out in conditions conducive to the formation of low-molecular formaldehyde oligomers. In this case, it is possible to identify the structure of the end groups. Adding 0.2 mL of the resulting initiating system to 1.2 mL of 37 wt% formalin solution resulted in the almost instantaneous white precipitate formation, while the reaction system was completely discolored. It was found that the sulfur solution in benzene and 1,3-dimethylimidazolium dimethylphosphate are inactive in the reaction with formalin. Thus, the initiator of oligomerization of formaldehyde is the product of the interaction of 1,3-dimethylimidazolium dimethylphosphate and elemental sulfur.

The isolated formaldehyde oligomerization product washed with benzene on the filter was characterized by MALDI-TOF, FTIR, ¹H NMR, ¹³C NMR, HSQC and HMBC spectroscopy methods. The FTIR spectrum was recorded in KBr tablets using the FTIR Nicolet 380 spectrometer. ¹H NMR and ¹³C NMR spectra were registered at the New Materials and Technologies Research Center at IBCP RAS on the Bruker Avance 500 spectrometer at an operating frequency of 500 and 126 MHz, respectively, in the DMSO-6d. MALDI-TOF of positively charged ions was recorded on an Ultraflex II mass spectrometer (Bruker, Germany) in the reflex mode with an accelerating voltage of 25 kV under the conditions of desorption by an Nd:YAG laser (355 nm) with a DHB matrix.

Results and discussion

Apparently, the mechanism of polymerization of formaldehyde (Scheme 2) is anionic and includes the stage of initiation as a result of nucleophilic attack by the polysulfide anion of the carbon atom of the carbonyl group of formaldehyde, followed by chain propagation due to the acts of formaldehyde addition. Chain termination is associated with reversible chain transfer to water molecules, and the dissociation constant of water (Kₐ = 1.58×10⁻¹⁶) is less than the dissociation constant of methoxymethanol (Kₐ = 1.58×10⁻¹⁵) (13), which should be very close to the dissociation constants of the terminal hydroxyl groups of formaldehyde oligomers. When the product is isolated by removing water and formaldehyde by vacuum drying, the equilibrium is mixed towards the formation of oligomeric alkoxides of 1,3-dimethylimidazolium.

In the area of 3300–3500 cm⁻¹ of the FTIR spectrum (Figure 1) there is a wide absorption band corresponding to the stretch vibrations of the terminal hydroxyl groups of oligooxymethylene fragments and water, which is also consistent with the presence of the corresponding bands of bending vibrations 1658.2 and 1641.5 cm⁻¹. The absorption bands 1237.3, 1091.0, 1130.6 and 934.6 cm⁻¹ are associated with skeletal vibration of oligooxymethylene fragments (14). The 1040.4 cm⁻¹ band corresponds to the typical dimethylphosphate anion vibrations associated with the joint stretching of C–O and P–O bonds, and the 625.2 cm⁻¹ band corresponds to the stretch vibration of the P–O bond (15). The 1383.3 cm⁻¹ band is the result of symmetrical stretch vibration of methyl groups (16), and the wide absorption with a maximum of 1471.0 cm⁻¹ can be considered as the result of overlapping signals caused by stretch vibration of methyl groups and stretch vibration of the

Scheme 1. Interaction of 1,3-dimethylimidazolium dimethylphosphate with S₈.
methylene groups of the polyoxymethylene chain (17). The 1579.1 cm\(^{-1}\) band is associated with skeletal vibration of the 1,3-dimethylimidazole cation ring, and the 809.4 cm\(^{-1}\) band corresponds to out-of-plane bending vibration of C–H bonds (18). The 749.7 and 473.3 cm\(^{-1}\) signals are probably caused by stretch vibration in S-O and S-S bonds (16).

In the \(^1\)H NMR spectrum of the isolated product, signals with chemical shifts of 9.2, 7.69 and 3.85 ppm are observed, which correspond to protons at positions 2 and 4, 5 (equivalent), as well as protons of methyl groups associated with nitrogen atoms at positions 1 and 3 of the 1,3-dimethylimidazolium cation. The proton signal of the equivalent methyl groups of the dimethyl phosphate residue splits into a doublet with a chemical shift of 3.31 ppm as a result of spin–spin interaction with the \(^{31}\)P core. All the described signals practically do not change their position in comparison with the initial 1,3-dimethylimidazolium dimethylphosphate (19). The 4.59 ppm singlet corresponds to the product of attaching a single formaldehyde molecule to the \(\text{Me}_2\text{PO}_4\text{S}^-\) initiating system, since otherwise it would have been split into a multiplet due to the spin–spin interaction realized in the spin system –
CH₂–O–CH₂– or as a result of the spin–spin interaction with the ⁳¹P core, if the oligosulfide chain was not part of the initiating anion. Multiplets with chemical shifts of 4.67 and 4.79 ppm they correspond to protons of methylene groups of oligooxymethylene chains, which is consistent with the results described in (20). A signal in the ¹³C NMR spectrum with a chemical shift of 81.82 ppm according to HSQC data (Figure 2) correlates only with the 4.59 ppm singlet in the ¹H NMR spectrum and refers to the carbon atom of the methylene group, the product of attaching a single formaldehyde molecule to Me₂PO₄S⁻. In addition, in this case, the smallest chemical shift of the ¹H and ¹³C nuclei is observed compared to other CH₂ groups, which is consistent with the presence of the fragment -S-CH₂-O-. A series of signals with chemical shifts from 83.55 to 88.95 ppm corresponds to the carbon atoms of the methylene groups of oligooxymethylene chains, which is also consistent with the HSQC and HMBC data (Figure 3). Comparison of the HSQC and HMBC spectra leaves no doubt about the presence of spin–spin interactions in the group of nuclei –CH₂–O–CH₂–. A signal with a chemical shift of 35.49 ppm corresponds to the carbon atoms of two equivalent methyl groups of the 1,3-dimethylimidazolium cation, and the signals 137.22 and 123.33 ppm correspond to the carbon atoms at positions 2 and 4, 5 (equivalent) of the imidazolium cycle. The signal with a chemical shift of 51.35 ppm refers to the carbon atoms of the methyl groups of the dimethyl phosphate residue. Thus, the given spectral data indicate that the resulting product is a low-molecular-weight polyoxymethylene alcohoholate with the Me₂PO₄S⁻ terminal group and the 1,3-dimethylimidazolium counter ion.

The data of MALDI-TOF spectroscopy with registration of cations make it possible to detect, against the background of the signal with the highest intensity m/z ≈ 97, related to the 1,3-dimethylimidazolium cation, signals characteristic of low-molecular-weight formaldehyde oligomers. As shown in Figure 4, in the m/z range from 550 to 1050, a series of signals with a difference of 30 was observed, corresponding to the formation of a mixture of formaldehyde oligomers. For example, a signal with m/z = 580.974 can be attributed to the cation Me₂PO₄S₁(CH₂O)₃CH₂⁺, which is consistent with the intended initiation mechanism (Scheme 2).

Therefore, oligomers with a degree polymerization of up to 20 were formed owing to the initiation of formaldehyde oligomerization by the products of the interaction of S₈ with 1,3-dimethylimidazolium dimethylphosphate.

Results of DSC/TGA (Figure 5) for the obtained oligomer, they are consistent with its structure established by MALDI-TOF, NMR and FTIR spectroscopy methods. The loss of 16% of the mass at a temperature less than 443 K is associated with the evaporation of water and is accompanied by a significant absorption of heat. An increase in temperature from 443 to 513 K
is accompanied by a loss of about 6% of the mass and low heat absorption, which indicates the development of slow depolymerization of formaldehyde oligomers and is consistent with a small value of the formaldehyde polymerization enthalpy ($21\text{\degree}$). In the temperature range from 513 to 603 K, there is a high rate of mass loss, which is presumably associated with the cleavage of the end groups due to homolysis of S-S bonds, which should also lead to the release of sulfur and rapid depolymerization of the remaining formaldehyde oligomers. The release of sulfur is consistent with the nature of the change in heat flow and the rate of mass loss in the temperature range from 698 to 763 K, in which it is assumed that the evaporation of sulfur occurs with the simultaneous involvement of its vapors in chemical transformations. The results

Figure 3. HMBC-spectrum of formaldehyde oligomers in DMSO-6d solution.

Figure 4. MALDI-TOF spectrum of formaldehyde oligomers in the m/z range from 550 to 1050.
obtained indicate the possibility of increasing the resistance of polyformaldehyde to short-term heat stress through the introduction of terminal oligosulfide phosphate groups (22).

In the absence of initiators, spontaneous polymerization of formaldehyde with the formation of insoluble products in an aqueous medium develops slowly and assumes the initial formation of soluble oligomers (20, 23–25). However, under the action of the interaction product of elemental sulfur and 1,3-dimethylimidazolium dimethylphosphate, the reaction proceeds with the formation of insoluble formaldehyde oligomers almost instantly. Consideration of the possibilities of using the product of interaction of 1,3-dimethylimidazolium dimethylphosphate with elemental sulfur as an initiator of polymerization in the green synthesis of polyoxymethylene and other polymers will be the subject of our further research.

Conclusions

It is shown that the initiation of anionic polymerization by the interaction products of 1,3-dimethylimidazolium dimethylphosphate and elemental sulfur opens a fundamentally new path to the green synthesis of polyoxymethylene. It was found that oligomers are formed in an aqueous solution of formaldehyde, which is probably the result of reversible chain breakage due to interaction with water. Using FTIR, MALDI-TOF, \(^{1}\)H NMR, \(^{13}\)C NMR, HSQC and HMBC spectroscopy methods, it was shown that the structure of the isolated product corresponds to polyoxymethylene alcoholes with the Me2PO4S\(^{-}\) terminal group and the 1,3-dimethylimidazolium counter ion, which is consistent with the results of DSC/TGA.

Disclosure statement

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