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PHYSICO-CHEMICAL STUDY OF HETEROGENEOUS SYSTEMS

Transformations of Chlorinated Organic Additives in Polystyrene in the Course of Oxidative Pyrolysis

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Abstract—Oxidative pyrolysis of polystyrene containing chlorinated organic additives was studied by synchronous thermal analysis combined with mass spectrometry of decomposition products. Commercial polystyrene foam sample with unknown composition of fireproofing additives and artificially prepared polystyrene with an admixture of chlorinated paraffins were chosen as investigation objects. Under the conditions of oxidative pyrolysis, both samples decompose to form chlorinated organic compounds, including highly toxic phosgene.

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The polystyrene production has considerably increased recently. In the past 15–20 years, polystyrene came into wide use for the production of foamed items for various purposes, from heat-insulating boards to packaging materials. The use of polystyrene foam ensures saving of power and materials [1]. However, there are also certain problems, one of which is the release of harmful substances in polystyrene foam combustion.

Polystyrene pyrolysis leads to the release of a large amount of volatile organic compounds, many of which are toxic. Under the conditions of a real fire, not only polystyrene itself but also its oxidation products are dangerous. Fireproofing additives significantly contribute to the toxicity of combustion products. Although today the majority of countries in North America and Europe virtually exclusively use halogen-free fireproofing additives, the market of fireproofing additives in Russia is oversaturated with halogenated products [2]. Polystyrene is mainly used a foam. Various chlorinated and brominated organic compounds are introduced as fireproofing additives into polystyrene foam [3]. Often the producers, for commercial reasons, do not indicate the chemical composition and concentration of the additives used.

The term combustion has broad meaning. It includes a set of complex physical and chemical processes. The combustion can occur as a chain or thermal process. The chemical nature of combustible substances and oxidants and the combustion reaction mechanisms are diverse. In common practice of using polystyrene foam, the oxidant is atmospheric oxygen. In the course of polystyrene foam combustion, complex physicochemical processes occur inside the condensed phase and on its surface: phase transitions, thermal and thermal oxidative degradation. Furthermore, polystyrene foam, like many polymers, degrades below the boiling point. Therefore, it forms gaseous products in the course of degradation.

To elucidate the relationship between structural characteristics of polymeric substances and relationships of their combustion, it is necessary to know and understand the physicochemical process of transformation of the initial material into final combustion products in all the steps of this transformation. This problem is very complex, especially in view of poor knowledge of the physical and thermal properties of polystyrene foam in a wide temperature interval and of the chemistry of its high-temperature degradation.

Polystyrene belongs to the group of polymers that degrade under the action of heat with the cleavage of bonds in the backbone and formation of low-molecular-weight gaseous and liquid volatile products [4]. Polymers of this type degrade at high temperatures (300–600°C) practically completely or form a very small amount of a nonvolatile residue (coke). The thermal stability of the majority of halogenated polymers is also poor [5]. Despite complex composition of volatile products, their formation can be attributed to the bond cleavage in the backbone and to participation of the arising active centers in the chain transfer. Furthermore, with an increase in temperature, the composition of the forming products becomes more and more complex because of complication of the degradation mechanism and occurrence of side reactions. Various additives and fillers also make the pyrolysis products more diverse, because they themselves can degrade and generate new radicals. Combustion of each of the forming compounds has its own specific features. The pattern becomes still more complex if we take into account that the components undergo combustion in a mixture [6].

Halogenated organic compounds are used in virtually all the fields of industry and agriculture, as well as in household devices. They are consumed by producers of plastics, synthetic fibers, resins, machines, electronic devices, pharmaceuticals, and household chemicals, and also by metal-working shops. Chlorine compounds are the most widely used. Virtually all the halogenated compounds are combustion inhibitors. Many of them are widely used as thermal stabilizers for polymeric materials. Three types of halogenated compounds are used most widely for reducing the combustibility of polymeric materials: aliphatic, aromatic, and cycloaliphatic derivatives. Both low- and high-molecular-weight compounds are used. Among fire retardants are chlorinated paraffins, hexachlorobenzene, hexachloroethane, hexabromocyclododecane, and tetrabromo-p-xylene. These compounds inhibit the chain degradation reactions by decomposing the peroxides formed and by deactivating the free radicals. The decomposition of fireproofing compounds leads to intense degradation of the polymer itself.

Chlorinated paraffins are difficultly combustible substances. The open cup flash point of a solid chloroparaffin is above 370°C. Liquid chloroparaffins are produced on the commercial scale by chlorination in a melt, and solid chloroparaffins, by chlorination of paraffin in a CCl_4 solution in the presence of an initiator [7].

The chlorination of paraffin hydrocarbons at high temperature in the gas phase and in the liquid phase in the presence of initiators occurs, as a rule, by the radical chain mechanism [8]. The energy required for homolytic cleavage of the chemical bond is determined both by the nature of the bond being cleaved and by the stability of the generated free radicals. Weak endothermicity of the hydrogen abstraction step and the independence of the reaction course from the nature of the C–H bond allow the chlorination to be considered as a low-selectivity reaction. Chloroparaffins occupy a prominent place among fire-proofing compounds, but the products of their thermal decomposition and combustion are toxic.

Saturated and unsaturated chlorinated compounds are oxidized with atmospheric oxygen to form complex mixtures of oxygen-containing oxidation products and peroxy compounds. For example, mono- and dichloromethanes are oxidized with oxygen to HCl, Cl_2, H_2O, and CO and to $COCl_2$, H_2, and Cl_2, respectively.

Depending on the structure, halogenated organic compounds either undergo pyrolysis in the condensed phase or vaporize and degrade already in the gas phase.

Most probably, free radicals can be generated in the course of thermal degradation of polystyrene foam with halogenated organic additives via cleavage of C–C bonds, both in the polymer and in molecules of additives. The cleavage of the C–H bonds as the primary event of the pyrolysis can be neglected. The radicals can be generated both in monomolecular and in bimolecular reactions.

The ratio of the dissociation energies of various C–C and C–H bonds in reactant molecules determines the rates of radical reactions along different pathways, the amount of different radicals generated, and ultimately the composition of the reaction products. The reactions subsequently occurring in the course of pyrolysis (substitution, addition, decomposition, isomerization, recombination, disproportionation) make the final products still more diverse.

The primary reactions of pyrolysis of halogenated organic compounds yield, as a rule, HX and RX_n, more seldom X_2, where X is a halogen atom. Low-molecular-weight compounds HX, RX_n (X_2) pass into the gas phase and participate in chain reactions.

Various mechanisms have been suggested to account for the inhibiting effect of halogen derivatives on the combustion. Below we present one of possible mechanisms [6]. It is believed that hydrogen halide plays an important role in inhibition of the gas-phase combustion.

When a halogenated hydrocarbon fragment RX gets into the gas phase, the primary formation reaction is

$$RX + H^{\cdot} \rightleftarrows R + HX.$$

When X_2 gets into the gas phase, the following reaction occurs:

$$X_2 + H^{\cdot} \rightleftarrows HX + X^{\cdot},$$

where R is an organic radical, and X is Cl or Br.

These reactions themselves reflect the inhibition reactions yielding less active radicals.

Hydrogen halide decreases the concentration of active species ($H^{\cdot}$, $^{\cdot}O^{\cdot}$, $^{\cdot}OH$, $HO_2^{\cdot}$) in the flame. Direct chain termination reactions:

$$\begin{gathered} H^{\cdot} + HX \rightleftarrows H_2 + X^{\cdot}, \\ ^{\cdot}O^{\cdot} + HX \rightleftarrows {}^{\cdot}OH + X^{\cdot}, \\ ^{\cdot}OH + HX \rightleftarrows H_2O + X^{\cdot}, \end{gathered}$$

where X = Cl or Br.

Thus, the compound HX can be considered as a kind of homogeneous catalyst of recombination of H atoms, preventing the participation of $H^{\cdot}$ in oxidation chain branching. HX, in turn, is formed in the reactions

$$\begin{gathered} H^{\cdot} + X^{\cdot} \rightleftarrows HX, \\ X^{\cdot} + HO_2^{\cdot} \rightleftarrows HX + O_2, \\ X_2 + H^{\cdot} \rightleftarrows HX + X^{\cdot}, \end{gathered}$$

where X = Cl or Br.

The above inhibition scheme does not take into account the nature of hydrocarbon radical R generated from RX. At the same time, this factor determines not only the strength of the C–X bond in the compound and the molecular or radical pathway of dehalogenation, but also the probability of the subsequent participation of the radical in the combustion.

Thus, in the course of thermal and thermal oxidative degradation, fire retardants decompose to form halogens, hydrogen halides, and halogenated hydrocarbon species, which, in turn, inhibit the combustion of materials owing to deactivation of free radicals and decomposition of peroxides formed.

Taking into account the fact that the pyrolysis occurring by the radical mechanism can yield complex chlorinated organic compounds, including highly toxic substances, we studied the products of oxidative pyrolysis of the commercially produced chlorinated organic fireproofing compound, of model blends of polystyrene with this compound, prepared in a laboratory, and of samples of commercially produced technical-grade polystyrene foam with unknown composition of combustion inhibitors.

Our goal was to identify the products of transformation of chlorinated organic compounds in a mixture with polystyrene in the course of oxidative pyrolysis and to evaluate the possibility of formation of highly toxic compounds in the course of polystyrene foam combustion.

EXPERIMENTAL

To obtain data on the products of oxidative pyrolysis of fireproofing additives that can be used in production of polystyrene foam with the aim to reduce its combustibility, we studied KhP-66T mixture of chlorinated paraffins C_{12}–C_{30} with the total weight fraction of chlorine of no less than 70% (Kaustik Public Joint-Stock Company, Volgograd, Russia), chemical formula $C_nH_{2n+2-x}Cl_x$, where $x = 18$–23, $n = 12$–30. This product is a light brown powder. It is used as an additive to polymeric materials (polystyrene, polyethylene, synthetic rubbers, plastics, etc.), reducing their combustibility (fire-proofing additive) and enhancing the self-extinguishing properties.

Pyrolysis of this mixture of chlorinated hydrocarbons was performed with an STA 449 F1 device for synchronous thermal analysis (Netzsch, Germany), allowing thermal analysis of a sample to be performed with simultaneous recording of thermal gravimetric and calorimetric characteristics. The gaseous products were analyzed with a QMS 303 CF Aeolos mass spectrometer (Germany). The results were processed using appropriate software.

A 7.57-mg sample was heated in air at a rate of 10 deg min^{-1} with simultaneous recording of the mass spectra. Thermal decomposition of KhP-66T mixture becomes detectable by thermal gravimetric analysis starting from 306°C, with the first decomposition step lasting up to 348°C. Further weight loss starts at approximately 500°C and can be attributed to oxidation of pyrocarbon residue to CO_2.

Thermal decomposition of hydrocarbons yields various products, including lower olefins, low-molecular-weight alkanes, and methane. At high temperatures, the decomposition occurs in the gas phase with the generation of radicals. Mass spectrometric identification of the pyrolysis products shows that the pyrolysis of the chlorinated paraffin mixture yields such chlorinated compounds as HCl, chloromethane, chloroethane, and $COCl_2$.

The active species in hydrocarbon oxidation are radicals $R^{\cdot}$, $RO^{\cdot}$, and $RO_2^{\cdot}$. The extent of participation of each active species in the process depends on the process conditions (temperature, pressure)

Methane is the simplest stable hydrocarbon product of pyrolysis of organic compounds generated in the course of combustion. Therefore, the methane combustion can be considered as a process simulating to certain extent the gas-phase flame reactions occurring in the course of polymer combustion [9].

The main reaction leading to the generation of a large amount of methyl radicals is as follows:

$$CH_4 + H^{\cdot} \rightleftarrows CH_3^{\cdot} + H_2.$$

Then, methyl radicals can recombine with chlorine radicals to form chloromethane, which, in turn, can undergo further chlorination up to the formation of chloroform and carbon tetrachloride.

Although the pathway of phosgene formation from chloroform has not been determined reliably, the following oxidative transformations of chloroform have been suggested [10]:

$$\begin{gathered} CHCl_3 + Cl^{\cdot} \rightarrow {}^{\cdot}CCl_3 + HCl, \\ {}^{\cdot}CCl_3 + O_2 \rightarrow CCl_3OO^{\cdot}, \\ CCl_3OO^{\cdot} \rightarrow COCl_2 + ClO^{\cdot} \end{gathered}$$

or

$$\begin{gathered} CCl_3OO^{\cdot} + CHCl_3 \rightarrow CCl_3OOH + {}^{\cdot}CCl_3, \\ CCl_3OOH \rightarrow CCl_3O^{\cdot} + {}^{\cdot}OH, \\ CCl_3O^{\cdot} \rightarrow COCl_2 + Cl^{\cdot}, \text{ chain propagation.} \end{gathered}$$

The mechanism of the CCl_4 oxidation has not been unambiguously determined either, but the following schemes, based on available data, are suggested:

$$\begin{gathered} CCl_4 + \rightarrow {}^{\cdot}CCl_3 + Cl^{\cdot}, \\ {}^{\cdot}CCl_3 + O_2 \rightarrow COCl_2 + ClO^{\cdot} \end{gathered}$$

or

$${}^{\cdot}CCl_3 + O_2 \rightarrow CCl_3OO^{\cdot} \rightarrow COCl_2 + ½\, O_2 + ½\, Cl_2.$$

This mechanism accounts for the formation of phosgene in the course of oxidative pyrolysis of a chloroparaffin.

Then, we prepared model polystyrene samples with preset chlorine content and studied the products of their high-temperature oxidative degradation. For this purpose, we performed styrene polymerization in the bulk. Various fireproofing additives were introduced. Halogenated compounds are main, or primary, fire retardants. The amount of the additives introduced was judged from the percent content of halogen in the polymer or material. It is known that the minimal chlorine content required to reduce the polystyrene combustibility is 10–15%. We prepared pure polystyrene and polystyrene containing 15 wt % chlorine. Styrene freed from the stabilizer was placed in ampules, KhP-66T mixture was added, and the ampules were sealed. The samples were polymerized at 80°C in the presence of azobis(isobutyronitrile) (AIBN), following the known procedure [11].

After that, the polystyrene samples were similarly subjected to pyrolysis in the presence of atmospheric oxygen, using an STA 449 F1 device for synchronous thermal analysis (Germany). The gaseous products were also analyzed with a QMS 303 CF Aeolos mass spectrometer (Germany).

In air, thermal decomposition of polystyrene with chlorinated additives becomes detectable by thermal gravimetric analysis at 303°C, and the first step of the degradation lasts up to 415°C. The weight loss in this step is 78%. Presumably, at this temperature only pyrocarbon framework remains, and it is virtually stable up to 530°C. Further weight loss is due to pyrocarbon oxidation and is accompanied by pronounced exothermic effect. The TG and DSC curves are identical to those obtained in oxidative pyrolysis of pure polystyrene.

Comparison of the results of thermal gravimetric analysis with the mass-spectrometric data allowed identification of a series of compounds formed in the course of the polymer degradation. In the pyrolysis products, we identified by mass spectrometry compounds with the following molecular weights: 36, 37 (HCl); 50, 51 (chloromethane); 64, 65 (chloroethane); 98, 99 ($COCl_2$); 102 (chlorofuran); 116 (methylchlorofuran). In pyrolysis of pure polystyrene, the compound with the molecular weight of 98 is not detected.

Commercially produced polystyrene foam was of particular interest. We chose five samples of technical-grade polystyrene foam from different producers. Two samples were prepared by pressing, and three samples, by extrusion. Because the producers frequently do not indicate what compounds, and in what amounts, are added to polymers as fire retardants, we preliminarily determined the content of halogens in the samples.

The content of bromine and chlorine was determined by X-ray fluorescence with an ELVaX device (USA, Ukraine). Three samples contained 1.0–1.5 wt % chlorine, and two samples contained 1.0–2.0 wt % bromine.

For the subsequent identification of products of high-temperature oxidative degradation, we chose the sample containing 1.5 wt % chlorine.

A 2.11-mg portion of the sample was heated in air at a rate of 10 deg min^{-1}, with mass-spectrometric monitoring. Thermal degradation of self-extinguishing polystyrene foam (SPSF) becomes detectable by thermal gravimetric analysis at 264°C, and the first step of the degradation lasts up to 421°C. Presumably, on reaching this temperature, only the pyrocarbon framework remains as residue; it is virtually stable up to 469°C. Further weight loss in the interval 470–574°C with a maximum at 500°C can be attributed to pyrocarbon oxidation with pronounced exothermic effect.

Comparison of the thermal effects with the mass-spectrometric data showed that actually all the organic compounds were released in the temperature interval of the first weight loss, except CO_2, which was released with two maxima.

In oxidative pyrolysis products, we detected compounds identified by molecular weights: hydrogen chloride, chloroethane, phosgene, chlorofuran, and methylchlorofuran. The mole fractions of SPSF pyrolysis products were determined from the areas of the corresponding peaks in the mass spectra. The results are given in Table 1.

To construct the material balance with respect to chlorine, we assumed that the chlorine present in the initial SPSF in an amount of 1.5 wt % fully passed into the six detected products: hydrogen chloride, chloromethane, chloroethane, phosgene, chlorofuran, and methylchlorofuran. In addition, we assumed that the ion current peak areas on the time scale correspond to the molecular amounts of the compounds. With these assumptions, it is possible to calculate the amount of the compounds released from SPSF. The calculation results are given in Table 2.

To estimate the amount of the phosgene formed, we assumed the SPSF density to be 30 kg m^{-3}. Then, the weight of 1 L of the material is 30 g, and 291.6 mg of phosgene is released in the course of its pyrolysis. Assuming that 2-min action of phosgene in a concentration of 3.2 mg L^{-1}

Table 1. Content of substances in SPSF pyrolysis products

Molecular weight, amu	Suggested compound	Peak area, arb. units	Content, mol %
18	Water	142.685	5.10×10^{-1}
26	Acetylene	4.459	1.59×10^{-2}
28	Carbon monoxide[a] + ethylene	27738.697	9.92×10^{-1}
37	Hydrogen chloride	1.480	5.29×10^{-3}
44	Carbon dioxide[b] + acetaldehyde	35.776	0.13
46	Ethanol	0.255	0.91×10^{-3}
51	Chloromethane	20.882	7.47×10^{-2}
58	Propionaldehyde	0.184	6.58×10^{-4}
65	Chloroethane	0.771	2.76×10^{-3}
78	Benzene	8.442	3.02×10^{-2}
92	Toluene	0.116	4.15×10^{-4}
98	Phosgene	0.067	2.40×10^{-4}
102	Chlorofuran	0.352	1.26×10^{-3}
104	Styrene	2.477	8.86×10^{-3}
106	Benzaldehyde	0.480	1.72×10^{-3}
116	Methylchlorofuran	0.011	3.93×10^{-5}

[a] Both CO and ethylene have molecular weight 28. However, the amount of CO was considerably larger in any case, so the peak was assigned to CO.

[b] Both CO_2 and acetaldehyde have molecular weight 44. However, the amount of CO_2 was considerably larger in any case, so the peak was assigned to CO_2.

Table 2. Chlorine balance

Molecular weight, amu	Suggested compound	Peak area, arb. units	Fraction of compound in total amount of chlorine derivatives		Weight of substance released per gram of bound Cl in the initial compound, mg
			mol %	wt %	
37	Hydrogen chloride	1.480	6.28	4.51	65.45
51	Chloromethane	20.882	88.63	87.77	1273.32
65	Chloroethane	0.771	3.27	4.13	59.87
98	Phosgene	0.067	0.28	0.53	7.72
102	Chlorofuran	0.352	1.49	2.95	42.80
116	Methylchlorofuran	0.011	0.05	0.11	1.62

is fatal [12], we can conclude that thermal degradation of 1 L of SPSF in air will produce the lethal concentration of phosgene in 92.2 L of air. Among products of oxidative degradation of the chlorine-containing polymer prepared in a laboratory, phosgene was also detected in amounts sufficient for poisoning.

CONCLUSIONS

(1) High-temperature oxidative decomposition of the mixture of chlorinated hydrocarbons yields a series of chlorinated products, including highly toxic phosgene.

(2) Polystyrene with preset chlorine content, prepared in a laboratory, undergoes oxidative pyrolysis with the formation of hydrogen chloride, chloromethane, chloroethane, phosgene, and chlorofuran.

(3) Pyrolysis of commercially produced polystyrene foam yields a series of products similar to those formed in pyrolysis of polystyrene with the chloroparaffin mixture.

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