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Self-Crosslinking Acrylic Latexes with Copolymerized Flame Retardant Based on Halogenophosphazene Derivative

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Abstract

In this study the synthesis of a novel flame retardant based on halogenophosphazene derivative and its application in waterborne coatings based on self-crosslinking latexes was investigated. Hexaallylamino-*cyclo*-triphosphazene was synthesized by nucleophilic substitution of hexachloro-*cyclo*-triphosphazene with allyl amine. Latexes of functionalized core-shell particles bearing in the structure hexaallylamino-*cyclo*-

triphosphazene molecules were prepared by the semi-continuous non-seeded emulsion polymerization of methyl methacrylate, butyl acrylate and methacrylic acid as main monomers. For interfacial crosslinking, diacetone acrylamide was copolymerized into the shell layer of latex particles to provide sites for subsequent reaction with adipic acid dihydrazide. The incorporation hexaallylamino-*cyclo*-triphosphazene did not affect transparency, flexibility, toughness and adhesive properties of resulting coatings. Moreover, the presence of the novel flame retardant decreased water sensitivity and increased the flame stability of coatings in terms of reduced total heat release, decreased amount of released smoke and drop in maximum average rate of heat emission which indicates a slower flame spread during the material combustion.

Keywords: Emulsion polymerisation; Core-shell latex; Diacetone acrylamide; Flame retardant; Phosphazene; Cone calorimeter

1. Introduction

Nowadays, the paint and varnish industries as well as consumers appreciate the technologies which reduce or eliminate the application of organic solvents in coating materials. Waterborne acrylic coating compositions belong to the most commonly used pro-ecological paints and varnishes. Latex and water reducible coatings are the two major types in the waterborne acrylic coating approaches, while latex coatings are the dominant type of waterborne technology. The film formation of the conventional latex coating is primarily based on coalescence of thermoplastic polymeric particles to provide mechanical properties and chemical resistance. Coalescence is a result of physical inter-diffusion and entanglement of polymeric molecules, and consequently it is not an adequate substitute for the chemical crosslinking. To improve the performance, crosslinking technology has been incorporated into latex coatings [1–3]. In addition, one component systems are preferred. This means that the crosslinking reaction must be blocked in the liquid phase [4,5].

Recently, crosslinking via the reaction between carbonyl groups in diacetone acrylamide (DAAM) repeat units and hydrazide groups from adipic acid dihydrazide (ADH) has attracted a tremendous amount of research activity and has been shown to be particularly effective [6–11]. This reaction is favored by the loss of water and the simultaneous decrease in pH arising from the evaporation of ammonia or amines during the film forming process. Since ADH is water soluble and added to the latex after its preparation, the crosslinking reaction occurs predominantly near the particle surfaces, giving rise to interfacial crosslinking between particles during film formation. As the ambient self-crosslinking latexes can get crosslinked rapidly at room temperature and do not need additional crosslinker to be added before use, this kind of latex can be used in a wide range of applications, starting from paints for the building industry [12], through wood paints and varnishes to paints for metal protection and decorative systems [13,14].

For special applications, increased flame stability of utilized coating materials may be appreciated. This requirement can be solved easily by using convenient inorganic pigments and additives in the case of paint formulations, whereas a serious problem may occur in the case of transparent varnishes and top coats. The incorporation of organic phosphorus for clear-coating applications has been referred in the literature [15]. Generally, there are two methods to bring organic phosphorus into polymeric materials: chemical reaction [16–21] and physical blending [22], being limited by the blending compatibility. Huang et al. utilized an aziridine and phosphorus-containing compound to serve both as a curing agent and as a flame retardant [23] for aqueous-based polyurethane resin. The resultant materials exhibited higher thermal stability and better flame-retardation properties than those of the plain polyurethane resin because of the phosphorus-containing crosslinkages formation among polyurethane backbones. Several authors investigated derivatives of halogeno-*cyclo*-phosphazenes linked into the structure of the film-forming polymers. Hexahalogeno-*cyclo*-triphosphazenes contain alternating phosphorus and nitrogen atoms in the cycle with two substituents attached to the phosphorus atoms. These compounds exhibit unusual thermal properties, such as flame retarding and self-extinguish ability [24,25]. During the endothermic thermal decomposition of phosphazene-based polymers, phosphate, metaphosphate and polyphosphate compounds are generated and a nonvolatile protective barrier layer on the polymer surface is formed, cutting off the supply of oxygen [26,27].

The most significant halogeno-*cyclo*-phosphazenes include hexachloro-*cyclo*-triphosphazene (HCCTP) which was first synthesized by J. von Liebig in 1834. The typical reaction of HCCTP is a nucleophilic substitution. The nucleophile, being able to pass its free electron towards the attacking electrophilic phosphorus atom, belongs usually to the group of amines, alcoholates, alcohols, or thiols. Several derivatives of HCCTP have already been synthesized and used as flame retardants and antioxidants in polymers [28,33]. Nevertheless, the covalent bonding of HCCP derivatives into emulsion polymers and their utilization as flame retardants has not been reported so far to the best of our knowledge.

In the present work, we focused on the synthesis of a novel flame retardant based on HCCTP derivative and its incorporation into self-crosslinking latexes based on DAAM and ADH crosslinking system. The flame retardant was synthesized using nucleophilic substitution of HCCTP with allylamine resulting in hexaallylamino-*cyclo*-triphosphazene (HACTP). The latexes bearing in the polymeric structure covalently linked molecules of HACTP were further were investigated with respect to their potential application as transparent binders with improved flame stability.

2. Materials and methods

2.1. Materials

Allyl amine and hexachloro-*cyclo*-triphosphazene (HCCTP) were purchased from Sigma-Aldrich, Czech Republic and were used for the synthesis of the hexaallylamino-*cyclo*-triphosphazene (HACTP) flame retardant. Self-crosslinking latexes investigated in this research work were synthesized of methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), and 2-hydroxyethyl methacrylate (HEMA). All the monomers were purchased from Roehm (Germany). Disponil FES 993 IS (BASF, Czech Republic) was used as a surfactant and ammonium persulfate (Lach-Ner Company, Czech Republic) was utilized as an initiator of the polymerization reaction. Adipic acid dihydrazide (ADH) was utilized as the crosslinker and was purchased from Sigma-Aldrich, Czech Republic. Tetrahydrofuran (THF, Penta, Czech Republic) was stored under anhydrous conditions using activated molecular sieves. All the chemicals were utilized as received without any further purification.

2.2. Synthesis and characterization of HACTP

The synthesis of HACTP was performed under anhydrous conditions in an inert argon atmosphere using Schlenk containers. The synthesis reaction of the phosphazene derivative is shown in Fig. 1. A Schlenk flask was filled in with 0.0014 mol of HCCTP and 20 mL of THF under an inert atmosphere. 0.0073 mol of allylamine was slowly added dropwise into the stirred reaction mixture at the boiling point of THF. The reaction was terminated after 72 h followed by filtration of resulting salts. Three times washing with THF was followed by vacuum distillation to remove THF from the product. The preparation of HACTP was monitored during the synthesis by means of thin layer chromatography and the identity of the prepared derivative was confirmed also by measuring the melting point. The final product was characterized by $^{31}P(H)$

NMR, elemental analysis, mass spectrometry (MS) and Fourier transform infrared (FT-IR) spectroscopy.

$^{31}P(H)$ NMR spectra (δ, ppm; J, Hz) were recorded using a Bruker Advance DRX 300 instrument (Bruker Corp., Germany) at the frequency of ^{31}P: 202.46 MHz and 85 % H_3PO_4 (as the external standard). The samples were sealed in Simax tubes (diameter 4 mm), inserted in NMR cuvettes (diameter 5 mm) filled with D_2O (external lock). The spectra were measured in the coaxial NMR cuvette system. The elemental analysis was performed on a FLASH Organic 2000 Elemental Analyzer (Thermo Scientific, USA), which can detect carbon, hydrogen, nitrogen and sulphur. Determination of chlorine was carried out by combustion in oxygen atmosphere followed by titration with sulphuric acid according to Schöniger [34]. The method was tested on *o*-chlorobenzoic acid standard containing chlorine at the concentration 21.915 %. FT-IR spectroscopy of the samples was performed on a Nicolet iS50 (Thermo Scientific, USA) with integrated diamond ATR FT-Raman module. The FT-IR spectrometer with an integrated module and ATR fully reflective optics has a broadband DLaTGS detector to make measurements in the area 5000–100 cm^{-1}. The spectral resolution of the device is 0.09 cm^{-1}. MS was performed on the instrument MSD Model 5975B (Agilent Technologies, USA) with a probe for direct entry. Mass selective detector operated in electron impact ionization mode with the ionization energy of 70 eV. The samples for the MS analysis were prepared as methanol solution in the concentration of 0.01 wt.%.

2.3. Preparation and characterization of self-crosslinking latexes with copolymerized HACTP

Self-crosslinking latexes of core-shell particles containing various levels of HACTP were synthesized by the semi-continuous non-seeded emulsion polymerization comprising a variable content of acrylic monomers (see Table 1). The prepared HACTP was shown to be readily soluble in the utilized acrylic monomers and was incorporated into core, shell and core-shell structure of latex particles, respectively. The core/shell weight ratio of latex particles was 1/1, which means a shell thickness about 10 % of the particle diameter. The nature of acrylic monomers forming core and shell phases was chosen to achieve a calculated T_g (using the Fox equation [35]) of approximately 7 °C and 3 °C, respectively. The shell layer included a constant amount of DAAM repeat units to provide ketone carbonyl functionalities for interfacial crosslinking by reaction with ADH added during latex formulation. To improve the colloidal stability of latexes and to ensure the acid catalysis of keto-hydrazide crosslinking reaction, carboxyl functionalities were introduced into the structure of core and shell layers by copolymerization with a constant amount of MAA into all the prepared copolymers.

The latexes were produced in a 700 ml glass reactor under nitrogen atmosphere at 85 °C. The reactor charge was put into the reactor and heated to the polymerization temperature. Then the monomer emulsion was fed into the stirred reactor at the feeding rate about 2 ml/min in two steps (1. core preparation, 2. shell preparation). After that, during 2 hours of hold period the polymerization was completed. The recipe of emulsion polymerization is shown in Table 2. The pH was adjusted to 8.5 with ammonia solution. To produce the self-crosslinking latexes, a 10 wt.% aqueous solution of ADH, in the amount corresponding to the molar ratio ADH:DAAM = 1:2, was added to the latex under agitation. The solids content of final latexes was about 40 wt.%.

The apparent viscosity of final latexes was measured according to CSN ISO 2555 using a Brookfield viscometer, Model DV-1 at 100 rpm at 23 °C. The average particle sizes of structured microgels in the water phase were obtained from dynamic light scattering (DLS) experiments performed using a Coulter N4 Plus instrument (Coulter, Corp., UK). The DLS measurements were conducted at 25 °C. The concentration of the measured polymer dispersion was approximately 0,05 wt.% of solids. The minimum film-forming temperature (MFFT) was measured using the MFFT-60 instrument (Rhopoint Instruments, UK) according to ISO 2115. The MFFT is defined as the minimum temperature at which a film cast from the polymer dispersion becomes continuous and clear.

For the glass transition temperature (T_g) and gel content measurements, specimen were prepared by pouring the self-crosslinking latexes into a silicone mould. Films were formed by water evaporation at room temperature for a month. T_g values were determined by means of differential scanning calorimetry using a Pyris 1 DSC instrument (Perkin-Elmer, USA). The measurements were carried out at the heating rate of 10 $°Cmin^{-1}$ with N_2 atmosphere. The testing temperature range was -80 to 120 °C. The gel content was determined according to CSN EN ISO 6427 using a 24-hr extraction with THF in a Soxhlet extractor. Around 1 g of the dried latex sample was put into the thimble. After the extraction, the thimble was dried in an oven at 75 °C for 6 h, cooled in a desiccator overnight, and the gel content was calculated from the initial and final weights, assuming that the gelled material remained in the thimble.

2.4. Characterization of emulsion copolymers from the point of view of HACTP incorporation

Glass transition temperature (T_g) and gel content values of the synthesized emulsion copolymers without ADH addition were determined in the same manner as described above. The presence of the copolymerized HACTP in the emulsion copolymers was investigated using two methods, namely the inductively coupled plasma optical emission spectrometry (ICP-OES) and $^{31}P(H)$ NMR. Before ICP-OES and NMR testing, 24-hr THF extraction of dried copolymer samples without ADH addition was performed. Both the high-molar mass polymer material (gel fraction) and the low-molar mass soluble material (sol fraction) were analyzed by means of $^{31}P(H)$ NMR, whereas in the case of ICP-OES analysis the copolymer samples without performing THF extraction and their corresponding gel fraction (after THF extraction) were measured and compared. The elemental analysis of phosphorus was carried out with the sequential, radially viewed ICP (Inductively Coupled Plasma) atomic emission spectrometer INTEGRA XL 2 (GBC, Dandenong Australia), equipped with the concentric nebulizer and the glass cyclonic spray chamber (both Glass Expansion, Australia). The analytical line used was 213,618 nm. The operation conditions of the ICP-OES analysis were: the sample flow rate 1.5 $mL.min^{-1}$, plasma power 1000 W, plasma, auxiliary and nebulizer gas flow rate were 10, 0.6 and 0.65 $L.min^{-1}$, respectively, photomultiplier voltage 600 V, view height 6.5 mm, three replicated reading on-peak 1s, fixed point background correction. For an instrumental calibration, calibration standards containing 10 - 5 - 1 - 0.5 – 0.1 $mg.dm^{-3}$ of P was used. The calibration standards were prepared using a commercially available stock standard solution of P, both containing 1 $g.dm^{-3}$ (SCP, Baie D'Urfé, Canada). The limit of detection (the concentration equal to three times standard deviation in the place of background correction) was 50 $\mu g.dm^{-3}$.

In the case of $^{31}P(H)$ NMR, only two representative copolymers, namely $C_{0.4}S_0$ (containing theoretically 0.4 wt.% of phosphazene derivative in the core structure of latex particles) and $C_0S_{0.4}$ (bearing theoretically 0.4 wt.% of HACTP in the shell structure of latex particles) were investigated. The presence of HACTP in sol fraction was determined using a Bruker Advance DRX 300 instrument (Bruker Corp., Germany) at the frequency of ^{31}P: 202.46 MHz and 85 % H_3PO_4 (as the external standard), whereas the incorporation of HACTP in the gel fraction was studied by means of $^{31}P(H)$ NMR using a Bruker Advance III(tm) spectrometer (Bruker Corp., Germany) at the frequency of ^{31}P: 500 MHz equipped with MAS VTN 500SB BL4 N-P/F-H probe. The samples were filled into 4 mm ZrO_2 rotor with the rotation speed 10 kHz. The hydrogen atoms splitting were not observed because of using zgig - inverse-gated decoupling program.

2.5. Coating preparation and evaluation

The non-pigmented coating films with a wet thickness of 120 μm were cast on glass and metallic panels by drawing the self-crosslinking latexes using a blade applicator. No coalescing solvents were used. The resulting coating films based on latex particles containing variable amount of HACTP in their core and shell structures, respectively, were evaluated for their gloss, hardness, adhesion, impact resistance, water sensitivity and flame stability. The dry film thickness was determined using a three-point instrument (BYK-Gardner, Germany) in the case of films prepared on glass panel, thickness of specimen on metallic panels was measured by the Sauter TE 1250-0.1 F Digital Coating Gauche (Sauter, Germany). The gloss of coatings was measured by a micro TRI-gloss μ instrument (BYK-Gardner, Germany) using a gloss-measuring geometry 60°. The hardness of test films was measured by the pendulum hardness tester "Perzos" pendulum (BYK-Gardner, Germany) following the CSN EN ISO 1522. The adhesion was determined using the cross-cut tester (Elcometer Instruments, UK) following the CSN ISO 2409 and the impact resistance was evaluated according to CSN EN ISO 6272 using the Elcometer 1615 Variable Impact Tester (Elcometer Instruments, UK). All experiments were carried out at room temperature (23 ± 1 °C).

For evaluating the water sensitivity, specimens were prepared by pouring the self-crosslinking latexes into a silicone mould. Films were air-dried at room temperature (23 °C) for a month. The water sensitivity expressed in terms of water absorption by latex films was measured by immersing samples in distilled water at 23 °C. The water absorption, A is given by $A = 100(w_t - w_0)/w_0$, where w_0 is the sample weight before immersion and w_t is the sample weight after immersion in water during given time. The swollen films were carefully removed from water, and water from the film surface was removed by touching the polymer with a filter paper. For each sample, three specimens of the approximate dimensions 20 × 20 × 0.75 mm^3 were tested and averaged values of the results were collected as a function of time.

For testing the flame stability using the dual cone calorimeter (Fire Testing Technology, UK), specimens of the approximate dimensions 80 x 50 x 4 mm^3 were prepared by pouring the self-crosslinking latexes into a silicone mould. Films were air-dried at room temperature (23 °C) for 30 days. The measurements were performed in a sample holder suitable for testing of thermally thin materials. The centre of a measured sample was situated 6 cm from the lowest part of the cone heater. The heat release rate was calibrated by burning methane. The cone radiancy 25 kWm^{-2} corresponds to a cone temperature 680 °C. It was set from the calibration diagram for a distance of the sample from the cone edge 6 cm [36]. For each sample, three specimens were tested and averaged values of the results were collected.

3. Results and discussion

3.1. Characterization of synthesized HACTP

The prepared hexaallylamino-*cyclo*-triphosphazene was characterized by means of elemental analysis; the elements C, H, N present in the compound were determined. The determination of chlorine was made by combustion in an oxygen atmosphere to verify the full substitution of Cl atoms. The amount of phosphorus elements was calculated additionally. The obtained data are listed in Table 3. It is evident that the theoretical contents of individual elements C, H, N, P, Cl in the synthesized HACTP molecule are consistent with the experimental results, which confirms the theoretical structure of the prepared derivative. Further, the synthesized derivative was characterized by means of

^{31}P(H) NMR analysis. The full substitution of HCCTP was demonstrated by a singlet in the ^{31}P(H) NMR spectrum at a chemical shift δ (S) = 18.79 ppm, as shown in Fig. 2.

The synthesized HACTP was also characterized by FT-IR spectroscopy. FT-IR spectrum is shown in Fig. 3. The P–N cycle vibration is located at 1213 and 1190 cm^{-1}, the vibration for the N–H bond correspond to 3273 and 1607 cm^{-1}. Valence vibrations (υ_{as} and υ_{s}) of C–H$_x$ groups (x = 1–3) were found between 2849 and 2932 cm^{-1}. Bands of deformation vibrations δ_{as} of C–H$_x$ groups (x = 1–3) occurred in the region between 1508 to 1553 cm^{-1}. Vibrations (υ_{as}) at 551 cm^{-1} corresponding to P–Cl groups are missing, which confirms the full nucleophilic substitution of HCCTP. The successfulness of the synthesis of HACTP was monitored by mass spectrometry as well. The MS spectrum is presented in Fig.4. The theoretical molar mass of HACTP is 471.45 g/mol. MS results revealed that almost the identical value of 471.9 g/mol was obtained, which correspond to a fully substituted derivative.

3.2. Characterization of latex copolymers

Latexes with negligible amount of coagulum (0.1 – 0.5 %) were synthesized by the semi-continuous non-seeded emulsion polymerization process with varying amount and location of HACTP molecules in core-shell compositions. The prepared latex copolymers were studied from the point of view of glass transition temperature and gel content with respect to HACTP concentration and location inside the latex particles. These characteristic properties are listed in Table 4. T_g and gel content values were shown to be influenced markedly by the content of HACTP in latex particles. Although the pendant allyl double bonds of HACTP were supposed to remain partly unreacted (because of steric hindrance effects and lower reactivity in comparison to vinyl groups of acrylic monomers) and therefore the crosslinking ability of the phosphazene derivative was believed to be suppressed, the glass transition temperature and gel content of emulsion copolymers were found to be increased with the growing content of HACTP. This phenomenon clearly reveals the formation of crosslinks and leads us to suppose that in the process of emulsion polymerization of common acrylic monomers, HACTP may act as an efficient crosslinker leading to the formation of latex particles of microgel structure. It was found further that the crosslinking ability of HACTP was supported in the case of HACTP incorporation into monomer feeds forming core structures. This effect may be related to swelling of the HACTP-crosslinked core by monomers fed in the shell stage of emulsion polymerization and polymerization of these monomers inside the polymer network of the pre-formed core structure, since unreacted allyl double bonds of HACTP are present. When comparing the results of the gel content for the emulsion copolymers before and after post-crosslinking using ADH, the ADH-crosslinked copolymers exhibited increased T_g and gel content values as a result of increasing the network density owing to keto-hydrazide crosslinking.

It should be noted that due to the low reactivity of allyl double bonds present in HACTP molecules, some unreacted allyl groups are probably left in the emulsion copolymers at the end of the polymerization and may react during the storage with the radicals generated from the unreacted persulfate initiator, thus modifying the film-forming properties of emulsion polymers. Nevertheless, the results of T_g and gel content measurements proved that no significant changes in the structure of latex copolymers occurred after the testing period of 12 months, which was manifested by negligible differences between T_g and gel content values of samples tested after 1 and 12 months-long storage of latexes. Hence, it can be assumed that the final properties of the studied copolymers will not be changed markedly even after a long-term storage. This fact may be attributed to decrease of mobility and steric hindrance effects caused by the HACTP-crosslinked structure of emulsion copolymers, which hinders proceeding of the above-mentioned reaction inside latex particles in large scale.

The presence of the copolymerized HACTP in the synthesized emulsion copolymers was tested using ICP-OES and ^{31}P(H) NMR. The results of the elemental analysis of phosphorus using ICP-OES are summarized in Table 5. It is evident that phosphorus concentration in the tested samples correlates well with the amount of HACTP applied during the synthesis of emulsion copolymers. The copolymer samples which were not subjected to THF extraction exhibited higher phosphorus concentration in comparison with the corresponding copolymers that were analysed after the extraction. Nevertheless, the calculated values of phosphorus remaining in gel fraction clearly reveal that the major part (80 % and more) of HACTP was present in ultra-high-molar mass insoluble copolymer structures.

In the case of ^{31}P(H) NMR analysis it was found that the spectra of $C_0S_{0.4}$ and $C_{0.4}S_0$ samples for the extracted low-molar mass molecules showed the absence of phosphazene derivative, whereas almost the identical ^{31}P NMR spectra were obtained in the case of gel fractions of both investigated emulsion copolymers,; the representative spectrum of the $C_{0.4}S_0$ crosslinked copolymer is shown in Fig. 5. It can be seen that a singlet at a chemical shift δ (S) = 19.89 ppm occurred in the spectrum of the high-molar mass polymer fraction, which indicates the presence of HACTP molecules. Hence, it can be stated that HACTP was successfully incorporated into the macromolecular structure of acrylic polymers via the emulsion polymerization technique proceeding at standard conditions.

3.3. Characterization of self-crosslinking latexes

All the prepared self-crosslinking latexes (after ADH addition) were stable for over 12 months. They were evaluated from the point of view of particle size in the water phase, minimum film-forming temperature and viscosity with respect to HACTP concentration and location inside the latex particles. These characteristic properties are listed in Table 1. For proving the core-shell morphology of latex particles, the diameters of core particles (samples taken after finishing the core polymerization step) and resulting core-shell particles were determined. Diameters of core particles varied from 123 to 140 nm, whereas particle sizes of core-shell particles were between 156 – 172 nm, which is in a good accordance with the calculated dimension of shell thickness about 10 % of the particle diameter. The DLS results indicated further that the latex particle size was not affected significantly by both the amount and the location of HACTP in emulsion copolymers. Similarly, MFFT and viscosity values were shown not to be influenced by presence of HACTP in latex particles. All the synthesized self-crosslinking latexes exhibited low viscosities and values of MFFT suggesting good application and film-forming properties.

3.4. Evaluation of latex coatings

Non-pigmented coating films cast from thermosetting one-package latexes based on the HACTP-modified emulsion microgels were prepared and their properties were tested. All the coating systems were able to form transparent films. Dry film thickness of the coatings was approximately 60 μm. The effect of HACTP on final coating properties is presented in Table 6. It was shown that the tested coating films can be characterized by high gloss (gloss value at 60 ° geometry above 70 %) or semi-gloss (below 70 %). A decrease in gloss appeared especially with higher amounts (0.2 and 0.4 wt.%) of HACTP being copolymerized in the core structure of latex particles, whereas in the case of coatings based on latex particles with HACTP copolymerized in the shell structure, the deterioration of gloss was observed for all samples with the exception of coatings made of $C_0S_{0.2}$ (comprising 0.2 wt.% of HACTP in monomer feeds forming shell layer). These coatings exhibited even higher gloss than the HACTP-free coatings. The gloss deterioration might be related to coalescence worsening due to increased network density and polarity changes of latex particles caused by presence of HACTP molecules. Nevertheless, the HACTP influence on surface character of coating films is still the subject of additional studies.

It was observed further that hardness of coating films was enhanced with the increasing content of HACTP in microgel particles, which was more pronounced in the case of latex particles with HACTP copolymerized in the core structure. This fact can be attributed to increased network density of resulting polymer materials, which is consistent with T_g elevation of the corresponding emulsion copolymers (see Table 4). It was shown as well that all the tested coatings containing copolymerized HACTP exhibited superior impact resistance and high adhesion suggesting the formation of crosslinked and elastic polymer materials in which sufficient coalescence of latex particles had been achieved before the ADH-crosslinking took place. In spite of the fact that the conventional cross-cut test does not enable to distinguish small differences in adhesion, it was observed that the coatings based on copolymers containing HACTP exhibited slightly higher adhesion in comparison with HACTP-free coatings. The reason of this phenomenon may be associated with polarity changes of emulsion copolymers due to the presence of phosphazene derivative containing polar amino groups and nitrogen-phosphorus cycles. The enhancement of coating adhesion was shown to be more pronounced at higher amounts of HACTP being copolymerized in the core of latex particles in contrast to HACTP being located in the shell of emulsion particles. This effect can be associated with higher conversion of allyl double bonds of HACTP copolymerized in core of latex particles due to longer polymerization time. This was confirmed by the elevation of T_g and gel content in the case of emulsion copolymers based on core-located HACTP microgels. Converting of allyl functionalities into saturated hydrocarbons attached to acrylic polymeric chains might lead to the increase in polarity effects of HACTP-integrated amino groups. Nevertheless, the above mentioned statements are based mainly on speculations and the mechanism of HACTP effect on coating adhesion still needs further investigation.

The coating films were tested from the point of view of water sensitivity. In comparison with the HACTP-free coatings, water sensitivity of the coating films comprising the novel phosphazene derivative (expressed in terms of water absorption) was decreased with the growing concentration of HACTP, being more pronounced in the case of copolymerizing HACTP in the core of emulsion particles. This fact suggests inferior coalescence of latex particles comprising HACTP. The open film structure facilitates the extraction of emulsifier and other water soluble components by water, which results in a lower water uptake due to decreased osmotic pressure [37].

As our system of interest was focused primarily on the evaluation of flame retardancy of the prepared phosphazene derivative in the resulting coatings, the effect of HACTP amount and location inside latex particles on combustion of coating films was studied in particular. The results obtained from measurements using dual cone calorimeter are presented in Table 7 and Fig. 6. Fig. 6 indicates that the coating material containing HACTP (C_0-$S_{0.4}$) ignited later than the coating based on microgels without phosphazene derivative (C_0S_0). The other coatings containing the phosphazene derivative exhibited a similar behavior. Table 7 reveals that the coatings comprising HACTP exhibited lower values of mean heat release rate, mean effective heat of combustion and total heat release. This phenomenon is more pronounced with increasing HACTP content, which indicates a slower flame spread due to incorporated HACTP. Decreased values of total smoke release during combustion of samples containing HACTP may reflect a more efficient oxidation of hydrocarbon chains in the presence of the phosphorus compound. It is assumed that the phosphorus atom reacts in the gas phase where the PO• radical is playing the main role [38]. In the case of values of total oxygen consumed, no significant effect of HACTP presence was proved. Nevertheless, one of the most important criterions of the flammability evaluation is the maximum average rate of heat emission (MARHE) that decreased markedly by the growing content of HACTP in the tested coating materials. These results lead us to conclude that HACTP did act as a flame retardant in the investigated coating materials. The flame stability was influenced mainly by the HACTP content while the HACTP location inside emulsion microgels was not proved to be of great importance.

4. Conclusions

HACTP was successfully prepared by nucleophilic substitution of HCCTP with allyl amine using the one-step synthesis. The structure of HACTP was verified using ^{31}P(H) NMR, elemental analysis, mass spectrometry and FT-IR spectroscopy. The prepared phosphazene derivative was incorporated into the macromolecular structure of acrylic polymers via the emulsion polymerization technique proceeding at standard conditions, which was evidenced by ^{31}P(H) NMR and ICP-OES. During the emulsion polymerization of acrylic comonomers, HACTP performed the function of an efficient crosslinker leading to the formation of latex particles of microgel structure. In addition to that, the basic objective of this work was to evaluate the flame retardancy of the prepared phosphazene derivative in the keto-hydrazide self-crosslinking aqueous coatings based on the HACTP-modified emulsion microgels. The presence of HACTP was found to cause decreased amount of produced smoke and a slower flame spread during the material combustion without affecting transparency, flexibility and adhesive properties of resulting coatings. Moreover, water sensitivity of the coating films comprising the novel phosphazene derivative was decreased. Thus, it can be concluded that HACTP acted as a flame retardant and one-package thermosetting transparent coating systems with increased flame stability and enhanced water resistance were developed, having a potential application as primer as well as topcoats.

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Table 1

Composition and characteristics of self-crosslinking latexes based on core-shell particles containing HACTP

Sample	Composition of monomer feeds (wt.%) MMA/BA/MAA/DAAM/HACTP		Particle size in the water phase (nm)		Viscosity (mPa.s)*	MFFT (°C)
	Core	*Shell*	*Core*	*Core-shell*		
C_0S_0	49/49/2/0/0	42/51/2/5/0	126	156	9.2	5.1
$C_{0.1}S_0$	48.95/48.95/2/0/0.1	42/51/2/5/0	136	172	8.3	5.6
$C_{0.2}S_0$	48.9/48.9/2/0/0.2	42/51/2/5/0	137	165	8.7	5.6
$C_{0.4}S_0$	48.8/48.8/2/0/0.4	42/51/2/5/0	140	170	9.9	5.8
$C_0S_{0.1}$	49/49/2/0/0	41.95/50.95/2/5/0.1	128	165	8.8	5.5
$C_0S_{0.2}$	49/49/2/0/0	41.9/50.9/2/5/0.2	136	169	9.1	5.6
$C_0S_{0.4}$	49/49/2/0/0	41.8/50.8/2/5/0.4	123	158	9.3	5.8

[*] Value obtained after 6-months storage at room temperature (23 ± 2 °).

Table 2

Recipe of emulsion polymerisation

Reactor charge:	
Water (g)	80
Disponil FES 993 IS (g)	0.5
Ammonium persulfate (g)	0.4
Monomer emulsion (core):	
Water	75
Disponil FES 993 IS (g)	7.3
Ammonium persulfate (g)	0.4
Monomers (g)	100
Monomer emulsion (shell):	
Water (g)	75
Disponil FES 993 IS (g)	7.3
Ammonium persulfate (g)	0.4
Monomers (g)	100

Table 3

Results of elemental analysis of HACTP

Element	Theory (%)	Experiment (%)
C	45.86	45.18 ± 0.03
H	7.70	7.67 ± 0.02
N	26.74	25.15 ± 0.03
P	19.71	19.82 ± 0.02
Cl	-	-

Table 4

Effect of HACTP and post-crosslinking using ADH on T_g and gel content values of emulsion copolymers

Sample	HACTP content (wt.%)		Copolymers without ADH		Copolymers after crosslinking with	
	Core	Shell	T_g (°C)	Gel content (%)	T_g (°C)	Gel content (%
C_0S_0	0	0	12.2	8.3	18.9	75.1
$C_{0.1}S_0$	0.1	0	14.5	32.9	18.9	84.3
$C_{0.2}S_0$	0.2	0	15.6	70.0	19.3	89.2
$C_{0.4}S_0$	0.4	0	18.1	83.9	20.9	97.0
$C_0S_{0.1}$	0	0.1	12.8	22.5	16.1	80.9
$C_0S_{0.2}$	0	0.2	14.2	36.7	20.5	83.7
$C_0S_{0.4}$	0	0.4	16.0	72.0	19.1	87.4

Table 5

ICP-OES results of phosphorus analysis for emulsion copolymers, differing in the amount and location of HACTP, and the calculated amount of phosphorus remaining in gel fraction of copolymers. Data for copolymers without extraction (comprising ultra-high-molar mass gelled material as well as soluble low-molar mass fractions) are compared with data for copolymers after THF extraction (comprising only insoluble crosslinked macromolecules).

Sample	Theoretical content of HACTP in copolymer (wt.%)		P concentration (mg/l)	
	Core	Shell	Without extraction	After extra
C_0S_0	0	0	0	0
$C_{0.1}S_0$	0.1	0	108	87
$C_{0.2}S_0$	0.2	0	181	149
$C_{0.4}S_0$	0.4	0	339	315
$C_0S_{0.1}$	0	0.1	108	95
$C_0S_{0.2}$	0	0.2	170	136
$C_0S_{0.4}$	0	0.4	352	341

Table 6

Comparison of final properties of coating films based on self-crosslinking latexes differing in the amount and location of HACTP in emulsion particles

Sample	Gloss 60° (%)	Hardness (%)	Adhesion[a] (degree of flaking)	Impact resistance[b] (cm)	W
C_0S_0	84.7 ± 2.7	22.0 ± 0.7	1	95	53
$C_{0.1}S_0$	82.7 ± 0.3	23.7 ± 0.5	1	above 100	43
$C_{0.2}S_0$	58.4 ± 0.4	26.4 ± 0.3	0	above 100	40
$C_{0.4}S_0$	69.9 ± 1.8	34.3 ± 1.1	0	above 100	35
$C_0S_{0.1}$	58.5 ± 3.6	19.9 ± 0.8	1	above 100	52
$C_0S_{0.2}$	87.2 ± 0.5	24.3 ± 1.3	0	above 100	50
$C_0S_{0.4}$	59.2 ± 1.3	27.0 ± 1.6	1	99	49

[a] Adhesion scale: 0 – 4, where 0 corresponds to the best property.
[b] Maximum evaluative value (representing the best property) is 100 cm.
[c] Value determined after 30-days-long immersion in distilled water.

Table 7

Results of combustion in a cone calorimeter for coatings based on self-crosslinking latexes containing structured particles differing in the amount and location of HACTP molecules

Evaluated parameter[a]	C_0S_0	$C_{0.1}S_0$	$C_{0.2}S_0$	$C_{0.4}S_0$	$C_0S_{0.1}$	$C_0S_{0.2}$	$C_0S_{0.4}$
Mean heat release rate (kW/m^2.g)	52.8	46.2	34.1	29.3	32.8	32.4	25.4
Mean effective heat of combustion (MJ/kg.g)	2.48	2.16	2.74	2.63	2.62	3.11	2.68
Total heat release (MJ/m^2.g)	15.01	7.52	7.38	6.90	7.29	8.11	7.19
Total oxygen consumed (g/g)	1.44	1.62	1.61	1.55	1.57	1.63	1.49
Total smoke release (m^2/m^2.g)	141.1	78.6	64.5	58.5	75.0	71.8	68.8
Maximum average rate of heat emission (kW/m^2.g)	45.9	33.6	32.2	31.9	37.7	33.8	31.4

[a] All evaluated parameters are related to the initial mass of a tested sample.

Figure captions:

Fig. 1. Schematic representation of the synthesis reaction of hexaallyamino-*cyclo*-triphosphazene (HACTP).

Fig. 2. ^{31}P(H) NMR spectrum for the synthesized HACTP.

Fig. 3. FT-IR spectrum for the synthesized HACTP.

Fig. 4. MS spectrum for the synthesized HACTP.

Fig. 5. ^{31}P(H) NMR spectrum for the gel fraction of the $C_{0.4}S_0$ copolymer containing theoretically 0.4 wt.% of HACTP in the core structure of latex particles.

Fig. 6. Comparison of combustion of (1) the coating formed by the HACTP-free latex particles C_0S_0 with (2) the coating based on the $C_0S_{0.4}$ latex particles comprising 0.4 wt.% of HACTP in monomer feeds forming the shell layer.

Fig. 1

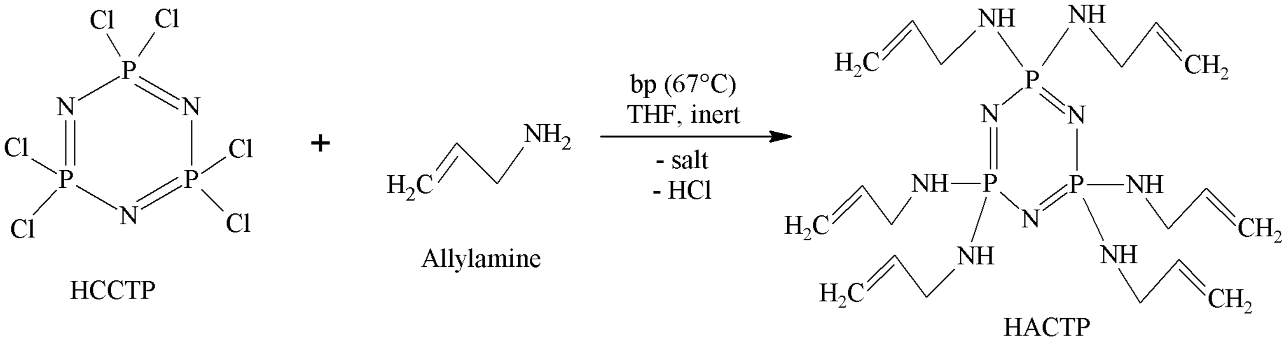
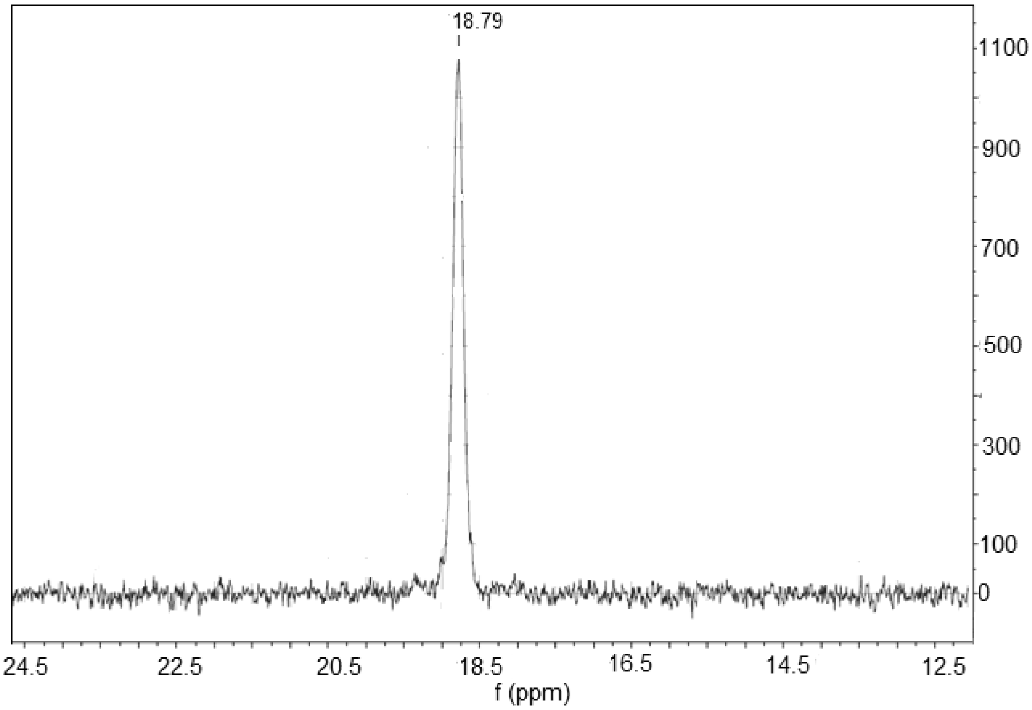


Fig. 2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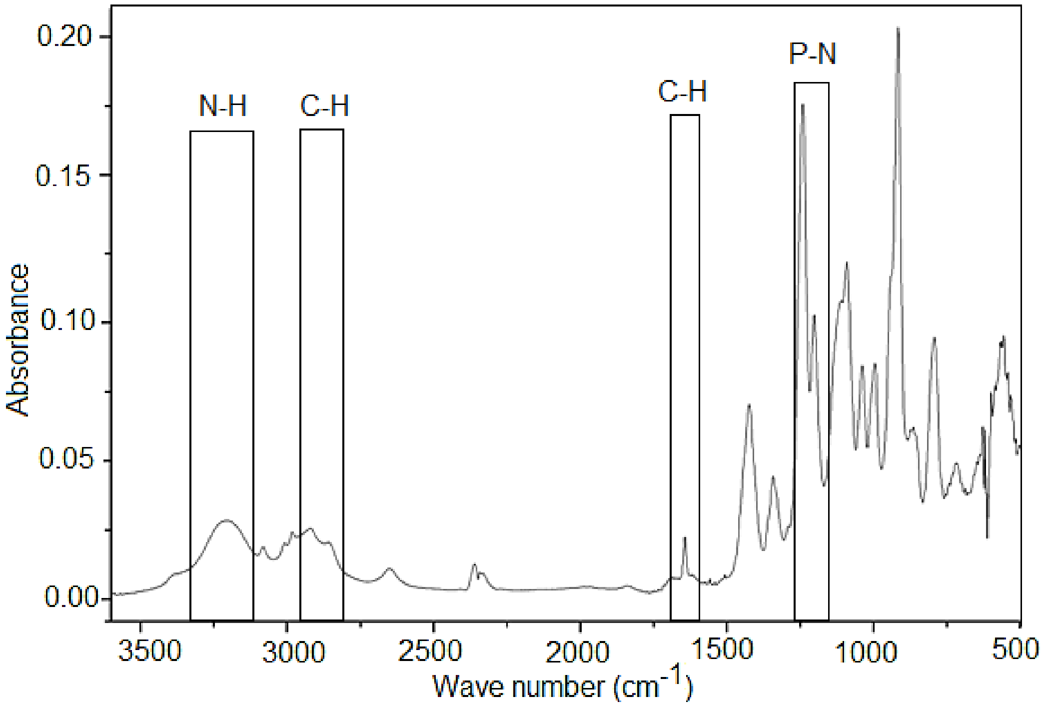
900
700
500
300
100
0
24.5
22.5
20.5
18.5
16.5
14.5
12.5
f (ppm)

Fig. 3


N-H
C-H
C-H
P-N
0.20
0.15
0.10
0.05
0.00
Absorbance
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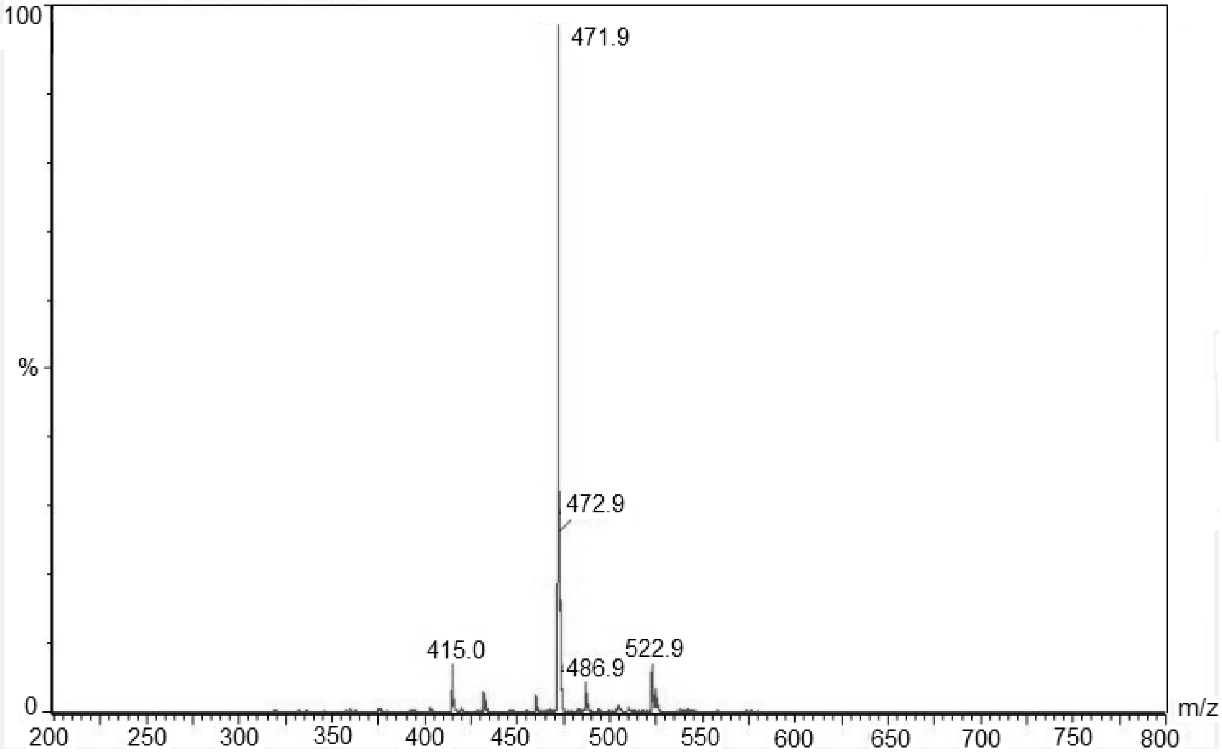
3000
2500
2000
1500
1000
500
Wave number (cm⁻¹)

Fig. 4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%
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472.9
415.0
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250
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350
400
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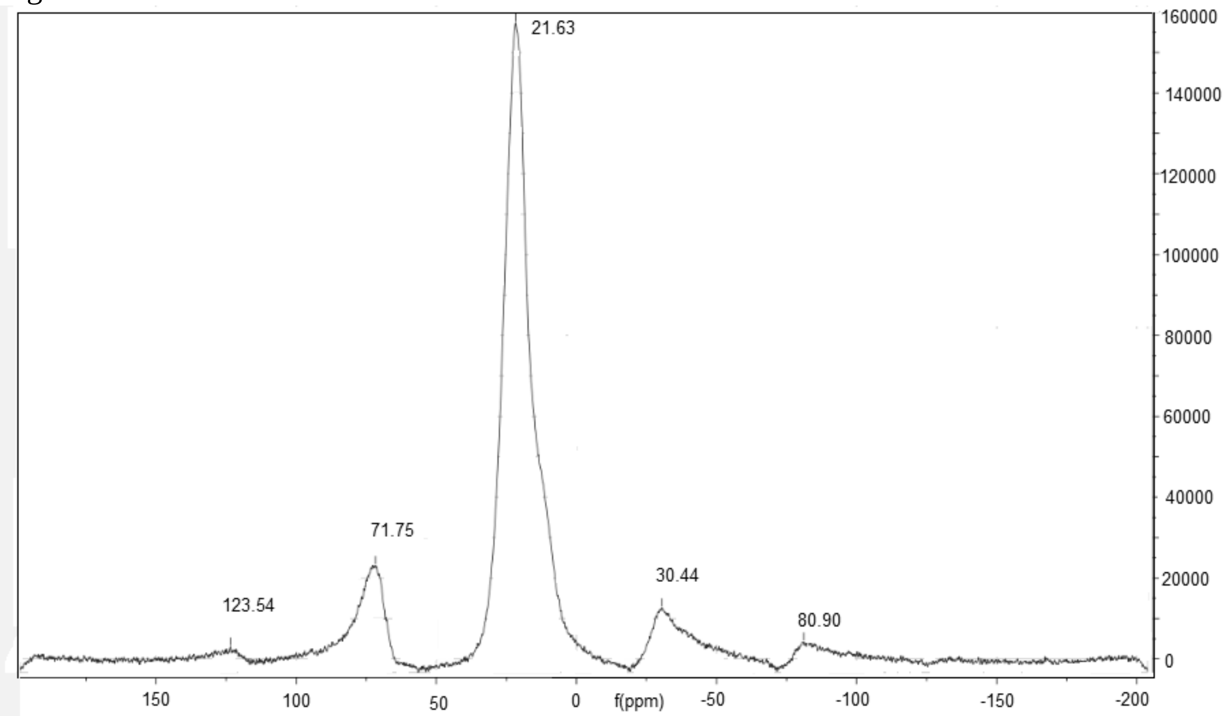
500
550
600
650
700
750
800
m/z

Fig. 5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30.44
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140000
120000
100000
80000
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20000
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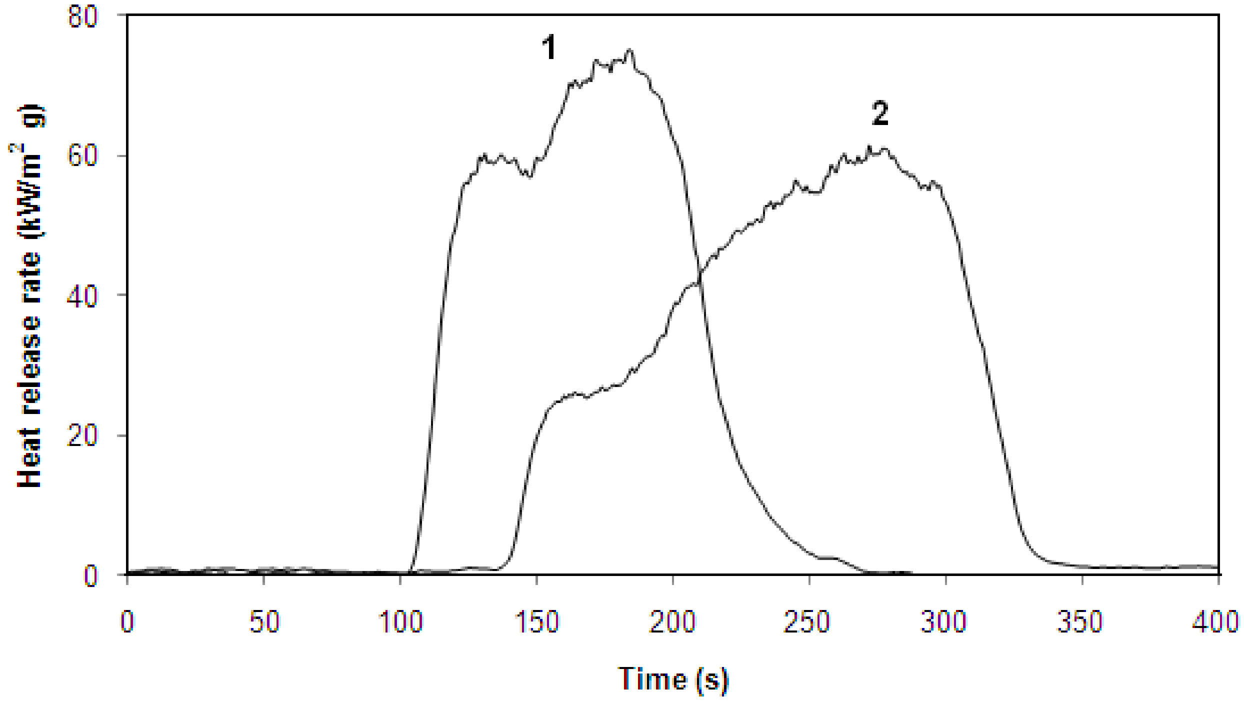
150
100
50
0
f(ppm)
-50
-100
-150
-200

Fig. 6


1
2
80
60
40
20
0
Heat release rate (kW/m^2 g)
0
50
100
150
200
250
300
350
400
Time (s)