



# Self-crosslinking acrylic latexes with copolymerized flame retardant based on halogenophosphazene derivative



Jana Machotova<sup>a,\*</sup>, Lucie Zarybnicka<sup>a</sup>, Radka Bacovska<sup>b</sup>, Josef Vrstil<sup>c</sup>,  
Martina Hudakova<sup>d</sup>, Jaromir Snuparek<sup>a</sup>

<sup>a</sup> Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

<sup>b</sup> Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic

<sup>c</sup> SYNPO, Ltd., S. K. Neumannova 1316, 532 07 Pardubice, Czech Republic

<sup>d</sup> Fire Research Institute, Ministry of Interior of the Slovak Republic, Rožňavská 11, 83104 Bratislava, Slovakia

## ARTICLE INFO

### Article history:

Received 22 March 2016

Received in revised form 6 June 2016

Accepted 5 September 2016

### Keywords:

Emulsion polymerisation

Core-shell latex

Diacetone acrylamide

Flame retardant

Phosphazene

Cone calorimeter

## 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.

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## 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].

\* Corresponding author.

E-mail address: [jana.machotova@upce.cz](mailto:jana.machotova@upce.cz) (J. Machotova).

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 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  $^{31}\text{P}$ (H) NMR, elemental analysis, mass spectrometry (MS) and Fourier transform infrared (FT-IR) spectroscopy.

$^{31}\text{P}$ (H) NMR spectra ( $\delta$ , ppm; J, Hz) were recorded using a Bruker Advance DRX 300 instrument (Bruker Corp., Germany) at the frequency of  $^{31}\text{P}$ : 202.46 MHz and 85%  $\text{H}_3\text{PO}_4$  (as the external standard). The samples were sealed in Simax tubes (diameter 4 mm), inserted in NMR cuvettes (diameter 5 mm) filled with  $\text{D}_2\text{O}$  (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  $\text{cm}^{-1}$ . The spectral resolution of the device is 0.09  $\text{cm}^{-1}$ . 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

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