

# SAMOSÍŤUJÍCÍ LATEXY OBSAHUJÍCÍ RETARDÉR HOŘENÍ

## SELF-CROSSLINKING LATEXES CONTAINING A FLAME RETARDANT

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### Summary

The paper describes the development of transparent one-component coating systems based on the core-shell acrylic aqueous dispersions prepared using emulsion polymerization technique. Latexes of functionalized core-shell particles bearing in the structure a covalently linked hexachloro-*cyclo*-triphosphazene 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 presence of the flame retardant increased the flame stability of coatings in terms of total heat release, amount of released smoke and maximum average rate of heat emission which indicates a slower flame spread during the material combustion.

**Key words:** phosphazene, flame retardant, emulsion polymerization, acrylic monomers

### Introduction

Currently, an increasing interest in exploiting of waterborne polymer coatings is related to the growing pressure on environmental protection, especially the need to comply with legislation restricting the volatile compounds (VOC) and emissions related to the use of solvent-based polymer coating systems. The aqueous colloidal polymer dispersions, i.e. latexes are used in many applications such as adhesives, additives for paper, paints and cosmetics, synthetic rubbers, floor polishes and sealants. The colloidal polymeric particles can be prepared to exhibit a desired morphology, composition, particle size distribution, surface groups and a molecular weight<sup>1</sup>.

For special applications, increased flame stability of utilized coating materials may be appreciated. 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<sup>2,3</sup>.

In the present work, we focused on the synthesis of a flame retardant based on hexachloro-*cyclo*-triphosphazene (HCCTP) 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.

## Experimental

### *Synthesis 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.

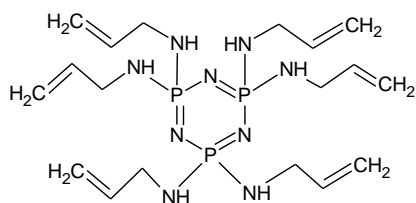


Fig. 1: The structure of hexaallylamino-*cyclo*-triphosphazene.

### *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. 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 described in the reference<sup>4</sup>. 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 minimum film-forming temperature (MFFT) was measured using the MFFT-60 instrument (Rhopoint Instruments, UK) according to ISO 2115. 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 gel content was determined according to CSN EN ISO 6427 using a 24-hr extraction with THF in a Soxhlet extractor. The presence of the copolymerized HACTP in the emulsion copolymers was investigated by means of

$^{31}\text{P}$  NMR 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).

## Discussion and result analysis

### *Characterization of latex copolymers*

Latexes were synthesized by the semi-continuous non-seeded emulsion polymerization process with varying amount and location of HACTP molecules in core-shell compositions. All the prepared self-crosslinking latexes (after ADH addition) were stable for over 12 months. MFFT values were shown not to be influenced by presence of HACTP in latex particles. All the synthesized self-crosslinking latexes exhibited low values of MFFT suggesting good application and film-forming properties. 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.  $T_g$  and gel content values were shown to be influenced markedly by the content of HACTP in latex particles. 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.

The presence of the copolymerized HACTP in the synthesized emulsion copolymers was tested using  $^{31}\text{P}$  NMR. It was found that almost the identical  $^{31}\text{P}$  NMR spectra were obtained in the case of gel fractions of the investigated emulsion copolymers; a singlet at a chemical shift  $\delta$  (S) = 21.63 ppm occurred in the spectrum of the high-molar mass polymer fraction, which indicated the presence of HACTP molecules (Fig 2). 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.

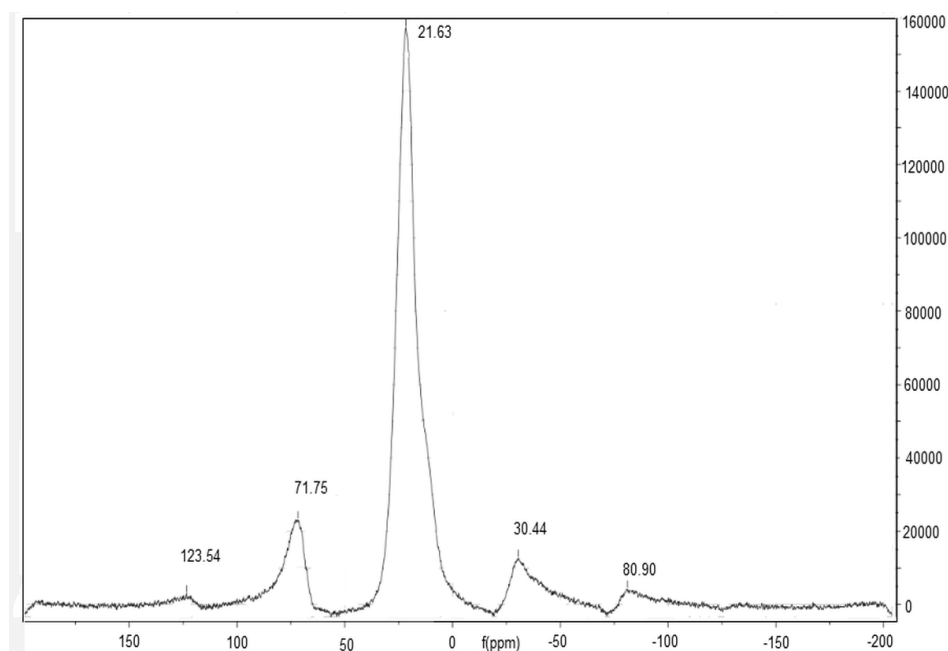


Fig. 2:  $^{31}\text{P}$  NMR spectrum for the gel fraction of the  $\text{C}_{0.4}\text{S}_0$  copolymer containing theoretically 0.4

wt.% of HACTP in the core structure of latex particles.

### *Characterization of latex coatings*

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. 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. 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  $PO\bullet$  radical is playing the main role. 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.

### **Conclusion**

HACTP was successfully prepared by nucleophilic substitution of HCCTP with allyl amine using the one-step synthesis. 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  $^{31}P$  NMR. 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.

## **Acknowledgement**

The Technological Agency of the Czech Republic (TA02000011) is gratefully acknowledged for supporting this work.

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