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SELF-CROSSLINKING LATEXES WITH IMPROVED FLAME STABILITY

Machotová J.[1], Zárybnická L.[1], Rückerová A.[1], Večeřa M.[1], Puková K.[2]

[1]*Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*
[2]*Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*
jana.machotova@upce.cz

Abstract

In this contribution the application of a novel flame retardant based on halogenophosphazene derivative 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 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 incorporation hexaallylamino-*cyclo*-triphosphazene did not affect transparency, flexibility, toughness and adhesive properties of resulting coatings. Moreover, the presence of the novel 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.

Introduction

Nowadays, the coating industries as well as consumers appreciate the technologies which reduce or eliminate the application of organic solvents in paint and varnish materials. 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. 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, through wood paints and varnishes to paints for metal protection and decorative systems[1-3].

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[4]. Huang et al. utilized an aziridine and phosphorus-containing compound to serve both as a curing agent and as a flame retardant for aqueous-based polyurethane resin[5]. 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[6,7]. 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[8,9].

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

Experiment

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.

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.

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 (Table I). 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[10]. 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}P(H) NMR 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).

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 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. 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.

Table I
Composition and MFFT values of self-crosslinking latexes based on core-shell particles containing HACTP

Sample	Composition of monomer feeds (wt.%) MMA/BA/MAA/DAAM/HACTP		MFFT (°C)
	Core	*Shell*	
C_0S_0	49/49/2/0/0	42/51/2/5/0	5.1
$C_{0.1}S_0$	48.95/48.95/2/0/0.1	42/51/2/5/0	5.6
$C_{0.2}S_0$	48.9/48.9/2/0/0.2	42/51/2/5/0	5.6
$C_{0.4}S_0$	48.8/48.8/2/0/0.4	42/51/2/5/0	5.8
$C_0S_{0.1}$	49/49/2/0/0	41.95/50.95/2/5/0.1	5.5
$C_0S_{0.2}$	49/49/2/0/0	41.9/50.9/2/5/0.2	5.6
$C_0S_{0.4}$	49/49/2/0/0	41.8/50.8/2/5/0.4	5.8

Discussion and result analysis

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. 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 (see Table I). 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. These characteristic properties are listed in Table II. 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. 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.

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

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

The presence of the copolymerized HACTP in the synthesized emulsion copolymers was tested using $^{31}P(H)$ NMR. It was found that almost the identical ^{31}P NMR spectra were obtained in the case of gel fractions of the investigated emulsion copolymers (Figure 5); a singlet at a chemical shift δ (S) = 21.63 ppm occurred in the spectrum of the high-molar mass polymer fraction, which indicated 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.

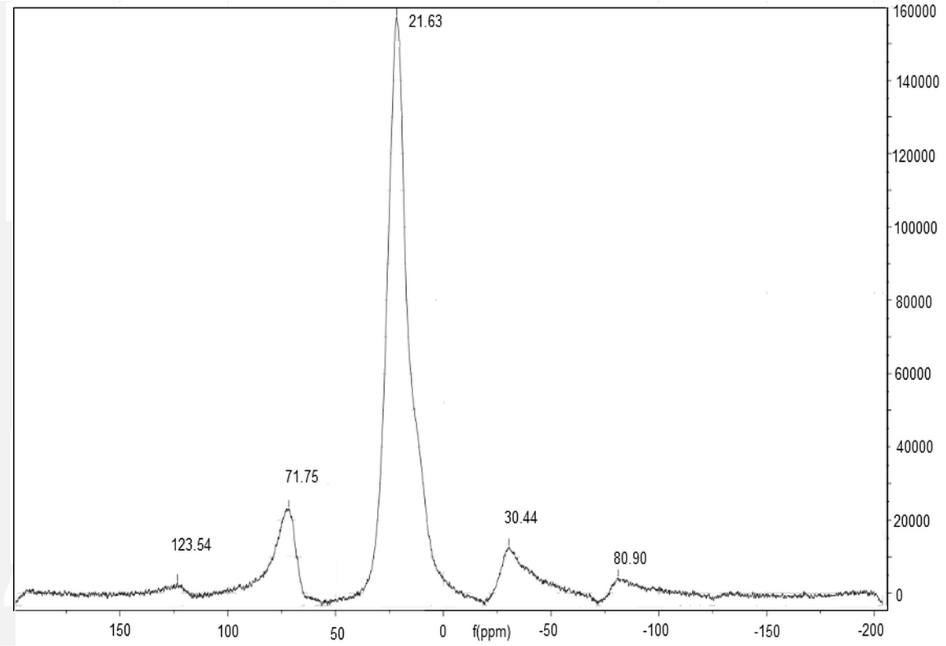

Figure 1. ^{31}P(H) NMR spectrum for the gel fraction of the $C_{0.4}S_0$ copolymer containing theoretically 0.4 wt.% of HACTP in the core structure of latex particles.

Characterizatition 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 III. 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 II). 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. Moreover, 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.

Table III

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]	Impact resistance[b] (cm)	Water absorption[c] (%)
C_0S_0	84.7 ± 2.7	22.0 ± 0.7	1	95	53.4 ± 2.1
$C_{0.1}S_0$	82.7 ± 0.3	23.7 ± 0.5	1	above 100	43.3 ± 1.7
$C_{0.2}S_0$	58.4 ± 0.4	26.4 ± 0.3	0	above 100	40.7 ± 0.9
$C_{0.4}S_0$	69.9 ± 1.8	34.3 ± 1.1	0	above 100	35.9 ± 1.1
$C_0S_{0.1}$	58.5 ± 3.6	19.9 ± 0.8	1	above 100	52.7 ± 1.6
$C_0S_{0.2}$	87.2 ± 0.5	24.3 ± 1.3	0	above 100	50.2 ± 1.8
$C_0S_{0.4}$	59.2 ± 1.3	27.0 ± 1.6	1	99	49.3 ± 0.7

[a] Adhesion is expressed as the degree of flaking in the 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.

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 IV and Figure 2. Fig. 2 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. 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.

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.

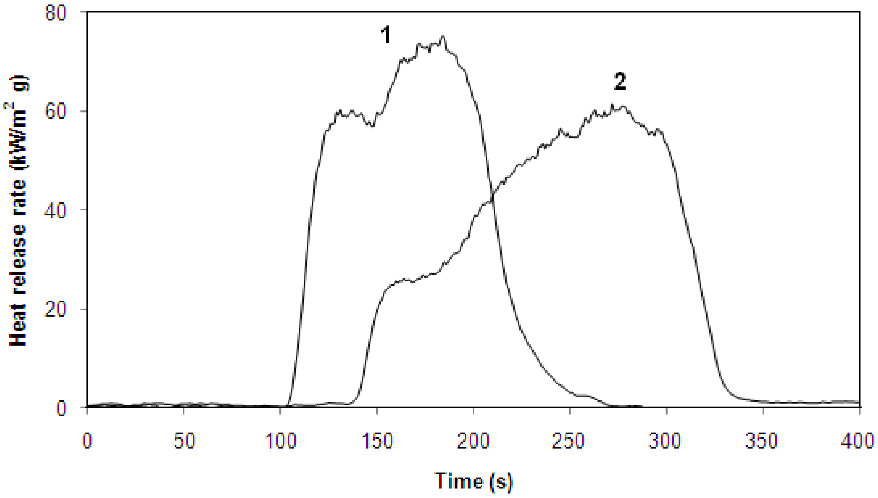

Figure 2. Comparison of combustion of (1) the coating based on the $C_0S_{0.4}$ latex particles comprising 0.2 wt.% of HACTP in monomer feeds forming their shell layer with (2) the coating formed by the HACTP-free latex particles C_0S_0.

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 $^{31}P(H)$ 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.

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