Phosphonated Oligoallylamine: Synthesis, Characterization in Water, and Development of Layer by Layer Assembly

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ABSTRACT: The work focuses on the synthesis and layer by layer (LbL) assembly of oligoallylamine and phosphonated oligoallylamine. To this aim, the synthesis of oligoallylamine and the phosphonated form have been done by free radical polymerization in aqueous media. First, radical polymerization of acid salt of allylamine was performed. This charged polymer could not be characterized using classical analytical techniques such as size-exclusion chromatography and matrix-assisted laser desorption/ionisation-time of flight mass spectroscopy due to presence of cations. This work demonstrated the interest of capillary electrophoresis (CE) to analyze charged oligomers, using very small amounts of samples. Entangled polymer solution CE was used as a size-based separation technique for the characterization of the molar mass distribution using indirect ultraviolet detection and calibration based on vinyl pyridine standards. Phosphorus-containing oligoallylamines having a number-average molar mass of 1600 g mol⁻¹ and a 2.3 polydispersity index were obtained. When combined using the LbL approach, prepared polymers showed an exponential growth regime as demonstrated by Fourier transform infrared spectroscopy measurements. Furthermore, thermogravimetric analyses of the LbL-assembled polymers showed an extraordinary thermal and thermo-oxidative stability. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. 51, 1244–1251, 2013

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INTRODUCTION Plastic materials, even though they are used for thousands of applications, have a major inconvenience: their flammability. A widely known method to impart flame retardancy is to add halogen-containing compounds to the basic resin. Nevertheless, halogenated flame retardants are recognized as highly toxic compounds and lead to environmental problems. Thus, enormous efforts have been made to develop halogen-free flame retardant systems. New organophosphorous (P) flame retardants in conjunction with nitrogen (N) compounds have a weak toxicity and a good efficiency. These compounds are efficient even with a low content of phosphorus or nitrogen. Generally, a good synergistic effect was observed between N and P, even if they are located on different molecules: during a combustion process, P−N bonds are formed and the new species protect the material against the fire. Nowadays, these commercially available azo-phosphonated flame retardants such as phosphanes, phospham, or phosphorimides are synthesized in extreme conditions (high temperatures).

Vinyl polymers containing both nitrogen and phosphorus groups can be used alternatively. These macromolecules can generally be obtained via a two-step synthetic procedure according to two distinct strategies: either the synthesis of azo-phosphonated monomer followed by its polymerization or the polymerization of amine-containing monomer followed by azo-phosphonation postfunctionalization. In this work, the second strategy was selected.

In this study, we have undertaken the radical polymerization of allylamine. Indeed, despite its well-known poor reactivity due to the stability of allyl radical, its polymerization affords primary amine-containing oligomers, which can be further functionalized from azo-phosphonation. The resulting

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phosphonated oligomers have been coupled with nonfunctionalized oligoallylamine through a layer by layer (Lbl) assembly (Scheme 1). Indeed, in recent years, the Lbl technique has been proven to be a valuable tool for surface modification and nanostructuration. This self-assembly technique, that was first presented by Ilavsky in 1966 and rediscovered by Decher in the 1990s, simply consists in an alternate adsorption of chemical species on a selected substrate. Until now most of the multilayer films have been built using mainly electrostatic attraction as the driving force for multilayer buildup but this is not a prerequisite. Recently, the Lbl assembly has been adopted to confer flame retardant properties to different kind of substrates such as natural and synthetic fabrics, foams, and rigid plastics.

Moreover, the Lbl approach represents an innovative and valuable alternative to current flame retardant treatments most of which have recently been prohibited due to environmental and health risks. Indeed, when compared with more traditional treatments the Lbl present several advantages: (i) easy incorporation of functional materials, (ii) processing under ambient conditions (room temperature and atmospheric pressure), and (iii) environmental friendly characteristics (solvent is mostly water, concentrations of the solutions/dispersions are below 1 wt %, possibility to recycle suspension baths after use).

In this scenario, the phosphonated oligomers synthesized in this work represent suitable products for the growing of Lbl assembly with an intumescent-like behavior.

Oligoallylaminos have been chosen as counterpart in the Lbl architectures taking in consideration the results published in the literature. Indeed, linear polyelectrolytes bearing allylamine groups exhibited an exponential growth when coupled with sodium phosphates or sodium monomorillonites with promising flame retardant properties.

In this paper, the synthesis and characterization of the above species has been thoroughly detailed as well as the Lbl growth. The latter aspect has been monitored by Fourier transform infrared (FTIR) spectroscopy and the resulting coatings imaged by scanning electron microscopy (SEM). Furthermore, the thermal and thermo-oxidative stability of the adopted oligomers and the assembled Lbl coating has been assessed trough thermogravimetric analyses (TGA) under nitrogen and air atmosphere, respectively.

**EXPERIMENTAL**

**Reagents**

All the solvents and reagents (Sigma-Aldrich or Acros) were of a purity of 98-99%. Allylamine, ammonium persulfate, formaldehyde, phosphonic acid, and didodecyl(dimethylammonium) bromide (DDAB) were used without purification. Chlorohydric acid was used as a 35% aqueous solution. Branched polyethyleneimine (average $M_w$ is approximately 25,000 g mol$^{-1}$) by laser scattering, average $M_w$ is approximately 10,000 g mol$^{-1}$ by gel permeation chromatography, as reported in the material datasheet; BPEI was purchased from Sigma Aldrich (Milwaukee, WI). All the products were used for preparing 0.1 wt % suspensions for Lbl assembly, using 18.2 MQ deionized water supplied by a Q20 Millipore system (Milano, Italy). Single side polished (1 0 0) silicon wafers were used for infrared (IR) growth characterization and cross-section SEM observation.

**Instrumentation**

Proton ($^1$H) and phosphorous ($^{31}$P) nuclear magnetic resonance (NMR) spectra were recorded in deuterium oxide solution, (using 5-10 mg of each compound dissolved in 0.6 mL of solvent), on a Bruker Avance 400 MHz spectrometer. $^1$H and $^{31}$P chemical shifts are expressed in ppm/tetramethylsilane (TMS) and ppm/H$_3$PO$_4$.

Capillary electrophoresis (CE) experiments were performed using an Agilent Technologies 3DCE system. Separation capillaries were prepared from bare silica tubing purchased from Composite Metal Services. Capillary dimensions were 33.5 cm (25 cm to the detector) $\times$ 50 $\mu$m internal diameter (i.d.). New capillaries were conditioned with the following flushes: 1 M NaOH for 20 min, 0.1 M NaOH for 20 min, pure water for 10 min, 0.25 M DDAB in water for 15 min, and finally 5 min with BGE1. BGE1 is a Background Electrolyte composed of 12 mM H$_3$PO$_4$, 6 mM creatinine, and 0.15 mM DDAB at pH 2.58. DDAB was used to obtain a positively charged capillary surface leading to strong anodic electrophoretic flow. For the determination of the molar mass distribution by entangled polymer solution CE, BGE2 was prepared by adding 5% (w/w) of dextran (Aldrich; $M_w$ = 400,000–500,000 g mol$^{-1}$) to BGE1. The samples were introduced hydrodynamically by application of a positive pressure on the inlet side of capillary (17–50 mbar for 5–10 s depending on the sample). The applied voltage was 7 kV. Poly vinyl pyridine (PVP) standard polymers were detected at 250 nm. Monomer and polymers were detected by indirect ultraviolet (UV) detection at 193 nm using creatinine as a chromophore. The temperature of the capillary cartridge was set at 25 °C. Mesityl oxide (approximately 0.1% (v/v) in the sample) was added as a neutral marker to determine the
electro-osmotic mobility. Electropherograms were plotted in effective mobility scale (\( \mu_{eq} \)) using the following eq (1):

\[
\mu_{eq} = \mu_{app} - \mu_{eo} = (L/V_{app}) \cdot (L/V_{eo})
\]

(1)

where \( \mu_{eo} \) is the electroosmotic mobility, \( \mu_{app} \) is the apparent mobility, \( t_{eo} \) is the migration time of a neutral molecule, \( L \) is the total capillary length, \( l \) is the migration length, \( V \) is the applied voltage, and \( t_{app} \) is the apparent migration time of the solute.

The seven PVP standard samples were dissolved at 2.5 g L\(^{-1}\) in pure water. The polymer samples were prepared at 2.8 g L\(^{-1}\) in BGE1. Each solution was injected and monitored separately. Note that the phenyl trimethylammonium chloride was used as a mobility marker to correct for any electroosmotic flow fluctuations.

Attenuated total reflectance (ATR) spectroscopy was used to acquire the spectra of pure materials. ATR spectra were recorded at room temperature in the range 4000-600 cm\(^{-1}\) (32 scans and 4 cm\(^{-1}\) resolution), using a Frontier FTIR/FIR spectrophotometer (Perkin Elmer, Italy), equipped with a Ge/Ge crystal (depth of penetration 0.65 \( \mu \)m, as stated by the producer).

Single side polished (1 0 0) silicon wafers were used as a substrate for monitoring the evolution of the Lbl assembly by means of a FTIR spectrophotometer (32 scans and 4 cm\(^{-1}\) resolution, Perkin Elmer SPECTRUM GX).

Cross-sections of the deposited coatings on Si wafers were imaged using a scanning electron microscope (model 1450VP by Leo). TGA were performed on a Q500 TA Instruments apparatus, in the range 50-800 °C, at 10 °C min \(^{-1}\), using approximately 10 mg of sample in alumina pans, in nitrogen or air atmospheres (60 mL min \(^{-1}\) flux).

Syntheses

**Synthesis of Allylamine Salt**

A two-neck round-bottomed flask equipped with reflux condenser, a nitrogen purge and a magnetic stirrer was charged with 175 mmol (9.975 g) of allylamine and was cooled at 0 °C. 175 mmol (6.38 g, i.e., 18.3 mL of 35% aqueous solution) of hydrochloric acid were added dropwise for 30 min. The mixture was stirred for 1 h at room temperature.

**Polymerization of Allylamine Salt**

The polymerization was conducted in the same system as the monomer synthesis: 90 mmol (8.42 g) of allylamine hydrochloride with 5 g of water were mixed under nitrogen atmosphere; 13 mmol (2.96 g) of ammonium persulfate diluted with 6 g of water were added dropwise in three fractions. The mixture was subsequently stirred at 90 °C during 7 hs. Polysalt of allylamine (PAAHCl) was separated by precipitation in methanol. A white solid was obtained in 60 % yield.

\[^{1}H\text{ NMR: 400 MHz, D}_2\text{O, } \delta \text{ (ppm): 1.41 (m, H}_1\text{); 1.92 (m, H}_2\text{); 2.95 (m, H}_3\text{) (Fig. 1)}}\]

**FIGURE 1** \[^{1}H\text{ NMR} \text{ (D}_2\text{O) of PAAHCl and deconvolution of the first zone in 4 peaks using Origin.}\]

**Synthesis of Phosphonated Polymer**

To a stirred solution of 57 mmol (5.33 g) of PAAHCl (2) and 125 mmol (10.25 g) of phosphoric acid in water (10 mL) heated at 100 °C, 240 mmol (7.2 g) of formaldehyde was added dropwise for 1 h. An orange solid was obtained, which was soluble in basic aqueous solution. The phosphonated polymer (PAA-P) oligomer was purified by precipitation in acidic solution.

\[^{1}H\text{ NMR: 400 MHz, D}_2\text{O, } \delta \text{ (ppm): 1.45 (m, CH}_2\text{); 1.90 (m, CH); 2.98 (m, CH}_2\text{-N); 3.45 (m, OCH}_2\text{); }^{31}\text{P NMR: 400 MHz, D}_2\text{O, } \delta \text{ (ppm): 5.7}}\]

**Lbl. Deposition**

To activate the Si surface and prepare it for the further Lbl deposition the very first layer was grown by dipping for 20 min into BGE1 (0.1% wt, pH 10) solution followed by a washing step with water to extract the residues of counterions. After this first step, the substrate was alternately immersed into negatively and positively charged baths (Scheme 1). The negative solution was prepared with phosphonated oligomers (0.1% wt, pH 3) that bear negative charges due to the dissociation of phosphonated groups while the positive solution was prepared with PAAHCl (0.1% wt, pH 4.5) that bears positive charge due to the protonated amine.

The dipping time was set to 10 min for the first couple of layers and reduced to 5 min for subsequent layers. After each immersion step, the substrate was washed with deionized water to remove the excess of ionic species.

20 bilayers (BL) coatings were also deposited onto 100 \( \mu \)m PET films and removed by scratching to obtain samples of the Lbl assembled polymers for TGA.

**RESULTS AND DISCUSSION**

**Polymerization of Allylamine Salt in Water**

Prior to phosphonic acid function, allylamine was polymerized in acidic water-based medium. The acidification of allylamine monomer was first carried out by mixing a 1:1
monomer to acid molar ratio (i.e., hydrochloric acid). A stoichiometric amount of acid was added dropwise to the allylamine under stirring and by keeping the reaction temperature between 0 and 10°C. Quantitative yields were obtained for salt formation.

The radical polymerization was performed in water initiated with ammonium persulfate (8% molar ratio). The mixture was warmed to 70 °C and concentrated aqueous solution of ammonium persulfate (initiator) was added very slowly in three fractions. First addition was performed over 1 h, the temperature was then increased to 90 °C, and the two last fractions of initiator were successively injected. The polymerization was stopped after 7 h of reaction time. The polysalt (NH₄⁺ Cl⁻ form), was precipitated into methanol, filtered and dried at 45 °C under vacuum. A 60% reaction yield was obtained. PAAHCl was found highly soluble in acidic aqueous solution.

The ¹H NMR of PAAHCl in the D₂O (Fig. 1) shows the presence of the polymer (broad peaks): the CH₂ and CH on the polymer chain were centered to 1.41 and 1.92 ppm, respectively, and the signal of CH₂ next to the nitrogen atom appeared at 2.95 ppm. NMR spectrum between 1.3 and 2.4 ppm was deconvoluted using Gaussian functions with Origin program. This process leads to informative data about the relative area of the different peaks and so information on the number average molar mass of PAAHCl. The fit between real and calculated spectra was good (R² = 0.990). The 2' peak area characteristic of proton in β position of initiator (SO₄⁻) was used as reference. Two number-average degrees of polymerization DPn were calculated from the ratio between areas of peaks 2 (Ap₂) and 1,1' (Ap₁,1') to area of peak 2' (Ap2'). According to eqs (2) and (3) (theoretically, DPn1 = DPn2):

$$DPn1 = \frac{(Ap_{1,1'} - Ap_{1'})}{2 \times Ap_{2'}}$$  \hspace{1cm} (2)

$$DPn2 = \frac{Ap_{2'}}{Ap_{2'2}}$$  \hspace{1cm} (3)

where $Ap_{1'}$ was estimated equal to $2 \times Ap_{2'}$ (areas 1 and 1' correspond to CH₂ groups and areas 2 and 2' correspond to CH groups).

$DPn1$ and $DPn2$ were equal to 14 and 18 units, respectively, with the deconvolution of spectrum (Fig. 1). The monomer has a molar mass of 93.6 g mol⁻¹; so the number-average molar mass estimated by this calculation was comprised between 1300 and 1690 g mol⁻¹ for PAAHCl. The direct determination of the polymer molar mass could not be made by classic analytical method such as gel permeation chromatography because of the charge of polymer. Alternatively, CE was used.

Characterization of Allylamine Oligomers by CE

A major experimental difficulty is to characterize the resulting charged and water-soluble polymer. CE is a powerful separation technique for the characterization of synthetic or biopolymers,²⁹ such as oligomers,²¹,²² polyelectrolytes,²²,²⁴ copolymers,²⁵-²⁷ or end-charged polymers.²⁹ Depending on the polymer characteristics (end-charged or evenly charged polymer, homopolymer or copolymer, statistic or block copolymers), different CE modes (free solution CE, entangled polymer solution CE or gel CE, micellar electrokinetic CE) can be implemented. Important information relative to the polymer distributions (either the molar mass or the compositional distributions) or to the purity of the sample (residual monomer, homopolymer against copolymer) can be obtained. In a recent study, the molar mass distribution of a UV absorbing ionic polydiacetylene²⁸ has been studied by entangled polymer solution CE allowing the determination of polydispersity index and the average molar mass relative to PVP calibration. CE presents also the advantage of requiring only minute amount of sample (few nanoliters are injected).

In this work, entangled polymer solution CE with indirect UV detection has been used for the size-based separation of oligomers which are UV transparent. Creatinine was used as a cationic chromophore (BGE 1 and 2) and dextran was used as a separating polymer (entangled polymer solution acting as a sieving medium, BGE 2). DDAB was used to obtain a positively charged capillary surface and to avoid any polymer adsorption onto the capillary surface. In these electrophoretic conditions, negative peaks for the polymer samples are detected at 193 nm.

In free solution CE [Fig. 2], that is, in the absence of separating polymer (BGE 1), the effective mobility of the PVP standards was found to be a slightly decreasing function of the molar mass (between 1390 and 135,500 g mol⁻¹). Nevertheless, this dependence is much too weak to get sufficient size-based selectivity in accordance with the free draining polyelectrolyte behavior generally observed in free solution. However, the free solution effective mobility of polymer (46 × 10⁻⁹ m²/V s)
Using this equation, it was possible to convert the distribution of polymer from effective mobility scale to molar mass scale. From this distribution, it is possible to deduce the number and the weight average molar masses of polymer relative to PVP calibration using eq (4). Average molar mass values calculated by integration of the distributions were found as \( M_n = 1600 \text{ g mol}^{-1} \) and \( M_w = 3600 \text{ g mol}^{-1} \). The corresponding polydispersity index was \( M_w/M_n = 2.3 \). This \( M_n \) value corresponds to an average degree of polymerization of about 17 monomers. This analytical result confirmed the first estimation done with \(^1\text{H} \) NMR deconvolution and brings some additional information on the polymer polydispersity.

Post Functionalization into Phosphonated Function

The synthesis of azo-phosphonated compounds can be performed by using well-known Kabachnik-Fields,31,32 Mannich33 or Moedritzer34 reactions have been described. These reactions generate in a selective way, \( \alpha \)-aminomethylphosphonates products.35,36 The reaction of Moedritzer allows the addition between phosphonic acid, formaldehyde, and any kind of amines to form the corresponding \( \alpha \)-aminoethylphosphonic acids directly.

Functionalization of the polymer was made according to the Moedritzer reaction (Scheme 2). PAAHCl was dissolved in the acidic aqueous solution (\( \text{pH} = 1 \)). The phosphonic acid was added and the mixture warmed to 100 °C. The addition of formaldehyde was made dropwise and the mixture was stirred for 1 additional hour. After cooling, the PAA-P was precipitated into deionized water. The obtained yellow solid was characterized by \(^1\text{H} \) and \(^31\text{P} \) NMR in basic aqueous solution. The \(^31\text{P} \) NMR showed the presence of a wide peak toward 5.7 ppm.

LbL Assembly

As already described in Experimental section, multilayered films were prepared by the dipping method in a solution of polyanion PAA-P then a solution of polycation PAAHCl (Scheme 1). The growth of the assemblies on silicon wafers was evaluated by FTIR spectroscopy. Figure 4 reports both the collected spectra of the pure oligomers PAAHCl and PAA-P (4a) and the evolution of the spectra during LbL growth (4b).

The asymmetric and symmetric stretching vibrations of \( \text{NH}_3 \) for pure PAAHCl were found at 1605 and 1510 cm\(^{-1} \), respectively; whereas pure phosphonated oligoallylamine
Inlet of Figure 4(b) shows the absorbance increase in the signal at 1075 cm⁻¹; an overall linear growth, after 5 BL, can be easily detected. By comparing signals reported in Figure 4(b), the signals related to PAA-P appear to be more intense than the ones related to PAAHCl. As a consequence the coating composition is expected to be rich in PAA-P.

The cross-sections of Si wafer coated by 10 and 20 BL have been measured by SEM microscopy (Fig. 5). A homogenous coating was achieved after 10 BL with an average thickness of 0.9 μm, while with 20 BL, the coating thickness was increased to 2.6 μm. Such thicknesses are consistent with the IR growth.

The thermal and thermo-oxidative stability of both the pure oligomers and the assembled LBL coating (20BL) has been assessed through TGA under nitrogen and air atmosphere at a heating of 10 °C min⁻¹ (Fig. 6).

Under nitrogen, both synthesized PAAHCl and PAA-P oligomers present several degradation steps that lead to a final residue of 2 and 31%, respectively. This latter value is extremely interesting and suggests that, on heating, the PAA-P is capable of creating a structure that is thermally stable up to 800 °C. For assembled LBL, the final residue found at 800 °C is 37%, and it is higher than the one obtained with pure PAA-P. When the two oligomers are LBL assembled the behavior on heating under inert atmosphere is different from what can be expected from the simply additive contribution of both PAA-P and PAAHCl oligomers. Indeed, when

![Figure 4](image)

**FIGURE 4** Collected IR spectra of pure oligomers (PAA-P and PAAHCl) (a) and LBL growth (b).

(PAA-P) gives characteristics signals of P=O and P−O stretching vibrations at 1175 and 920 cm⁻¹, respectively.⁷⁷ Both elements present a small peak at 1075 cm⁻¹ that can be ascribed to both NH₃⁺ rocking and C−N stretching vibrations.

As far as the LBL assembly of PAAHCl and PAA-P is concerned, the above-mentioned characteristic peaks of both oligomers can be distinguished with some wavelength and intensity variations due to the LBL process. NH₃⁺ stretching vibrations are shifted at higher wavenumbers (1640 and 1550 cm⁻¹) probably due to the absence of Cl⁻ counterions (eliminated by rinsing with pure water) in the assembled polymers. Two peaks around 1175 and 1075 cm⁻¹ appears to be the most intense. Such signals can also be found in the spectra of the pure oligomers with lower intensities [Fig. 4(a)]; the former can be ascribed to P=O stretching vibration and the latter to both NH₃⁺ rocking and C−N stretching vibrations. The change in relative intensity found for the LBL assembled polymers can be linked to PO₃⁻ and PO₄²⁻ species related to partially dissociated phosphonated groups of PAA-P.⁷⁷

![Figure 5](image)

**FIGURE 5** SEM micrographs performed on the cross-section of Si wafers coated with 10 and 20 BL.
FIGURE 6 TG plots of pure PAA HCl and pure PAA-P in comparison with the 20 BL assembly of the two oligomers under nitrogen (a) and air (b).

oligomers are LBL assembled, the resulting thermal stability is unexpectedly higher than that of PAA-P, which can be ascribed to a synergistic effect of the LBL assembly. This synergy is due to the strong ionic interactions between oligomers during the LBL approach.

Under air atmosphere, pure PAA HCl shows a weight loss curve similar to the one found in inert atmosphere with the exception of a new degradation step found around 400 °C; the final residue is about 2% (Fig. 6(b)).

On the contrary, PAA-P shows exceptional thermo-oxidative stability with a 63% residue stable at 550 °C that, on reaching 800 °C, is reduced to 8%. Again, as observed under inert atmosphere, the LBL assembly of the two oligomers yields extraordinary results: indeed, the residue found around 550 °C (58%) is close to the one of pure PAA-P (63%), whereas the final residue at 800 °C is greatly enhanced (30%) by the LBL approach.

Such enhanced thermal-oxidation stability can certainly come in handy when designing LBL coatings to provide a thermally stable coating with an overall flame retardant effect. Preliminary studies performed in our laboratories have shown that once deposited on natural fabrics the coating under study are capable of reducing the burning rate as well as preserving the integrity of the fabric after flammability tests.

These latter promising results clearly demonstrate the flame retardancy potentialities of the LBL coatings under study and will be thoroughly investigated in a future study.

CONCLUSIONS

We have demonstrated the possibility to produce oligoallyl amines by radical polymerization in water with monomer masses about 1600 g mol⁻¹ [M_n]=3600 g mol⁻¹ [M_w]. CE was found to be well suited to characterize the charged oligoallylamines. Phosphonated oligoallylamines were obtained by postfunctionalization in one stage and gave original polymers with zwitterions functions that can be utilized for many applications.

We have successfully used the LBL technique for the fabrication of different films with oligoallylamines and phosphonated oligoallylamines. FTIR measurements have shown an exponential growth regime of LBL assemblies. Moreover, a homogeneous coating of 10 or 20 BL has been achieved, demonstrated by SEM observations.

TGA have revealed an exceptional thermal and thermo-oxidative stability of the LBL assembled oligomers that were able to yield residues of 37 and 31% at 800°C, under inert and oxidative atmosphere, respectively. Undoubtedly, this study provides the opportunity to use (PAA-P and PAA HCl) LBL assemblies as flame retardants.

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REFERENCES AND NOTES


