Synthesis and Characterization of Thermally Stable Flame Retardant Thermoplastic Polyphosphazenes

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Abstract

Different types of functionalized thermoplastic polyphosphazenes such as poly(bis(furfuroxy)phosphazenes) (PBFP), poly(bis(1-adamantanemethylamine)phosphazenes) (PBAP) and poly(bis(cyanophenoxy)phosphazenes) (PBCP) were synthesized and further characterized to study their flame retardant properties. Structural characterizations were carried out by using GPC, FTIR, ^1H & ^{31}P NMR and wide angle XRD. Beside this, the solubility behaviour of these synthesized polyphosphazenes was checked in various protic and aprotic solvents. Thermal analysis and combustion properties of synthesized polyphosphazenes were investigated using thermogravimetric analysis (TGA), differential scanning calorimetry, UL-94 (vertical burning test) and cone calorimetry. The Limiting Oxygen Index values of synthesized polyphosphazenes were also determined from their % char yield obtained in TGA. It was found that the LOI value was highest for PBCP and lowest for PBAP amongst all substituted polyphosphazenes. Further, all the polymeric samples showed high flame retardancy with UL-94 V-0 rating. The water uptake property of synthesized polyphosphazene polymers was also invested by measuring their water contact angles which showed that all the polymers were hydrophobic in nature with their water contact angles in the range of 137^o to 141^o. Copyright © VBRI Press.

Keywords: Functionalized polyphosphazenes, limiting oxygen index, flame retardancy, cone calorimetry, UL-94.

Introduction

Polyphosphazenes are the most versatile category of inorganic polymers which display very broad range of chemical and physical properties due to variety of substituents attached to their backbone phosphorous atoms [**1-4**]. Depending on the substituents, polyphosphazenes show significant amount of properties like oxidative stability, biocompatibility, high thermal stability and biodegradability [**5-7**]. Further, polyphosphazenes can be water soluble or repellent, flexible at low temperatures, flame retardant, stable at high temperatures, resistant to harsh chemicals & UV radiation, biologically active and biodegradable [**8-11**]. Moreover, P-N backbone in polyphosphazenes is flexible due to which it is possible for these polymers to undergo structural changes in the solid state. Crystalline polyphosphazenes generally exhibit polymorphism with a mesomorphic state between crystalline and melted state. Another characteristic common to nearly all the polyphosphazenes is their combustion behaviour. They exhibit high oxygen index, low smoke emissions, no corrosiveness and low toxicity of combustion gases [**12-15**]. This property has proven to be essential for the commercial development of polyaryloxyphosphazenes [**16**]. Polyphosphazenes have been exposed to have exceptional compatibility [**17-18**]. They have been productively proven as vehicles for drug delivery and tissue regeneration treatment [**19**]. Due to hydrolytic unsteadiness of P-N bond in the presence of definite side groups, certain animated polyphosphazenes are admirable candidates as biodegradable polymers. Polyphosphazenes substituted by amine group have higher sensitivity in acidic medium than neutral or basic medium. Their degradation rate is significantly quicker in acidic media [**20**]. Beside these, polyphosphazenes have also some qualities which make them precious for energy, aerospace or oil drilling purposes. These properties comprise of low temperature litheness and softness, resistance to various fuels, oils and hydraulic liquids, resistance to fire, radiation and ultraviolet permanence [**21-22**]. Polyphosphazenes have been also employed as a matrix material in thermal conductive composites [**23**].

Polyphosphazenes can be used as an active flame retardant additive since these materials display high LOI values [**24**]. Cyclotriphosphazenes are one of the interested material which exhibit main chain of –P=N- units and self-extinguishing nature in flame tests [**25**]. Phosphorous based flame retardant materials (PFRMs) are one of the promising members of multilateral halogen-free flame retardant materials which can be used in vapor and condensed phase reactions [**26-27**]. These materials furnish flame retardancy in the polymers by emboldening carbonization and char formation [**28**]. Allyl functionalized polyphosphazenes [**24**] and 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) are one of the proficient PFRMs which have engrossed interest due to their extraordinary thermal stability [**29-31**]. Aryloxy or allylamine substituted polyphosphazene is also highly thermal stable as well as potential flame retardant material [**32, 33**]. Beside these, fluoroalkoxy elastomers have been used as fire retardant materials due to their low Tg and insolubility [**34**]. Polyphosphazenes containing mixed substituents (alkoxy and aryloxy) elastomers have been used as fire retardant materials and foam expansion insulations [**35**]. Poly(fluorophosphazene) combined with organo-bromine compounds enhances the flame retardancy of polyethylene terephthalate [**36**]. Further, a multifunctional organic-inorganic hybrid polyphosphazene having melamine group wrapped ammonium phosphate has been also used as potential flame retardant material [**37**]. Even phospham [**38**], (poly)aminophosphazene [**39-40**], phosphorus oxynitride [**41**] have been utilized as flame retardant materials.

In the present investigation, we have synthesized thermoplastic polyphosphazenes by substituting the chlorine atoms of polydichlorophosphazene with furfuroxy, 1-adamantanemethylamine and cyanophenoxy side groups and study their structural, thermal and flame retardant and hydrophobic properties to use them as water repellant coating and flame retardant materials for defence applications.

Experimental

Materials

Materials used in the experiment were hexachlorotriphosphonitrile (99%), $CaSO_4.2H_2O$(99%), furfuryl alcohol (98%), 1-Adamantanemethylamine (99%), cyanophenol (98%), sodium hydride (60% dispersed in mineral oil), anhydrous THF (99%), hexane anhydrous (95%) & petroleum ether AR 60-80^{0}C. All of them were obtained from Sigma Aldrich and used without further purification.

Characterizations

FTIR spectra of polymers were performed on the JASCO FT-IR 4000 instrument & the spectra were recorded in the range from 500 to 4000 cm^{-1} by using KBr pellet method. The existence of various groups & linkages etc. is identified from spectra.

NMR spectra were obtained on a Bruker Advance III, 400 MHz spectrometer operating at various frequencies viz.400 MHz for ^{1}H spectra and 160 MHz for ^{31}P spectra. Standard pulse sequences were used for obtaining ^{1}H, and ^{31}P spectra. Samples were dissolved in deuterated DMSO. The reference standard for ^{1}HNMR was TMS & for ^{31}P NMR was 85% H_3PO_4 as external standard.

GPC of synthesized polyphosphazenes was carried out using Malvern Viscotek 350 HT gel permeation chromatograph module 350 A using tetrahydrofuran as a solvent. The GPC columns were calibrated with polystyrene standards (Waters).

Wide angle X-ray diffraction patterns of the synthesized polyphosphazene polymers were recorded on an XRD-6000 diffractometer with Cu/Ka target (40 kV, 15 mA) and having scanning rate was 50 min^{-1}.

Differential Scanning Calorimetry (DSC) analysis of polymer samples was performed with TA Instruments DSC-Q100 using Indium metal for calibration of the instrument according to standard procedures. The analysis was done under N_2 atmosphere with heating rate of 10ºC/min.

Thermo-gravimetric analysis was carried out using DuPont TGA-2100 thermal analyzer in the temperature range from room temperature to 800ºC with heating rate of 10ºC/min. in inert atmosphere. Limited oxygen index (LOI) was measured from the char yield of the synthesized polyphosphazenes using Van Krevelen and Hoftyzer equation [**42**].

$$LOI = 17.5 + 0.4\sigma \qquad (1)$$

where σ – Char yield at 800ºC (the data are reported in **Table 2**).

LOI was further investigated using Rheometric oxygen index instrument connected with nitrogen and oxygen pressure regulators. Samples having dimension of 15 × 5 cm^2 were prepared and ignited using propane gas burner in the combustion column. Average LOI value was calculated by testing three to four replicates of each sample.

The flame retardancy of the polymeric samples was further investigated using UL94 (Vertical burning test) where the samples were characterized into V0, V1 and V2 according to their ASTM D 3801. The test was used to find ignition response time and relapse time of the samples with each having 6 mm thickness.

Cone calorimetry studies of each polymeric sample were carried out on cone calorimeter (Fire Testing Technology, UK) using ISO 5660 standard. The dimensions of polymeric sheets were 100X100X3 mm^3. The external heat flux of 35 kWm^{-2} was exposed on each sample. The Water uptake property or wettability of each PPZ surface was further analyzed by investigating liquid droplet profile by calculating their water contact angle using contact angle goniometer (model No. HO-ED-M-1, India). The polymeric samples were cleaned using mixture of acetone/ethanol (1:1) and then placed on sample stage. A small water drop was further placed on polymeric sample with the help of clean syringe, and the contact angle was measured. It was assume that if contact angle θ was 0°, surface was completely wetted by the liquid. Besides this, if the contact angle lied between 0° and 90°, the surface was partially wetted by the liquid. Contact angle θ of 90° was assigned to absolute non-wetting of polymers by liquid [**43**].

Methods

Synthesis of polydichloropolyphosphazene

Fresh and dry hexachlorocyclotriphosphazene (HCCTP) 10 g (28.7 mmol) was taken in a dry pyrex glass tube along with catalyst ($CaSO_4.2H_2O$) 1.8mg (10.47mmol) & sealed under vacuum. The tube was then kept in a hot air rotatory oven and heated to 230°C for 1.5 hrs and then at 250°C for 15 hrs after which time, the molten material inside the tube almost stopped to flow. The tube was then allowed to cool at room temperature. After this, the tube was broken in an inert media and reacted contents were dissolved in 50mL of petroleum ether for removal of unreacted trimer. The obtained polymer was dissolved in 30mL of anhydrous THF as a pure product. The final product i.e. poly-dichlorophosphazene (PDCP) was separated as a light yellowish rubbery material. The yield of synthesized PDCP was obtained >83%. The scheme for synthesis of polydichlorophosphazene is provided in **Fig. 1**.

Synthesis of poly(bis(furfuroxy)phosphazene) (PBFP), poly(bis(1-adamantanemethylamine)phosphazenes) (PBAP) and poly(bis(cyanophenoxy)phosphazenes) (PBCP)

Furfuryl alcohol, 16.9 g (172.45 mmol), was added drop wise to a stirred solution of NaH, 13.98 g (582.25 mmol) in 60 mL anhydrous THF taken in three-necked round bottom flask equipped with a dropping funnel and inert gas inlet tube, over a period of two hrs. The solution mixture of furfuryl alcohol appeared transparent in colour which indicated the confirmation of furfuroxy anion in the solution. The prepared solution was then added drop wise to solution of polydichlorophosphazene, 10 g, in tetrahydrofuran contained in another three-necked round bottom flask equipped with a dropping funnel and inert gas inlet tube. The mixture was refluxed at 45°C for 20 hrs and 14.4 mL (103.4 mmol) triethylamine as a base was added and stirred for 2 hrs. Upon cooling to optimum temperature, the product was filtered through Whatman no.1 filter paper and the volume of the THF was reduced. The concentrated solution was then added to 100 mL water with stirring. The precipitated polymer was dissolved in dry THF and precipitated with dry hexane and dried in vacuum. The polymeric material was isolated as a dark brown solid product with yield of 75%. The similar procedure was adopted for the preparation of poly(bis(1-adamantanemethylamine) phosphazenes) (PBAP) and poly(bis(cyanophenoxy) phosphazenes) (PBCP) where 26g (172.2 mmol) adamantylamine and 20.51g (172.35 mmol) cyanophenol were added drop wise to a stirred solution of 21.51 g (896.25mmol) and 16.96 g (706.67 mmol) of NaH, respectively, in 70 mL anhydrous THF solvent, The yield of PBAP and PBCP were obtained as 80% and 70%, respectively. The scheme for the synthesis of PBFP, PBAP and PBCP is provided in **Fig. 1**.

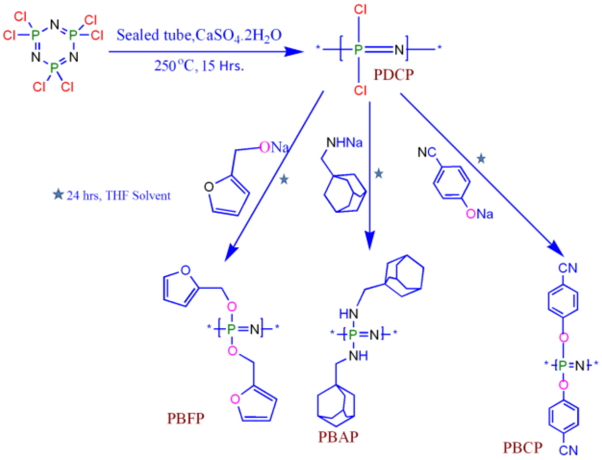

Fig. 1. Scheme for the synthesis of PDCP, PBFP, PBAP & PBCP.

Results and discussion

This section contains the results obtained from synthesis and characterization of synthesized polymers based on poly(bis(furfuroxy)phosphazenes) (PBFP), poly(bis(1-adamantanemethylamine)phosphazene) (PBAP) and poly(bis(cyanophenoxy)phosphazenes (PBCP).

GPC analysis of PBFP, PBAP and PBCP

The molecular weights of PBFP, PBAP and PBCP were taken in THF solvent with Viscotek 350 HT gel permeation chromatograph module 350 A instrument. The GPC profile of all the polymeric samples is shown in **Fig. 2**. The number average molecular weights (Mn) of synthesized polyphosphazene derivatives viz. PBFP, PBAP and PBCP were measured to be 1.38x105, 1.05x105 and 1.89x105 Da, respectively. On the other hand, the polydispersity indices of polyphosphazenes (PBFP, PBAP and PBCP) were measured to be 1.806, 1.028 and 1.026, respectively. It was reported that the trend in molecular weights (either Mn or Mw) of synthesized polyphosphazene samples viz. PBFP,

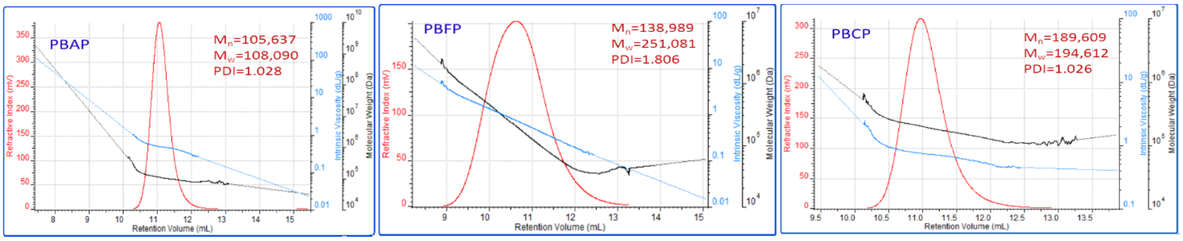

Fig. 2. GPC trace of the synthesized polyphosphazenes.

PBAP and PBCP followed decreasing order which could be due to the stability parameter of the substituted moieties. The aromatic molecules are rigid & stable and hence their respective polymers have higher molecular weights as compared to the aliphatic ones. Further, the intrinsic viscosities of the aforementioned polymers (PBFP, PBAP and PBCP) were obtained as 0.4768, 0.7380 and 0.4086 dL/g. The viscosity values of PBCP and PBFP were lower than PBAP which might be due to inter-electronic repulsions between the aromatic rings of the polymeric networks of PBCP and PBFB. PBAP does not have such type of repulsive interactions, so exhibits higher intrinsic viscosity values.

FTIR analysis

In the FTIR analysis of synthesized polyphosphazenes (provided in **Fig. 3**), important characteristic absorption peaks around 1293.8 and 1087.9 cm^{-1} are related to phosphorous nitrogen bond (-P=N-). For PBFP, the absorption band at 1421.5 cm^{-1} is assigned to C=C double bond of furan of furfuroxy group. Further, absorption bands at 2925 & 2957.9 cm^{-1} are the consequence of protons of furan moiety. Also, band at 2885 cm^{-1} appears due to methylene protons. The adamantylmethyl amine substituted polyphosphazene i.e. PBAP is showing absorption bands at 2885, 2925 & 2957.9 cm^{-1} for different methylene and methane protons of the admantyl ring. Besides this, the absorption band of N-H bond of amine group of admantyl amine appears at 3394.5 cm^{-1}. In case of cyanophenol based polyphosphazene, PBCP, absorption bands at 1461.8 and 1421.4 cm-1 are owing to the C=C double bond of aromatic group and bands at 2857.9 & 2924 cm^{-1} are due to its protons. In addition to this, CN bond is showing its characteristic band at 2343.5 cm^{-1}. All of these data are indicating the successful preparation of PBFP, PBAP and PBCP.

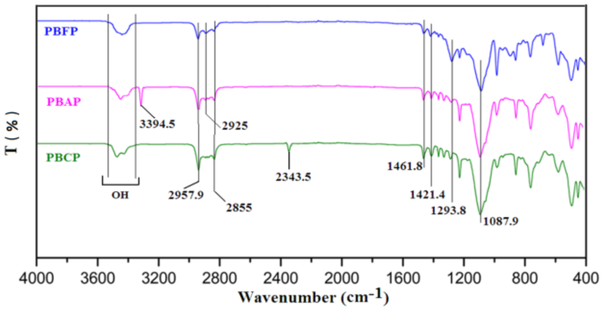

Fig. 3. FTIR spectra of synthesized polyphosphazenes.

NMR analysis

The formation of synthesized polyphosphazene polymer was confirmed by analyzing the ^{1}H and ^{31}P spectra recorded in CDCl$_3$ (**Fig. 4**). The important features of the ^{1}H NMR spectrum of PBFP are singlet signals at 4.06 ppm which are due to methylene protons next to oxygen of furfuroxy groups respectively. Further, two doublet signals (7.69 and 6.38 ppm) and a quartet (6.48 ppm) are attributed to the methine protons of furan moiety. In case of ^{1}H NMR spectrum of PBAP, signals around 0.9, 1.1 and 1.7 ppm correspond to different C-H protons and signal at 2.6ppm relates to the methylene protons. The N-H proton is exhibiting its characteristic peak at 3.45ppm. The ^{1}H NMR spectrum of PBCP is showing signals at 6.7 & 7.0 ppm, which assigned to the aryl protons. The ^{31}P NMR spectrum of PBFP, PBAP and PBCP gives sharp signals at -3.2, -13, 15 ppm, respectively, which confirmed that PBFP, PBAP and PBCP have been successfully synthesized.

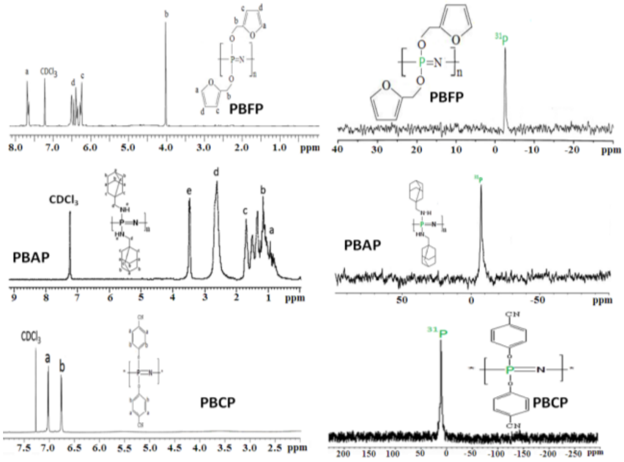

Fig. 4. ^{1}H & ^{31}P spectra of PBFP, PBAP & PBCP.

XRD analysis of synthesized polyphosphazenes

The wide angle X-Ray diffractograms of synthesized polyphosphazenes is provided in **Fig. 5**. All the measurements were taken at room temperature to study the crystalline or amorphous nature of polyphosphazenes. From the Fig. 6, we can see PBCP and PBFP are exhibiting a diffraction peaks between 15° to 28°, which indicates their crystalline nature. The crystalline nature of these polymers is due to the incorporation of rigid aromatic moieties like benzene and furan. Further, no such types of diffraction peaks are occurring for PBAP which confirms the amorphous nature of PBAP.

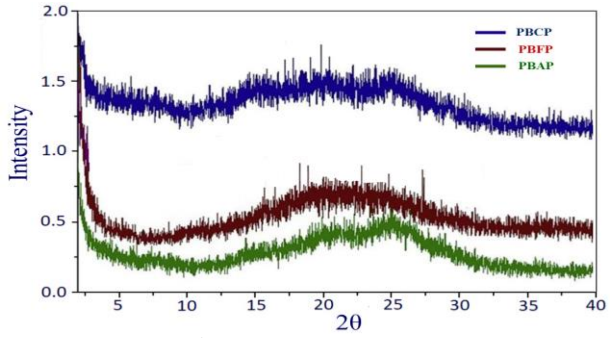

Fig. 5. XRD patterns of the synthesized polyphosphazenes.

Solubility behavior of synthesized polyphosphazenes

Solubility behavior of all the synthesized polyphosphazenes was analyzed in different solvents. One gram of each sample was put into 20 mL of different solvents and shaken well using magnetic stirrer. The temperature was increased to enhance their miscibility behavior. The results obtained are provided in **Table 1**. All the synthesized Polyphosphazenes are miscible in tetrahydrofuron, N, N-dimethyl formaide, N, N-dimethyl acetamide, N-methyl pyrrolidone, chloroform and dimethyl sulfoxide at room temperature while they are immiscible in benzene and methanol.

Table 1. Solubility* behaviour of polyphosphazenes in various protic and aprotic solvents#.

Nomenclature of poly-phosphazenes	THF	DMF	DMAc	DMSO	NMP	CHCl₃	C₆H₁₂	CH₃OH
PBFP	+	+	+	+	+	+	—	—
PBAP	+	+	+	+	+	+	—	—
PBCP	+	+	+	+	+	+	—	—

* Solubility (+) soluble at room temp., (-) insoluble
# THF: Tetrahydrofuron, DMF: N, N-dimethyl formaide, DMAc: N,N-dimethyl acetamide, NMP: N-methyl pyrrolidone, DMSO: dimethyl sulfoxide.

Thermal analysis

The thermal analysis of all synthesized polyphosphazenes was determined using DSC and TGA for a temperature range -100 to 100°C and room temperature to 800°C, respectively with heating rate of 10°C/min in inert atmosphere. The results are illustrated in **Fig. 6, 7** (**a** & **b**) and **Table 2**. The DSC scan is showing glass transition temperature at 3°C, -34°C and 26°C for PBFP, PBAP and PBCP, respectively. The decomposition temperature of all synthesized polyphosphazenes at 5% weight loss exhibits single step decomposition at temperatures 274, 304 and 350°C for PBFP, PBAP and PBCP, respectively. The final decomposition temperatures of 411,472 and 505°C are also obtained for PBFP, PBAP and PBCP, respectively. Further, the thermal stability of PBCP is higher than PBFB owing to the presence of greater number of pie bonds or structural stability of cyanobenzene ring than furan. Besides this, the char yields of respective polyphosphazenes are found in the range from 29 to 42 % at 800°C.

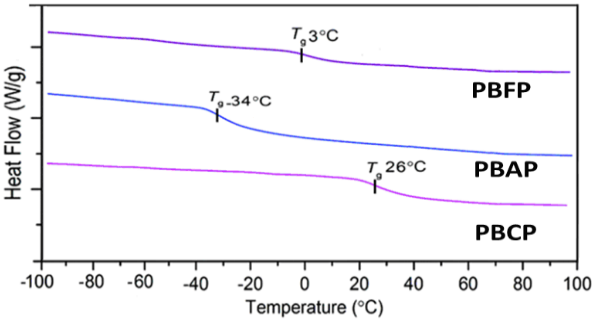

Fig. 6. DSC overlay curves of synthesized polyphosphazenes.

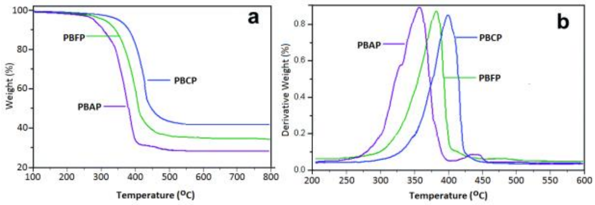

Fig. 7. (a) TGA & (b) DTG curve of synthesized polyphosphazenes.

Table 2. Thermal results of synthesized polyphosphazenes.

S. code	DSC	TGA (°C)			LOI
	T_g (°C)	$T_{5\%dt}$	T_{fdt}	Char Yield (%)	
PBFP	3	274	411	34 %	31.1
PBAP	-34	304	472	29 %	29.1
PBCP	26	350	505	42 %	34.3

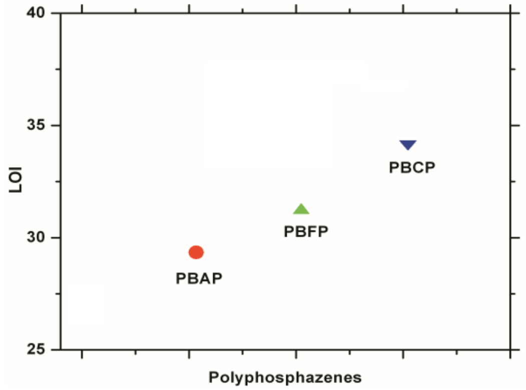

Fig. 8. LOI values of polyphosphazenes (PBAP, PBFP & PBCP).

Limiting Oxygen Index (LOI)

LOI values of the synthesized polyphosphazenes were estimated using char yield obtained from TGA and the results are provided in **Fig. 8** and **Table 3**.

$$LOI = 17.5 + 0.4\sigma \qquad (1)$$

The LOI values of various synthesized polyphosphazenes were obtained as 29.1, 31.1 and 34.3 for PBAP, PBFP and PBCP, respectively. Further, LOI values of each sample calculated by Rheometric oxygen index instrument were achieved as 28.7, 30.8 and 35.1 for PBAP, PBFP and PBCP, respectively. The values of calculated as well as experimental LOI values are nearly same. If we move from PBAP to PBCP via PBFB, we find that the bond stability of the synthesized polymers increases due to the incorporation of considerable amount of double or triple bonds in the side groups along with the formation of P-N or P-O bond in place of P-Cl bond in PDCP. The cyanophenoxy moiety is thermally more stable as compare to furfuryl group due to presence of homocyclic ring as well as higher bond order in PBCP as compare to PBFP. This thermal stability trend is the reason behind the variation in the LOI values of the synthesized polyphosphazenes. On comparing the LOI values of the synthesized polymers with the classification table of various materials based on their LOI (provided in **Table 3**) [**44**], we found that PBAP, PBFP and PBCP are self-extinguishing in nature.

Table 3. Classification of materials as flammable or self-extinguishing in nature on the based on their LOI values [**41**].

LOI	**Nature**
LOI < 20.95	Flammable
LOI = 20.95	Marginally stable
21 < LOI < 28	Slow burning
28 < LOI < 100	Self-extinguishing
100 < LOI	Intrinsically non-flammable

UL-94 (Vertical burning) test

UL-94 Test of above polymeric samples was done to study their flammability behavior. The Ignition response time (seconds) and ignition relapse time (seconds) are provided in **Table 4** along with the UL-94 rating. Besides this, photograph of tested samples of UL-94 test is depicted in **Fig. 9**. During the vertical burning test, five test bars of each polymeric samples PBAP, PBFP and PBCP were observed to quench within 5-8s, 4-6s and 3-5s, respectively, when ignition was stopped. It indicated that each polymeric sample were auto-extinguishable in nature. Further, No dripping was observed due to the structural stability of the polymeric materials. Hence, all the polymers are allotted a rating of V-0.

Table 4. UL 94 test values of (PBAP, PBFP & PBCP) polyphosphazenes.

Materials composition	Ignition response (sec)	Ignition relapse (sec)	Dripping	UL-94
PBAP	37-40	5-8	No	V0
PBFP	42-46	4-6	No	V0
PBCP	45-50	3-5	No	V0

Fig. 9. UL-94 vertical burning images of polyphosphazene samples.

Cone calorimetry

Cone calorimetry was used to study the flame retardancy of polyphosphazene polymers. Various parameters like heat release rate (HRR), total heat release (THR), total smoke release (TSR) and residue mass or wt% residue are plotted in **Fig. 10** and also provided in **Table 5**. The heat release rate, mainly peak heat release rate (PHRR), is one of the essential parameter to evaluate the fire hazards [**45**]. The PHRR values of PBAP, PBFP and PBCP are 177.8, 152.1, 126.3 kW/m^2, respectively. The lowest PHRR for PBCP suggests that it has better flame retardancy than other two polymers. The THR values of polyphosphazene polymers shows trend similar to their PHRR values. The THR values of PBAP, PBFP and PBCP are 36.1, 31.2 and 27.1 MJ/m^2, respectively. The rise of stability in polyphosphazenes from PBAP to PBCP due to enhancement of aromaticity is the possible reason for the decreasing trend in THR values. Further, the release of non-combustible gases like volatile phosphide, NH_3, N_2 and CO_2 during burning process [**46-48**] dilute the flammable gases and hence dimish the concentration of oxygen around the material.

Table 5. Cone calorimetric data of synthesized polyphosphazene

Sample	PBAP	PBFP	PBCP
TTI(s)	82±9%	80±7%	79±8%
PHRR(kW/m^2)	177.8±11%	152.1±13%	126.3±12%
THR(MJ/m^2)	36.1±9%	31.2±6%	27.1±7%
FGR (kW/m^{2}s)	2.82	2.61	2.52
TSR (m^2/m^2)	440.13±8%	326.23±5%	210±7%
Residue (wt. %)	34.6±5%	38.3±6%	44.9±3%

TTI: Time of ignition; PHRR: Peak heat release rate; THR: Total heat release; FGR: Fire growth rate; TSR: Total smoke release

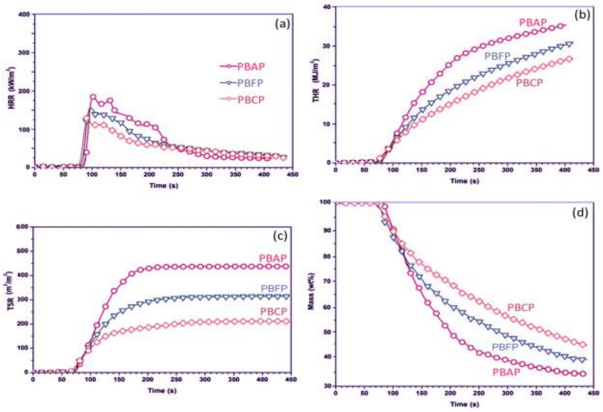

Fig. 10. Cone calorimetric plots of synthesized polyphosphazenes (a) HRR (b) THR (c) TSR (d) wt. % residue curves.

Fire growth rate (FGR) was also evaluated by dividing PHRR value by time to PHRR to estimate the ignitability of the materials, scale of a fire and flame spread in developing fire [**49**]. The FGR values of PBAP, PBFP and PBCP are 2.82, 2.61 and 2.52 kW/m^{2}s, respectively. It indicates the enhancement in fire safety of the polyphosphazene polymers due to increase in bond stability. TSR is also another important parameter used to measure the production of smoke during combustion. As shown in **Fig. 10** and **Table 5**, The TSR value of PBAP, PBFP and PBCP are 440.13, 326.23, 210 m^2/m^2, respectively. The phosphazene backbone in polyphosphazene polymers allows them to decompose at the early stage of combustion and stimulate the development of phosphorus-rich and solid char as a protective layer on the surface of the polymer. This protective layer prevents the heat transfer as well as restricts the formation of combustible gases. Due to this, the intensity of combustion pyrolysis reaction is suppressed and hence release of the amount of smoke is less. Moreover, the wt% residue for PBAP, PBFP and PBCP are 34.6%, 38.3%, 44.9%, respectively which is in agreement with the char yield behavior obtained from TGA analysis.

Water contact angle

The water uptake property of the synthesized polyphosphazenes i.e. PBAP, PBFP & PBCP is shown in terms of their water contact angles. It can be seen from **Fig. 11**, the water contact angles of PBAP, PBFP & PBCP are 140.80, 138.50 and 137.70, respectively which shows that all the synthesized polymers are hydrophobic in nature or are non-wetted by water molecules. A non-polar admantylmethy group in PBAP is highly bulky which repels water molecules to great extent and has highest water contact angle value. While furfuryl group is polar but due to the unavailability of lone pairs, no hydrogen bonding type interaction is present in PBFP. In fact, water molecules repel from the furfuryl group in PBFP. Cyanophenyl group in PBCP shows some short of hydrogen bonding interation with water and has least water contact angle but overall, the aromatic ring shows hydrophobic interaction with water and hence, PBCP is not wetted by water molecules.

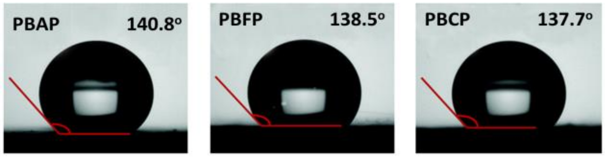

Fig. 11. Water contact angles of polyphosphazenes (PBAP, PBFP & PBCP).

Conclusion

Various types of thermoplastic polyphosphazenes with adamantylmethyl amine, furfuroxy and cyanophenoxy groups in their side chains were successfully synthesized and their structures were further analyzed using GPC, FTIR, NMR and XRD analysis. The molecular weights of synthesized polyphosphazenes were very high with higher intrinsic viscosity values. Thermal analysis showed the all synthesized polyphosphazenes were highly thermal stable with their final decomposition temperature range from 411 to 505ºC. Thermal analysis and combustion properties of the synthesized polyphosphazenes were evaluated which showed all the synthesized polymers were excellent flame retardant materials in nature since their LOI values exceeded 28% along with UL-94 rating of V0. PBCP showed lowest values of PHRR, FGR and TSR along with highest weight % residue due its highly thermally stable homocyclic aromatic ring. Further, all the polymers exhibited hydrophobic behavior in water shown by the water contact angle measurements.

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References

1. Allcock, H.R.; Chemistry and Applications of Polyphosphazenes. Wiley-Interscience: Hoboken, NJ, **2013**.
2. Allcock, H.R.; *Science*, **1976**, *193*, 1214.
3. Potin, P.; Jaeger, R.D.; *Eur. Polym. J.*, **1991**, *27*, 341.
4. Allcock, H.R.; Kugel, R.L.; *J. Am. Chem. So.c*, **1965**, *87*, 4216.
5. Allcock, H.R.; *Science*, **1976**, *193*, 1214.
6. Allcock, H.R.; *Macromolecules*, **1991**, *24*, 2024.
7. Allcock, H.R.; Kwon, S.; Pucher, S.R.; *Polym. Prepr.*, **1990**, *31*, 180.
8. Allcock, H.R.; *J. Inorg. Organomet. Polym.*, **1992,** *2*, 1971.
9. Wilson, A.; *J. Coated Fabrics*, **1978**, *7*, 233.
10. Thompson, J.E; Sicka, R.W., Patent 3994838A, USA, **1976**.
11. Crommen, J.H.L; Schacht, E.H; Mense, E.H.G.; *Biomaterials*, **1992**, *13*, 601.
12. Singler, R.E.; Hagnauer, G.L.; Schneider, N.S.; *Polym. News*, **1978**, *5*, 9.
13. Zhang, Q.; Lu, M.; Dong, X.; et al., *Environ. Sci. Technol.*, **2014**, *48*, 6995.
14. Gettleman, G.L.; Vargo, J.M.; Gebert, P.H.; et al., *Polym. Sci. Tech.*, **1987**, 35, 55.
15. Allen, C.W., *J. Fire Sci.*, **1993**, *11*, 320.
16. Allcock, H.R.; Hymer, W.C.; Austin, P.E.; *Macromol.*, **1983**, *16*, 1401.
17. Allcock, H.R.; Fuller, T.J.; Mack, D.P.; et al., *Macromol.*, **1977**, *10*, 824.
17. Singh, K.P.; Mishra, A.; Kumar N.; Tripathi D.N.; Shami, T.C.; *Polym. Bull.*, **2018**, *75*, 2415.
19. Allcock, H.R.; Pucher, S.R.; Scopelianos, A.G.; *Macromol*, **1994**, *27*, 1071.
20. Whitehead, P.M.; Propellant Testing - Metrology OSD Propulsion Data Sheet PDS245, DSTO, **1998**.
21. Kopecký, F.; Physics for Students of Pharmacy I. Bratislava UK, **1999**, p184.
22. Kavesh, S.; Schultz, J.M., A Review Polym Eng and Sci, **1969**. 9, 331.
23. Zou, W.; Basharat, M.; Ullah Dar, S.; Zhang, S.; Abbas, Y.; Liu, W.; Wu, Z.; Zhang, T.; *Composites: Part A*, **2019**.
24. Mayer-Gall, T.; Knittel, D.; Gutmann, J.S.; Opwis, K.; *ACS Appl. Mater. Interfaces*, **2015**, *7*, 9349.
25. Liu, H.; Wang, X.; Wu,D.; *Polym. Degrad. Stabil.*, **2014**, *103*, 96.
26. Perret, B.; Schartel, B.; Stoess, K.; Ciesielski, M.; Diederichs, J.; Doering, M.; Kraemer, J.; Altstaedt, V.; *Eur. Polym. J.*, **2011**, *47*, 1081.
27. Neisius, N.M.; Lutz, M.; Rentsch, D.; Hemberger, P.; Gaan, S.; *Ind. Eng. Chem. Res.*, **2014**, *53*, 889.
28. Butnaru, I.; Fernandez-Ronco, M.P.; Czech-Polak, J.; Heneczkowski, M.; Bruma, M.; Gaan, S.; *Polymers*, **2015**, *7*, 1541.
29. Xu, M.J.; Xu, G.R.; Leng, Y.; Li, B.; *Polym. Degrad. Stabil.*, **2016**, *123*,105.
30. Liu, S.; Fang, Z.P.; Yan, H.Q.; Wang, H.; *RSC Adv.*, **2016**, 6, 5288.
31. Qiu, S.; Wang, X.; Yu, B.; Feng, X.; Mu, X.; Yuen, R.K.K.; Hu, Y.; *J. Hazard. Mater.*, **2016**, *325*, 327.
32. Potin, P.; Jaeger, R.D.; *Eur. Polym. J.*, **1991**, *27*, 341.
33. Gabino, A.C.; Francisco, J.G.; Paloma, G.E.; Fidalgo, J.I.; Garcia, J.L.; *Chem. Eur. J.*, **2003**, *9*, 3833.
34. Allcock, H.R.; *Chem Mater.*, **1994**, *6*, 1476.
35. Allcock, H. R.; McDonnell, G. S.; Desorcie, J. L., Macromolecules, **1990**, *23*, 3874.
36. Shukla, L.; Arya, P.; *Text. Dyer Printer*, **1998**, *31*, 16.
37. Qiu, S.; Ma, C.; Wang, X.; Zhou, X.; Feng, X.; Mu, X.; Yuen, R.K.K.; Hu, Y.; *J. Hazard. Mater.*, **2018**, *344*, 839.
38. Levchik, G. F.; Grigoriev, Y. V.; Balabanovich, A. I.; Levchik, S.V.; Klatt, M.; *Polym. Int.*, **2000**, *49*, 1095.
39. Sasakura, T.; Ueda, T.; Method and Agents for Finishing Cellulosic Fabrics. JP02289175A, **1990**.
40. Tsujimoto, H.; Ishikuro, S.; Yonezawa, T.; Watanuki, T.; Aminophosphazene-based Fireproofing Agents for Cellulosic Fibers,their Manufacture and Treated Fabric Products. JP2000017574A, **2000**.
41. Levchik, S. V.; Levchik, G. F.; Balabanovich, A. I.; Weil, E. D.; Klatt, M.; *Angew. Makromol. Chem.*, **1999**, *264*, 48.
42. Barraa, G.; Vertuccioa, L.; Naddeoa, C.; Arenab, M.; Viscardib, M.; Guadagnoa, L.; Thermal degradation and fire properties of epoxy modified resins, AIP Conference Proceedings **1981**, 020149 (2018).
43. Zheng, W.; Surface wetting characteristics of rubbed polyimide thin films. In Polymer thin films; Abbass A Hashim (Ed.); In Tech. **2010**, pp.161-183.
44. Younis, A.A.; *Journal of Petroleum*, **2016**, 25, 161.
45. Schartel, B.; Bartholmai, M.; Knoll, U., *Polym. Degrad. Stab.*, **2005**. 88, 540.
46. Liu, R.; Wang, X; Polym. Degrad. Stab., **2009**, *94*, 617.
47. El Gouri, M.; El Bachiri, A.; Hegazi, S.E.; et al., *Polym. Degrad. Stab.*, **2009**, *94*, 2101.
48. Qian, L.J.; Ye, L.; Qiu, Y.; et at., *Polymer*, **2011**, *52*, 5486.
49. Morgan, A.B.; Bundy, M.; *Fire Mater.*, **2007**, *31*, 257.