

Synthesis, Characterization of Imide Substituted Polyphosphazenes and Evaluation of their Structural Properties

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Abstract: Imide functionalized polyphosphazenes (1P, 2P and 3P) have been synthesized from imide substituted *m*-aminophenol and then further characterized by FT-IR, NMR and GPC. The synthesized polyphosphazenes have been cured as thermally form cross linked networks. The thermal characterization of cured and uncured resins was done by DSC and TGA analysis. The DSC graph of a typical uncured resin 1P showed T_g at 49°C and T_m at 146°C, it also showed T_{ons} of curing at 290°C. The resin 1P, upon curing, showed increase in T_g upto 122°C due to cross linking. The TGA analysis of cured 1P showed onset of degradation at 285°C and maximum decomposition temperature T_{max} at 435°C. The synthesized resins have also been evaluated for their rheological, morphological, isothermal ageing and water uptake properties for end use application.

Keywords: *m*-aminophenol, imides, polyphosphazene, isothermal ageing and thermal stability

1. Introduction

Polyphosphazenes include a broad range of hybrid inorganic-organic polymers with a number of various skeletal architectures containing alternating phosphorous & nitrogen atoms [1]. Poly (dichlorophosphazene) which is reactive intermediate is utilized in the synthesis of polyphosphazenes by exchanging the chlorine atoms with nucleophiles. This unique property has led to the synthesis of very large number of different polyphosphazenes with variety of chemical and physical properties. By compounding the properties of the phosphorus-nitrogen backbone and the synthetic tailorability through macromolecular substitution, various different applications have been achieved for polyphosphazenes [2]. Substituting chlorine with 2-(2-methoxyethoxy) ethoxide side units reveals a high degree of free volume into the polymer leading to a very low T_g value [3-5]. Polymers that contain fluoroalkoxy side unit shows fire resistance, hydrophobicity and relatively low T_g values [6-7]. On the other hand, Polymers containing the carboxylate groups can be used for cross-linking sites in bone-regeneration composites [8]. The amino acid ester side unit bearing polyphosphazene is utilized to impart hydrolytic instability in the polymer. This results in the degradation of polymer into biologically favorable amino acids, phosphates & ammonia [9-10]. The phosphonic acid and protonated sulfonamide polymers have been used as polymeric fuel cell membranes and tissue engineering [11]. Besides this lithiated derivative of the sulphonamide polymer has been used as a single ion polymer electrolyte in the energy storage devices. The high acidity of sulfonimide acids has been well recorded [12]. Watanabe and co-workers have used a polymeric parallelism and prepared poly(2-oxo-1-difluoroethylene lithium sulfonimide) similar to

Lithium bis(trifluoromethanesulfonyl)imide salts (one of the largest weekly coordinating salts with very high transportation of ion) as a single ion conducting polymer and achieved highest ambient temperature conductivity in the range of 10-7 S/cm [13]. Further, siloxane-based polymers containing trifluoroethane sulfonamide and ethyleneoxy functionalized side chains have been prepared by Shriver and his co-workers and highest temperature conductivity in the range of 10-6 S/cm was achieved by them [14]. The synthesis of a novel styrene monomer bearing a sulfonimide group has been done by Feiring and co-workers. They described its homopolymerization and copolymerization with a variety of olefin monomers as possible electrolytes in the application of lithium battery [15-16]. Various trifluorovinyl aromatic ether monomers bearing both pendent sulfonimide groups can be incorporated into the monomer main chain [17-18]. These monomers can undergo thermal cyclopolymerization to give perfluorocyclobutane aromatic polyethers which are interesting materials as potential fuel cell membranes [19]. The main objective of this study was to determine the effect of imide groups on thermal stability of imides/trifluoroethoxy polyphosphazenes. Different imides groups were functionalized on the side chain of each phosphazene repeating unit to produce self curing behavior on thermal treatment for making free standing films

2. Materials

m-Aminophenol, maleic anhydride (MA), hexachloronadic anhydride (HA), nadic anhydride (NA), trifluoroethanol, hexachloro triphosphazene, N-methyl-2-pyrrolidone (NMP), sodium hydride, and dry THF were purchased from Aldrich Chem. Co. and used without purification.

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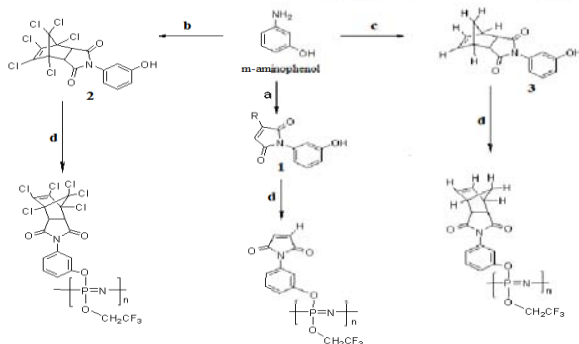
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3. Methods

¹H NMR spectra were recorded in CDCl₃ on a 400 MHz Bruker T spectrometer. Infrared measurements were performed on a Perkin Elmer spectrophotometer using KBr as a reference material or solution cast films for polymer. Thermo gravimetric analysis (TGA) and Differential calorimetry analysis (DSC) were performed on a TA instrument with a heating rate of 10⁰C/min under inert atmosphere. Gel Permeation Chromatography (GPC) was performed using THF at an ambient temperature with flow rate of 1.0 mL per minute. Weight-average and number-average molecular weights were calculated relative to polystyrene standards. Rheological test was conducted in NMP at 25⁰C using Anton par (MCR 301) Rheometer at room temperature, at constant shear rates, to investigate the effect of imides on polyphosphazene viscosity. Scanning Electron Microscopy (SEM) was done by a Carlzeissto (EVO 50 XVP) to analyze the morphology of the cured samples. Before the analysis, the samples were sputtered with gold to make the surface conducting.

3.1 Synthesis of 1-(3-hydroxyphenyl)-1H-pyrrole-2,5-dione (compound 1)

To a stirred solution of m-aminophenol (10.9 g, 100 mmol) in dry NMP (200 ml), maleic anhydride (1) (9.8 g, 100 mmol) was added and the reaction was allowed for 6 hrs at room temperature. The reaction mixture was then poured into benzene to obtain brown colour precipitate which was then further heated up to 200⁰C in vacuum oven for cyclization. The cyclized compound 1 was obtained with 90% (18 g) yield.



Reagents and conditions: Meta aminophenol; a) maleic anhydride, NMP, rt-200 °C, b) hexachloronadic anhydride, NMP, rt-200 °C, c) nadic anhydride, NMP, rt-200 °C, d) NaH, dry THF, CF₃CH₂OH, 0⁰C-50⁰C.

3.2 Synthesis of 1-(3-hydroxyphenyl)-1H-pyrrole-2, 5-dione/Trifluoroethanol substituted PPZ (1P)

Compound 1 (6.51g, 100m mol) was added to a stirred solution of NaH (60% in mineral oil) (6.62g, 100mmol) in dry THF under inert atmosphere and the reaction was allowed to stir at room temperature for 1 day and then trifluoroethanol (3 ml) was added and again the reaction was carried out at room temperature for further 24 hrs. This reaction mixture was then taken in dropping funnel and added drop wise to a stirred solution of dichloro polyphosphazene (4g, 100 m mol) in dry THF (100ml) and reaction mixture was stirred for

another 3 days at room temperature and at 50⁰C for next 2 days. The resulting mixture was then poured in water to remove sodium chloride salt & extracted with DCM (3x100). The solvent was evaporated and product was then precipitated by DCM/hexane. The obtained polymer was dried in a vacuum oven at 80⁰C for 2 hours. The final yield of the product was recorded as 75% (10 g).

3.3 Synthesis of 3-N-hexachloronadiimide-1-hydroxy benzene (Compound 2) and 3-N-nadiimide-1-hydroxy benzene (Compound 3)

All the reaction conditions used for the synthesis of 3-N hexachloronadiimide-1-hydroxy benzene and 3-N nadiimide-1-hydroxy benzene were same as used for 1-(3-hydroxyphenyl)-1H-pyrrole-2,5-dione but instead of maleic anhydride, hexachloronadic anhydride (37.1g,100 mmol) and nadic anhydride (16.4g,100mmol) were taken for synthesis of compound 2 and compound 3 respectively. The yield for the compound 2 and compound 3 was obtained as 38 g & 19 g respectively.

3.4 Synthesis of 3-N-hexachloronadiimide-1-hydroxy benzene /trifluoroethanol substituted PPZ (2P) and 3-N nadiimide-1-hydroxy benzene/ Trifluoroethanol substituted PPZ (3P)

For the synthesis of 2P and 3P, compound 2(10.62g, 100mmol) and compound 3(8.79g, 100mmol) were added in place of compound 1P in the reaction mixture respectively and same reaction methods and conditions were followed as in case of synthesis of 1P. The compound 2P was obtained as pale yellow precipitate with 85% yield (14g) and compound 3P was as brown color, solid product with a yield of 86% (15g).

4. Results and Discussion

The Imide functionalized Polyphosphazenes have been synthesized by using thermal ring opening polymerization and nucleophilic substitution reaction. The formation of precursor polymer has been confirmed by its FT-IR, ¹HNMR spectroscopy, TGA, DSC, and Rheometer.

4.1 FT-IR Analysis of 1P, 2P and 3P polyphosphazenes

It can be observed from the FT-IR spectra given in Fig.1 that for all synthesized polyphosphazenes viz. 1P, 2P & 3P, the bands in the range 1165 -1175cm⁻¹ relate to the phosphazene backbone. The occurrence of bands in the range 1085 -1095 cm⁻¹ corresponds to the P-O-C bond. Further the characteristic absorption bands ranging from 1290 to 1300 cm⁻¹ are for N=P stretching. Likewise multiple strong bands in the range 1350-1100cm⁻¹ & 2850-3000cm⁻¹ contain the characteristic bands for C-F bonds of trifluoro group and for C-H bonds for methylene protons for CH₂CF₃ group respectively. The band in the region of 690-900 cm⁻¹ consistent with the C-H out of plane bending vibrations of protons of meta-substituted benzene ring. In addition to this, the bands in the ranges 1400-1600 cm⁻¹ & 1620-1680 cm⁻¹ can be compared with the C=C double bonds of aromatic and non-aromatic rings. The anhydride group showing the

bands for C=O group in the regions $1820-1790\text{ cm}^{-1}$ and $1760-1730\text{ cm}^{-1}$ arise due to the asymmetric and symmetric stretching of carbonyl group. While in case of 1P the absorption band at 3010 cm^{-1} resembles to vinyl proton, the band at $650-810\text{ cm}^{-1}$ and 1286 cm^{-1} for 2P assigned for C-Cl bond and methine proton of sp^3 hybridized carbon respectively. At the same time, bands in the range from 2850 to 3010 cm^{-1} for 3P are due to the different protons of sp^3 and sp^2 hybridized carbons.

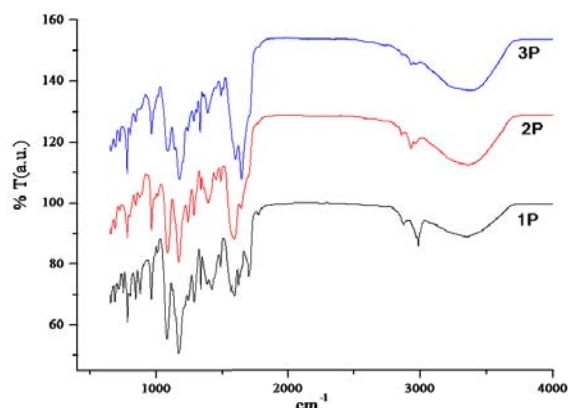


Figure 1: FTIR Spectra of 1P, 2P and 3P

4.2 ^1H NMR analysis of compound 1, 2 and 3

The proton NMR spectra of compound 1, 2, and 3, taken in CDCl_3 ($7.3\ \delta$), is shown in Figure 2. From the spectra, it can be inferred the multiple peaks in the range from δ value 6.9 to 7.2 are assigned to the protons of the aromatic moiety {i.e. $6.90 - 7.23\ \delta$ for compound 1; $6.92 - 7.21\ \delta$ for compound 2; $6.91 - 7.20\ \delta$ for compound 3}. Besides this the hydroxyl proton of all the compounds shows the small broad singlet peak in the range from 4.8 to $5.4\ \delta$ { 4.85 , 5.3 & $4.8\ \delta$ for compound 1, 2 & 3 respectively}. While for the compound 1; the intense singlet peak at $6.7\ \delta$ corresponds to the vinyl protons of the 1-H Pyrrole-2, 5-dione moiety, the sharp singlet peak at $3.2\ \delta$ for compound can be concurred to the methine protons at the junction carbons of the hexachloro norbornene and N-(3-hydroxyphenyl) succinamide ring. In case of compound 3, vinyl protons give the intense sharp peak at $5.54\ \delta$, where as peak at 2.67 and $2.71\ \delta$ are deduced for the protons of the bridgehead carbons of norbornene ring and protons at the junction carbons of the norbornene and N-(3-hydroxyphenyl) succinamide ring respectively. Moreover the two singlets at 1.75 and $1.90\ \delta$ are figure out for the diastereotopic methylene protons of the carbon in the single carbon bridge.

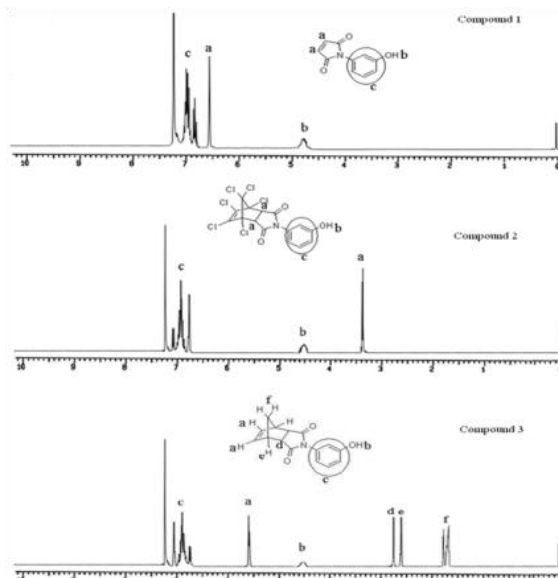


Figure 2: ^1H NMR spectrum of compound 1, 2 and 3

4.3 Rheological analysis

Rheological test was carried out at Anton par (MCR301) Rheometer using parallel plate geometry of diameter 25mm. We have carried out two types of test for all the three samples. Oscillatory test was performed by giving time swipec to all the samples. The results showed that 3P exhibited highest storage modulus as well as loss modulus shown in (Figure 3). Similarly 2P and 1P demonstrated slightly less storage modulus. Hence it can be said that 3P displayed good elastic behavior with better retention properties which may be supported by thermal and morphological studies. Viscosity of all the three types of PPZ showed more or less similar behavior which is well suited for the further processing criteria.

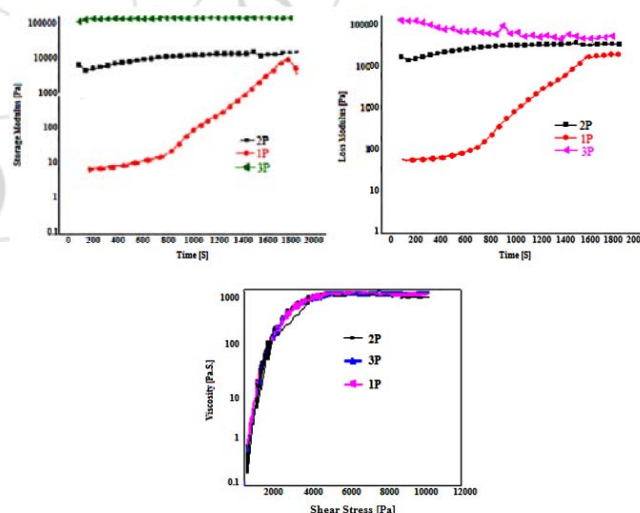


Figure 3: Rheological spectra of 1P, 2P and 3P Polyphosphazene

4.4 Thermal Analysis

The glass transition/melting temperature, curing behavior and thermal stability of the synthesized polymer namely 1P, 2P and 3P (graphically represented in Figure 4, 5 and 6) were noticeably detected by differential scanning calorimetry

(DSC) taken in temperature range from 30°C to 400°C with a heating rate of 10°C/min under inert flow. The thermal data of all the synthesized polyphosphazenes 1P, 2P and 3P is given in Table 1.

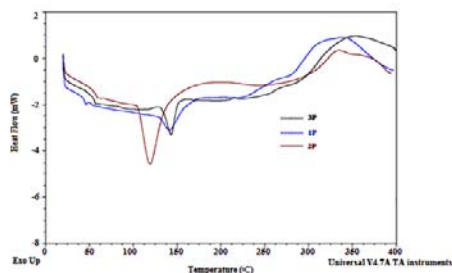


Figure 4: DSC graph of uncured sample of 1P, 2P and 3P PPZ

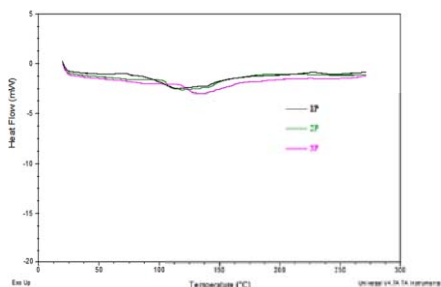


Figure 5: DSC graph of cured sample of 1P, 2P and 3P PPZ

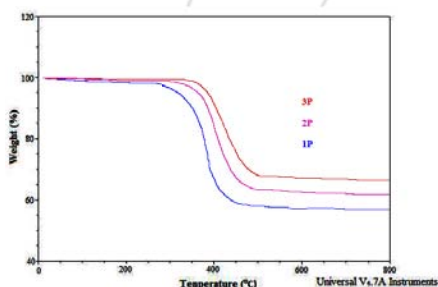


Figure 6: TGA graph of cured sample 1P, 2P and 3P PPZ

Table 1 Thermal properties and molecular weights of 1P, 2P and 3P PPZ

S.C.	T _g (°C) Uncured /Cured	T _m (°C)	T _{ons} /T _{max} (°C)	*M _w	M _n	Char yield (%)
1P	49/122	146	285/435	12204.5	12435	55
2P	53/135	125	320/470	9055	10768	67
3P	54/130	147	345/498	14009	14852	73

*Molecular weight determined by GPC.

Polyphosphazenes are striking polymer due to their higher thermal stability and flame retardant properties when compared to their organic homologues. Due to the excellent thermal stability and char yield performance, imide substituted polyphosphazene has gained attention for its possible submission in flame retardants. For such reasons we have investigated the thermal stability of the compounds 1P and 2P and compared the results with polymer 3P by determining the weight loss of the sample upon linearly increasing the temperature by conventional TGA at the rate of 10°C/min up to 800°C under inert flow. From the TGA graphs, it is concluded that polymers 1P to 3P exhibited very good thermal stability with decomposition temperatures (T_d) in the range 285–498°C. The decomposition onset

temperatures (T_{ons}) of cured resin 1P, 2P, 3P are 285, 320 and 345°C, and maximum decomposition temperature T_{max} are 435, 470, 498°C respectively. Further the char yields of cured resins reached to 55%, 67%, and 73% at 800°C respectively.

4.5 Isothermal Ageing

The isothermal ageing, in air, for 1P, 2P and 3P was carried out by keeping their films at 200°C weighing them at 0 h, 100 h and 200 h on a microbalance after each thermal operation. The % mass loss for nth hour was calculated from the following equation;

$$\text{Mass loss (\%)} = (W_0 - W_n) * 100 / W_0$$

Where W₀ is initial mass of sample at 0 h and W_n is the mass at nth h.

The results of isothermal ageing are summarized and depicted in table 2 and Figure 7. The isothermal ageing of 1P showed 4.2 & 6.3 % mass loss when measured after 100 & 200 h respectively at 200°C, while 2P showed 5.5 & 7.7 % mass loss respectively after similar intervals when kept at 200°C. The sample of 3P showed 4.9 & 5.5 % mass loss under the similar conditions. These results revealed that in all two cases the initial mass loss for first 100h was substantial in comparison to mass loss after 200h. These results showed that the percentage of mass loss decreased with time. The decrease in mass loss with respect to time was attributed to the stabilization of matrix by initial loss due to volatile degradation by products.

Table 2: Isothermal ageing of cured samples for 100h and 200 h at 200 °C

S. C.	Mass loss after 100 h (%)	Mass loss after 200 h (%)
1P	4.2	6.3
2P	5.5	7.7
3P	4.9	5.5

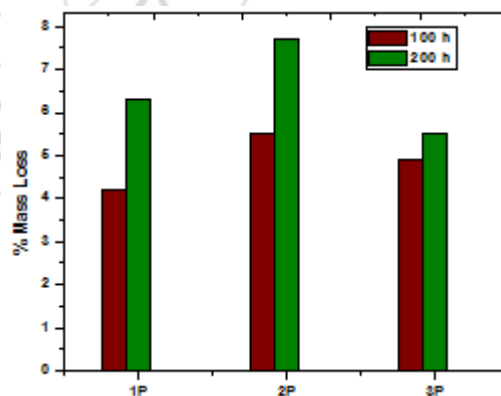


Figure 7: Bar graph of isothermal ageing of samples for 100h, 200h at 200 °C

4.6 Water Uptake

The % water absorption of 1P, 2P & 3P was measured by immersing their casted films into deionised water for 24 h at room temperature (~ 30 °C). The films coated on glass Petri dish were then taken out and wiped with tissue paper and quickly weighted on a microbalance. The water uptake of

these glass coated films was calculated from the following equation;

$$\text{Water uptake (\%)} = (W_{24} - W_0)100 / W_0$$

Where W_0 is initial mass of sample at 0 h and W_{24} is the mass at 24 h.

The water uptake of 2P was 0.25 % which was relatively low due to the presence of high halogen content in polymer skeleton. The water uptake by 3P was found to be 0.29 % which was expected due to hydrophobic nadic group. Further 0.38 % water uptake by 1P showed less hydrophobic maleic group (data depicted in table 3)

Table 3: Water uptake of cured samples after 24 h

Sample Code	Water uptake after 24 h (%)
2P	0.25
3P	0.29
1P	0.38

4.7 Scanning electron Microscopy (SEM)

The surface of the polymers was examined by SEM (Figure 8). The polydichlorophosphazene was an amorphous rubbery and exhibited a uniform surface while the different imides showed distinctive characteristics. 1P, 2P and 3P demonstrated an interaction of imide characteristics with phosphorus moieties; it is possible that synthesized polyphosphazenes had a cross linking reaction with itself which is favorable to a geometry structure. Thus, morphology depends on the type of the substituent attached to the polyphosphazene backbone.

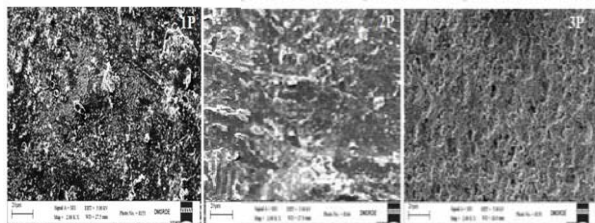


Figure 8: SEM images of 1P, 2P, and 3P Polyphosphazene

5. Conclusions

In these studies three novel imides substituted polyphosphazenes (1P, 2P, and 3P) have been synthesized via nucleophilic substitution reaction of the chlorine atoms and their further characterization was done. The structure property relationship chart showed an enhancement in the thermal and water uptake properties with increased in bulkiness of the side groups. The thermal properties of the resulting polymer systems have excellent thermal stability and high char yields at 800°C for making retardant systems. SEM analysis depicted that the cross linking effects of 1P, 2P, 3P for their cured morphology. An advantage of this synthesis system is the freedom to tune up the polymer composition and properties by different co-substitution and the side group ratios variations.

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