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Selective mono substitution of cyclotri-phosphazene by 2-Hydroxyethylacrylate producing new acrylate cyclo-triphosphazene

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Abstract

In this work, new acrylate cyclotriphosphazene moiety (PN-A) was successfully synthesized starting from cyclotriphosphazene (PN) compound. This compound reacted with 2-hydroxyethylacrylate utilizing 1:1 mole ratio to increase the priority of one substitution reaction and forming PN-A molecule. The crud product was purified by recrystallization using n-hexane and column chromatography using cyclohexane: ethyl acetate 60:40 mL ratio as eluent. The obtained pure target product was characterized using FTIR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR techniques. All spectra demonstrates the chemical structure of the product hence the showed all required peaks to identify it.

Keywords: Cyclotriphosphazene; Column chromatography; ^{1}H NMR; ^{31}P NMR; Acrylate

1. Introduction

Phosphazenes are interesting substrates having chemical structures based on –P=N– repeated units possessing 3 or 4 units in low molecular weight cyclic derivatives to more than 10,000 in high molecular weight polymers (Figure 1). Further, two substituent groups, which are chosen among a large number of different candidates, are attached to the phosphorus atoms in both these classes of compounds hence producing materials that are able to cover an unbelievably large number of practical applications [1].

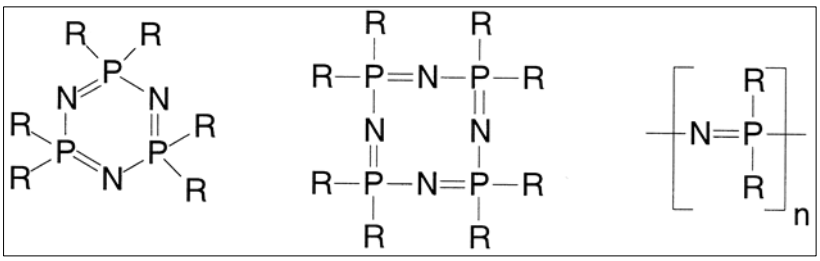

Figure 1 General structures of cyclo- and poly(organophosphazenes)

It has been mention, that phosphazene chemistry has brought much attention since 1960[2][3]. Especially, hexachlorocyclotriphosphazene (N3 P3 Cl6, trimer) which has a particular interest to both theoretical and experimental researchers concerning phosphazene-based chemistry. Due to its tendency to react with the nucleophilic mono-, di-, or

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multi-functional groups[4]–[7]. cyclophosphazenes was used in the syntheses of a considerable range of organocyclotri/tetraphosphazene derivatives with diverse applications [8] [9].

On the other hand, hexachlorocyclotriphosphazene (HCP) is suitable for extrapolation of functional properties and reaction activity to linear polymers. It has been mention that cyclophosphazenes are beneficial substsnces , [10]–[12]. This is due to the characteristic that it has in terms of being self-sufficient materials and contributes as curing agents for polymer resins. As modifiers for polymers to improve their inflammability[13], and mechanical characteristics[13] [14]; as building blocks for porous materials[15]; as cores of star-shaped polymers[16]–[18]. Further, phosphazenes are used as coordination ligands for metal ions [9], [19], [20] or as building blocks in preparation of porous materials [21].

2. Materials and method

2.1. Materials

Hexachlorcyclotriphosphazene $(NPCl_2)_3$ [HCP]. (Sigma-Aldrich) was purified by recrystallization from n-hexane. 2-hydroxy ethyl acrylate [HEA] (Sigma-Aldrich) was distilled under vacuum pressure to remove the inhibitor (mono ethyl ether hydroquinone).

2.2. Instruments

Fourier transformer infrared (FTIR) spectra in the range of 4000-400 cm^{-1} were recorded on a SHMADZU 8400_S FTIR spectrophotometer, KBr Window, ^1H ,^{13}C and ^{31} P-NMR spectra were recorded using an Oxford- Varian 300 NMR spectrometer operated at 300 MHz for proton and 75 MHz for carbon. Chemical shifts were recorded in parts per million relative to TMS (0.00 ppm) for H,C NMR and to 85% H_3PO_4(0.00 ppm) for ^{13} PNMR.

2.3. Synthesis of PN-A

Inside (100 ml) round flask a solution of (20 ml) 1,4-freshly dioxane, (5 gm, 14.00 mmol) (HCP) was stirred for 5 min. To this solution a mixture of (20 ml) dioxane, (1.653 ml, 14 mmol) 2-hydroxy ethyl acrylate, (2.021 ml , 0.014 mol) triethylamine dissolved in (30 ml) of 1,4-dioxane, was added via addition funnel over a period of 20 min. A white salt precipitate after 5 min, the contents stirred for 24 hr. At room temperature, the solvent was removed by using rotary evaporator and further dried under vacuum pressure at 60 ℃ [22].

3. Results and discussion

3.1. Synthesis of new acrylate cyclotriphosphazene moiety (PN-A)

Acrylate cyclotriphosphazene (PN-A) was done by using 1 mole of PN, 1 mole of cyclotriphosphazene (PN) to 1 mole of 2-hydroxyethylacrylate which was purified by using distillation under vacuum pressure (see Figure 2). Dioxane was used as a moderate polar solvent and dried before using *via* a distillation system using drying tube. The purpose of using drying dioxane is the highly sensitivity nature of PN towards humidity, when it exposed to air, it will readily suffered from hydrolysis. Thus, the reaction between PN and 2-hydroxyethylacrylate include loss of one proton from 2-hydroxyethylacrylate and one chlorine atom from PN molecule. The result is forming of HCl as a side product, and according to Le Chatelier's principle (A+B ⇋ C+D). Since C is the main product while D is the side product, in order to make the reaction move forward we must get rid of D, so HCl has been removed *via* the using of triethylamine. This compound reacts with HCl and produce triethyl ammonium chloride salt which can be removed *via* filtration. The crud product was firstly purified via recrystallization using n-hexane (b.p 69 ℃). Then it was purified utilizing column chromatography technique by performing TLC technique first to determine the best eluent system. Cyclohexane, ethyl acetate were used in ratio 60:40 mL as a mixture since cyclohexane considered non polar and ethyl acetate is moderate polar solvent.

Important note: In the beginning after preparing the PN-A compound according to the approved method, and after completing the additions and checking the IR, it was found that the result was incorrect. The reason is that the available 2-hydroxyethylacrylate compound may have absorbed moisture as a result of improper storage and turned into acrylic acid, or it may have polymerize through exposure to some light leading to wrong results. Therefore, a distillation was carried out under vacuum pressure, and the result product of the distillation process was kept, closed in a tight way, covered well and kept in a dark place. After that it gives satisfactory results as was demonstrated by various techniques.

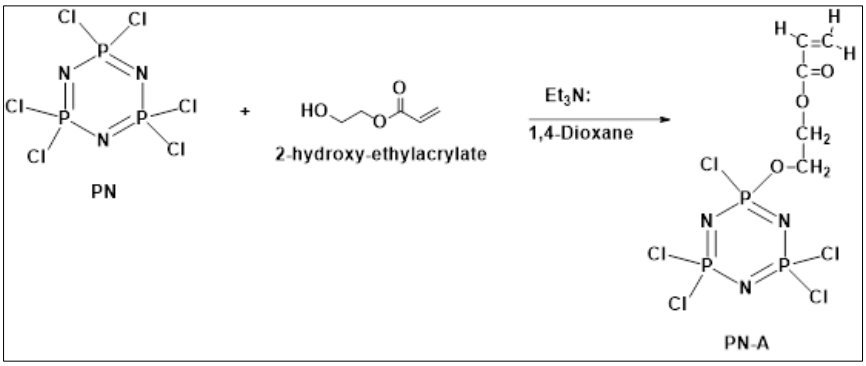


Figure 2 Synthesis of PN-A

3.2. Characterization of PN

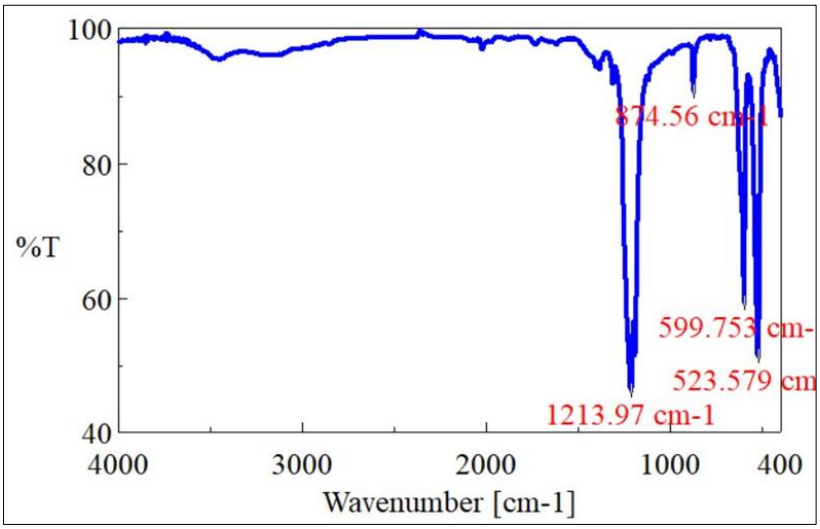


Figure 3 FTIR spectrum of PN

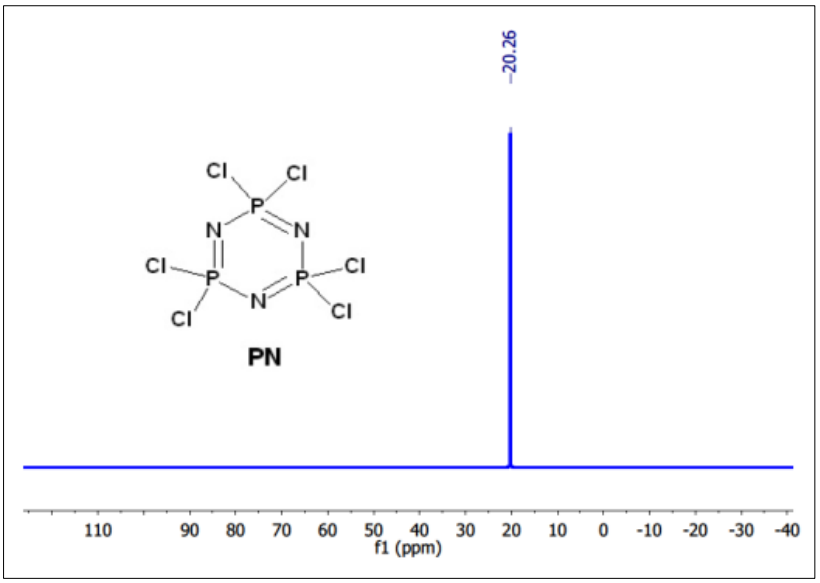


Figure 4 ^{31}P NMR spectrum of PN

The starting compound hexachlorocyclotriphosphazene $(NPCl_2)_3$ or PN was characterized by infrared spectroscopy. An interesting absorption peaks are display at 1213.9 and 1192.7 cm^{-1} refer to asymmetric and symmetric stretching vibration of P=N groups, respectively. The band at 874.5 cm^{-1} assigned to P=N skeletal vibration. The characteristic absorption at 599.7, 523.5 cm^{-1} are related to asymmetric and symmetric vibration of P-Cl bonds, as shown in Figure 3.

Figure 4 depicts the ^{31}P NMR spectrum of PN, hence it has showed only one strong peak at chemical shift 20.26 ppm for all three phosphine atoms [23]. This is because these phosphine atoms have exactly the same environment so they resonate at the same frequency.

3.3. Characterization of PN-A

A characteristic bands display in Figure 5 FTIR spectrum refer to the phosphazene ring, mainly at 1212 and 1194 cm^{-1}, which represent the asymmetric and symmetric stretching of the (P=N) group, sequentially. While the band at 1041 cm^{-1} is assigned to the PO-C group. The absorption at 599 cm^{-1} and at 525.5 cm^{-1} refers to the asymmetric and symmetric vibration of P-Cl. The band at 1728 and at 1635 cm^{-1} represent the C=O and C=C characteristic absorption of (2-ethoxyethylacrylate). The FTIR important peaks of PN-A moiety were tabulated in Table 1.

Table 1 Infrared spectral data of PN-A.

Frequency (cm^{-1})	Assignment
1212 ,1194	P=N (asymmetric and symmetric stretching)
1041	PO-C (stretching of PO-C)
599, 525.5	P-Cl (stretching of P-Cl)
1728	C=O (stretching of ester group of acrylate)
1635	C=C (stretching of acrylate group of ethylacylate)

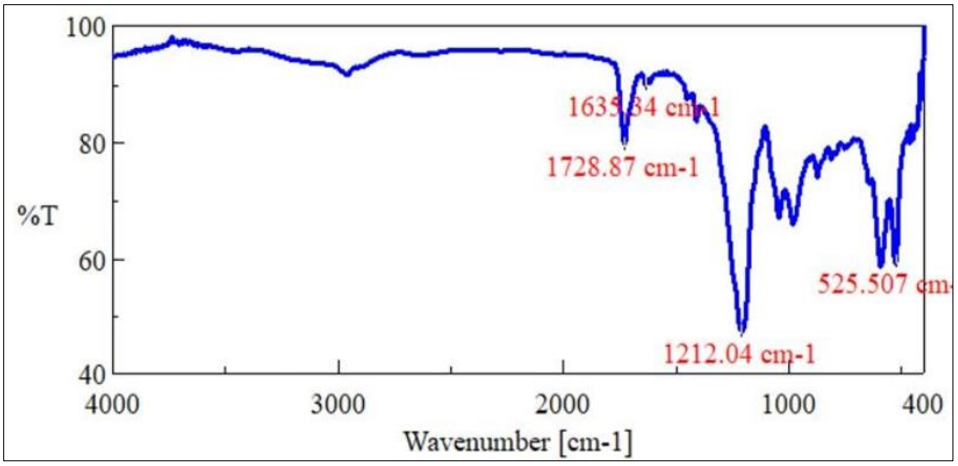
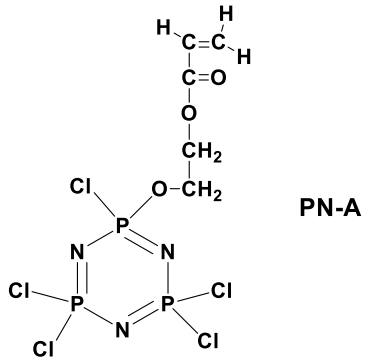


Figure 5 FTIR spectrum of PN-A

Synthesised PN-A compound was characterized using ^1H NMR technique, hence the spectrum has showed all required peaks to demonstrate the chemical structure of target compound as shown in Figure 6. The proton NMR spectrum showed seven hydrogen atoms in four different environments. One atom gives double duplet peak within the unsaturated region with *J*-coupling 10.72 and this is clear that this hydrogen atom is related to C=CH group. This proton gives double duplet peak because it is affected by the adjusted tow protons. The carbon atoms of alkene group have SP^2 hybridization then each hydrogen atom has different environment and effect differently by each other. This is why it was notice double duplet peak for C=CH group and multiple peak for $C=CH_2$ group. In addition, it was observed two nice triplet peaks at 4.16 ppm and 3.65 ppm which are belong to the two CH_2 groups next two oxygen [80][81].Therefore, it is demonstrated by 1H NMR spectrum that the reaction happens and target product PN-A has been got in high purity. All NMR data of synthesised PN-A compound have been summarized in Table 2.

Table 2 NMR spectral data of PN-A

Technique	 PN-A
^{1}H-NMR (400 MHz: DMSO-d_6, δ, ppm, *J* in Hz).	6.17 (dd, *J* = 10.72, 2.12 Hz, 1H, HC=C), 5.81-5.72 (m, 2H, C=CH_2), 4.16 (t, *J* = 5.70, 2H, O-CH_2), 3.65, (t, *J* = 5.70, 2H, O-CH_2).
^{13}C-NMR (100 MHz: DMSO-d_6, δ, ppm).	177.21, 140.48, 138.58, 80.26, 71.86.
^{31}P-NMR (162 MHz: DMSO-d_6, δ, ppm).	25.77, 22.60.

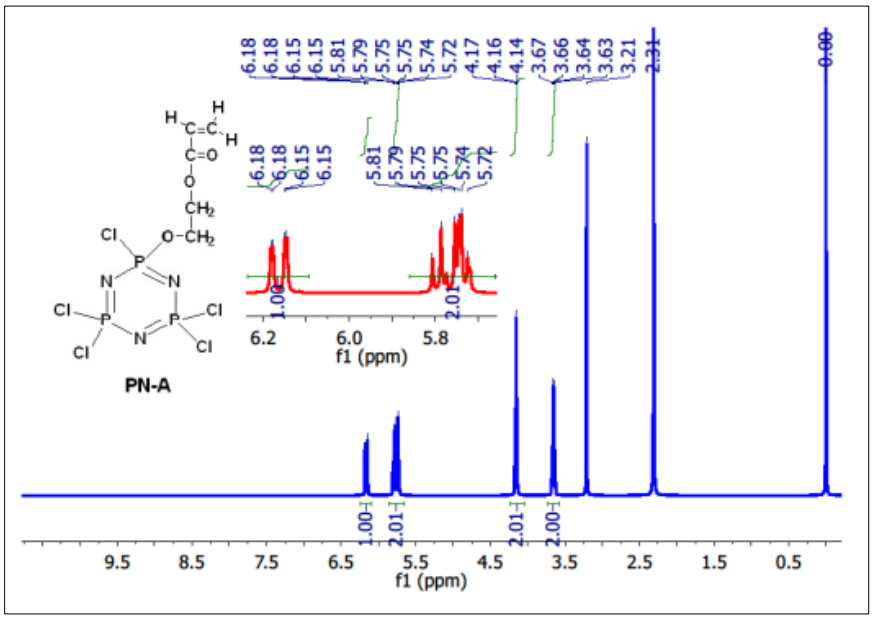


Figure 6 ^{1}H NMR spectrum of PN-A

Figure 7 shows the ^{13}C NMR of PN-A compound. Since it has showed five peaks, one at 177.21 ppm which is definitely for carbon of carbonyl group (C=O) [80]. This carbon atom has high chemical shift because it has unsaturated double bond with SP^2 hybridization and in the same time it is next to high electronegative molecule (oxygen) which is de-shielded the carbon atom then it becomes highly effected by magnetic field. Two peaks appear at aromatic or alkene region 140.48 ppm and 138.58 ppm which are related to C=C alkene group. Moreover, it is observed two peaks at 80.26 ppm and 71.86 ppm belongs to carbon atoms next oxygen. The ^{13}C NMR spectrum shows that it was obtained the product with high percentage of purity. Since the chart shows only needed peaks to demonstrate the structure without any further peaks.

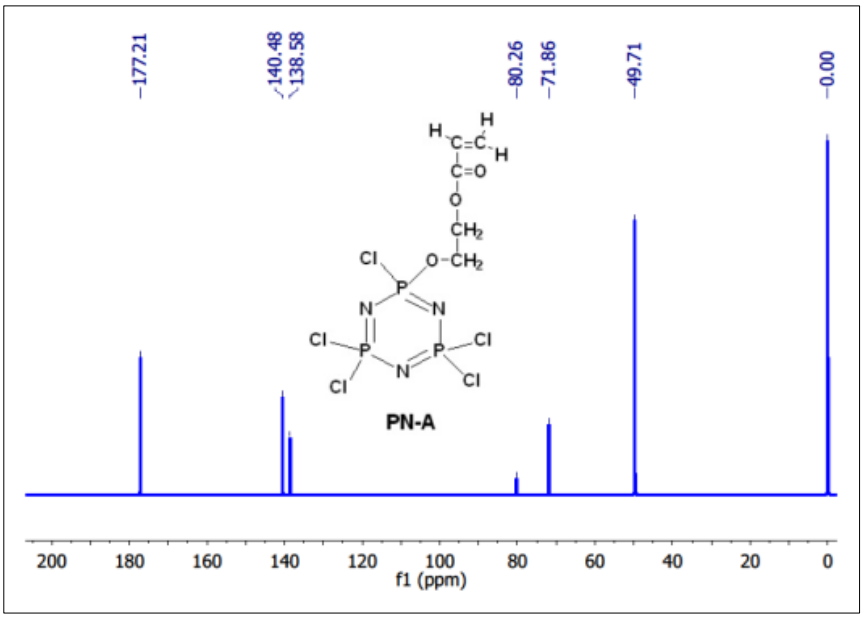


Figure 7 ^{13}C NMR spectrum of PN-A

Phosphine NMR was also employed to exhibit the chemical structure of synthesised PN-A compound. Hence 31P NMR spectrum showed two peaks at 25.77 ppm and 22.60 ppm because there are only two environments of phosphine atoms [23], as shown in Figure 8. The lowest chemical shift (22.60 ppm) could be belongs to phosphine atom which links to oxygen thus oxygen has lower electronegativity than oxygen and cause shielding for phosphine atom.

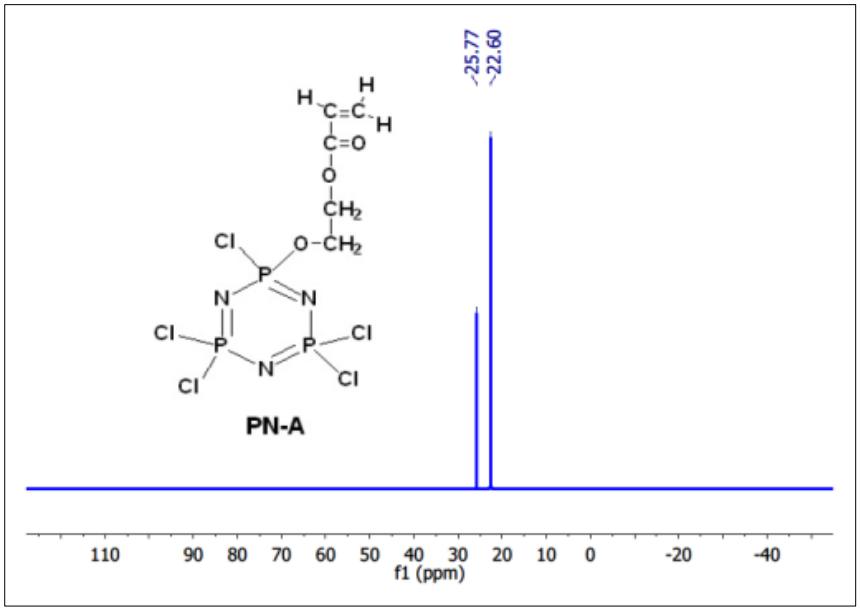


Figure 8 ^{31}P NMR spectrum of PN-A.

4. Conclusion

To conclude, starting with the cyclotriphosphazene (PN) molecule, three novel polymers (poly PN-A, poly PN-P, and poly PN-B) were effectively produced. Cyclotriphosphazene (PN) reacted with 2-hydroxyethylacrylate at a 1:1 mole ratio to give the priority of a mono substitution process, resulting in the formation of PN-A molecule. The product was purified using n-hexane recrystallization and column chromatography with a 60:40 mL ratio of cyclohexane:ethyl acetate as the eluent. The pure product was confirmed using FTIR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR techniques. All spectra demonstrates the chemical structure of the product hence the showed all required peaks to identify it.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

All authors of the manuscript have no conflict of interests to declare.

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