(RESEARCH ARTICLE)

Check for updates

Synthesis and full characterizations of poly acrylate cyclotriphosphazene and blended it with PMMA

Maha F. Abbass [1, *], Salah Al-Shukri [1] and Ahmed A. Ahmed [2]

[1] Department of Chemistry, College of Science, Mustansiriyah University, Baghdad 10052, Iraq.
[2] Polymer Research Unit, College of Science, Al-Mustansiriyah University, Baghdad 10052, Iraq.

Abstract

Poly acrylate cyclotriphosphazene (poly PN-A) was successfully synthesized by polymerization reaction using benzoyl peroxide as an initiator in dry 1,4-dioxane to form poly PN-A. After that the blended polymer with poly(methyl methacrylate) (PMMA) were prepared for synthesized polymer (poly PN-A) by using ratio 10:1 per weight of synthesized polymer to PMMA hence they were mixed using dioxane. Many techniques were used to characterize the chemical structures of synthesized material. Infrared spectroscopy was used to identify the functional groups within the chemical structure of the compounds. Three types of nuclear magnetic resonance (1H NMR, 13C NMR, and 31P NMR) were used to confirm the chemicals structures of the products. 31P NMR was used because all units and their polymers have phosphine atoms in their chemical structures. Thus, all used spectra confirmed the chemical structure of synthesised materials with high percentage of purity.

Keywords: Polymerization; PMMA; ^{1}H NMR; Blended polymer; FTIR

1. Introduction

Polyphosphazene is one of the most important and interesting class of inorganic polymers containing –P=N– basic units in their structures [1-3]. The nitrogen and phosphorus atoms are at alternating positions and two side-groups are attached to the phosphorus. Polyphosphazeneare is essentially inorganic polymer consisting of a wide range of organic, inorganic and organometallic molecules. Further, it is containing of a broad variety of different polymers, groups that attached to the polyphosphazenes skeleton having different nature. Phosphazene polymers can be synthesized with different side-groups to get a large number of different products with different properties [4-7]. The side groups are the ones on which the physical properties depend on, for example, if the side group are methoxy or ethoxy, then polymers are rubbery elastomers, and if fluoroalkoxy, or phenoxy and amino-substituted side groups are present, then polymers are flexible and film forming [8]. The general structure of polyphosphazenes is shown in Figure 1 [9-11].
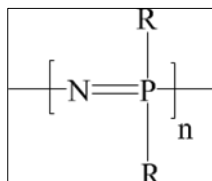
Figure 1 General structure of polyphosphazenes

* Corresponding author Maha F. Abbass
Mustansiriyah University, Department of Chemistry, College of Science, Baghdad 10052, Iraq.

Polyphosphazenes possess a numerous properties that are attractive for the following applications: elastomeric application, biomedical application, optical properties, proton conducting polymers, membranes, phosphazenes as lubricant stabilizers and additives, fuel cells, fluorinated polyphosphazenes elastomers, ceramics, military application, dyes and resins [12]. However, the macromolecular substitution of $[NPCl_2]_n$ gives ready access to copolymers, they are only random copolymers by cause of the nucleophilic substitution of the chlorine atoms along the polyphosphazene backbone is non-selective. Block copolymers, withal this, have proven fundamental for a wide number of applications, and they have widespread use, so a considerable effort has been made in order to be able to also prepare block copolymers of polyphosphazenes [13]. Attributed to the living nature of the cationic polymerization routes to $[NPCl_2]_n$, described above, the polymer chain ends remain active and enable further polymerisation upon addition of a second monomer.

A block copolymer can be synthesized which combining polyphosphazene blocks with blocks from a second polymer, for example, the organometallic–inorganic block copolymer poly(ferrocenylsilane-*b*-polyphosphazene), [14] prepared *via* end group functionalization of PFS with diphenylphosphine groups which could then act as a macroinitiator for the cationic polymerization of $Cl_3PNSiMe_3$ [15, 16].

2. Materials and method

2.1. Materials

The reagent grade triethyl amine (ET3N) (Merck) was predried over grinded potassium hydroxide, distilled and received over molecular sieves type 4A° (2.5-5.0 mm beads). 1,4-dioxane (LAB-SCAN) was freshly distilled prior to use from sodium benzophenone ketyl in an atmosphere of nitrogen gas. Ethyl-4-hydroxybenzoate (Sigma-Aldrich) was purified by re-crystallization from hot toluene, anhydrous sodium sulfate (Romil), methylene chloride (Scharlau) 99.9 % pure, chloroform (Romil) 99.5% pure, phenol (Scharlau) 99.5% pure, tetrahydrofuran (Lab-Scan) 99.8 % pure, PMMA (Fluka) 98.9% pure, were used received without further purification. sodium metal (Merck) rods were protected in petroleum oil. The rods were sliced into thin pieces prior to use.

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 relatives to TMS (0.00 ppm) for ^1H, ^{13}C NMR and to 85% H_3PO_4 for ^{13}P NMR.

2.3. Polymerization of PN-A

In three necks round bottom flask (30 ml) of freshly distilled 1,4-dioxane, (0.008 gm) benzoyl peroxide were added to (5 gm) PN-A. The contents were stirred for 5 min, then refluxed at (102 ℃) with continuous stirring for 72 hrs. The contents of the solution become concentrated then the solution was filtered and the solvent was removed by using a rotary evaporator. Finally, a viscous material was obtained.

2.4. Preparation of poly PN-A blend with PMMA

In around bottom flask (30 ml) of freshly distilled 1,4-dioxane, (0.5 gm) PMMA were added to (5 gm) PN-A, the contents stirred for 5 min, then refluxed for 0.5 hr after that the mixture filtrated and the solvent is removed by using a rotary evaporator.

3. Results and discussion

3.1. Synthesis of poly PN-A and blend it with PMMA

The polymerization of PN-A to poly PN-A was achieved *via* using freshly re-distilled 1,4-dioxane which was added to the content of the flack (PN-A) and benzoyl peroxide (see Figure 2). That was chosen as an initiator in this case because of its ability to decompose at a temperature of more than 60 ℃ and yield free radical products that are highly reactive as shown in below Figure 3. The contents stirred for 5 min, then refluxed at (102 ℃) with continuous stirring for 72 h. It was observed that the density of the mixture was increase and the solution becomes more viscous. The solvent is removed by using a rotary evaporator and finally a viscous material was obtained.
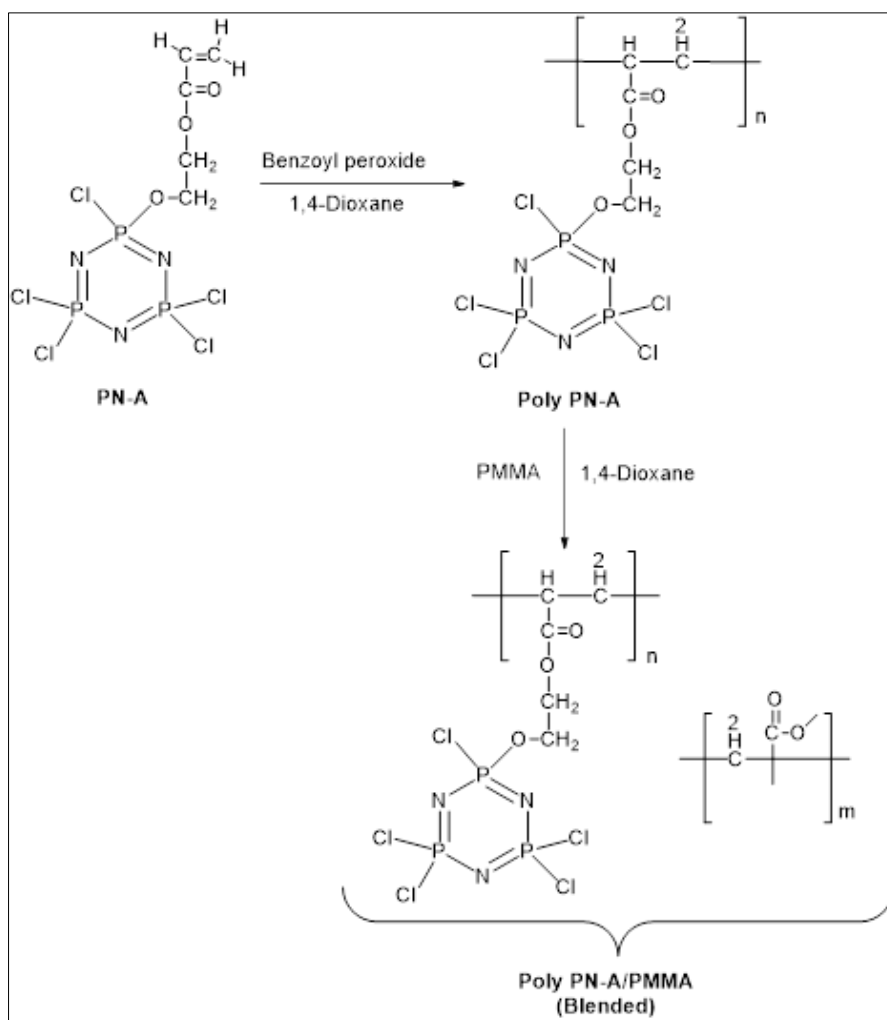
Figure 2 Synthesis of PN-A, poly PN-A and poly PN-A/PMMA
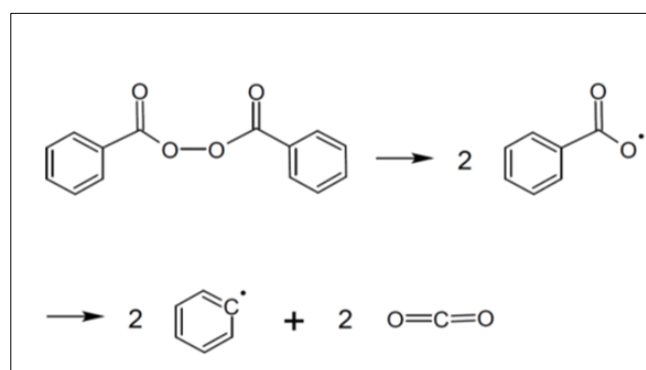
**Figure 3** Benzoyl peroxide as an initiator

A blend of poly PN-A, PMMA was prepared with ratio 1:10 per weight where it was used 0.5 gm of PMMA to 5 gm of poly PN-A; both dissolved in 30 mL of 1,4-dioxane, the contents stirred for 5 min, then refluxed for 30 min. After that the mixture filtrated and the solvent is removed by using a rotary evaporator. Since refluxed is carry out this lead to formation of tightly bound polymeric chains, the nature of the bonding is physical and not chemical. In the beginning, (FTIR) spectrum display incorrect result for the product. This is due to the presence of the residues of salt and solvent in the polymer. Therefore the crude product was dissolved in minimum amount of 1,4-dioxane then was added to vigorously stirred benzene. The blended polymer was precipitated and the residue was separated by using centrifuge then decantation the final result was good with very interesting spectrum.

3.2. Characterization of poly PN-A by FTIR

Figure 4 shows the interesting band of P=N group at 1203 and 1189 cm^{-1} which assigned to the asymmetric and symmetric stretching vibration respectively. The peak at 1035 cm^{-1} refers to PO-C group and the characteristic peak at 585 and 528 cm^{-1} assigned to asymmetric and symmetric vibration of P-Cl group. The band at 1736 cm^{-1} refers to C=O group of ethoxyethylacrylate. The important FTIR bands of poly PN-A are summarized in Table 1 as shown below.

Table 1 Infrared spectral data of poly PN-A

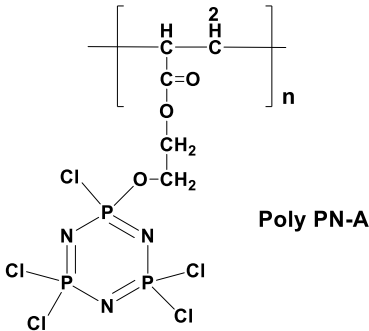| Frequency (cm^{-1})	Assignment
1035	PO-C (stretching of PO-C)
1736	C=O (stretching of ester group of acrylates)
1203, 1189	P=N (asymmetric and symmetric stretching)
585, 528	P-Cl (stretching of P-Cl)
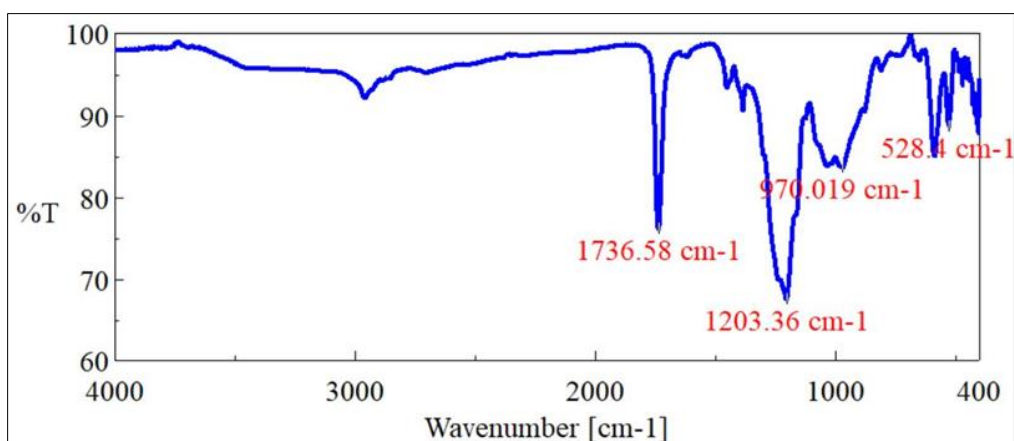
Figure 4 FTIR spectrum of poly PN-A

3.3. Characterization of poly PN-A by NMR

Prepared PN-A moiety was polymerized to get homo polymer (poly PN-A). The product was identified using ^{1}H NMR technique. The ^{1}H NMR spectrum showed seven hydrogen atoms by integration in four different environments (see Figure 5), two peaks at 4.11 ppm and 3.71 ppm for protons next to oxygen (O-CH$_2$)$_2$. As it was demonstrated for the monomer unit PN-A this is because these groups do not affected by polymerization reaction. Even though the peaks become multiplet instead of triplet for monomer unit, which is expected due to forming polymer then each unit within the polymer structure has very slightly different environment which leads to form multiplet rather than triplet peaks. However, the peaks belong to alkene group have completely shifted from unsaturated region to saturated region at 2.36-2.30 multiplet peak for aliphatic CH group, and 1.09 multiplet peak for aliphatic CH$_2$ group. This is obvious because polymerization happens at the alkene groups hence it becomes fully saturated after the reaction [17, 18].

In comparison of ^{13}C NMR spectra of PN-A and poly PN-A both spectra have showed five peaks one at the highest chemical shift above 180 ppm for carbonyl group (C=O) group and two peaks between 70-81 ppm which are belongs to carbon atoms next to oxygen (see Figure 6). However, two peaks have been shifted from aromatic or alkene region for PN-A monomer to aliphatic region below 40 ppm for poly PN-A polymer. This is clear evidence that polymerization happens through alkene groups and converted to saturated groups. All NMR data of synthesised poly PN-A homo polymer have been summarized in Table 2.

Table 2 NMR spectral data of poly PN-A

Technique	
	Poly PN-A
¹H-NMR (400 MHz: DMSO-d₆, δ, ppm, *J* in Hz)	4.11-4.07 (m, 2H, O-CH₂), 3.71-3.66, (m, 2H, O-CH₂), 2.36-2.30 (m, 1H, CH), 1.09-1.05 (m, 2H, CH₂).
¹³C-NMR (100 MHz: DMSO-d₆, δ, ppm)	185.00, 80.15, 70.93, 36.43, 18.54.
³¹P-NMR (162 MHz: DMSO-d₆, δ, ppm)	26.86, 23.69
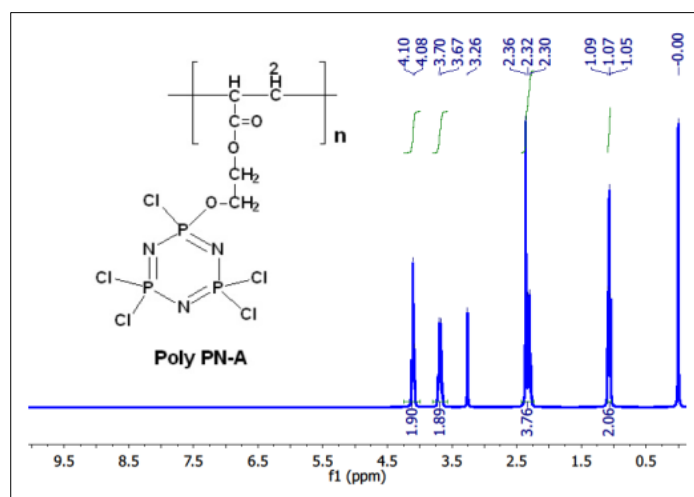
Figure 5 ¹H NMR spectrum of poly PN-A
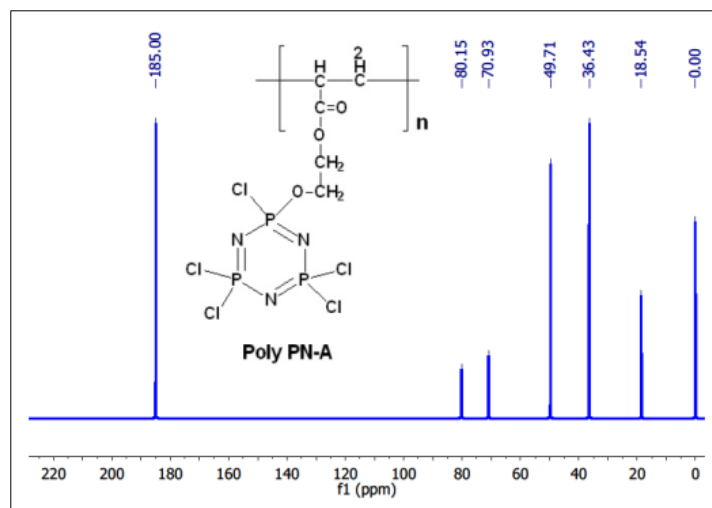
Figure 6 ¹³C NMR spectrum of poly PN-A

For ^{31}P NMR spectrum of poly PN-A, it has showed as well two peaks the same what was noticed for PN-A monomer unit due two phosphine atoms has two environments in both cases. Thus it was notice a little bit of shifted to higher frequency by about 2 ppm for poly PN-A in comparison to PN-A moiety, which might be because of polymerization. Figure 7 shows ^{31}P NMR spectrum of synthesised poly PN-A.
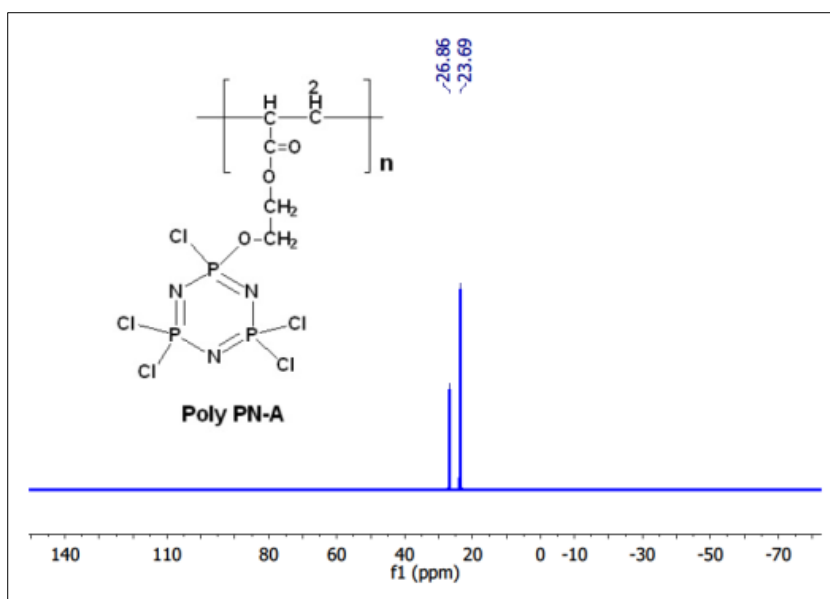
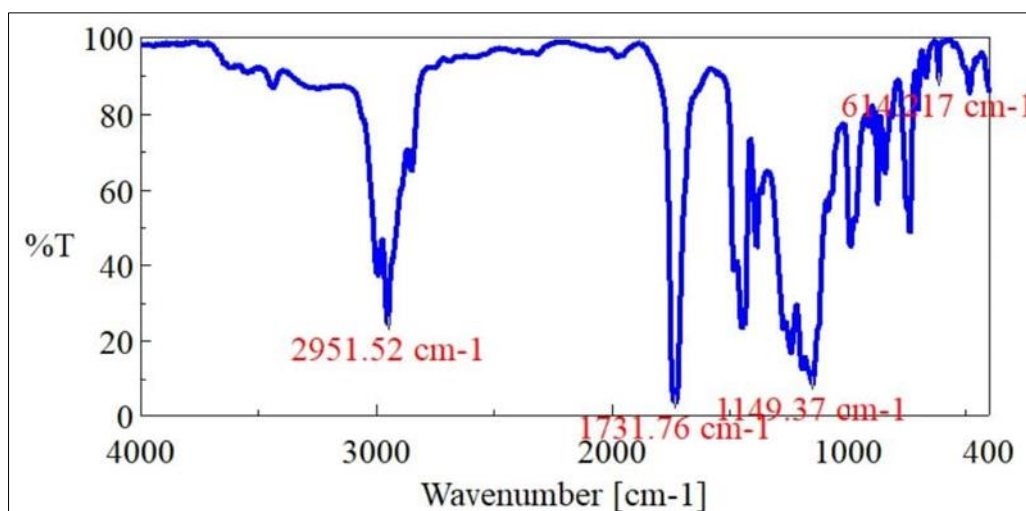**Figure 7** ^{31}P NMR spectrum of poly PN-A

3.4. Characterization of poly PN-A/PMMA by FTIR

Poly PN-A/PMMA was characterized by FTIR technique to demonstrate the chemical structure of this blended polymer. It was observed peaks at 1161.9, and 1149 cm^{-1} refer to asymmetric and symmetric stretching vibration of P=N group. In addition, the adsorption band at 668, 614 cm^{-1} fits to stretching vibration of P-Cl group. An interesting peak was also noticed at 1731 cm^{-1} refers to stretching of C=O group of PMMA. Thus, band at 1240.9 cm^{-1} refers to stretching vibration of C-O group for PMMA part. While peaks at 2951.5 and 1721 cm^{-1} belong to stretching vibration of C-H group of PMMA and stretching of C=O group of acrylate ester respectively [19]. However, band at 1038 cm^{-1} refers to stretching vibration of PO-C group as shown in Figure 8. The FTIR data of blended polymer poly PN-A/PMMA were tabulated in Table 3.

Table 3 Infrared spectral data of poly PN-A/PMMA

Frequency (cm^{-1})	Assignment
1161.9, 1149	P=N (asymmetric and symmetric stretching)
668, 614	P-Cl (stretching of P-Cl)
1731	C=O (stretching of aster group of PMMA)
1240.9	C-O (stretching of aster group of PMMA)
2951.5	C-H (stretching of PMMA)
1721	C=O (stretching of acrylate group)
1038	PO-C (stretching of PO-C)

Figure 8 FTIR spectrum of poly PN-A/PMMA

3.5. Characterization of poly PN-A/PMMA by NMR

Figure 9 shows the 1H NMR spectrum of poly PN-A/PMMA blended co-polymer by 10:1 equivalent per weight of poly PN-A polymer and PMMA polymer respectively. In comparison of poly PN-A homo-polymer to polyPN-A/PMMA blended polymer 1H NMR spectra, it can be seen the appearance of new peaks related to PMMA polymer. Hence it was noticed overlapped singlet peak at 3.59 belongs to OCH3 group and another nice singlet peak at 1.23 returns to aliphatic CH3 group [20]. In addition, it was noticed one more peak at aliphatic region for CH2 group. Obviously, from the integration of protons the blend polymerization happened successfully by ratio 10:1 per weight. All NMR data of synthesised polyPN-A/PMMA blended polymer have been summarized in Table 4.

Table 4 NMR spectral data of poly PN-A/PMMA

Technique	
	Poly PN-A/PMMA (Blended)
^{1}H-NMR (400 MHz: DMSO-d$_6$, δ, ppm, J in Hz)	4.06-4.02 (m, 2H, O-CH$_2$), 3.65-3.56 (m, 2H, O-CH$_2$, and OCH$_3$ of PMMA), 2.23-2.15 (m, 1H, CH), 2.05-1.96 (m, CH$_2$ of PMMA), 1.70-1.51 (m, 2H, CH$_2$), 1.23 (s, CH$_3$ of PMMA).
^{13}C-NMR (100 MHz: DMSO-d$_6$, δ, ppm)	186.30, 183.81, 80.15, 70.93, 61.81, 49.71, 43.73, 42.01, 31.30, 26.86.
^{31}P-NMR (162 MHz: DMSO-d$_6$, δ, ppm)	26.96, 23.79.

In the case of ^{13}C NMR spectrum, it was demonstrated the existence of five new peaks for poly PN-A/PMMA blended polymer comparing to poly PN-A homo-polymer (see Figure 10). Since, it appears two peaks at very large chemical shift above 180 ppm instead of one peak; they fit to carbonyl groups [21]. Appearance of three peaks at region between 60-81 ppm instead of two peaks which are fit to carbon atoms next to oxygen C-O groups. Furthermore, it exhibited the presence of five peaks between 0-50 ppm instead of two which are return to aliphatic CH, CH$_2$, and CH$_3$ groups.

For phosphine NMR spectrum of polyPN-A/PMMA blended polymer, there is no much difference between starting polymer polyPN-A and the product blended polymer polyPN-A/PMMA. Hence there is not any change in the chemical structure of both compounds regarding phosphine atoms. Figure 11 shows the ^{31}P NMR of polyPN-A/PMMA blended polymer.

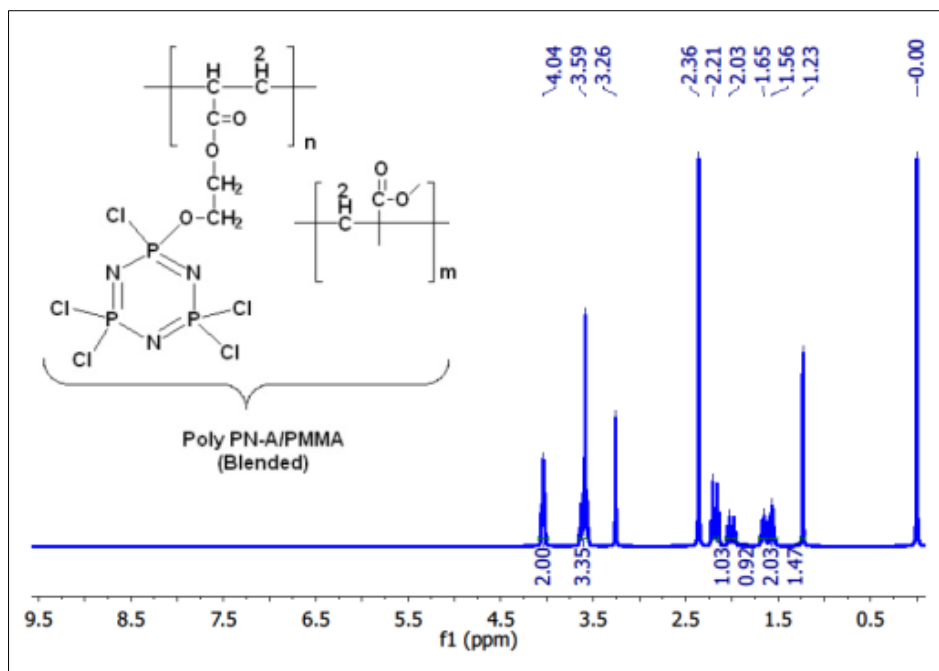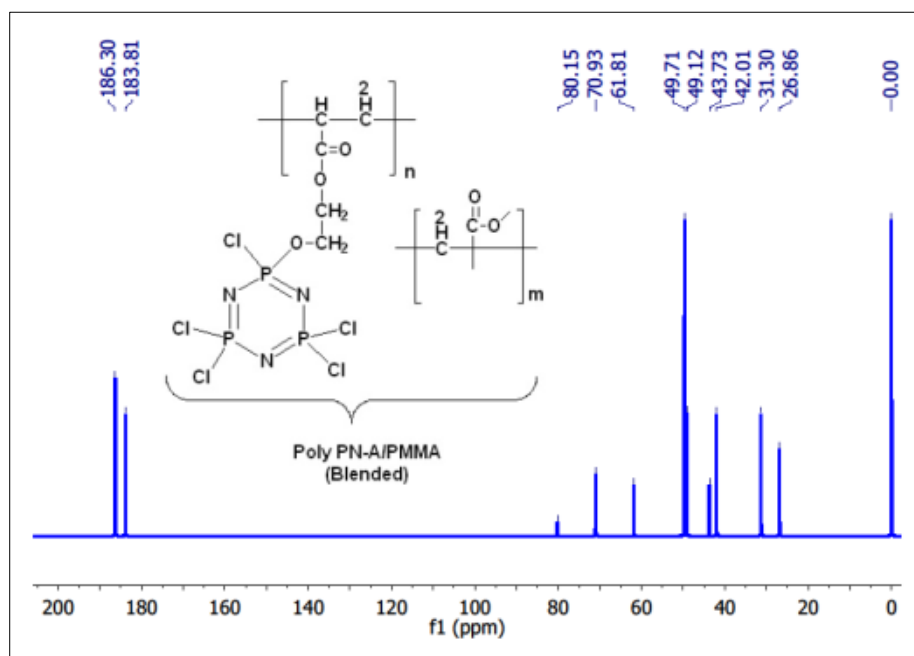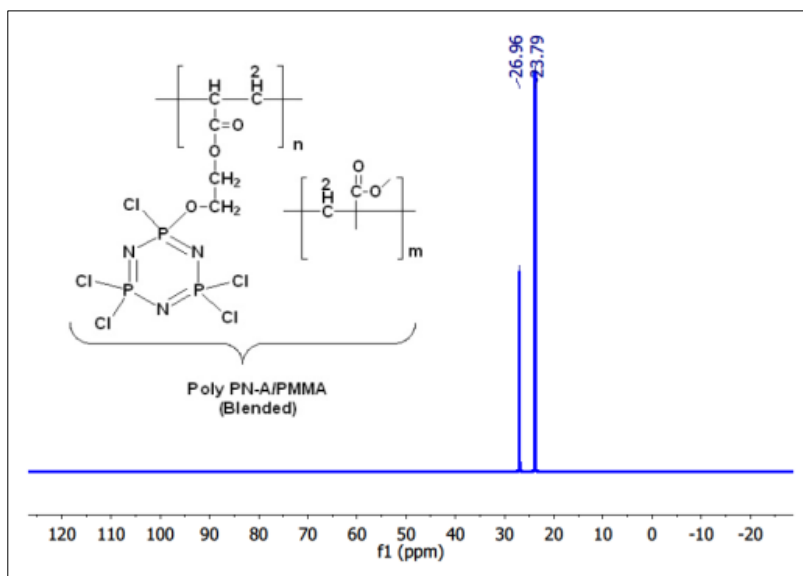**Figure 9** ^{1}H NMR spectrum of poly PN-A/PMMA

Figure 10 ^{13}C NMR spectrum of poly PN-A/PMMA

Figure 11 ^{31}P NMR spectrum of poly PN-A/PMMA

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 demonstrate the chemical structure of the product hence the showed all required peaks to identify it.

Compliance with ethical standards

Disclosure of conflict of interest

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

References

[1] Cheng H, Richard A, Patrick B, Green polymer chemistry: new products, processes, and applications. Vol. 1310. Washington, DC: American Chemical Society, 2018.

[2] K. K. Ajekwene, Properties and Applications of Acrylates, Acrylate Polym. Adv. Appl., pp. 1–12, 2020.

[3] K. M. Takashi Ohara, Takahisa Sato, Noboru Shimizu, Günter Prescher, Helmut Schwind, Otto Weiberg, Acrylic Acid and Derivatives, 2003.

[4] V. E. and S. Chimjarn†, Synthesis and Isolation of Methacrylate- and Acrylate-Functionalized Polyhedral Oligomeric Silsesquioxanes (T8, T10, and T12) and Characterization of the Relationship between Their Chemical Structures and Physical Properties, vol. 52, no. 22, 2013.

[5] J.J. Gallagher, M.A. Hillmyer, and T.M. Reineke Acrylic triblock copolymers incorporating isosorbide for pressure sensitive adhesives ACS Sustainable Chemistry & Engineering. 2016 Jun 6;4(6):3379-87.

[6] P. Simona, S. Iliescu, G. Ilia, N. Plesu, A. Popa, A. Visa, and L. Macarie. Solid polymer electrolytes based on phosphorus containing polymers for lithium polymer batteries. European Polymer Journal.,2017; 94; 286-298.

[7]   Z. Mitra, M. Vojdani, S. Mohammadi, and A.-A. Khaledi. Comparison of the water sorption and solubility of four reline acrylic resins after immersion in food-simulating agents. Journal of International Society of Preventive & Community Dentistry 2019; 9; 40.

[8]   V. K. Gupta, M. Gupta, and S. Sharma, Process development for the removal of lead and chromium from aqueous solutions using red mud - An aluminium industry waste, Water Res., 2001; 35(5): 1125–1134. 2001, doi: 10.1016/S0043-1354(00)00389-4.

[9]   H. R. Allcock, Recent advances in phosphazene (phosphonitrilic) chemistry, 1971.

[10]   V. C. and A. Chakraborty, Organophosphorus Chemistry., R. Sciety Chem., 2019; 48,400-423.

[11]   D. Kumar, J. Singh, and A. J. Elias, cyclophosphazene cores : synthesis , characterization and complexation studies †, pp. 13899–13912, 2014, doi: 10.1039/c4dt01741b.

[12]   A. M. Amin et al., Recent research progress in the synthesis of polyphosphazene and their applications, Des. Monomers Polym., vol. 12, no. 5, pp. 357–375, 2009, doi: 10.1163/138577209X12486896623373.

[13]   AP Soto and I Manners. Poly(ferrocenylsilane-b-polyphosphazene) (PFS-b-PP): A new class of organometallic-inorganic block copolymers. Macromolecules, 2009; 42(1):40–42, 2009, doi: 10.1021/ma8016713.

[14]   S. Rothemund and I. Teasdale, Preparation of polyphosphazenes: A tutorial review, Chem. Soc. Rev., 2016; 45 (19): 5200–5215. doi: 10.1039/c6cs00340k.

[15]   HR Allcock, JD Bender, Y Chang, M Mckenzie, and MM Fone, Controlled Refractive Index Polymers : Polyphosphazenes with Chlorinated- and Fluorinated- , Aryloxy- and Alkoxy- Side-Groups, no. 2003; 10, 473–477.

[16]   M. Olshavsky and HR Allcock, Polyphosphazenes with High Refractive Indices: Optical Dispersion and Molar Refractivity, 1997; 9297(96): 4179–4183.

[17]   A Papan, A Tarassoli and Z Shahidian, Synthesis and structure determination of novel derivative of cyclotriphosphazene with phloroglusine ligand with two protected position, Iran. J. Chem. Chem. Eng., 2016; 35 (2): 1–7.

[18]   L. Carolin, M. Horn, F. Berger, C. Fauhl-Hassek, M. A. Glomb, and Susanne Esslinger. Quality control of spectroscopic data in non-targeted analysis–Development of a multivariate control chart. Food Control, 2022; 133; 108601..

[19]   E Vargün and A Usanmaz, Polymerization of 2-hydroxyethyl acrylate in bulk and solution by chemical initiator and by ATRP method, J. Polym. Sci. Part A Polym. Chem. 2005; 43(17): 3957–3965. doi: 10.1002/pola.20867.

[20]   RB Koizhaiganova, VB Sigitov, LA Bimendina and SE Kudaibergenov, Synthesis and characterization of novel linear and crosslinked polyelectrolytes derived from the acetoacetic ester and acrylic acid, Polym. Bull., 2005; 53(3):161–168, 2005, doi: 10.1007/s00289-004-0328-3.

[21]   NAA Rossi, RG Jones and SJ Holder, Synthesis and Characterization of Poly (methyl methacrylate) - block -Poly (methylphenylsilane) - block -Poly (methyl methacrylate) by Atom Transfer Radical Polymerization, pp. 30–40, 2003