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The synthesis and characterization of o-dianisidine derived crosslinked trimeric and tetrameric polyphosphazene microspheres

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ABSTRACT

Phosphazenes can react with compounds with various functional groups to form compounds with different properties, and polymers with various usage areas can be obtained under suitable conditions. A class of materials known for its versatility and sophisticated nature, crosslinked polyphosphazenes combine a phosphorus-nitrogen backbone with a variety of organic side groups to form a unique inorganic-organic hybrid structure. The crosslinking process, whether it be chemical, photochemical, or thermal, results in notable improvements in mechanical strength, chemical resistance, thermal stability, and biocompatibility. These properties make crosslinked polyphosphazenes highly suitable for a range of applications including biomedical devices, drug delivery systems, controlled drug release, enzyme activities, tissue engineering scaffolds, surgical materials, hydrophilic-hydrofobic materials, liquid crystals, sensors, thermal resistant materials, ion transfer membranes, catalysis support, dye adsorption for green chemistry environmental remediation technologies, and advanced coatings and adhesives. Their potential utility is further expanded by the capacity to modify the side groups and crosslinking density of these materials to tune their physical and chemical features. Crosslinked polyphosphazenes are being explored and optimized for synthesis and use in several sectors of research, thereby placing them as essential materials for future technological breakthroughs.

In this study, cyclomatrix polyphosphazene microspheres were synthesized from the reactions of o-dianisidine (o- DNSD) as monomer and hexachlorocyclotriphosphazene (trimer, $N_3P_3Cl_6$) /octachlorocyclotetraphosphazene (tetramer, $N_4P_4Cl_8$), as crosslinking agents, according to the precipitation polymerization method. The characterization of the products were elucidated by SEM (Scanning Electron Microscopy), FT-IR (Fourier- Transform Infrared Spectroscopy) and XRD (X-Ray Diffraction Spectroscopy) and TGA (Thermogravimetric Analysis) spectral techniques.

1. Introduction

Phosphazene compounds are characterized by double bonds between phosphorus and nitrogen atoms in their structures and have been the subject of studies for years due to their superior properties [1–3]. Polyphosphazenes are examined under four general groups as straight chain, cyclolinear, cyclomatrix and linear matrix polymers. Cyclic phosphazenes are more stable than straight-chain phosphazenes due to resonance-like electron delocalization in the benzene molecule [4,5]. Hexachlorocyclotriphosphazene (trimer) and tetrachlorocyclotetraphosphazene (tetramer) are the two most often utilized cyclic phosphazene compounds. Different groups attached to phosphorus atoms in these compounds will cause the bond lengths and angles of the cyclic structure to change [5–8]. Polyphosphazenes with cyclomatrix structure are synthesized as a result of the reaction of cyclic phosphazenes with alcohols or phenols having more than one functional group, under appropriate conditions [9].

High cross-linking levels of cyclomatrix polyphosphazene compounds are produced by treating trimer or tetramer with phenols, alcohols, or di- or polyfunctional amines [11–13]. This type of phosphazenes are obtained by the precipitation polymerization method. This method; It is an easy and multi-purpose approach in which fully cross- linked polymeric nano/microspheres with similar shape and size are produced by replacing multifunctional organic nucleophiles with trimer or tetramer. Determination of surface morphology and particle size can be controlled by ratio variation of the starting material [14].

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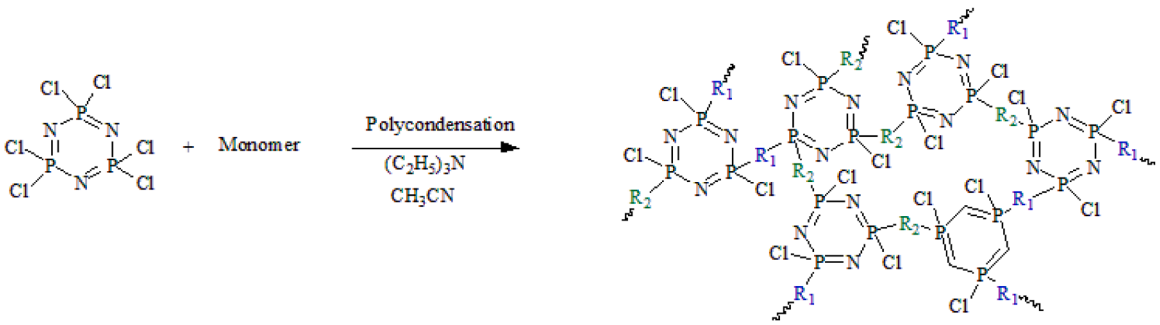


Fig. 1. The formation route for cross-linked trimeric polyphosphazenes.

Cyclomatrix polyphosphazenes are obtained by precipitation polymerization method. In these reactions, cyclic phosphazene compounds act as crosslinkers and polyfunctional alcohols/amines act as monomers [15–17]. As a result of the substitution of the cyclic phosphazenes used in this method with nucleophiles, it is possible to realize the formation of cross-linked nano/microspheres of the same size. Particle sizes and surface morphologies can be controlled by changing the molar ratio of the amount of crosslinker or monomer [10,14,15,18]. Crosslinking polyphosphazenes involves creating covalent bonds between polymer chains, enhancing the material's mechanical strength, thermal stability, and resistance to solvents. Common methods for crosslinking polyphosphazenes include: Thermal Crosslinking: Heating the polymer can induce crosslinking reactions between functional side groups. In the realm of advanced materials, crosslinked polyphosphazenes have emerged as a fascinating and highly versatile class of polymers. Characterized by their unique backbone structure of alternating phosphorus and nitrogen atoms, these materials offer a remarkable combination of properties that make them suitable for a wide range of applications, from biomedical devices to high-performance coatings [6]. Crosslinked polyphosphazenes have improved characteristics that make them very useful for novel applications. Their biocompatibility and capacity to be functionalized with bioactive molecules have made them useful in the biomedical industry for applications such as medical implants, scaffolds for tissue engineering, and drug delivery systems [19]. Additionally, their excellent chemical resistance and selective permeability are exploited in filtration and separation membranes, while their durability and stability make them ideal for protective coatings and adhesives in industrial applications [20].

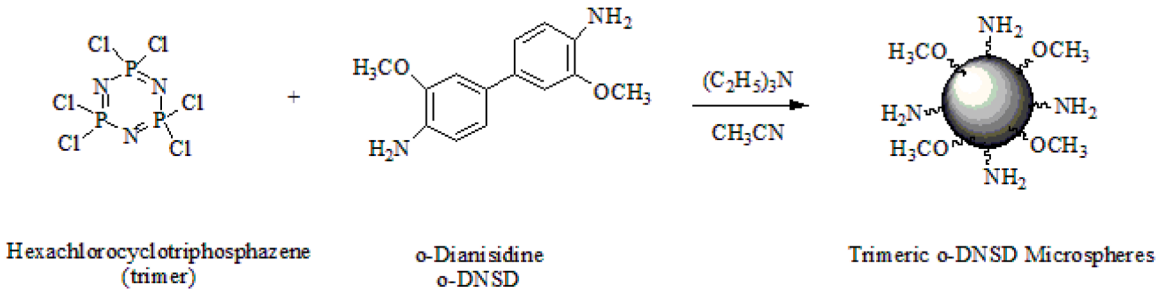
The formation mechanism of cyclomatrix polyphosphazene nano/microspheres can be explained as the polycondensation reaction between the crosslinker hexachlorocyclotriphosphazene (trimer) and monomers with more than one functional group and the formation of oligomeric species. The steps for formation mechanism can be expressed as Initial monomer synthesis, Nucleophilic substitution, Crosslinling and cyclization, Curing and network formation. Triethylamine (TEA) is used as a salt scavenger and to regulate the pH of the reaction medium, and TEA.HCl is formed during the reaction . The oligomers come together and grow, as a result of which precursor core particles are formed. These particles interact through hydrogen bonds to obtain more stable particles and combine with oligomers to form nano/microspheres [6,21,22], (Fig. 1).

In this study, cross-linked polyphosphazene microspheres were synthesized by polycondensation reactions under suitable conditions using hexachlorocyclotriphosphazene, trimer ($N_3P_3Cl_6$) / octachlorocyclotetraphosphazene, tetramer ($N_4P_4Cl_8$) and o-dianisidine. Hexachlorocyclotriphosphazene, trimer ($N_3P_3Cl_6$) and octachlorocyclotetraphosphazene, tetramer ($N_4P_4Cl_8$) were used as the crosslinkers. Cross-linked polyphosphazene microspheres were obtained by changing the mole ratios of crosslinkers and monomer at constant conditions and their structures were elucidated by SEM, FT-IR and XRD spectral techniques. This article explores the synthesis, features, and range of uses of crosslinked polyphosphazenes, emphasizing how their special and improved qualities have the potential to transform a number of industries. These materials have the potential to be extremely important in the creation of next-generation technology as long as research on them continues.

2. Experimental methods

2.1. Materials and methods

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$, trimer) was purchased from Alfa Aesar and recrytallized from n- Heptane and its purity checked by measuring the melting point. O-dianisidine (o-DNSD), triethylamine (TEA) and acetonitrile (CH_3CN) and ethanol (C_2H_5OH) were purchased from Acros Organics, Fischer, Sigma Aldrich respectively and used without further purification. Scanning electron microscopy (SEM) measurements were performed on a ZEISS Ultra Plus (ZEISS ULTRA 55) electron microscope at an accelerating voltage of 2 kV by coating with gold before analysis. Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer Spectrum 100 Spectrometer) was used to determine the functional groups of microspheres and changes in groups attached to the phosphazene rings. KBr pellets of the reactants and products were used for analysis and scans were performed in the range f 400–4000 cm^{-1}. X-ray diffraction (XRD) pattern was recorded on PANALYTICAL/EMPYREAN instrument equipped with Cu Kα radiation at 40 kV and 40 mA.



Scheme 1. Synthesis Reaction of Trimeric o-DNSD Microspheres.

Table 1
Trimeric microsphere compositions at constant o-DNSD concentration.

Molar ratio (ODNSD:Trimer)	ODNSD (g)	Trimer (g)	TEA (mL)
1:1	0.250	0.356	7.130
1:2	0.250	0.712	14.260
1:3	0.250	1.068	21.400
1:4	0.250	1.424	28.520
2:1	0.250	0.177	3.600
3:1	0.250	0.118	2.410
4:1	0.250	0.088	1.800

Table 2
Tetrameric microsphere compositions at constant o-DNSD concentration.

Molar ratio (o-DNSD:Tetramer)	ODNSD (g)	Tetramer (g)	TEA (mL)
1:1	0.250	0.474	7.120
1:2	0.250	0.948	14.240
1:3	0.250	1.422	21.360
1:4	0.250	1.896	28.480
2:1	0.250	0.237	3.560
3:1	0.250	0.158	2.370
4:1	0.250	0.118	1.780

2.2. Synthesis of microspheres

2.2.1. The synthesis of trimeric o-DNSD microspheres and change in the mole ratio of hexachlorocyclotriphosphazene

o-Dianisidine (o-DNSD; 0.25 g, 1.023 mmol) was dissolved in 50 mL acetonitrile (CH_3CN). Triethylamine (TEA) (7.130 mL, 50.380 mmol) was added to the solution under ultrasonic radiation. After ten minutes, the reaction media were mixed with a solution of hexachlorocyclotriphosphazene (trimer, $N_3P_3Cl_6$; 0.356 g, 1.023 mmol) (Scheme 1). The reaction mixture was kept at a temperature between 35 and 50 °C for two hours under ultrasonic radiation. Then, a magnetic stirrer was used to agitate the mixture for four hours at room temperature and allowed to settle. Following a 30-minute centrifugation run at 3000 rpm to separate the precipitated product, acetonitrile (CH_3CN), distilled water and ethanol (C_2H_5OH), and were used as wash agents. Finally, obtained o-DNSD microspheres were dried at 50 °C under vacuum. The same procedure was repeated for other molar ratios of trimer (Table 1).

2.2.2. The synthesis of tetrameric o-DNSD microspheres and change in the mole ratio of octachlorocyclotetraphosphazene

o-Dianisidine (o-DNSD; 0.25 g, 1.023 mmol) was dissolved in 50 mL acetonitrile (CH_3CN). Triethylamine (TEA) (7.130 mL, 50.380 mmol) was added to the solution under ultrasonic radiation. A solution of octachlorocyclotetraphosphazene (tetramer, $N_4P_4Cl_8$; 0.474 g, 1.023 mmol) was added to the reaction media after ten minutes. The reaction mixture was maintained at the temperature range of 35–50 °C for 2 h under ultrasonic radiation. Then, a magnetic stirrer was used to agitate the mixture for four hours at room temperature and allowed to settle. Following a 30-minute centrifugation run at 3000 rpm to separate the precipitated product, acetonitrile (CH_3CN), distilled water and ethanol (C_2H_5OH), and were used as wash agents. Ultimately, o-DNSD microspheres were produced and vacuum-dried at 50 °C. For different molar ratios of tetramer, the same process was performed (Table 2).

3. Results and discussion

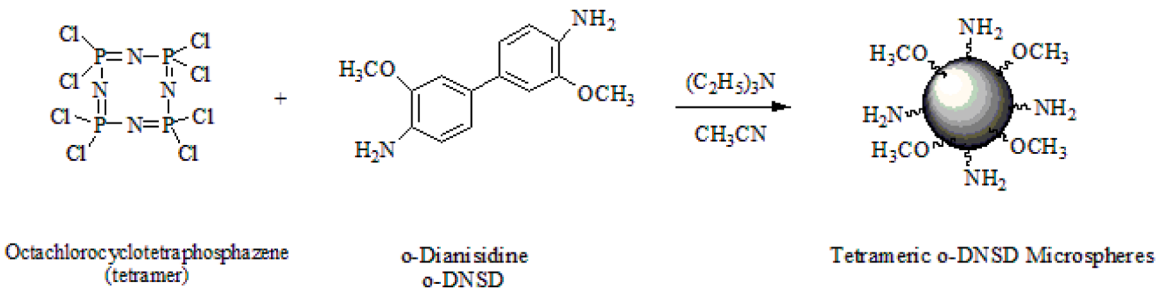
Four distinct types of crosslinked polyphosphazene were attempted to be synthesized in these studies using the precipitation polymerization process. Meanwhile, ratio experiments were carried out with o-DNSD as monomer and trimer and tetramer as crosslinkers. The aim of these ratio experiments is to obtain proper and homogeneous spheres. Some parameters were specifically tried to be kept constant like solvent amount, temperature and ultrasonic bath as reaction media. SEM morphologies were used by looking at the initial experiments to determine the reaction durations. These parameters were kept constant for each experiment. o-DNSD-microspheres were prepared via self- assembly one-pot polycondensation polymerization of hexachlorocylotriphosphazene (trimer, $N_3P_3Cl_6$) trimer and tetramer octachlorocyclotetrahosphazene (tetramer, $N_4P_4Cl_8$). In order to obtain the best morphological surface, the use of reagents in different mole ratios was tried. It was tested using chemicals in various mole ratios to get the optimal morphological surface. Utilizing SEM, FT- IR, and XRD, the polymeric microspheres were characterized. [15,23,24]. o-DNSD-MS synthesis was accomplished via one-pot basic polymerization. Synthetic routes for the formation o-DNSD-miscospheres were given in Scheme 1 and Scheme 2. The crosslinker molecules trimer and tetramer are flexible rings with six and eight chlorine atoms, respectively. So these features of both phosphazene rings give them high cross-linking ability against o-DNSD. Excessive amounts of TEA were used as an acid acceptor during polymerization operations, generating TEA.HCl. Stabilizing agent or surfactant was not needed for the polymerization process.

According to the previously described process, trimeric and tetrameric polyphosphazenes with cross-linked networks self-assemble. During the initial phase of polymerization, ODNSD, acting as the monomer, reacts with the crosslinker trimer/tetramer to create oligomers. Oligomers aggregate together to form primary nucleus particles at the next step. Subsequently, hydrogen bond interactions cause the primary nucleus particles to aggregate and become stable primary particles. Following that, oligomeric species are absorbed by the particles, causing them to grow larger than initial particles. The resulting microspheres are pore-free both inside and outside. SEM images of the cyclomatrix type o-DNSD-trimer microspheres are presented in Fig. 2.

The crystalline or amorphous nature of the microspheres is ascertained using XRD spectral technique. The 1:1 o- DNSD-trimer XRD Spectrum is shown in Fig. 3. The broad peak displays the product's amorphous structure at about 25° that emerged in accordance with the XRD diffraction pattern.

Fig. 4 displays the FT-IR spectra of the trimer, o-DNSD, and 1:1 o-DNSD-trimer.

SEM images of the cyclomatrix type o-DNSD-tetramer microspheres are shown in Fig. 5.



Scheme 2. Synthesis reaction of tetrameric o-DNSD microspheres.

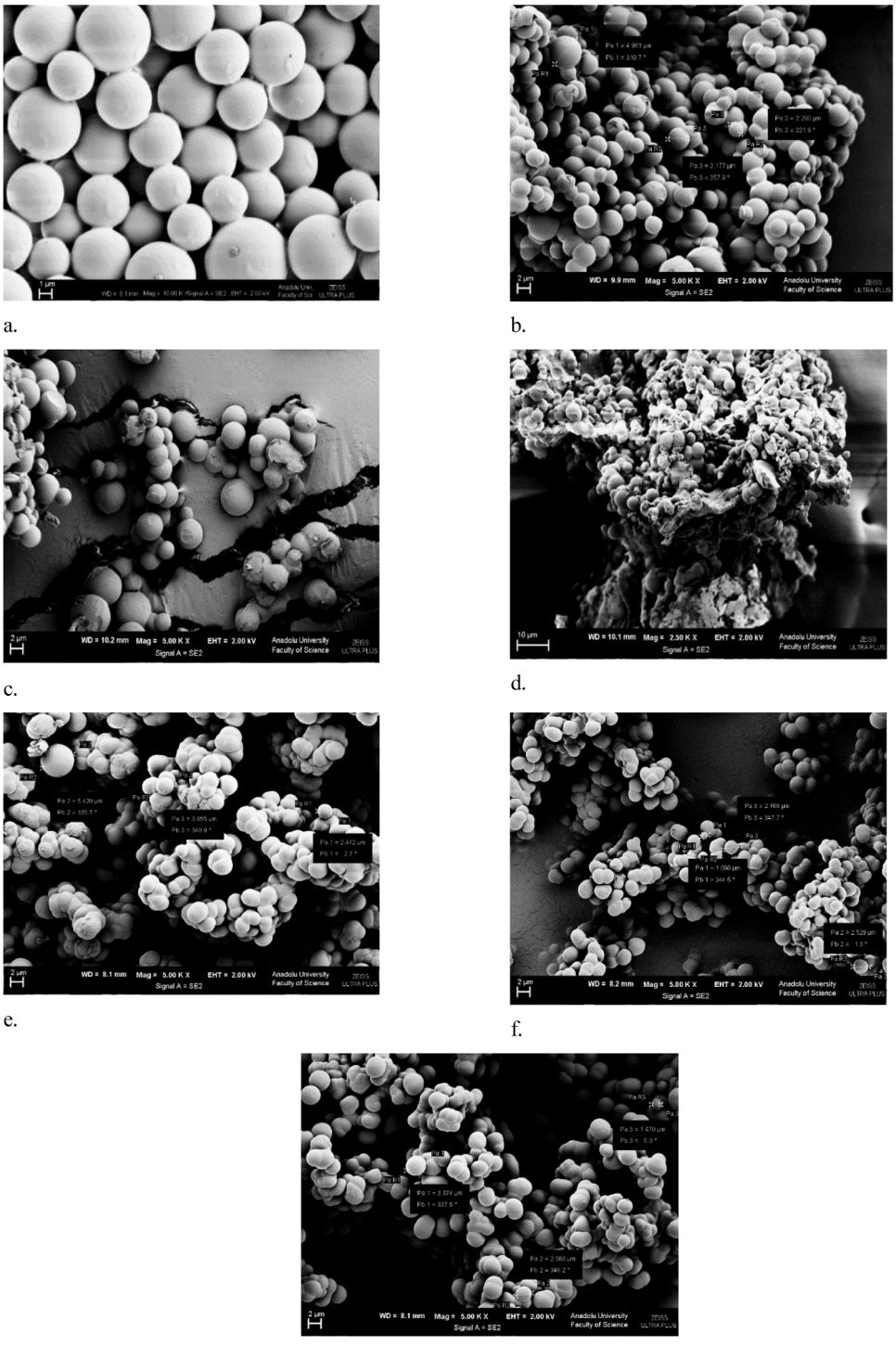


Fig. 2. SEM images of the cyclomatrix type o-DNSD-trimer microspheres: a. 1:1, b.1:2, c. 1:3, d. 1:4 e. 2:1, f. 3:1, g. 4:1.

The crystalline or amorphous nature of the microspheres is ascertained using XRD diffraction analysis. The 1:1 and 1:2 o-DNSD-tetramer XRD Spectrum is shown in Fig. 6. The product's amorphous structure is displayed by the broad peak that emerged in accordance with the XRD diffraction pattern. Additionally, there is no peak in the 2:1 o-DNSD-tetramer microspheres pattern that belongs to the $(C_2H_5)_3N.HCl$ salt that was produced during the polycondensation reaction, which corresponds to the product's purification with work-up procedure.

FT-IR spectra of 1:1, 1:2 1:3 and 1:4 o-DNSD- tetramer are given in Fig. 7.

TGA was used to determine the thermal stability of o-DNSD-tetramer microspheres generated by precipitation polymerization (Fig. 8). It is obvious that the release of adsorbed water and solvent at about 120 °C is the root of the mass loss. There were actually two stages to the mass loss of o-DNSD: 81.787 % between 269.548 and 307.985 °C and 70.509 % between 599.846 and 602.982 °C.

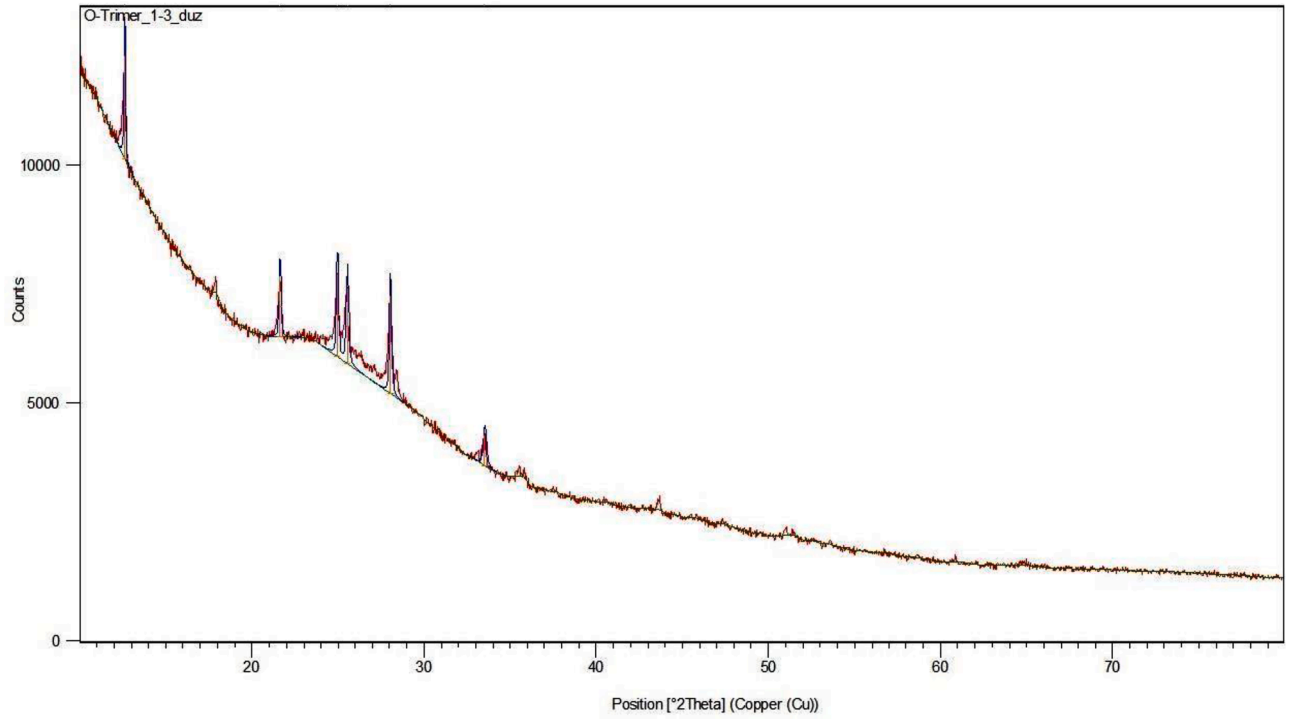


Fig. 3. 1:1 XRD spectrum of o-DNSD-trimer.

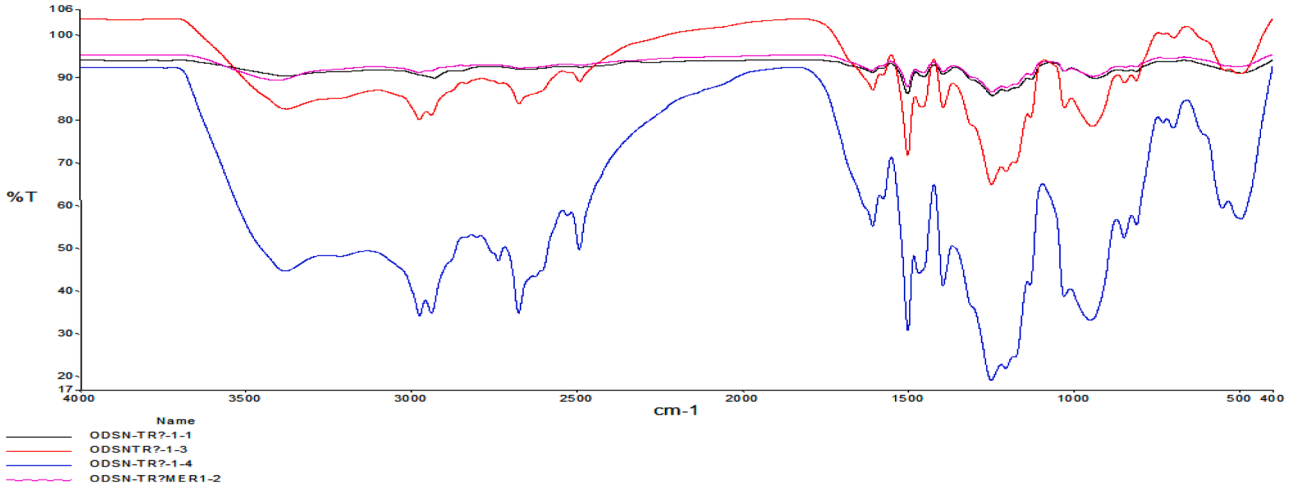


Fig. 4. FT-IR spectra of trimer, o-DNSD and 1:1 o-DNSD-trimer.

4. Conclusion

Cyclomatrix polyphosphazenes have special qualities that allow them to be used in a range different ways:

Thermal Stability: Some C-PPZs exhibit stability up to 900 °C, exhibiting strong thermal stability. C-PPZs produced at 200 °C, for instance, revealed only roughly 10 % mass loss, demonstrating their high-temperature performance. Flame Retardancy: These polymers are well-known for their ability endure flames, which enables them for uses where fire resistance is essential. Biocompatibility: Poly(organo)phosphazenes have demonstrated advantageous biological properties, indicating that they may find use in biomedical applications.

Cyclomatrix polyphosphazenes are used in a variety of fields as Biomedical Applications: C-PPZs are being investigated increasingly for drug delivery systems, scaffolds in tissue engineering, and other biomedical devices owing to their biocompatibility. Coatings and Flame Retardant Materials: These materials can be used in coatings that improve fire safety in a variety of materials since they have flame-retardant qualities. Optical Applications: Recent research has brought attention to C-PPZs' optical characteristics, such as their refractive index, implying that they may find application in optical platforms [25–29].

For the o-DNSD-trimer and o-DNSD-tetramer tests, it was noted from the SEM images that the sphere surfaces were distorted in accordance with the increasing crosslinker concentration. Based on an assessment of the SEM images, it can be assumed that, for the most part, experiments are successful in generating microspheres. XRD analyzes of crosslinked polyphosphazene microspheres were performed. These analyses exhibit the crystalline or amorphous characteristics of the products. As a result, polymerization was seen, and the graph developed an amorphous structure with a large peak and a $2\theta(^{o})$ value between 20 and 30. The peaks observed for some product types are an indication that small

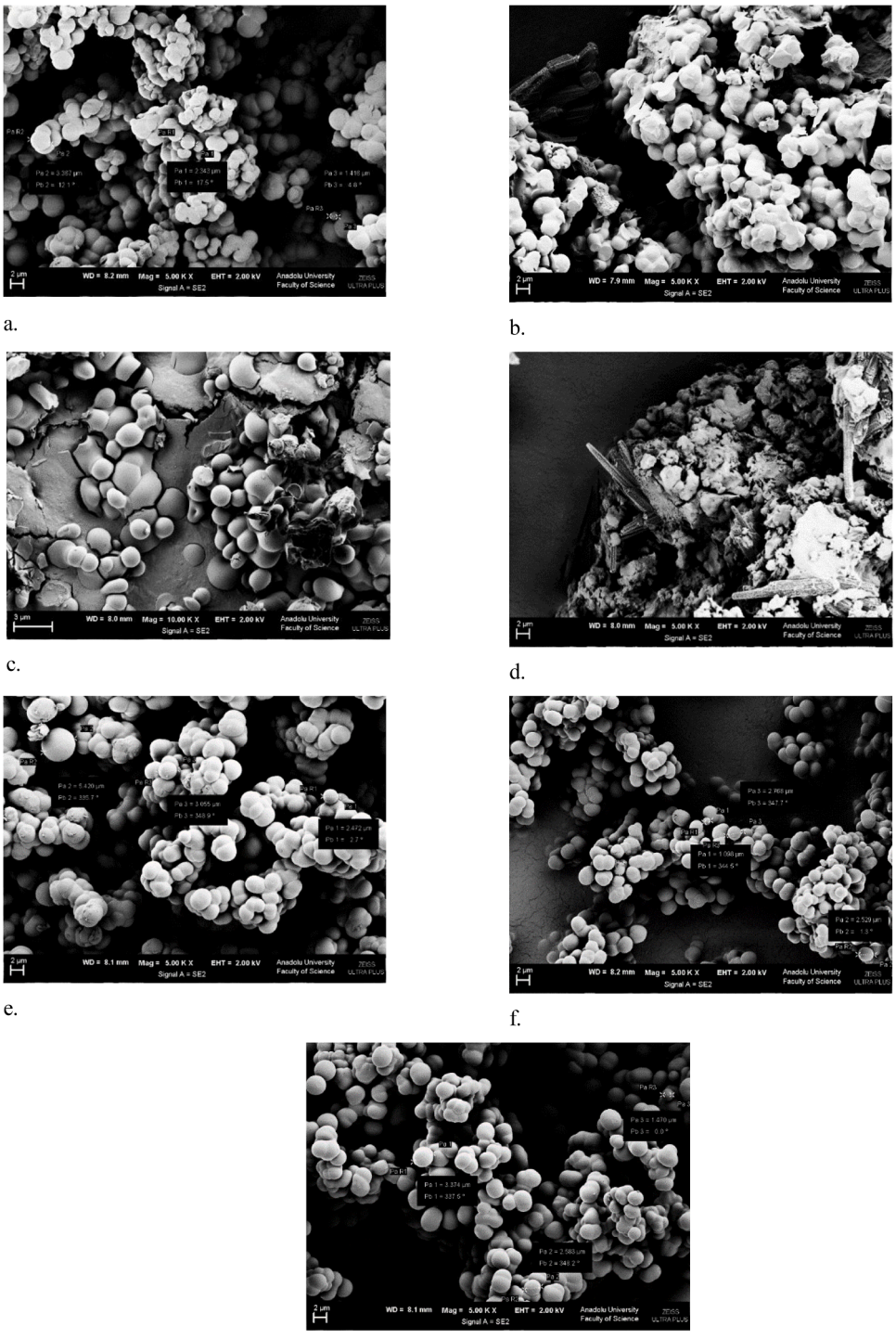


Fig. 5. SEM images of the cyclomatrix type o-DNSD-tetramer microspheres: a. 1:1, b.1:2, c. 1:3, d. 1:4 e. 2:1, f. 3:1, g. 4:1.

amounts of different non-polymeric products formed as a result of the reaction and/or effective work-up procedure is not performed during the purification of the products.

FT-IR spectra show the binding states of the monomer and the crosslinker. The spectra showed characteristic (P=N, N-H) peaks for polyphosphazene compounds. Besides, the P-Cl bond peak values in the trimer and tetramer either reduced their intensity or vanished entirely. The presence of the binding can be confirmed by looking for specific bands in the microsphere's spectra which match those of monomers. Thus, in FT-IR spectra, the following stretching is attributed to microspheres with o-DNSD: the band at 3350–3410 cm^{-1} is thought to be related to N- H stretching; the band at 2932–2987 cm^{-1} to C-H aliphatic stretching; the band at 1610–1616 cm^{-1} to C=N stretching; the band at 1503 cm^{-1} to C-O stretching; the band at 1450–1460 cm^{-1} to C-C aromatic stretching; the band at 1390 cm^{-1} to C=C aromatic stretching; the band at 1240–1245 cm^{-1} to P=N stretching; the band at 810–930 cm^{-1} to C-H aromatic stretching; and the band at 490–508 cm^{-1} to P-Cl stretching. As a result, the desired polyphosphazene microspheres were

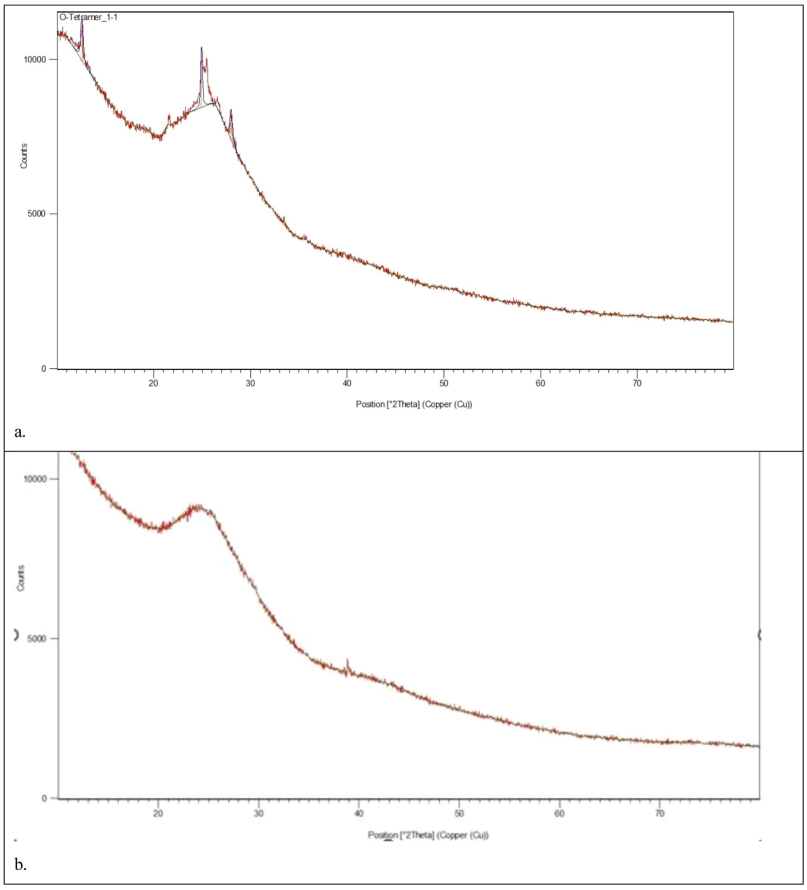


Fig. 6. XRD spectra of cyclomatrix type o-DNSD-tetramer microspheres: a) 1:1, b) 2:1.

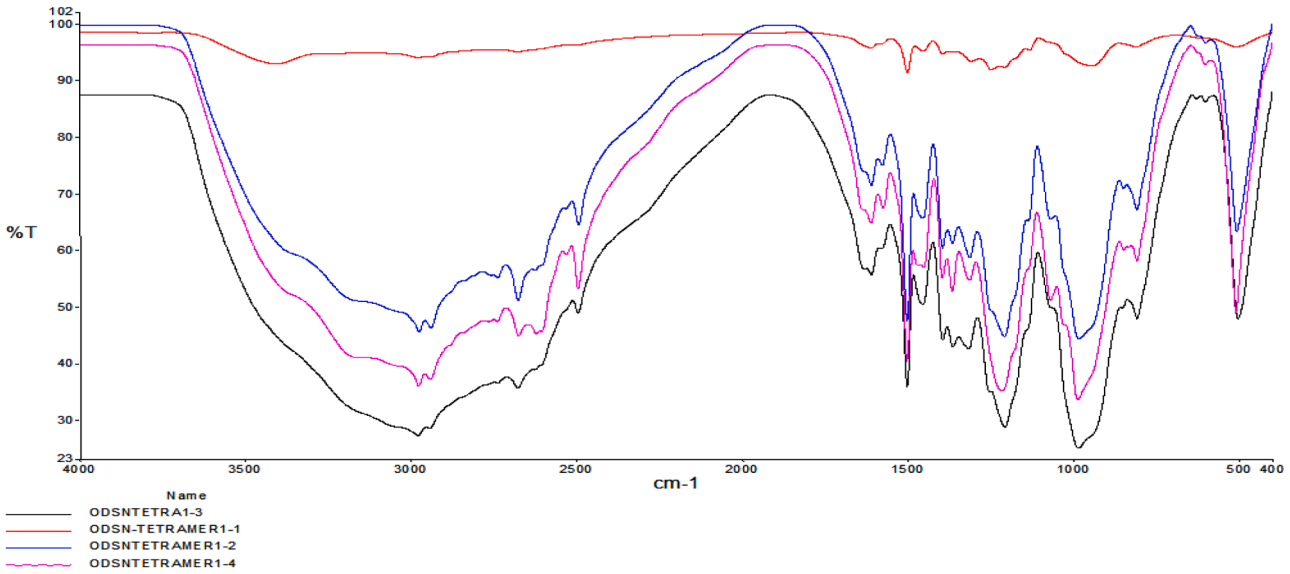


Fig. 7. FT-IR spectra of 1:1, 1:2, 1:3 and 1:4 o-DNSD- tetramer.

synthesized and spectrally characterized.

Synthesized microspheres are anticipated to be valuable materials for a variety of applications, including drug release, heavy metal or dye adsorption, and others, provided their desirable surface shape and other spectrum aspects.

CRediT authorship contribution statement

Yasemin Süzen Demircioğlu: Writing – review & editing. **Zafer Karaçiray:** Investigation.

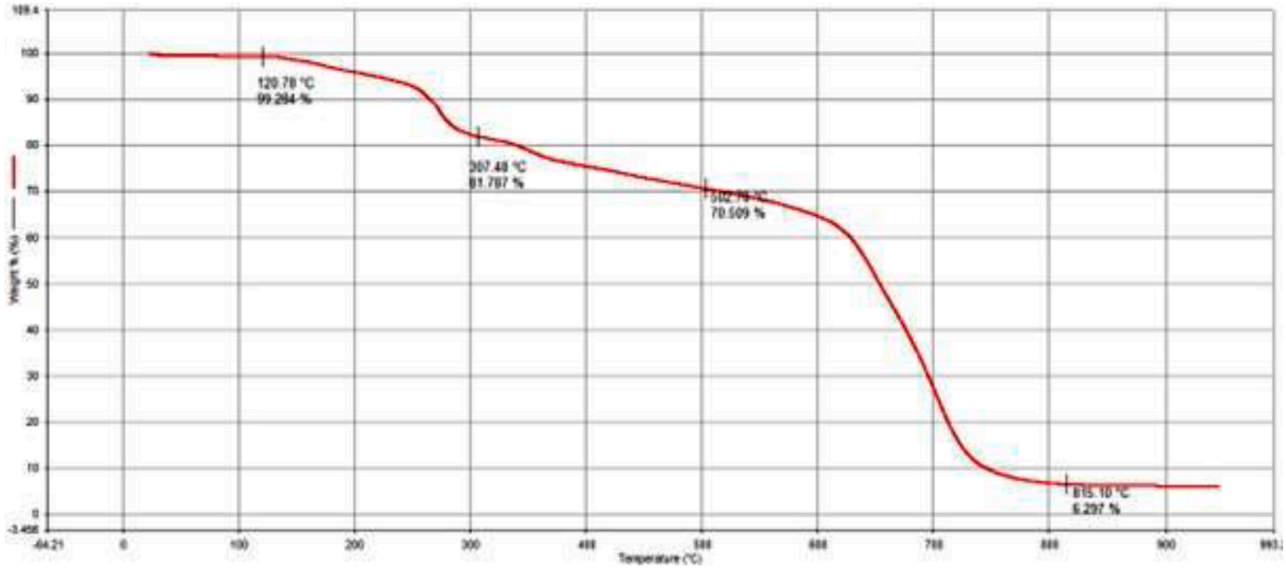


Fig. 8. TGA Curve of 1:2 o-DNSD-tetramer.

Declaration of competing interest

The authors declare the following financial or non-financial interests which may be considered as potential conflicts of interest:

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Data availability

No data was used for the research described in the article.

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