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Synthesis and Characterization of Novel Inorganic and Organic Hybrid Poly[cyclotriphosphazene-co-(4,4'-diaminophenylmethane)] Microspheres via One-Pot Self-Assembly Polycondensation Approach

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Abstract: Cross-linked cyclomatrix polyphosphazene microspheres have been successfully synthesized via self-assembly polycondensation reaction between hexachlorocyclotriphosphazene (HCCP) and 4,4'-diaminodiphenylmethane (DADPM) in acetonitrile. The absence of any stabilizing agent or surfactant and usage of only an ultrasonic bath have been the advantages for this reaction. HCCP and DADPM ratios have been attempted to obtain the best morphology by SEM-EDX. The size of microspheres were ranging from 4.46 to 4.74 µm. The inorganic-organic hybrid microspheres were characterized by FTIR, TGA, UV, Fluorescence and XRD.

Keywords: Cyclomatrix microspheres, polyphosphazene, self-assembly, precipitation polymerization.

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INTRODUCTION

Recently, research for synthesizing micro or nano-sized particles have paid notable attention with the development of science and technology [1-2]. Among these particles, phosphazene-based polymers have attracted great interest due to their chemical stability, excellent thermal/flame-retardant properties [3-7] and also their applications in biomedical delivery systems [8] and tissue engineering [9]. Apart from the most known linear poly(dichloro)phosphazene containing polymers, cyclomatrix type polyphosphazenes comprise of highly crosslinked framework and can be synthesized by the reaction of hexachlorocyclotriphosphazene (HCCP), which is one of the important inorganic rings and a building block for development of new polymers because of high tunability of its backbone and structural diversity [10-12] with various difunctional alcohols, phenols and diamines [11,13-15].

Fully crosslinked nano/microspheres are generally synthesized via precipitation polymerization approach which has some advantages like avoiding the use of any surfactant or stabilizer [16]. Besides, particle size and morphologies of microspheres can controlled by changing some experimental conditions such ratio of HCCP or reagents, temperature, reaction time and ultrasonic power [17]. In this article, we have synthesized novel inorganic-organic hybrid polyphosphazene microspheres by the reaction of HCCP (hexachlorocyclotriphosphazene) and DADPM (4,4'-diaminodiphenylmethane) in acetonitrile using an ultasonic bath. Otherwise, the effect on formation of microspheres were investigated by storing in darkness and light. Then, characterizations of the microspheres were elucidated by FTIR, SEM-EDX, TGA, ZETA, UV, Fluorescence and XRD.

MATERIALS AND METHODS

HCCP (Aldrich) was recrystallized from dry hexane followed by double sublimation before use. The melting point of the purified HCCP was 113-114°C. 4,4'-diaminodiphenylmethane (DADPM), triethylamine (TEA), acetonitrile and tetrahydrofuran (THF) were purchased from Sigma-Aldrich Company and were used as received. Also, distilled water was used in all experiments.

Characterization of DADPM-MS Microspheres

Scanning electron microscopy (SEM-EDX) measurements were performed on an ZEISS Ultra Plus (ZEISS ULTRA 55, APOLLO XP3) electron microscope. The samples were coated with gold before SEM analyses. Fourier Transform Infrared spectroscopy (FT-IR, Perkin Elmer Spectrum 100 spectrometer) and Thermogravimetric analysis (SETARAM LABSYS, N_2 atmosphere and a heating rate of 20 °C/min) were used to explain the structure and thermal features of the microspheres. Ultraviolet-visible (UV-Vis) absorbance spectra were measured on a Shimadzu UV-3150 spectrometer. The fluorescent spectra measurements were performed on a Varian Cary Eclipse Fluorescence spectrophotometer. Particle size measurements were performed with a Malvern ZEN 3600 instrument. X-ray diffraction (XRD) patterns were recorded by using a Bruker AXS, S8 TIGER Advance instrument equipped with Cu Kα radiation performed at 40 kV and 40 mA.

Synthesis of the DADPM-MS Microspheres

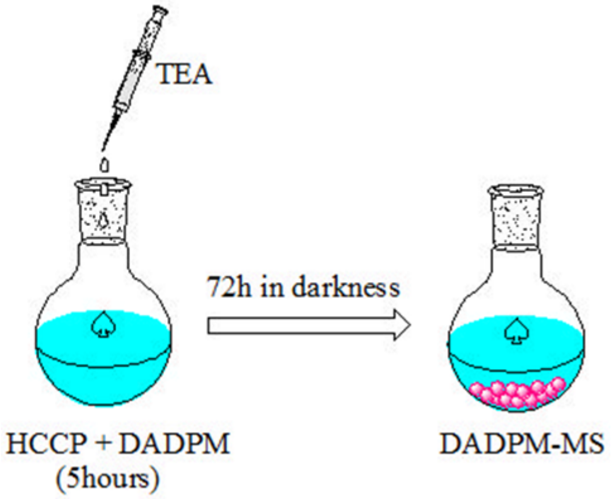
The microspheres were synthesized using precipitation polymerization technique (Tables 1 and 2) [16,18-20]. HCCP and TEA were used as a crosslinker and an acid acceptor, respectively. In a typical synthetic procedure, 3.5 mL of TEA was added to a solution of HCCP and DADPM in acetonitrile (50 mL), in a flask (100 mL). The reaction mixture was stirred at 40°C in an ultrasonic bath (100 W, 53 kHz) for 5 hours. Then, it was stored in darkness for 72 h (Scheme 1). The precipitated polyphosphazene microspheres were isolated by centrifugation (5000 rpm, 30 min), then washed first with THF and afterwards with distilled water three times. Finally, the product was dried under vacuum at 40 °C. The same procedure was used for other molar ratios of HCCP and DADPM.

Table 1. Compositions of microspheres at constant HCCP concentration.

Molar ratio (HCCP:DADPM)	HCCP (g)	DADPM (g)	TEA (mL)
1:1	0.175	0.1	3.5
1:2	0.175	0.2	3.5
1:3	0.175	0.3	3.5
1:4	0.175	0.4	3.5

Table 2. Compositions of microspheres at constant DADPM concentration.

Molar ratio (HCCP:DADPM)	HCCP (g)	DADPM (g)	TEA (mL)
1:1	0.175	0.1	3.5
1:2	0.35	0.1	7.0
1:3	0.52	0.1	10.5
1:4	0.70	0.1	14.0



Scheme 1. Preparation of DADPM-MS polyphosphazene microspheres.

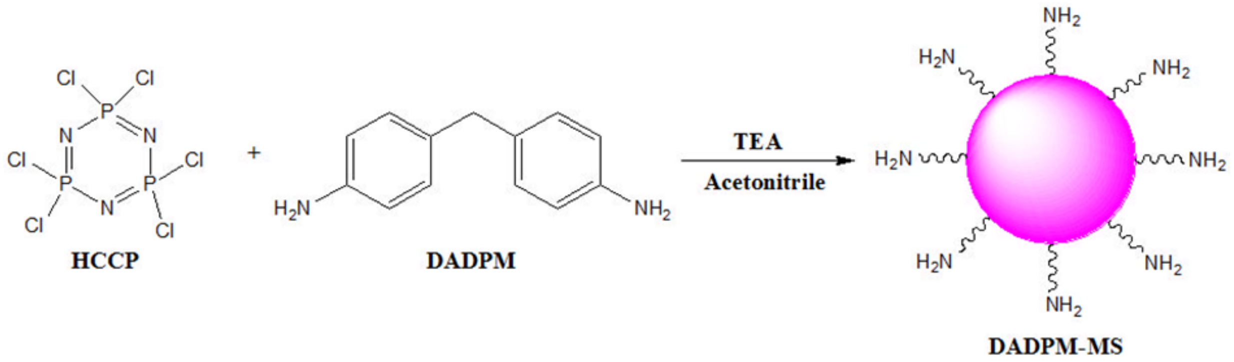
RESULTS

The formation of DADPM-MS microspheres was achieved via self-assembly polycondensation reaction of HCCP and DADPM. The optimization of DADPM-MS was made by changing concentrations of HCCP and DADPM in order to obtain the best morphology. Besides, some experiments were performed to determine light and darkness effects on formation of microspheres. Finally, characterization of microspheres was investigated by FTIR, SEM-EDX, TGA, ZETA, UV, Fluorescence and XRD.

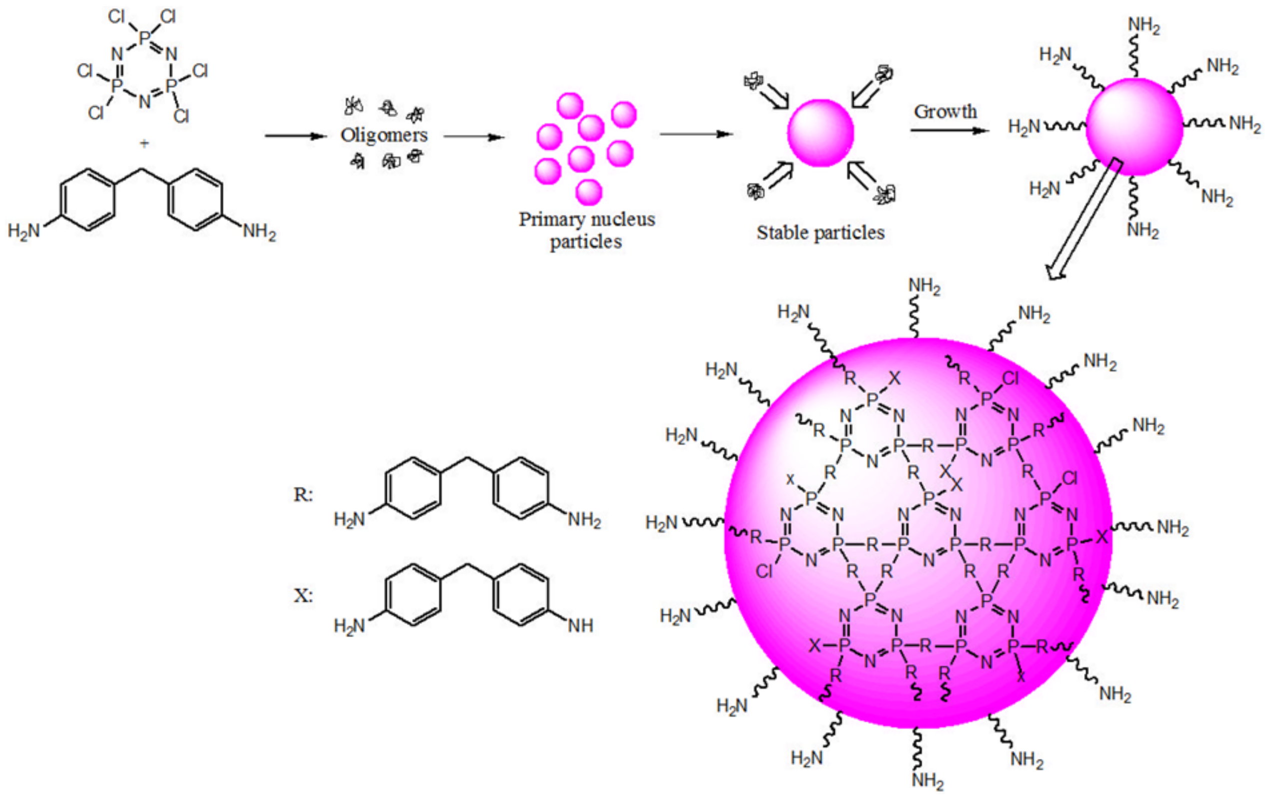
Preparation of the DADPM-MS microspheres

Synthetic route and formation mechanism of the DADPM-MS polyphosphazene microspheres are shown in Schemes 2 and 3. HCCP and DADPM were reacted with excessive amount of TEA as an acid acceptor, using acetonitrile as solvent, under ultrasonic conditions via precipitation polymerization without using any stabilizing agent or surfactant [11,17,21]. During the polycondensation, hydrochloric acid (HCl) formed from the nucleophilic substitution reaction between P-Cl bonds and terminal amino groups and was absorbed by TEA to afford TEA.HCl. The generation of TEA.HCl spontaneously accelerated the nucleophilic replacement. HCCP shows function as a cross linker molecule to obtain fully cross-linked polyphosphazene microspheres [24].

In previous studies, formation mechanism of cross-linked polyphosphazene microspheres had been explained as follows [18,22]. At the first stage of the precipitation polymerization, oligomers are formed by reaction between monomer and crosslinker. Then, oligomers aggregate together to form primary nucleus particles. Afterwards, primary stable microspheres are generated through the aggregation of the primary nucleus particles with each other by hydrogen bonds. As soon as the stable particles are generated, the particles grow in size by absorbing oligomeric species instead of primary particles. Hence, microspheres which were acquired at the end of the polymerization, do not have pores inside (see Scheme 3).



Scheme 2. Synthesis of DADPM-MS polyphosphazene microspheres.



Scheme 3. Schematic illustration of the formation mechanism of the DADPM-MS microspheres.

On the purpose of obtaining the best morphology of microspheres, experiments were performed using different concentrations of HCCP and DADPM. It was observed that in the trials, when DADPM concentration was increased, morphologically better microspheres were obtained (Figure 1). Because DADPM has two functional groups whereas HCCP has six functional groups. So, when DADPM concentration was increased, crosslinking between DADPM and HCCP was better. Besides, it was thought that sizes of obtained primary nucleus particles were approximate. So, the growth of primary nucleus particles are same rate and obtained microspheres were smooth. The Dn value ranged from 4.510 to 4.737 µm and the particle size of the microspheres did not change remarkably with increasing molar ratios of DADPM. The particle-size distribution of as-synthesized microspheres have narrow size distribution as shown in Figure 2. However, it was determined that when HCCP concentration was increased, the crosslinker in polymerization reaction, the formation of microspheres was not smooth and sphericity was broken down (Figure 3). DADPM ratio was the determining factor to form oligomers. When DADPM were run out of in polycondensation reaction, oligomers and primary nucleus particles will not be obtained. Because of oligomers were not form sufficiently, particles could not grow and were not smooth. Besides, multiplet particles were observed increased with molar ratios crosslinker HCCP. Because primary particles can come into collision with each other [16]. SEM images revealed that the best molar ratio was 1:4/HCCP:DADPM (Figures 1 and 3). Thus, all characterization studies were performed using microspheres with obtained from 1:4 molar ratio of HCCP:DADPM.

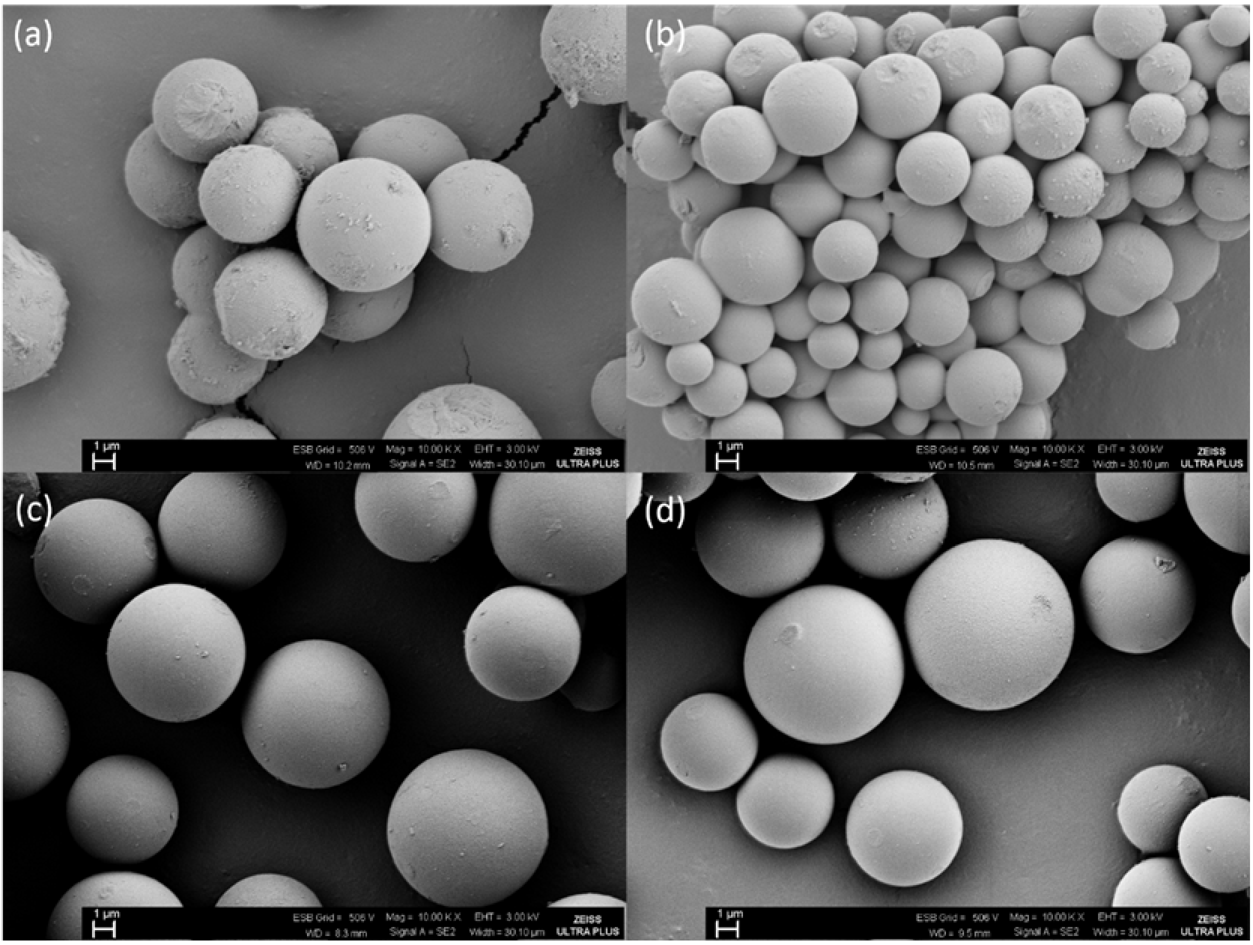
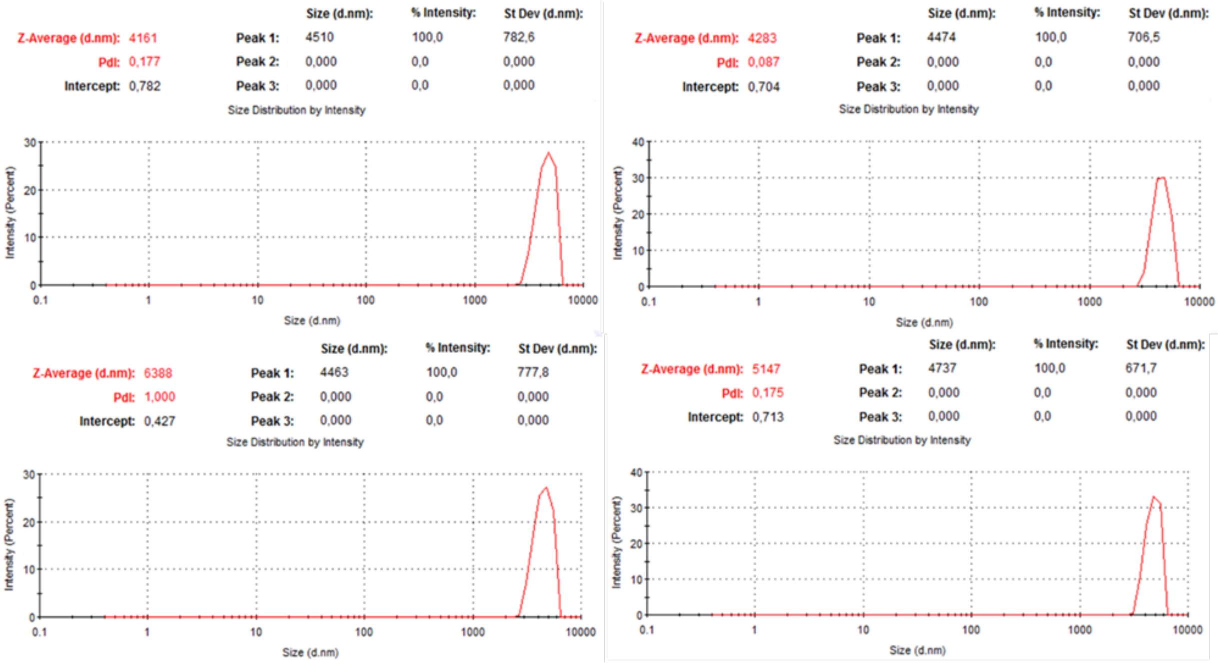


Figure 1. SEM images of (a) 1:1, (b) 1:2, (c) 1:3 and (d) 1:4 (molar ratios) HCCP:DADPM microspheres.



Z-Average (d.nm): 4161
PdI: 0,177
Intercept: 0,782

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Peak 1:	4510	100,0	782,6
Peak 2:	0,000	0,0	0,000
Peak 3:	0,000	0,0	0,000

Z-Average (d.nm): 4283
PdI: 0,087
Intercept: 0,704

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Peak 1:	4474	100,0	706,5
Peak 2:	0,000	0,0	0,000
Peak 3:	0,000	0,0	0,000

Z-Average (d.nm): 6388
PdI: 1,000
Intercept: 0,427

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Peak 1:	4463	100,0	777,8
Peak 2:	0,000	0,0	0,000
Peak 3:	0,000	0,0	0,000

Z-Average (d.nm): 5147
PdI: 0,175
Intercept: 0,713

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Peak 1:	4737	100,0	671,7
Peak 2:	0,000	0,0	0,000
Peak 3:	0,000	0,0	0,000

Figure 2. Particle size distributions of microspheres by precipitation polymerization. (a) 1:1, (b)1:2, (c)1:3, (d)1:4 HCCP:DADPM molar ratios.

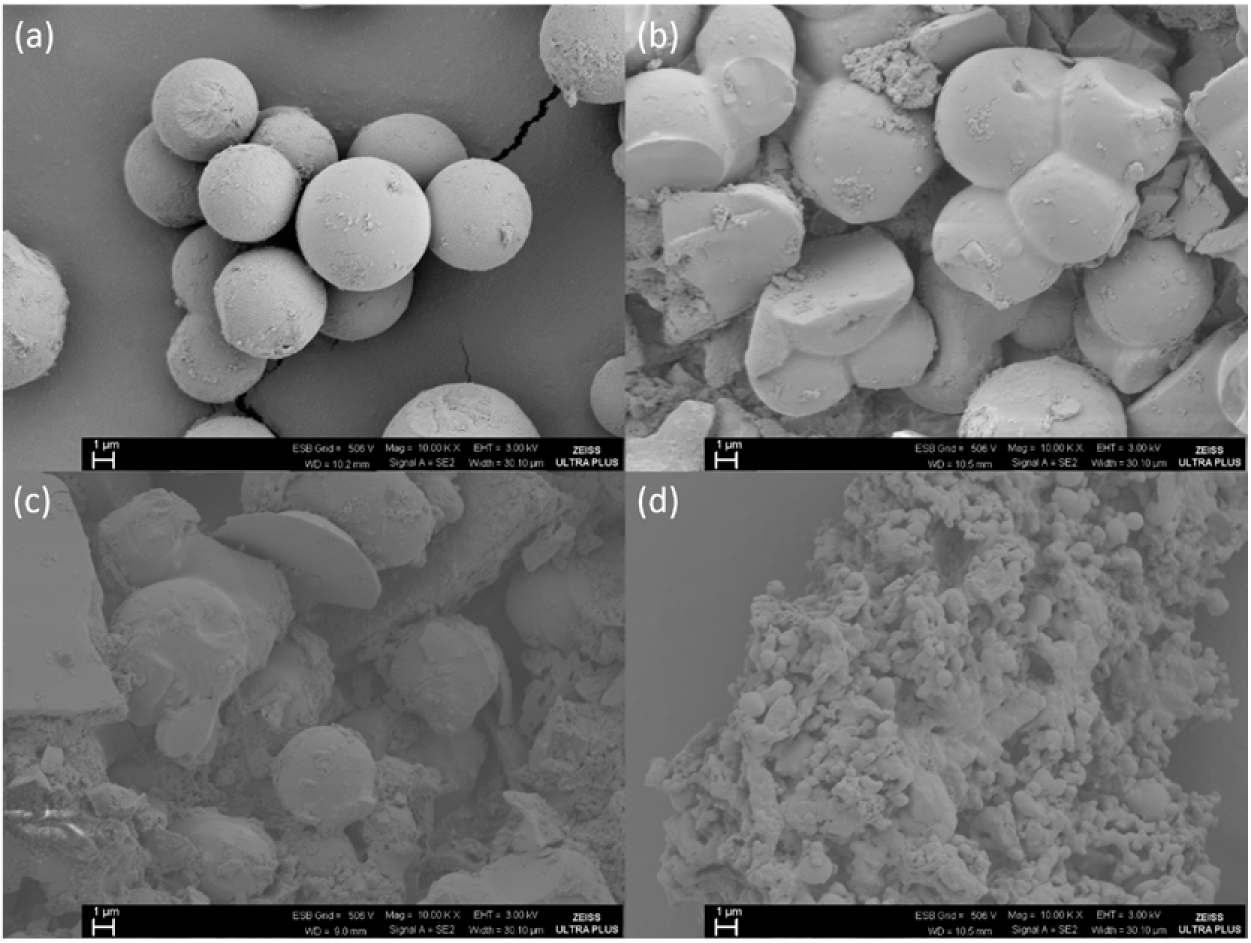


Figure 3. SEM images of (a) 1:1, (b) 2:1, (c) 3:1 and (d) 4:1 (mol. ratios) HCCP:DADPM microspheres.

Besides, it was thought that during the 5-hour reaction, only the oligomers obtained by polycondensation reaction of HCCP and 4,4′-DADPM and primary nucleus particles did not precipitate by aggregation of oligomers in 5 hours. Therefore, the reaction medium was stored in darkness and precipitation began to form in the flask. After storing for 18 hours in the dark, the precipitated product was analyzed by SEM and it was observed that formation of the microspheres were started but was not totally completed yet. On the other hand, after 72 hours in the dark, when the precipitated product was analyzed by SEM, it was seen that the formation of microspheres were completed and were morphologically good spheres (Figure 4). Also, when compared the EDX results of microspheres which were stored in the darkness for both 18 and 72 hours, it was determined that in EDX spectrum of microspheres which were stored 72 hours in the darkness, P (13.46%) and N (13.69%) ratios were similar and chloride ratio (3.99%) was lower (Figure 5a). However, the EDX spectrum of microspheres, which were stored 18 hours in the darkness, indicated the following values: P (08.56%), N (14.39%) and Cl (04.29%) (Figure 5b). When the reaction medium was stored in light for 72 hours, instead of darkness, it was seen that sphericity did not totally complete and formed a different morphology except sphericity (Figure 6a). Moreover, the yield of microspheres which were obtained in light was lower (59%) than that in the darkness (76%).

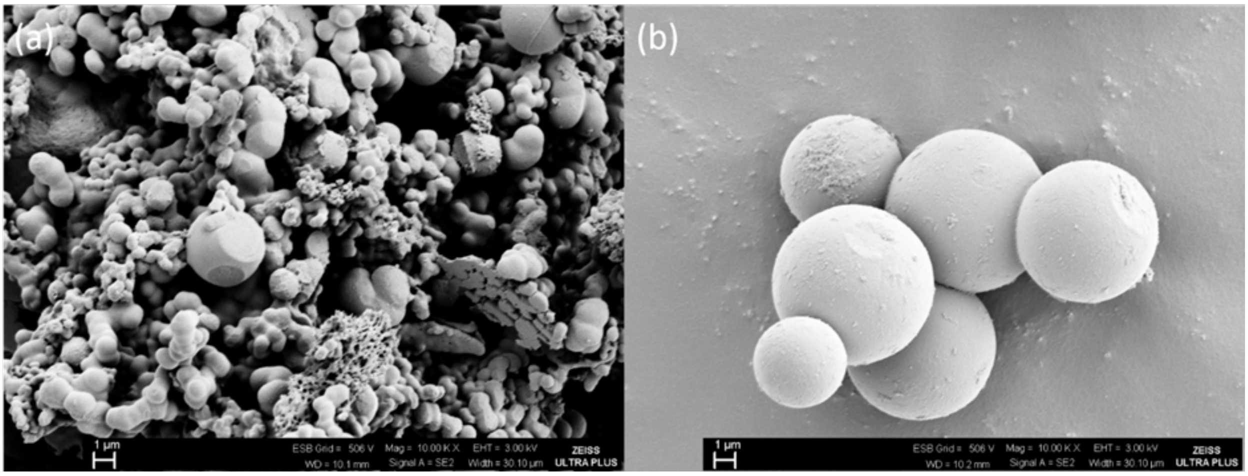
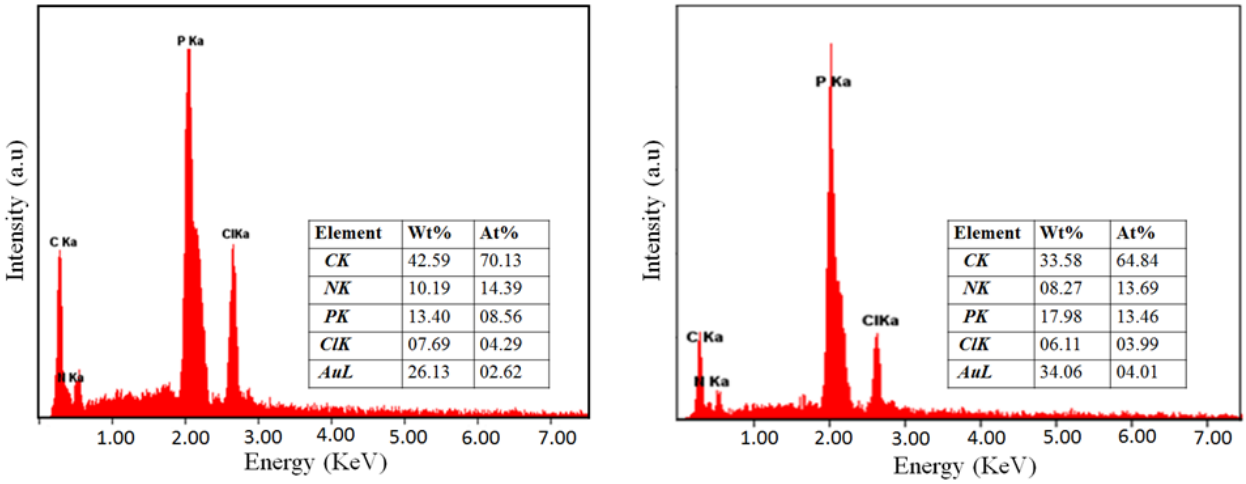


Figure 4. SEM images of DADPM-MS (1:1) which were stored in darkness (a) 18 hours (b) 72 hours.



Element	Wt%	At%
CK	42.59	70.13
NK	10.19	14.39
PK	13.40	08.56
ClK	07.69	04.29
AuL	26.13	02.62

Element	Wt%	At%
CK	33.58	64.84
NK	08.27	13.69
PK	17.98	13.46
ClK	06.11	03.99
AuL	34.06	04.01

Figure 5. EDX spectra of DADPM-MS (1:1) which were stored in darkness for (a) 18 hours (b) 72 hours.

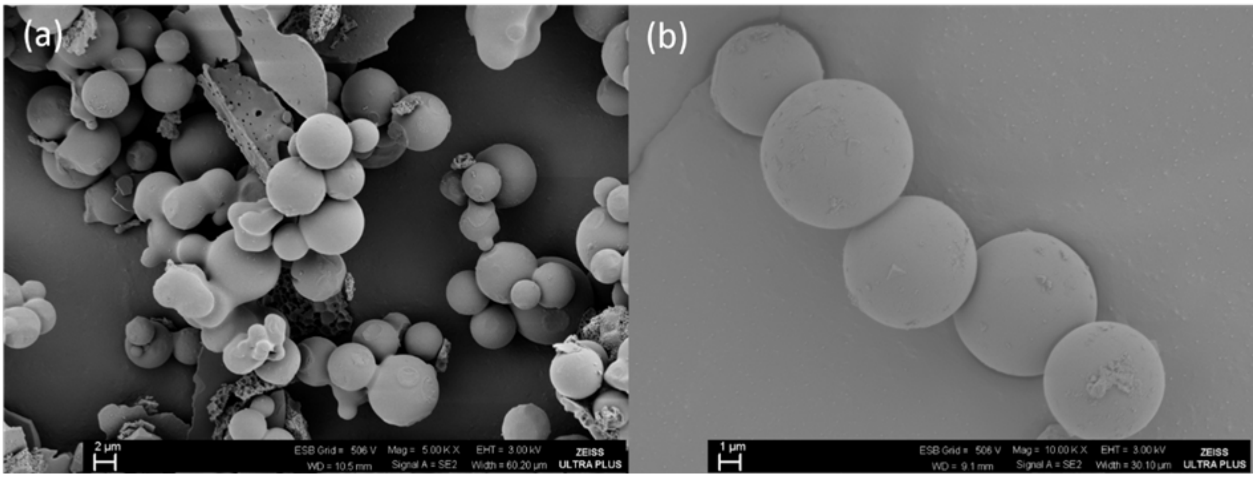


Figure 6. SEM images of DADPM-MS (1:1) which were stored in light (a) and darkness (b) 72 hours.

FTIR spectral analysis

The chemical structure of the microspheres (1:4 HCCP:DADPM) was characterized by FT-IR. As shown in Figure 7, N-H stretching and bending bands indicating the existence of primary amine groups on the microspheres were observed at 3336–3182 (1, 2) and 1613 cm^{-1} (6), respectively. The absorption at 3027 cm^{-1} (3) was assigned to the aromatic C–H stretching vibration of aromatic rings. Aliphatic C-H stretching vibrations can be seen at 2905 and 2841 cm^{-1} (4, 5). Aromatic C-C stretching bands correspond to 1509, 1452 and 1378 cm^{-1} (7, 8, 9). C-N stretching band was observed at 1288 cm^{-1} (10). Furthermore, the characteristic P=N and P-N absorption bands of HCCP were observed at 1253, 1166 and 934 cm^{-1} (11, 12, 13), respectively. The weak P-Cl bands at 568 and 504 cm^{-1} (14, 15) showed that microspheres still contain chloride atoms in small quantities [16, 19]. Obviously, the FTIR spectrum of DADPM-MS contain characteristic bands which are expected from the polymeric structure synthesized from HCCP and DADPM molecules. Thus, the polycondensation reaction between HCCP and DADPM has been successfully achieved.

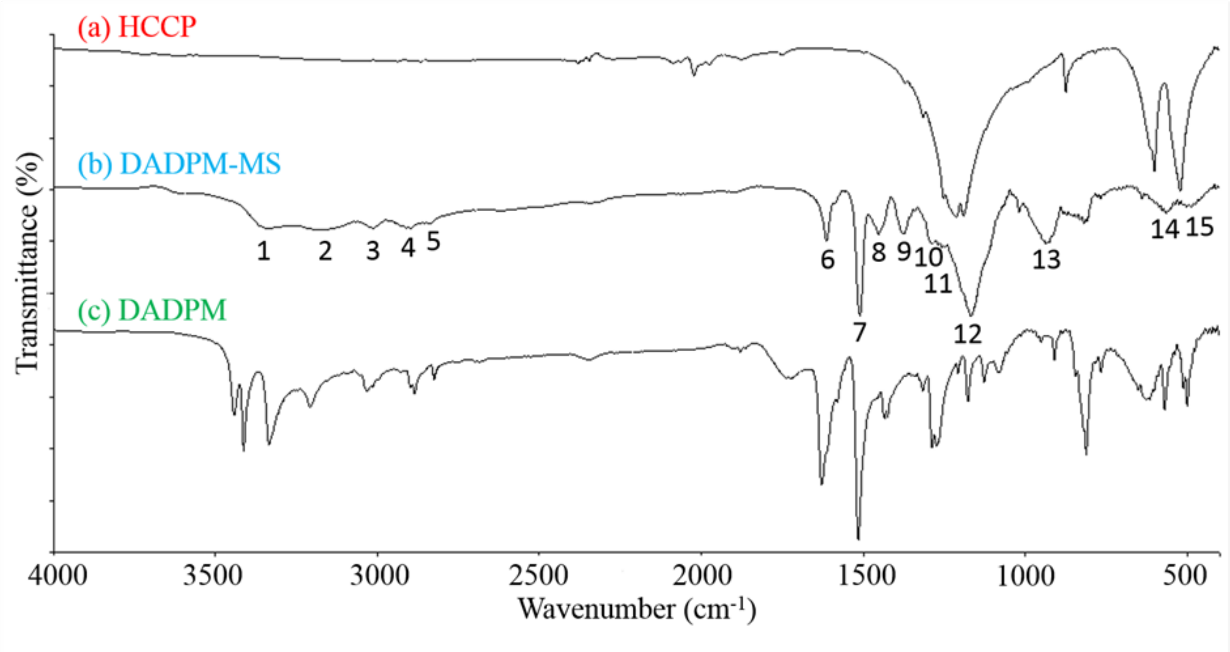


Figure 7. FT-IR spectra of HCCP, DADPM-MS, and DADPM.

Thermal properties

The thermal properties of the DADPM-MS obtained from the precipitation polymerization were also characterized with thermogravimetric analyses (Figure 8). A mass loss of 5% below 100 °C was observed due to the desorption of adsorbed water. Remarkably, under nitrogen atmosphere, it was indicated that the material was thermally stable up to a temperature of 415 °C and a sharp mass loss was observed from 415 to 784 °C that is likely to be associated with carbonization of the organic groups and the depolymerization of the P–N framework in the fully crosslinked structures [23,27].

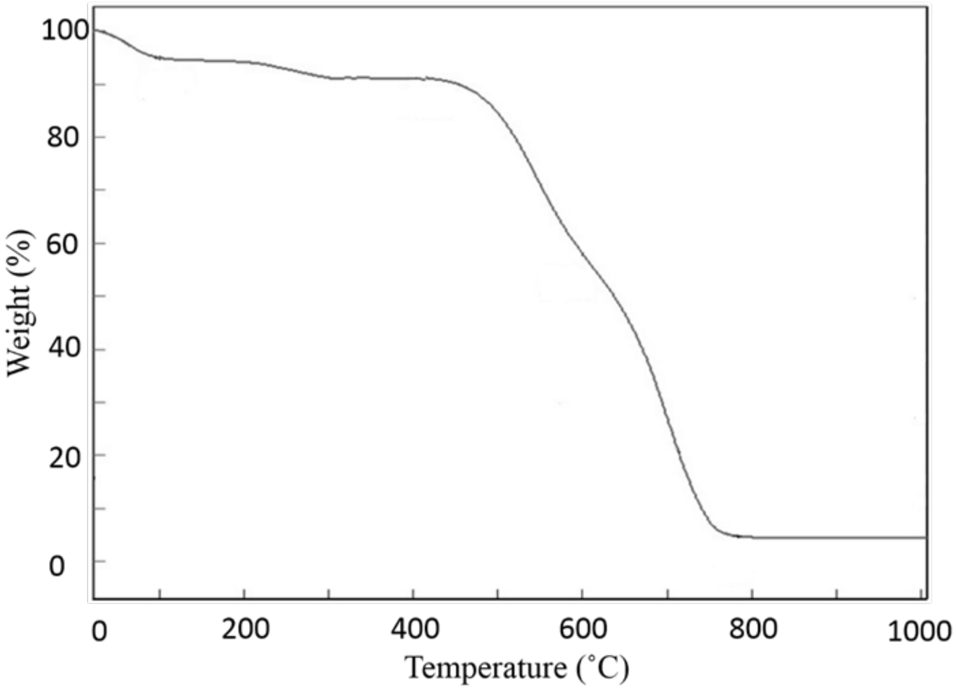


Figure 8. TGA curve of DADPM-MS (1:4).

Optical and crystallographic properties

Microspheres (DADPM-MS) were dispersed in methanol under ultrasonic conditions and the UV and fluorescence properties were investigated. DADPM and DADPM-MS displayed absorption peaks at 290 and 245 nm in methanol, respectively (Figure 9). It was understood that DADPM-MS does not absolutely have an absorption of light in the visible range. The fluorescence emission spectra of DADPM and DADPM-MS of which were dispersed in methanol are shown in Figure 10. DADPM revealed a fluorescent emission peak at 349 nm when excited with 280 nm light. Similarly, DADPM-MS displayed a fluorescence emission peak at 347 nm when excited with 240 nm light because of π-conjugation in the polymeric structure.

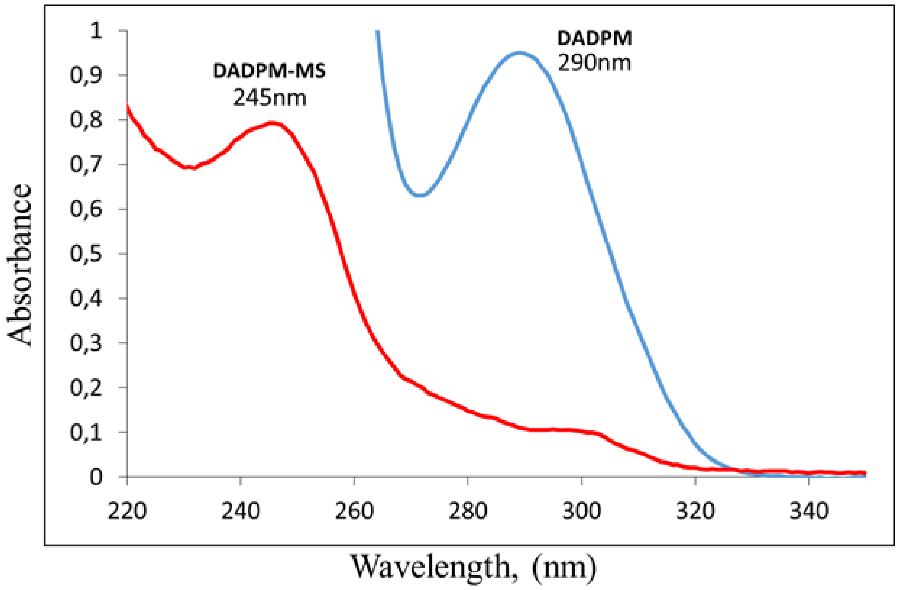


Figure 9. UV absorption spectra of DADPM-MS (a) and DADPM (b) in methanol.

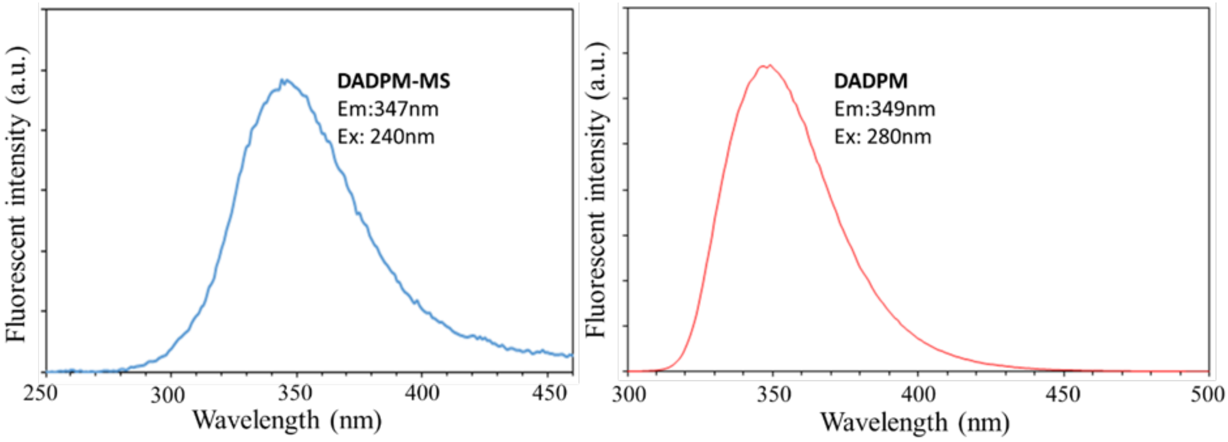


Figure 10. Fluorescent emission spectra of DADPM-MS (left) and DADPM (right) in methanol.

The XRD patterns of the powder DADPM-MS microspheres indicated a broad diffraction peak corresponding typical amorphous structure (see Figure 11) [17, 25, 26].

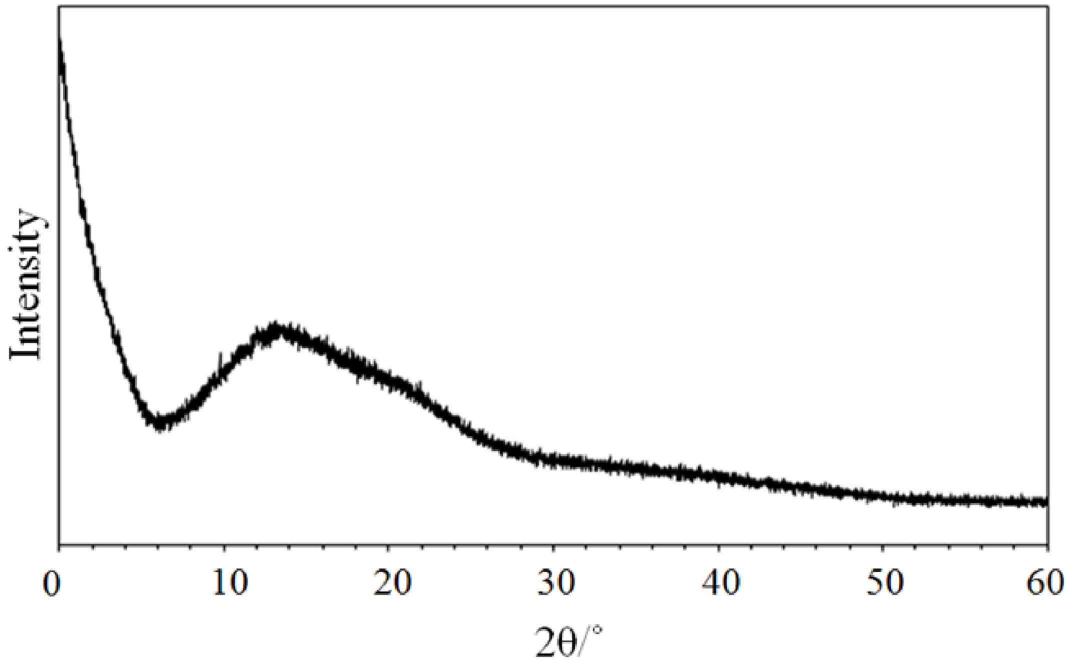


Figure 11. XRD spectrum of DADPM-MS.

CONCLUSION

In conclusion, inorganic-organic hybrid cross-linked polyphosphazene microspheres, DADPM-MS, were synthesized by polycondensation reaction between HCCP and DADPM. Variable HCCP and DADPM mol ratios were studied and morphologically the best ratio was determined as (1:4) HCCP:DADPM. The size range of obtained microspheres were 4.510 to 4.737 µm. The storage time in darkness was determined 72 hours to complete the formation of microspheres by SEM-EDX. It was seen that storing in darkness is more effective than light to obtain morphologically good spheres by SEM. FTIR spectra demonstrated that the formation of the microspheres were achieved succesfully when compared with the FTIR spectra of HCCP and DADPM molecules. On the other hand, the TGA measurement showed that the obtained microspheres have perfect thermal stability and the thermal degradation temperature was determined as 415 ºC. DADPM-MS indicated UV and fluorescent property because of π-conjugation of aromatic rings in the polymeric structure. Also, it was understood, from the XRD spectrum, that microspheres have characteristic amorphous structure.

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YENİ ANORGANİK VE ORGANİK HİBRİD POLİ[SİKLOTRİFOSFAZEN-co-(4,4'-DİAMİNODİFENİLMETAN)] MİKROKÜRELERİNİN TEK ORTAM İÇERİSİNDE KENDİLİĞİNDEN DÜZENLENMELİ POLİKONDENZASYON YAKLAŞIMI İLE SENTEZİ VE KARAKTERİZASYONU

Öz: Çapraz bağlı siklomatriks polifosfazen mikroküreler, hekzaklorosiklotrifosfazen (HCCP) ile 4,4'-diaminodifenilmetanın (DADPM) asetonitril ortamında kendiliğinden düzenlenmeli polikondenzasyon tepkimesi sonucu, başarı ile sentezlenmiştir. Herhangi bir stabilize edici ajan veya surfaktant gerektirmemesi ve sadece ultrasonik banyo kullanımı bu reaksiyonun avantajlarıdır. SEM-EDX ile en iyi morfolojiyi elde etmek için, HCCP ve DADPM oranları değişimi denenmiştir. Mikrokürelerin boyutları 4,46 ile 4,74 μm arasında değişmektedir. Anorganik-organik hibrid mikroküreler FTIR, TGA, UV, Fluoresans ve XRD ile karakterize edilmiştir.

Anahtar kelimeler: Siklomatriks mikroküreler, polifosfazen, kendiliğinden düzenlenme, çöktürme polimerizasyonu.

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