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Research Article

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Synthesis of Epoxy Functional Porous POSS Microparticles

Epoksi Foksiyonel Gözenekli POSS Mikropartikülerin Sentezi

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ABSTRACT

Epoxy-functional porous polyhedral oligomeric silsesquioxane (POSS) microparticles were synthesized by templated polymerization in two steps by using monodisperse 2µm poly(GMA) seed latex particles as a template. In the first step, templated polymer latex was swollen in emulsion medium to obtain micron size porous POSS particles. In the second step, the hydrophobic monomers metharcyl-POSS, epoxy-functional monomer glycidyl methacrylate (GMA), the crosslinking agent glycerol dimethacrylate (GDMA), and the thermal initiator diffused into the swollen template in emulsion medium for free-radical polymerization. The resultant poly(POSS-co-GDMA-co-GMA) microparticles were obtained in polydisperse form due to the high molecular weight of the silica cage core of POSS created difficulty in the diffusion step. However; monodisperse composite microparticles were obtained around 5.8 ± 0.4µm in size via centrifugal post-separation. The spherical fine porous hybrid structure was fully characterized as morphological, thermal, chemical composition, and crystalline form by SEM, TGA, FTIR, and XRD respectively.

Key Words

Polyhedral oligomeric silsesquioxane (POSS), glycidyl methacrylate (GMA), porous structure, monodisperse.

ÖZ

Epoksi fonksiyonlu gözenekli polyhedral oligomerik silseskuioksan (POSS) mikropartikülleri, şablon olarak monodispers 2 um poli(GMA) lateks partikülleri kullanılarak iki aşamada şablon polimerizasyon ile sentezlendi. İlk aşamada, şablon polimer lateks, mikron boyutunda gözenekli POSS parçacıkları elde etmek için emülsiyon ortamında şişirildi. İkinci aşamada, hidrofobik monomerler; metakril-POSS monomeri, epoksi-fonksiyonel glisidil metakrilat (GMA) monomeri, çapraz bağlayacı gliserol dimetakrilat (GDMA) ve termal başlatıcı serbest radikal polimerizasyonu için emülsiyon ortamında şişmiş şablona difizlendi. Elde edilen poli (POSS-co-GDMA-co-GMA) mikropartiküller, POSS'un silika kafes çekirdeği yüksek molekül ağırlığı nedeniyle, difüzyon aşamasında güçlük yarattığı için polidispers formda elde edildi. Ancak eş boyutlu kompozit mikropartiküller, üretim aşamasından sonra santrifüj ayırma yoluyla yaklaşık 5.8 ± 0.4 um boyutunda elde edildi. Küresel mezo-gözenekli hibrit yapı sırasıyla SEM, TGA, FTIR ve XRD ile morfolojik, termal, kimyasal bileşim ve kristal yapı analizleri ile tamamen karakterize edildi.

Anahtar Kelimeler

Polyhedral oligomerik silseskuioksan (POSS), glisidil metakrilat (GMA), gözenekli yapı, eş boyutlu.

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INTRODUCTION

Organic-inorganic functional hybrid materials have always been attractive for material science due to their superior physical and chemical properties. Polyhedral oligomeric silsesquioxane (POSS) has gained attention with hybrid three-dimensional (3D) nanocage structure $(RSiO_{3/2})n$, where R is hydrogen or hydrocarbon-based (alkyl, aryl, alkylene, vinyl, amine, etc.) functional end groups [1]. POSS molecules are also known as the smallest hybrid structure of silica (1-3 nm in diameter), where the cage silica structure is located at the center and surrounded by organic functional groups in Figure 1. While the inorganic part of the molecule provides extreme thermal resistance and enhances mechanical properties, the organic part presents functional properties on the surface such as biocompatibility, wettability [2, 3].

Epoxy functionality has one of the top desired features on composite materials for many engineering applications especially coatings and adhesives because of their thermoset properties, mechanical resistance, corrosion resistance, and chemical resistance [1, 4-6]. Until now, the POSS hybrid structure was combined with epoxy functionality in many chemical routes to produce membranes, coating materials, fillers, or adhesives [1]. Epoxy networks were reinforced with POSS blending to obtain better thermal stability and surface properties [7-9]. In the study of Matejka et al, the epoxy-POSS hybrid network was prepared by utilizing mono epoxy-POSS or amine-POSS precursors incorporation with polymeric networks via chemically bound or physically admixed [10]. Methacryl-POSS monomer and glycidyl methacrylate (GMA) were prepared as film coating via free radical polymerization. Another type of epoxy-POSS hybrid copolymers was obtained by copolymerization of GMA and other methacrylate-based crosslinkers via atom transfer radical polymerization (ATRP) and used for gene delivery [7]. Ma et al. obtained the GMA-POSS monomer via ring-opening reaction which was used for emulsion polymerization with the copolymer of polymethylmethacrylate to produce a new composite under 100nm particles as film structure [11]. Most recently, multiple epoxy-functional POSS groups incorporated with gelatine were synthesized by a complete hydrolysis and condensation method as a porous matrix [12].

In our previous work, we managed to obtain the uniform shape POSS latex particles from 200nm to 20µm in size via one-step-emulsion polymerization [13]. However, there was no porosity on these particles for advanced applications. Scientific literature commonly reported on the use of the porous structure of epoxy-functional POSS materials for many critical engineering applications such as catalysis [14, 15], drug delivery [16], tissue engineering [17], dental resins [18], separation [19], nanofiltration [20], antifouling [21], carbon dioxide uptake [22] and hydrogen purification [23]. Therefore, we aimed to produce novel porous functional organic-inorganic hybrid particles.

In this study, the metharcyl-POSS monomer was copolymerized with GMA and glycerol dimethacrylate (GDMA) monomers to fabricate highly spherical and uniform morphology around 6µm in size. The porous structure of POSS-based particles was obtained via templated polymerization in two-step emulsion: (I) the chosen template as 2µm non-crosslinked poly(GMA) seed latex particles were swollen (II) the monomers and thermal initiator diffused into the swollen template and free-radical polymerization. The resultant porous particle poly(POSS-co-GDMA-co-GMA) was characterized by Fourier transform infrared (FTIR), scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDAX), thermogravimetric analysis (TGA), and x-ray diffraction XRD.

MATERIALS and METHODS

The hybrid monomer, methacryl-Polyhedral Oligomeric Silsesquioxane (M-POSS) cage mixture (MA-0735) was purchased from Hybrid Plastics Inc. The crosslinking agent glycerol dimethacrylate (GDMA), the template, and functional co-monomer glycidyl methacrylate were purchased from Sigma-Aldrich. An emulsifying agent sodium dodecyl sulfate (SDS) and stabilizers polyvinyl alcohol (PVA, 87–89% hydrolyzed, Mw = 85,000–146,000) and polyvinylpyrrolidone K30 (PVP-K30) were obtained from Sigma-Aldrich. The thermal initiator 2,2′-Azobisizobutyronitrile (AIBN) and benzoyl peroxide (BPO) were also bought from Sigma-Aldrich, which were recrystallized from methanol before use. Solvents ethylbenzene (EB), ethanol (EtOH), tetrahydrofuran (THF), acetone were obtained from Sigma-Aldrich. Deionized water (dH_2O) used in all experiments was obtained by using Millipore/Direct Q-3UV.

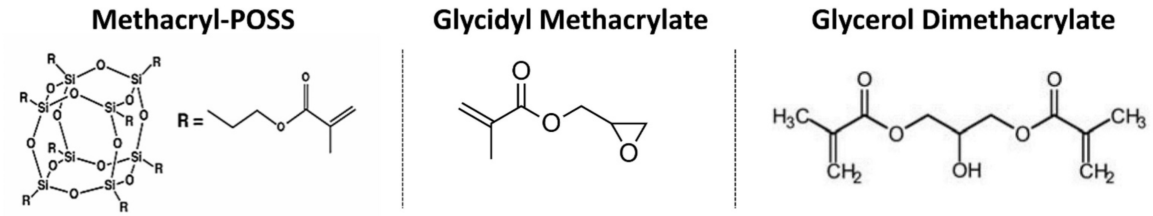


Figure 1. The chemical structures of monomers: the main monomer methacryl-polyhedral oligomeric silsesquioxane (POSS), co-monomer glycidyl methacrylate(GMA), crosslinking agent glycerol dimethacrylate (GDMA).

Synthesis of porous epoxy-functional POSS microparticles

The functional porous POSS microparticles were synthesized by templated polymerization in Figure 2. The template particles poly(GMA) were synthesized around 2µm in size by dispersion polymerization [24]. The dispersion medium was obtained by dissolving epoxy-functional monomer GMA (3ml), stabilizer PVP-K30 (0.45g), and initiator AIBN(0.24g) in absolute EtOH (30ml). The polymerization was carried out at 70°C in a shaking-bath for overnight. The poly(GMA) latex was collected by centrifuged and washed with EtOH and water several times.

The swelling step: The template latex 0.15g poly(GMA) were swollen by 2.5ml EB in 0.25% (w/w) SDS containing 25ml water. The emulsion medium was obtained by probe sonication (Qsonica, Q500 sonicator) for 6min and magnetically stirred for 24h at room temperature.

The diffusion step: The main monomer 0.5g M-POSS, epoxy-functional co-monomer 0.5g GMA and crosslinker monomer 1.0ml GDMA were mixed. The thermal initiator 0.03g BPO was added onto this monomer mixture and dissolved in the ultrasonic bath. The emulsion medium was prepared by probe-sonication of this organic mixture in 0.25% (w/w) SDS containing 25ml water. This emulsion was added into the swelling step emulsion and magnetically stirred for 24h at room temperature for the diffusion of the organic mixture into poly(GMA) seeds. After the diffusion process, 5ml of 8.0% (w/v) PVA solution were added into the final emulsion and put into a 200rpm shaking-water bath at 80°C overnight. At the end of the polymerization, the final product was collected by centrifuge and washed by EtOH, THF, EtOH, and water respectively.

Characterization

The size, morphology, and elements of the particles were characterized by scanning electron microscope-energy-dispersive X-ray spectroscopy SEM-EDAX (Quanta 450 Akishima, Tokyo, Japan). The samples were prepared by 2µl water-dispersed particles dispersed onto double-sided sticky carbon tapes fixed to a flat sample holder and kept for 5 min to air-dry. The samples coated 6nm Au-Pt thin film to create a conductive metal layer and protect the sample from thermal degradation during SEM analysis. The average size of the particles was evaluated by the image processing program ImageJ (National Institute Health, USA) via measu-

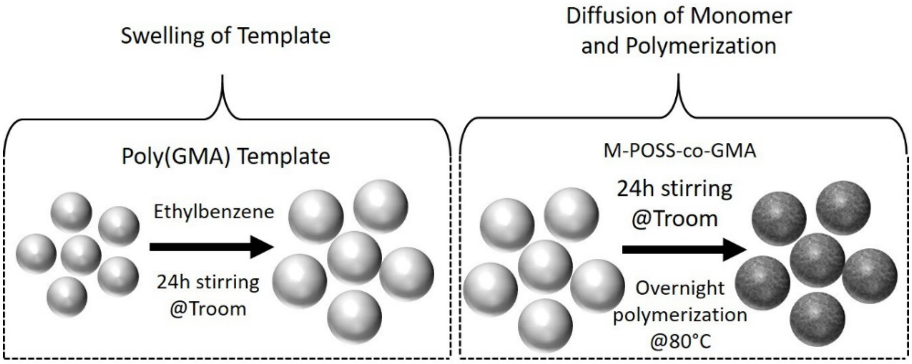


Figure 2. Schematically representation of templated polymerization.

Table 1. Composition in emulsion medium.

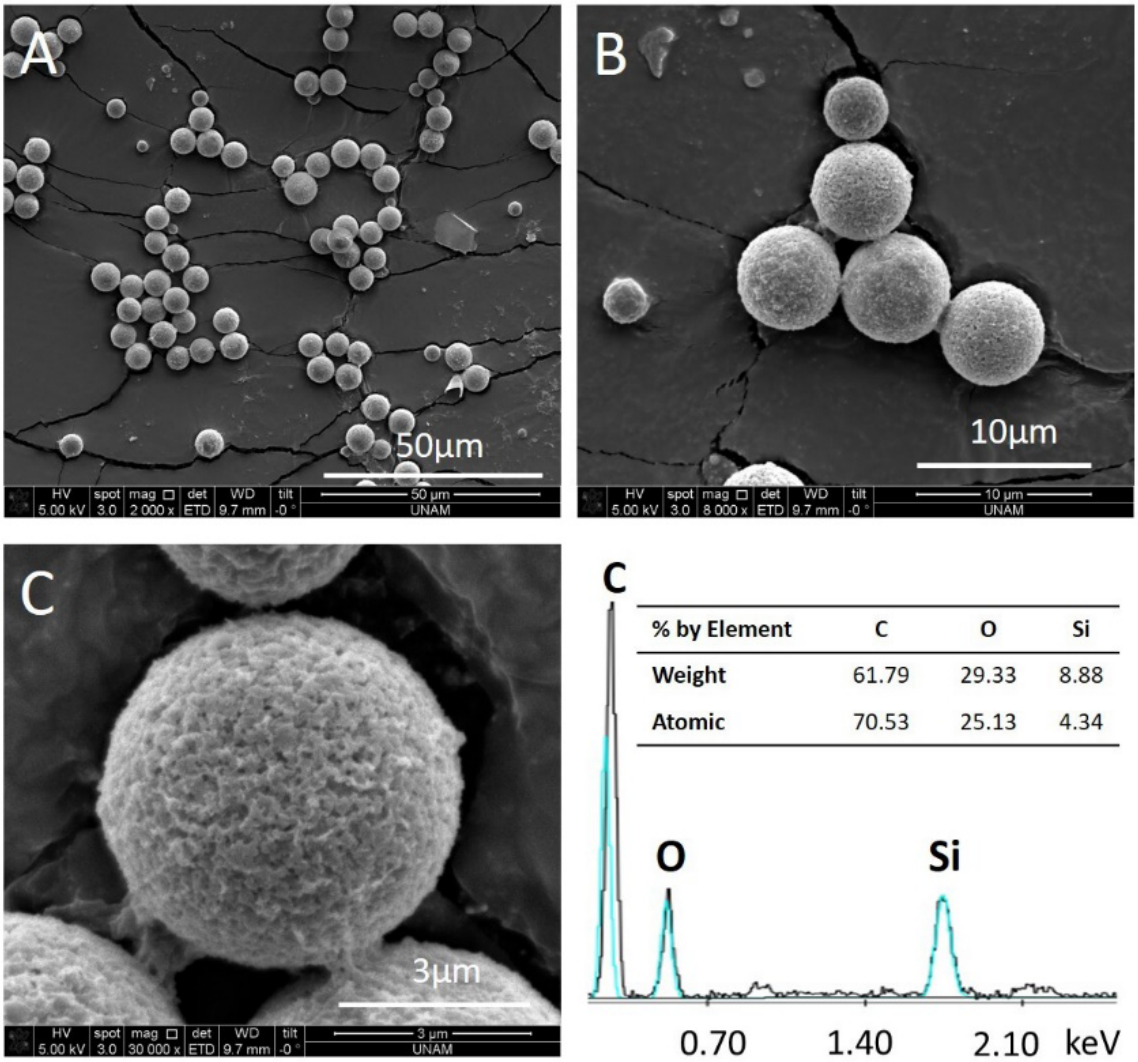
Components	STEP 1	STEP 2
Organic phase		
Poly(GMA) (g)	0.15	
EB (ml)	2.5	
POSS (g)		0.5
GMA (ml)		0.5
GDMA (ml)		1.0
BPO (g)		0.03
EtOH (ml)		0.50
Water Phase		
dH2O (ml)	25.0	25.0
SDS (g)	0.0625	0.0625
8% (w/v) PVA (ml)		5.0

ring 50 particles from SEM images. The chemical-bond structure of monomers and the synthesized particles were analyzed by Fourier-transform infrared spectroscopy-attenuated total reflection FTIR-ATR (Nicolet™ iN™ 5 FTIR Microscope, Thermo Fisher Scientific, USA). The thermal degradation analysis was performed by using a Thermogravimetric analyzer (Hitachi STA7300) in a nitrogen atmosphere with a heating rate of 10°C/min ranging approximately from 30 to 550°C for each sample. The crystalline form of synthesized particles was determined by XRD (Rikagu Miniflex 600 X-ray diffraction) by scanning the angles from 5° to 90°.

RESULTS and DISCUSSION

The epoxy-functional hybrid microparticles were synthesized via templated polymerization in given amounts in Table 1. The synthesized microparticles were obtained around 5.8 ± 0.4µm in size analyzed by image processing program ImageJ (National Institute Health, USA). Even though the polymerization end-product was obtained polydisperse, the smaller size of the particles was separated from microparticles via centrifugal forces. In Figure 3-B the non-separated smaller size of particles could be clearly seen. The polydispersity could be explained by the diffusion step. The methacrylate base monomers and monomer soluble initiators were generally diffused into swollen poly(GMA) seed particles [25]. However, the M-POSS monomer was created its own micelles forms in emulsion that resulted in the smaller size of particles [13]. Additionally, the high molecular weight of the M-POSS hybrid monomer could create difficulty during the diffusion step into swollen poly(GMA) template particles. The porous morphology was obtained at the final product in Figure 3-C by removal of template particles poly(GMA) by washing THF. The EDAX results showed the inorganic and organic elements of microstructure in Figure 3.

The chemical bonds of poly(POSS-co-GDMA-co-GMA) particles could be seen in Figure 4. Here, the vinyl end group -C=C- stretching around 1640cm-1 indicated the active monomer sides for the free radical polymerization. The diminished vinyl end showed the polymerization successfully done in Figure 4-d. Particularly the strong band at 1151 cm-1 indicated -C-O- bending in Figure 4-a and 4-b. The -C-O- the peak was overlapped with a wide Si-O-Si peak around 1100 cm-1 belonging to the POSS monomer in Figure 3-d. The POSS monomer gave an inorganic part to final copolymer particles as Si-O-Si cage structure, which could be obviously seen at 1100cm-1 peak in Figure 3-c and 3-d [13]. However, this wide Si-O-Si peak at 1100cm-1 partly overlapped the strong -C-O- peak at 1151 cm-1 belonging to GMA and GDMA monomers, so the -C-O- peak cannot be observed in Figure 4-d. The peak at 1730 cm−1 which indicated -C=O- bonds was associated with the main characteristic of methacrylate structure [13]. CH3-CH2 bonds were appeared as weak stretching vibration in the 2,960–2,890 cm−1 in Figure 4 [13]. The fingerprint region of the final product demonstrated the co-monomer properties of the epoxy ring around 915 cm−1, 830 cm−1, and 527 cm−1in Figure 4-a and Figure 4-d [26].



% by Element	C	O	Si
Weight	61.79	29.33	8.88
Atomic	70.53	25.13	4.34

Figure 3. The SEM images of poly(M-POSS-co-GMA-co-GDMA).

The thermal degradation steps (inflection points) of poly(POSS-co-GDMA-co-GMA) were obtained from Figure 5 and given in Table 3. The first step of degradation was obtained at 255°C, where the organic content was removed from the structure with a weight loss of 4.5%. The sharp peak indicated that the main degradation step around 410°C produced less than 50% residue in Figure 5. This degradation step could be explained by the cleavage of C-C and Si-C bonds. The backbone of the structure Si-O-C-Si-O was decomposed at the last step around 490°C. Total degradation was analyzed until 550°C where almost 65% of the material was decomposed. The hybrid structure of the particles provided high thermal resistance properties

The crystalline form of particles was analyzed by an XRD diffractogram in Figure 6. The wide peak appearing at 2θ=21° indicated the amorphous silica form of the particles. The other small angel peaks were simply matched the amorphous hydrated silicon dioxide form known as opal mineral, which is made of tightly packed silica spheres. Due to the poly(POSS-co-GDMA-co-GMA) particle arrangement during XRD analysis, the small-angle XRD patterns have appeared as same as opal mineral which contains α-cristobalite and α-tridymite XRD reflection positions (opal-CT) [26].

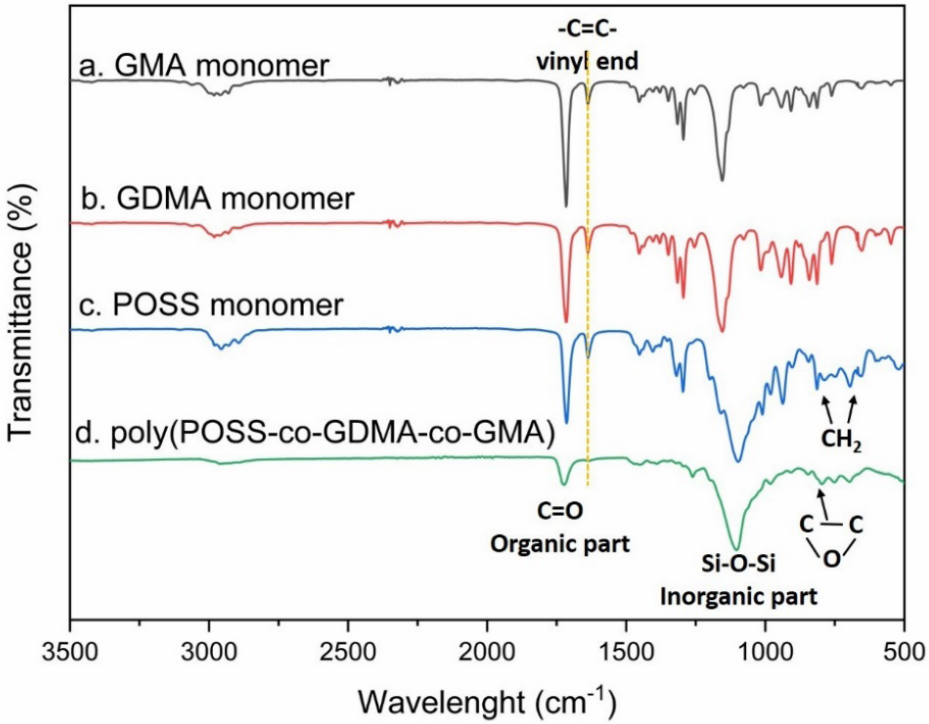


Figure 4. FTIR analysis of monomer and final product a) GMA monomer b) GDMA monomer c) POSS monomer d) poly(POSS-co-GDMA-co-GMA)

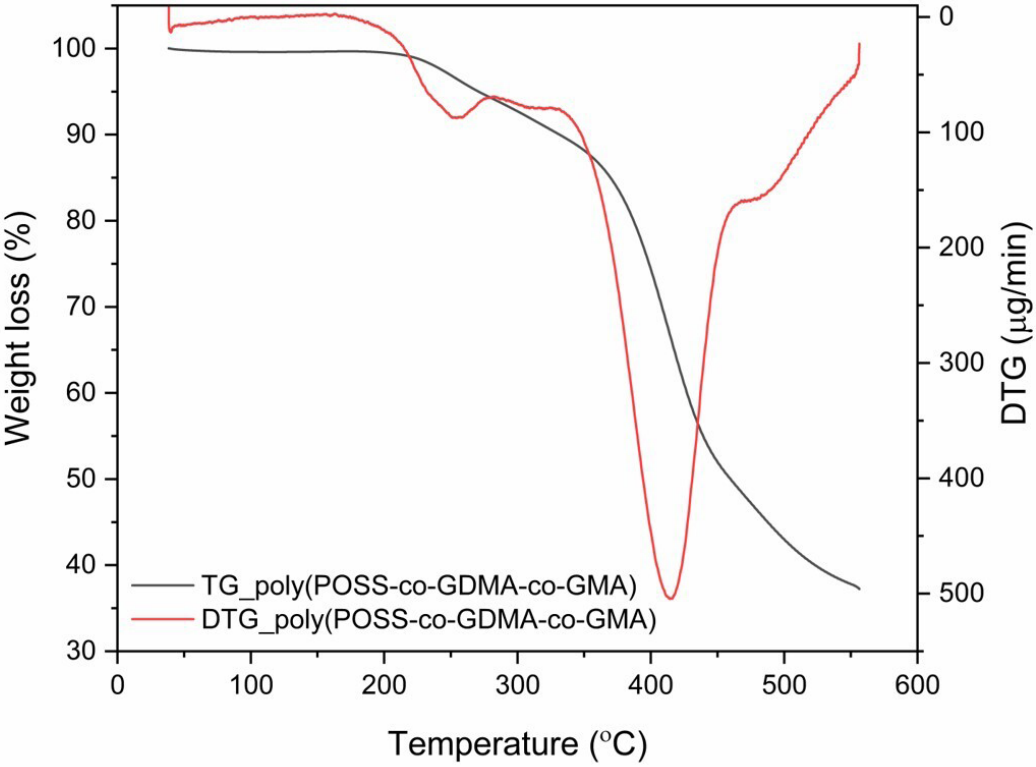


Figure 5. Thermogravimetric analysis TG (weight loss %) and differential thermogravimetric analysis DTG (µg/min) of synthesized poly(POSS-co-GDMA-co-GMA) microparticles.

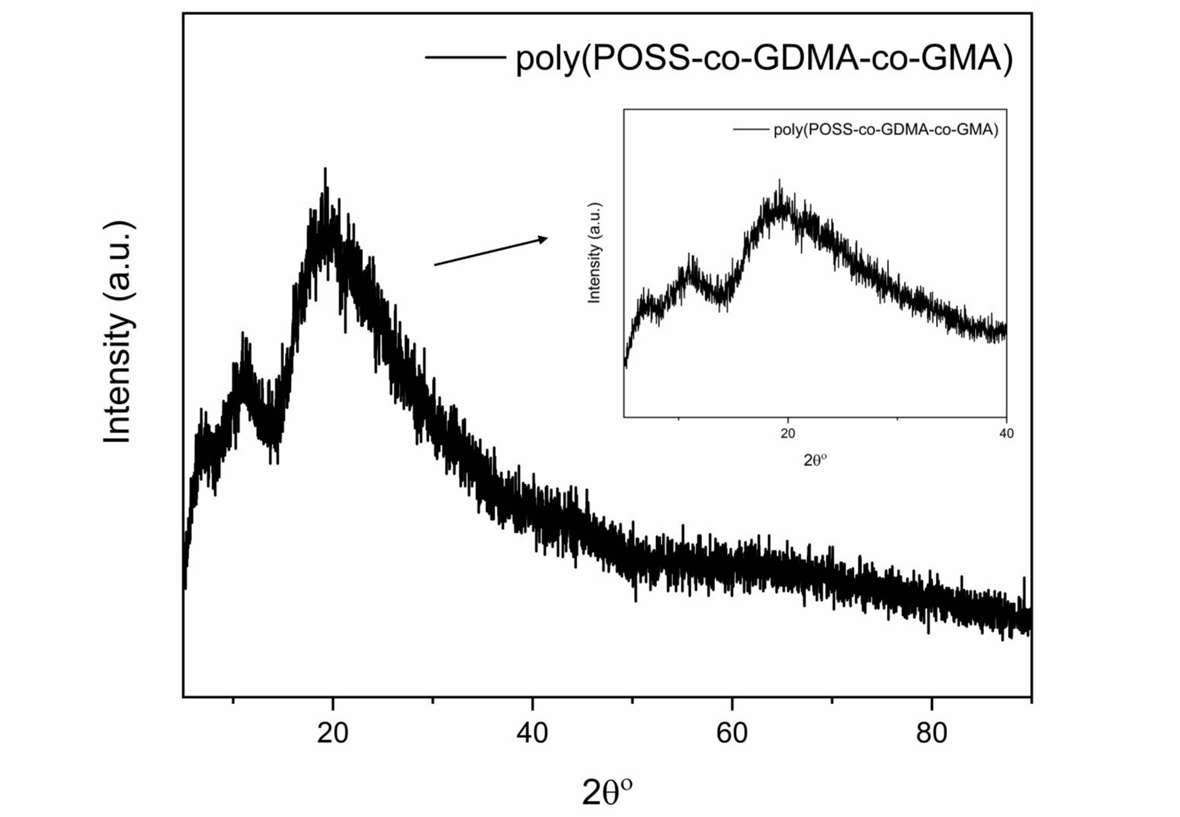


Figure 6. Diffractogram of poly(POSS-co-GDMA-co-GMA) particles.

Table 2. Percentage weight loss of poly(POSS-co-GDMA-co-GMA).

	Inflection Points					
Poly(POSS-co-GDMA-co-GMA	Step I (°C)	Δy%	Step II (°C)	Δy%	Step III (°C)	Δy%
	255	4.6	410	54.2	489	4.2

Δy% Percentage of decomposition

CONCLUSION

The first time, spherical porous uniform epoxy-functional POSS microparticles were synthesized around 6 µm via templated polymerization in two-step emulsion. These novel epoxy-functional hybrid microparticles have extremely flame-retardant properties up to 400°C with a silica-cage structure. The desirable thermal characteristic of the microparticles could be potentially useful as fillers or coating materials. Additionally, the incorporation of silica and epoxy organic parts provides a promising material to scientific communities for protein or/and DNA purification systems. The new porous microparticles could also perform in chromatographic columns as a stationary phase or catalyst support. The organic part is highly active any further modifications for preferable applications.

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