Supporting Information

Exploring maleimide-anchored halloysites as nanophotoinitiators for surface-initiated photografting strategies

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Experimental

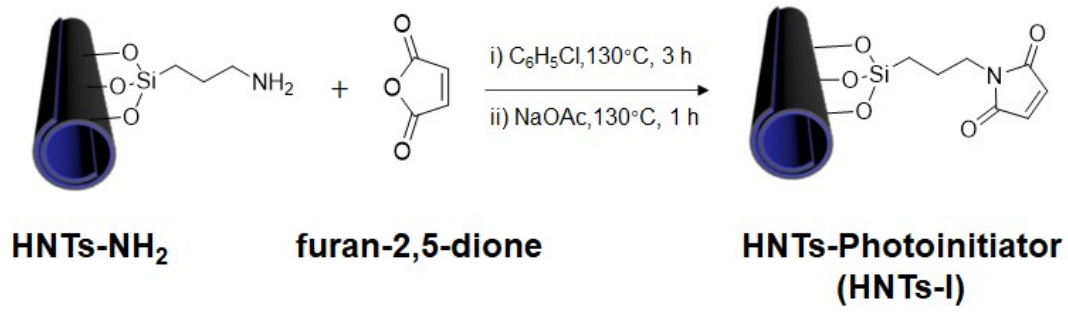
Materials

HNTs were purchased from GuangZhou Shinshi Metallurgy and Chemical Co., Ltd. and purified before used according to our previous work [1]. Furan-2,5-dione was purchased from Sigma-Aldrich. Chlorobenzene, ethanol and acetone were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Sodium acetate and acetic anhydride were obtained from Fuchen Chemical Reagent Co., Ltd. and Sinopharm Chemical Reagent Co., Ltd., respectively. N-methyldiethanolamine and Polyethyleneglycoldiacrylate (PEGDA, M. W. 400) were purchased from Energy Chemical. Hydroxypropylmethyl cellulose (HPMC E5) was kindly supported by Colorcon®. Distilled water was used throughout the study. High-purity argon was used for degassing procedures.

Synthesis and Preparation

HNTs-I

A mixture of HNTs-NH_2 (300 mg) [2] and furan-2,5-dione (1.50 g, 15.3 mmol) was added into 25 mL chlorobenzene in a 50 mL round-bottom flask and heated at 130°C for 3 h. Then, the flask was removed from heat bath and cooled to room temperature. 5 mL sodium acetate/ acetic anhydride solution (20 mg/mL) was added into the solution. The mixture was then heated at 130°C for another hour. After cooling to room temperature, residue was collected after centrifugation at 8000 rpm for 3 min and then washed sequentially with ethanol and water. After dried in vacuum, the product HNTs-I was obtained as white solid (Scheme 1).



Scheme 1. Synthesis of HNTs-photoinitiator (HNTs-I)

Surface grafting of HNTs via photopolymerization

Accurately weighed HNTs-I (50 mg) was added into 3 mL DMF or water. Ultrasound was used to make the it well dispersed. 1.0 g monomer (MMA, styrene, HEMA or acrylamide) were added into the system under argon atmosphere. Then the system was exposed to 365 nm LED light (Power: 35 W; Intensity: 10^2mW/cm^2; Distance: 10 cm) for a certain time. The residue was thoroughly washed by THF and then collected by centrifugation., the grafted products were obtained after dried in vacuum.

Characterizations

The morphological characterizations were performed by using a Tecnai G2 F20 S-TWIN transmission electron microscope (TEM) with an accelerating voltage of 200 kV. A JEOL Ltd.

SIGMA 300 field emission scanning electron microscopy (SEM) was used to characterize the micromorphology of grafted products. The fluffy samples were carefully put on flat substrates precoated with carbonic glues and then were coated with gold for SEM observations.

FTIR spectra were recorded in the region of 400-4000 cm-1 for each sample on a Thermo Fisher Scientific NICOTET IS10 FTIR spectrophotometer i. Samples were previously ground and mixed thoroughly with KBr.

The 13C Solid-state NMR spectra were obtained on a Bruker Advance III spectrometer.

X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific ESCALab 250Xi using 200 W monochromated Al Ka radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3 × 10-10 mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing.

TGA was performed on Perkin-Elmer Pyris 6 at a scanning rate of 10oC/min from 40 to 800oC under nitrogen.

Pore size distribution was measured by a V-Sorb 2800P porosity analyzer.

Data

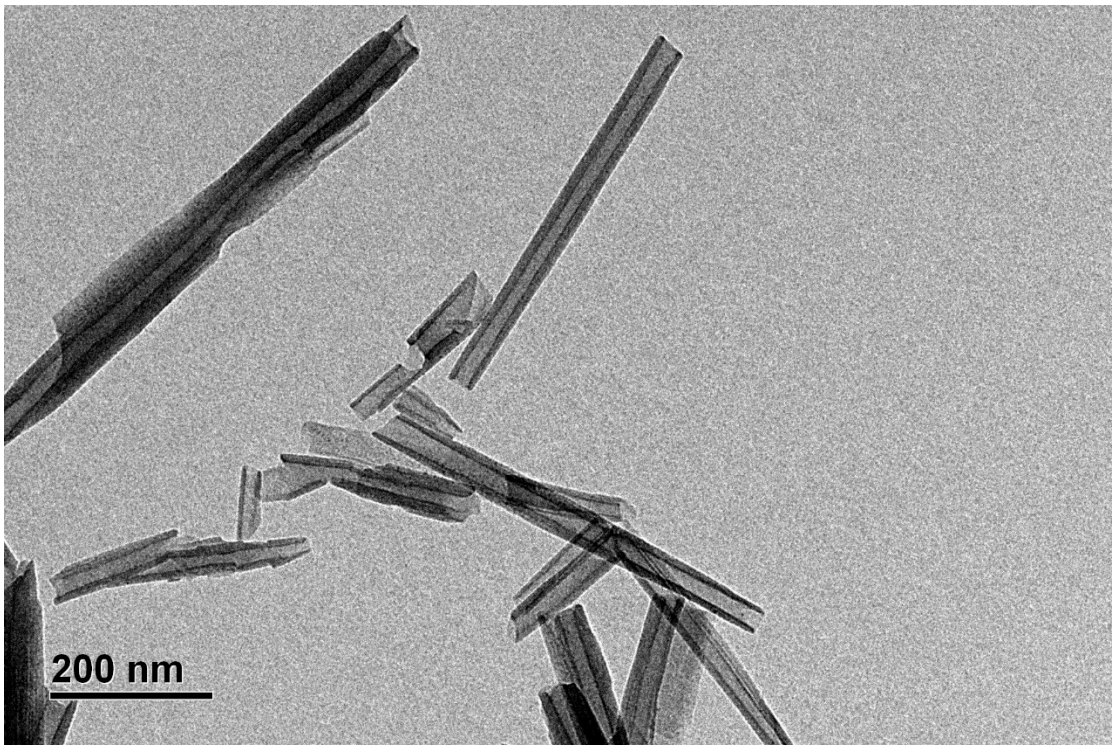


Figure S1. TEM image of pristine HNTs

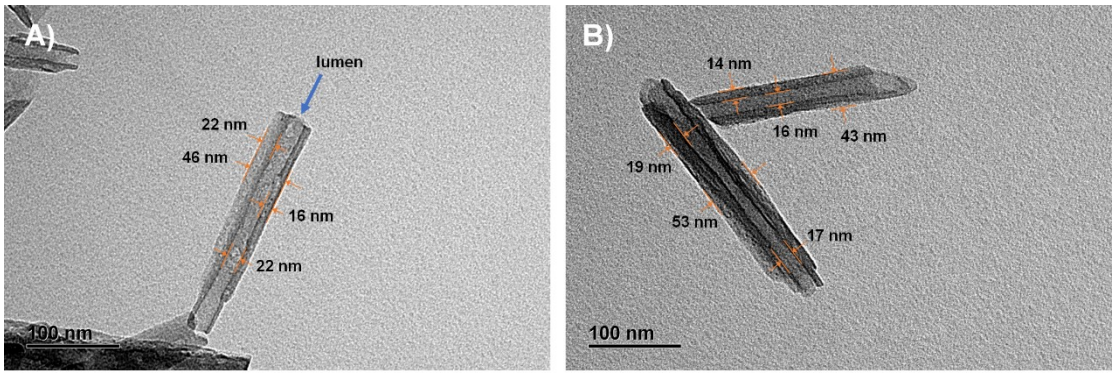


Figure S2. TEM images of pristine HNTs with calculated lumen diameters, outer diameters and walls thickness

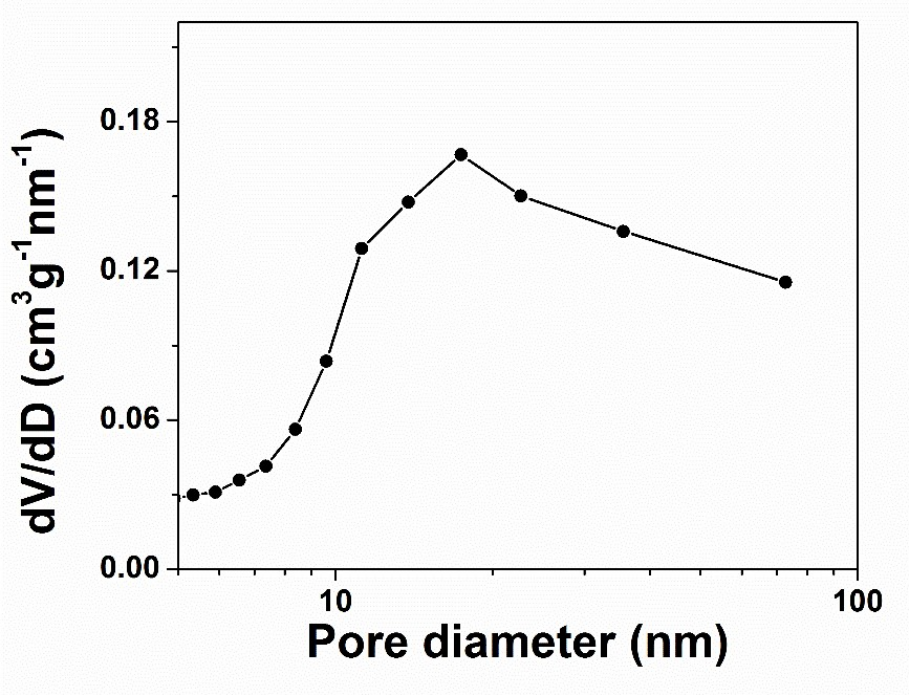


Figure S3. pore size distribution of HNTs

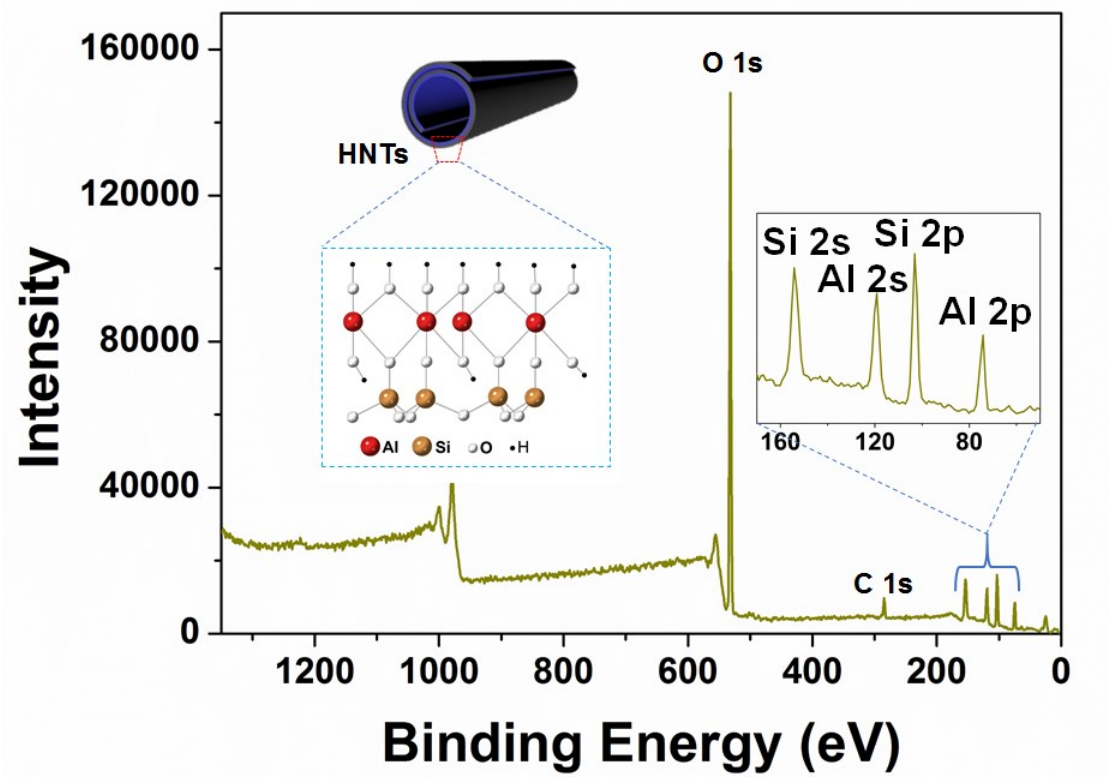


Figure S4. Schematic illustration of crystalline structure [3] and XPS spectrum of HNTs

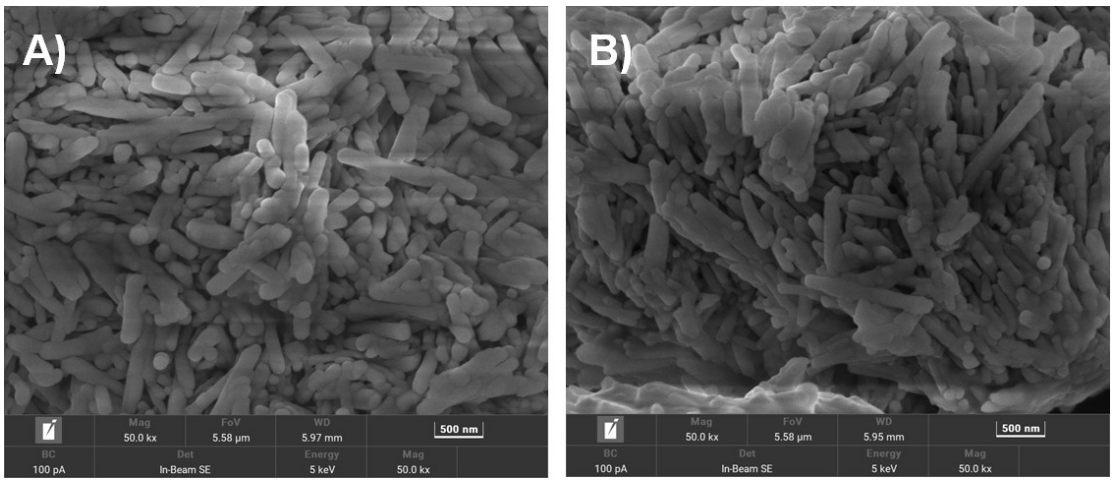


Figure S5. SEM images of HNTs-I

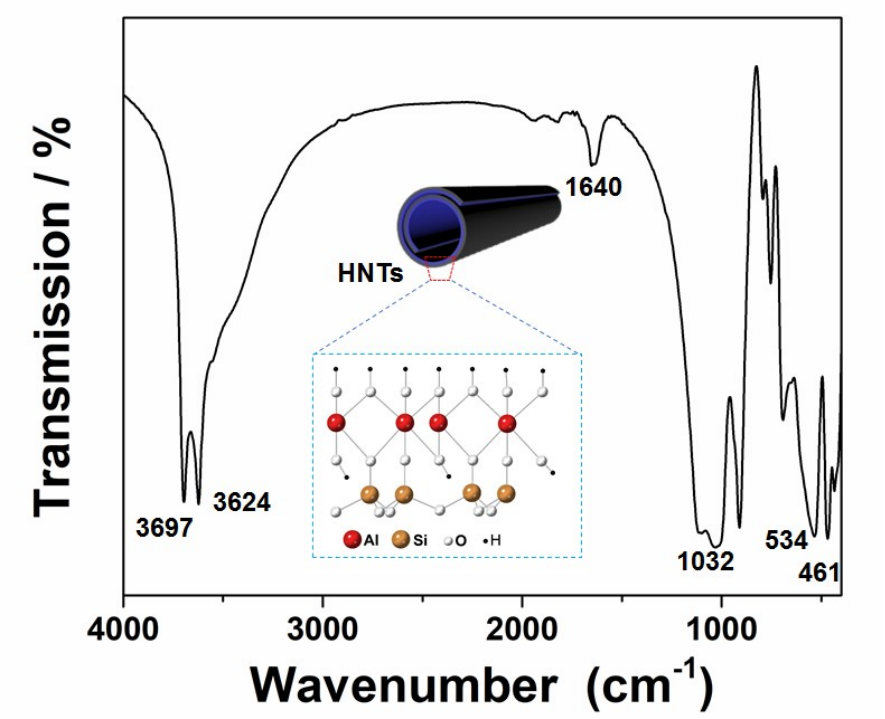


Figure S6. FTIR spectrum of pristine HNTs

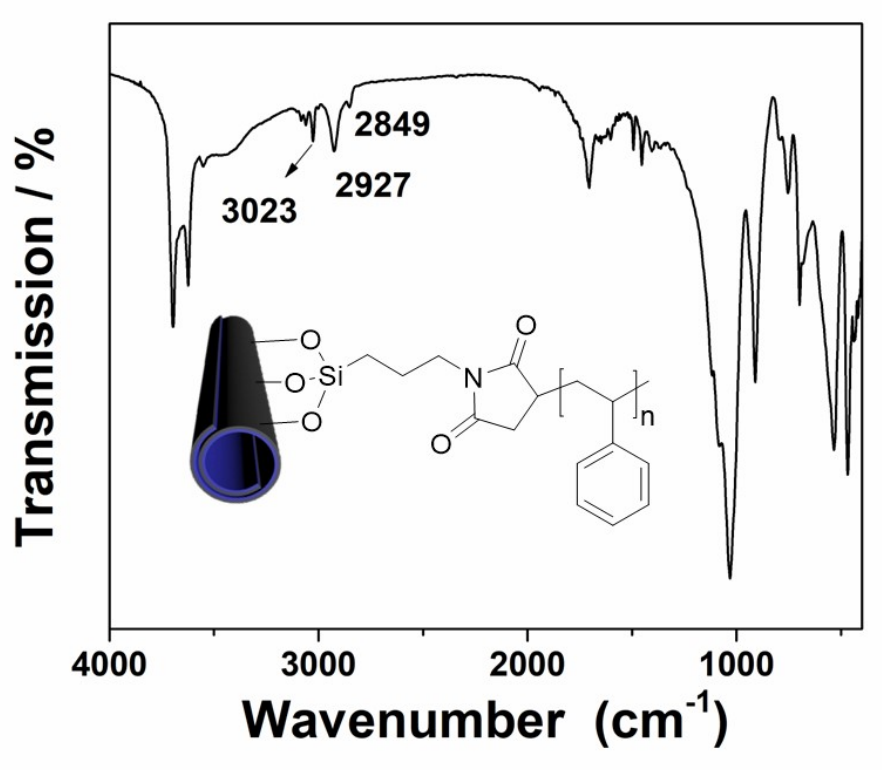


Figure S7. FTIR spectrum of HNTs-I-PS (Case.No.4 in Tab.1)

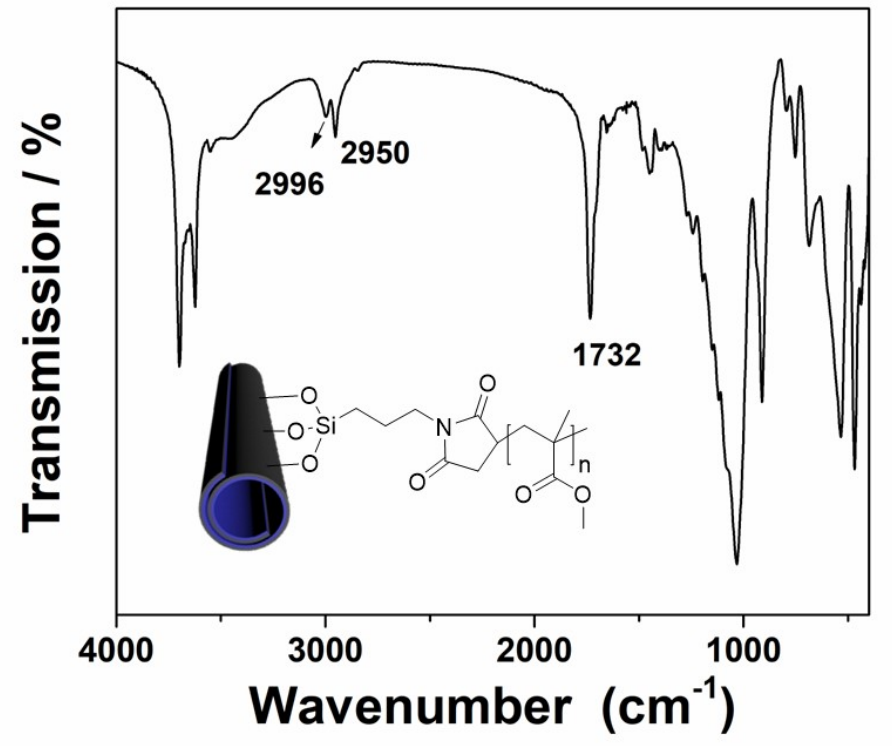


Figure S8. FTIR spectrum of HNTs-I-PMMA (Case.No.1 in Tab.1)

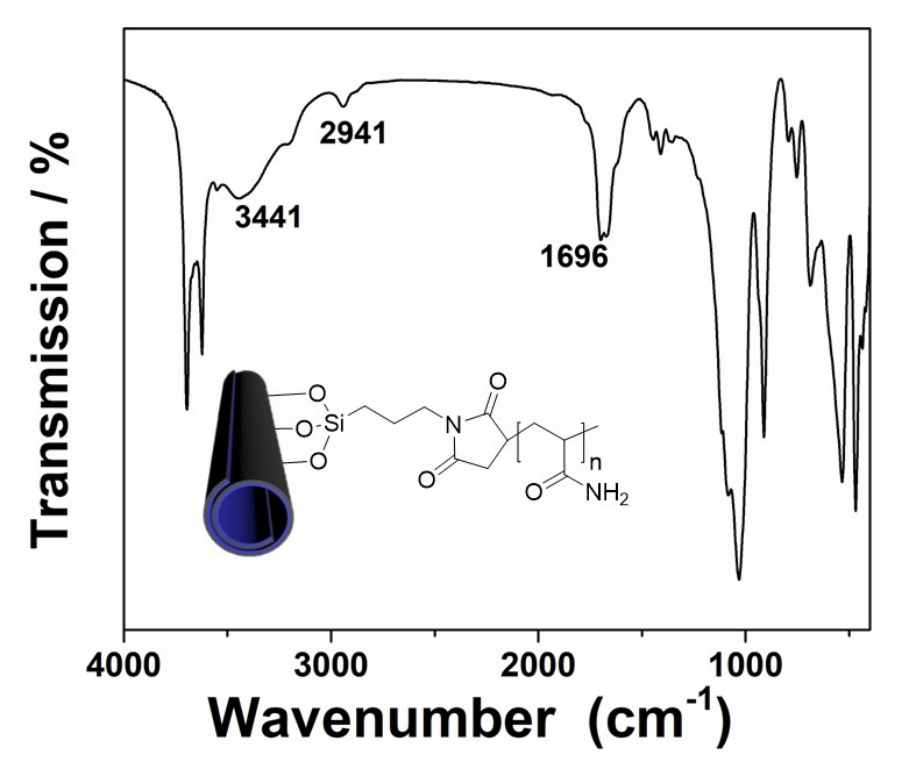


Figure S9. FTIR spectrum of HNTs-I-PAM (Case.No.10 in Tab.1)

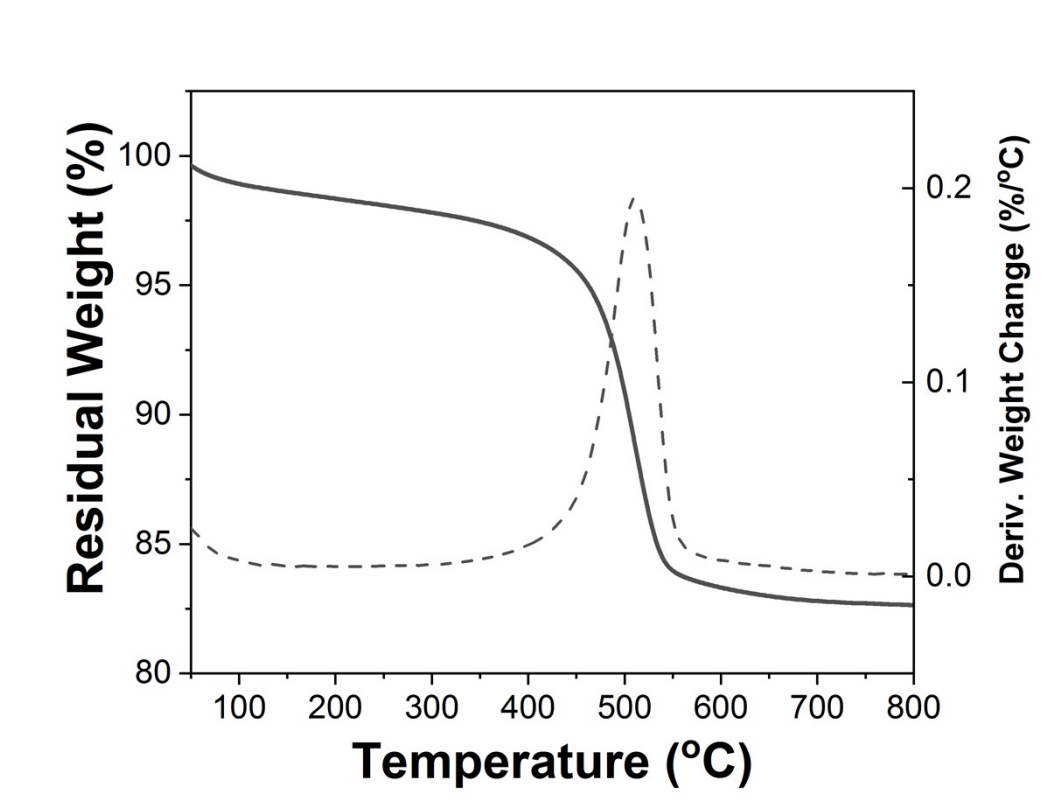


Figure S10. TG and DTG curves of HNTs

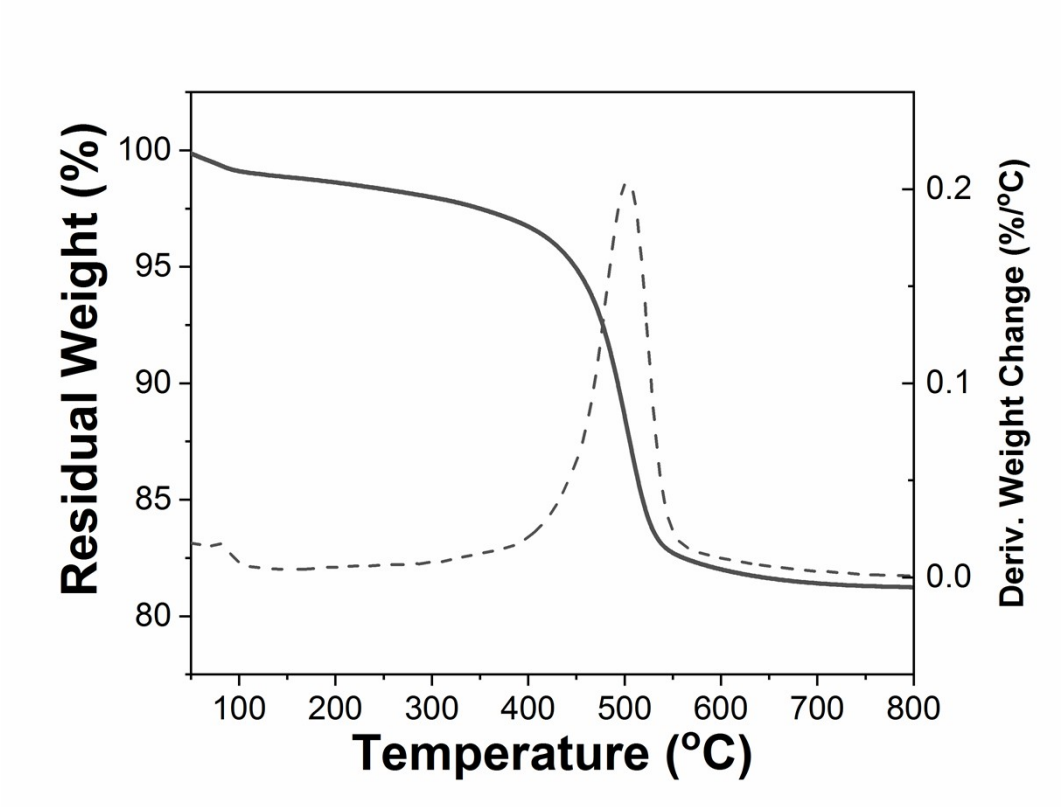


Figure S11. TG and DTG curves of HNTs-NH_2

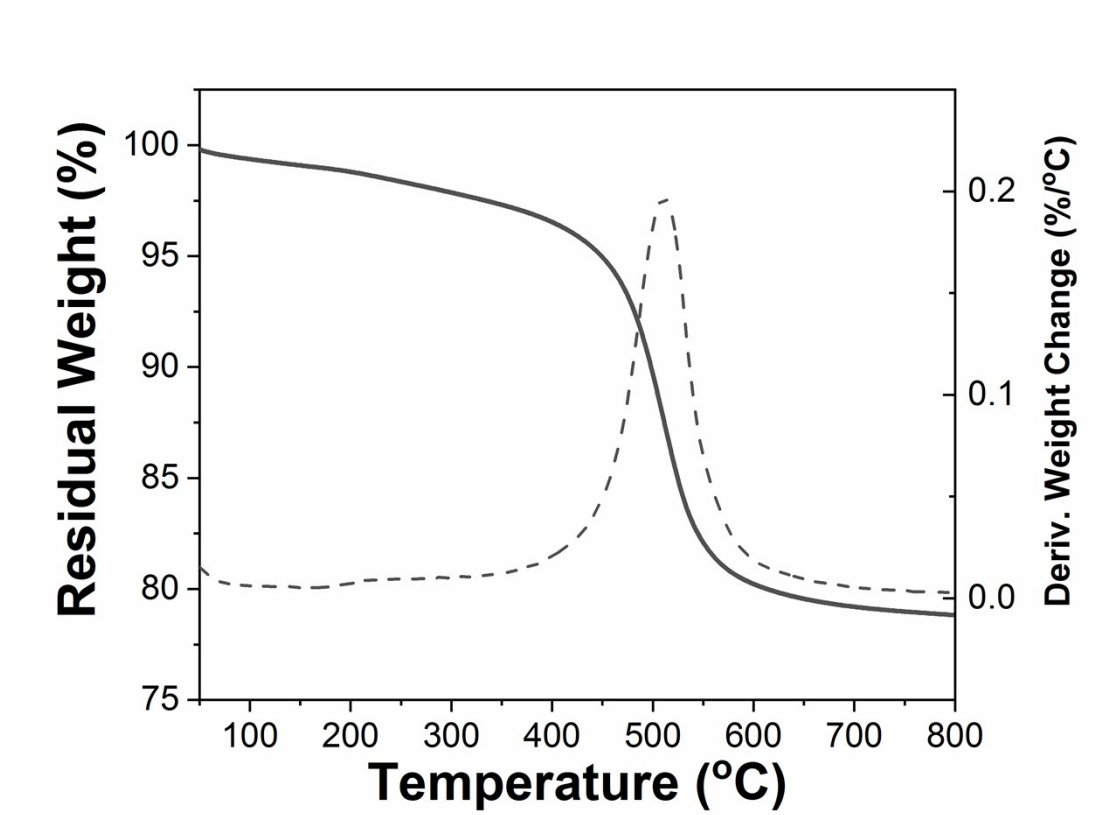


Figure S13. TG and DTG curves of HNTs-I

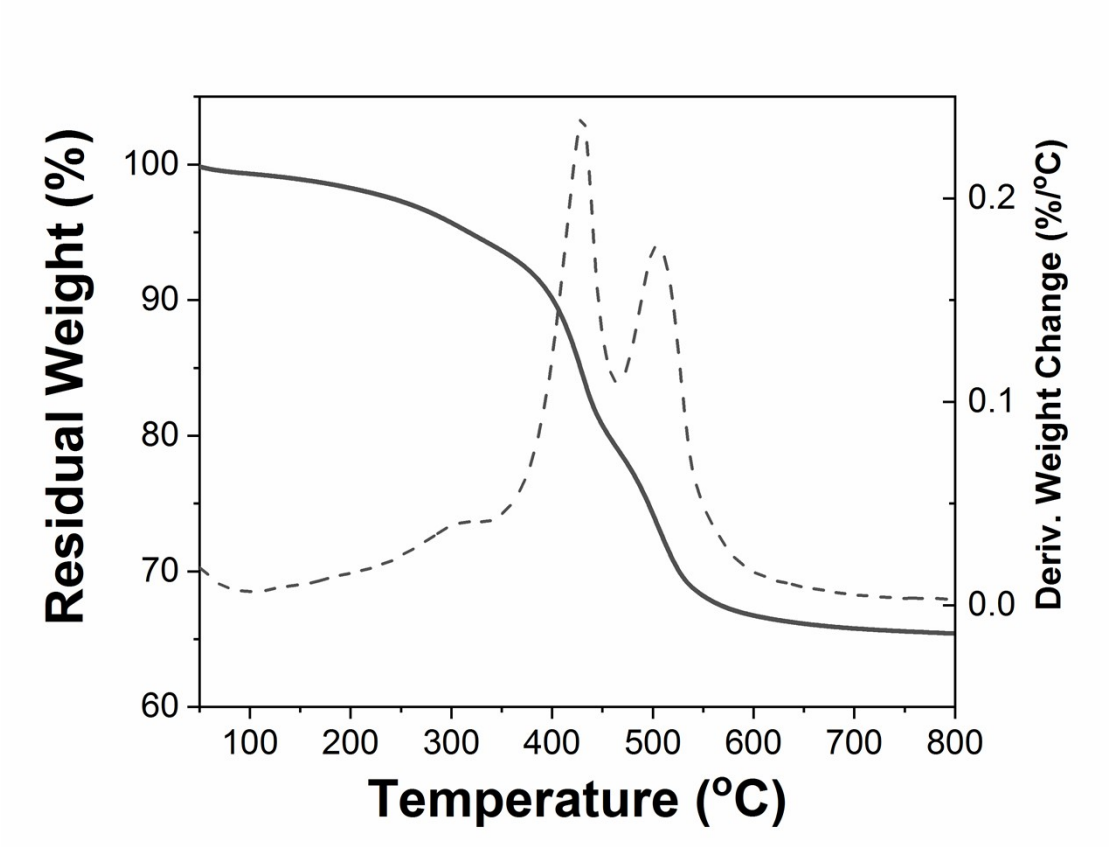


Figure S12. TG and DTG curves of HNTs-I-PMMA (Case.No.1 in Tab.1)

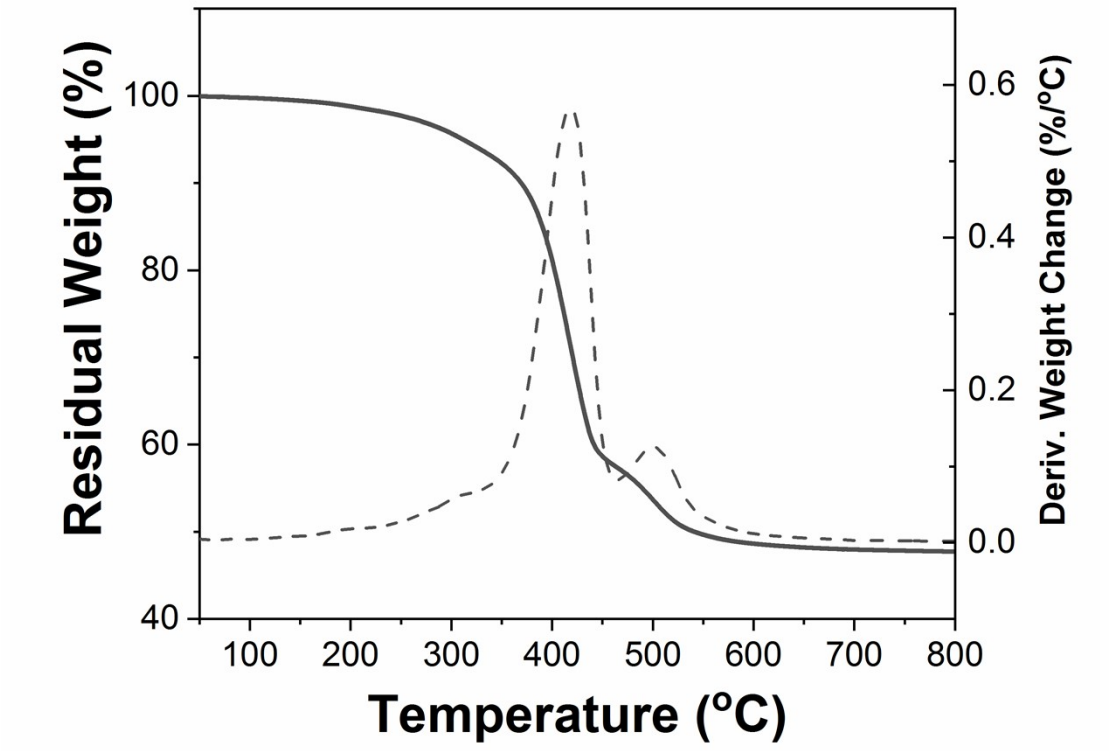


Figure S14. TG and DTG curves of HNTs-I-PMMA (Case.No.2 in Tab.1)

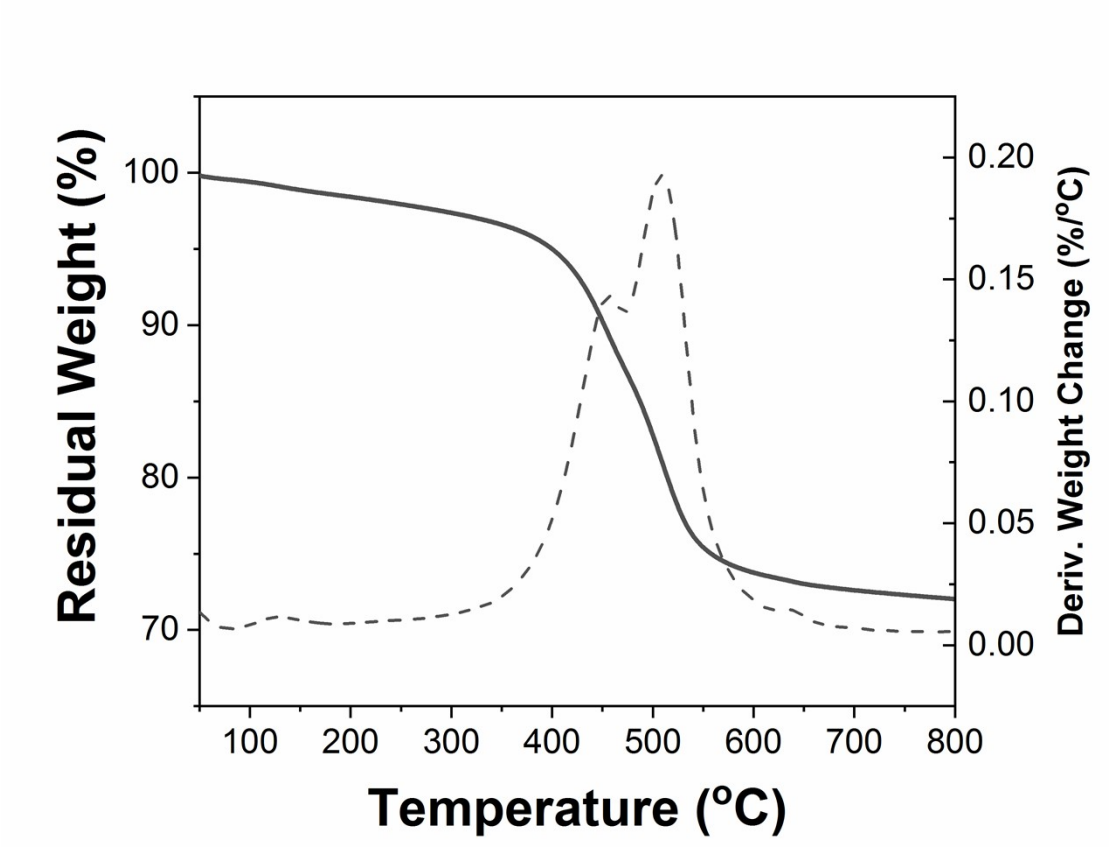


Figure S15. TG and DTG curves of HNTs-I-PS (Case.No.4 in Tab.1)

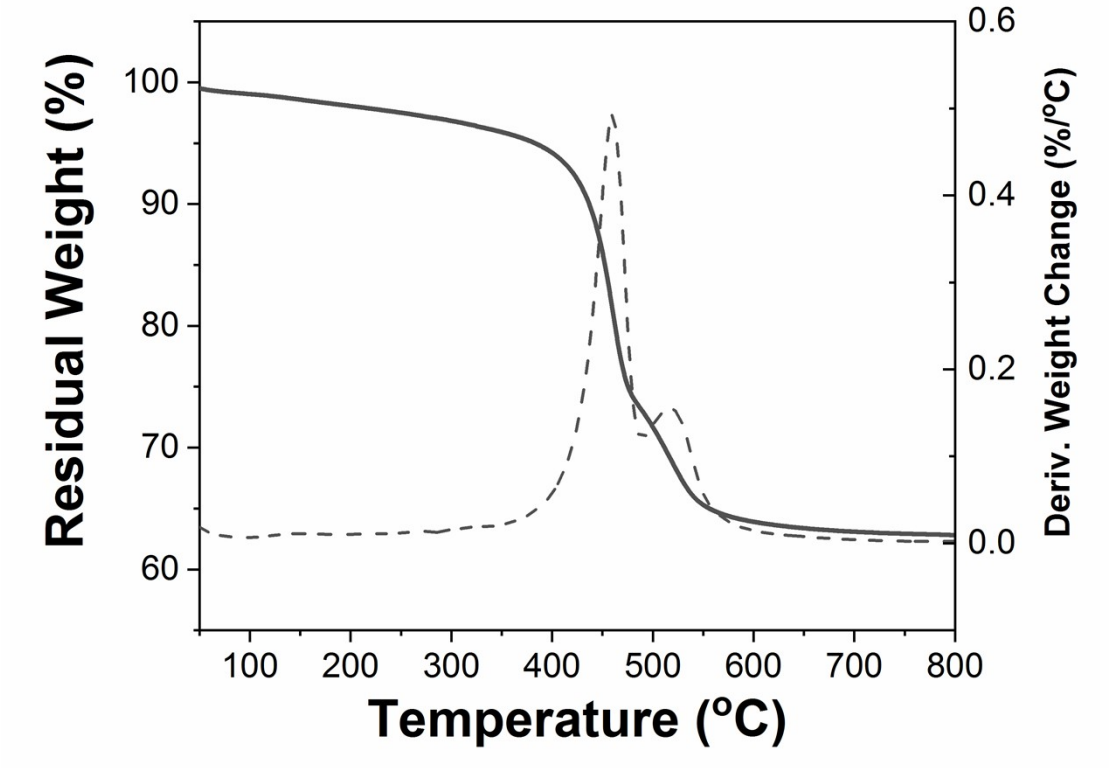


Figure S16. TG and DTG curves of HNTs-I-PS (Case.No.5 in Tab.1)

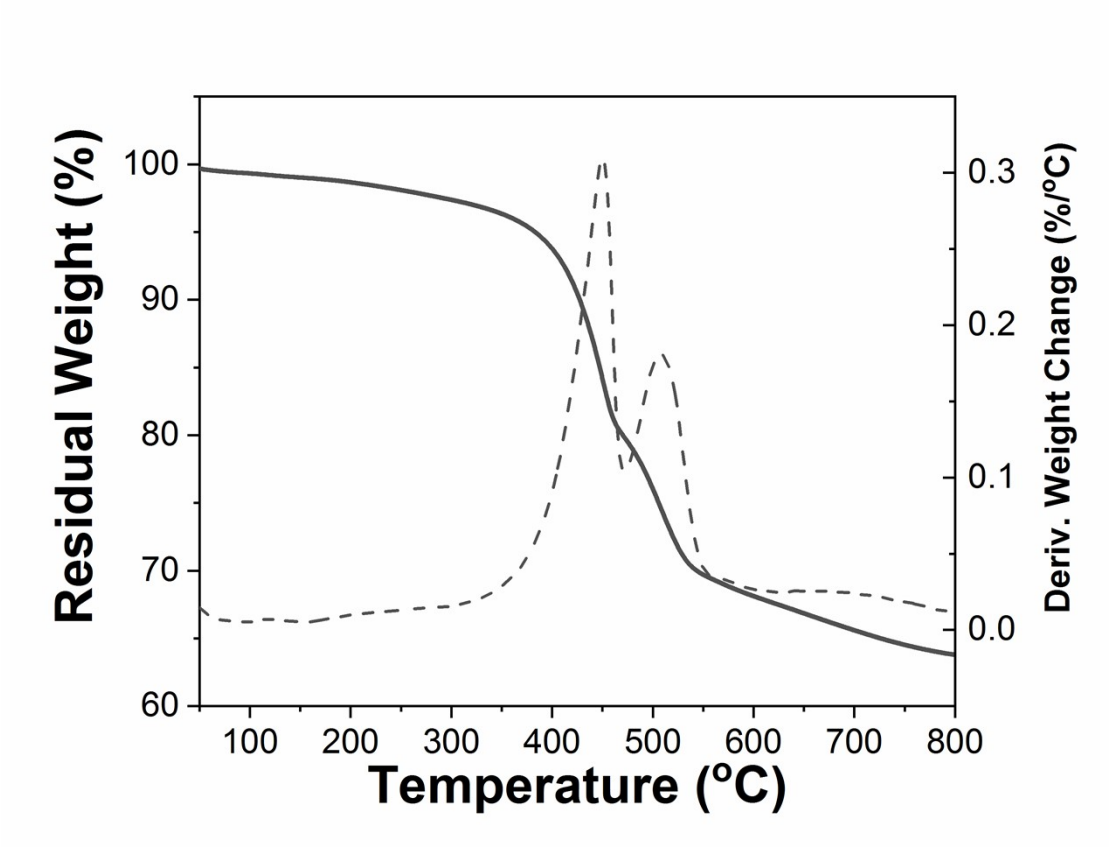


Figure S17. TG and DTG curves of HNTs-I-PS (Case.No.6 in Tab.1)

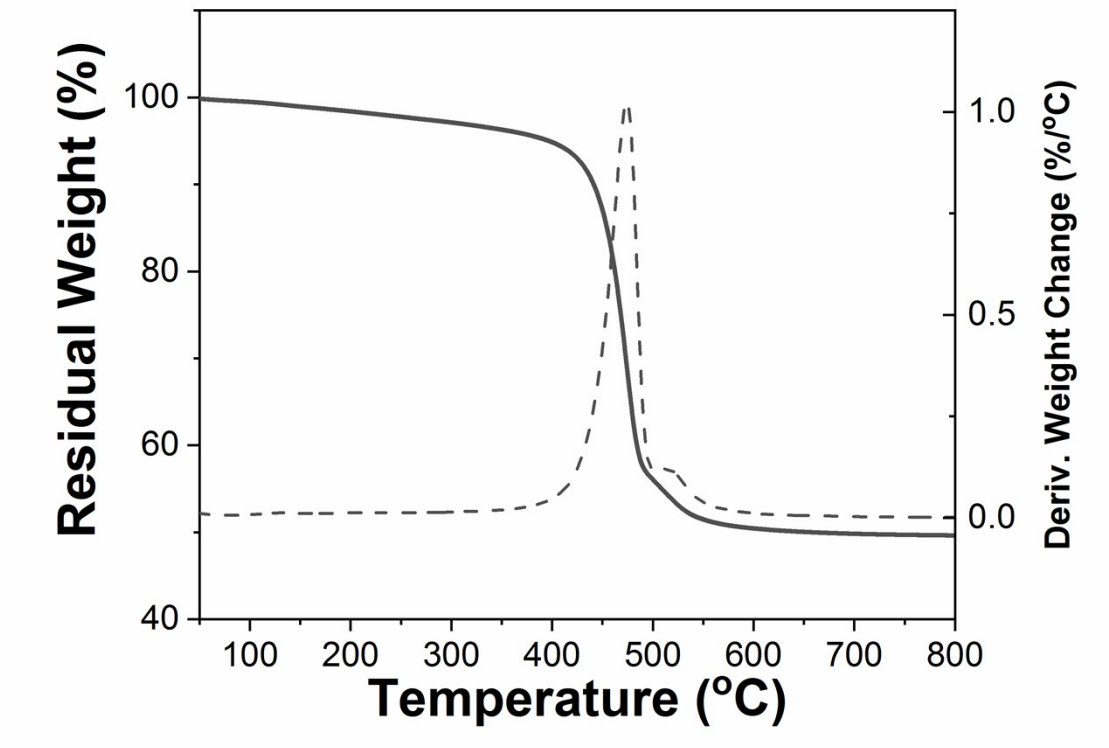


Figure S18. TG and DTG curves of HNTs-I-PS (Case.No.7 in Tab.1)

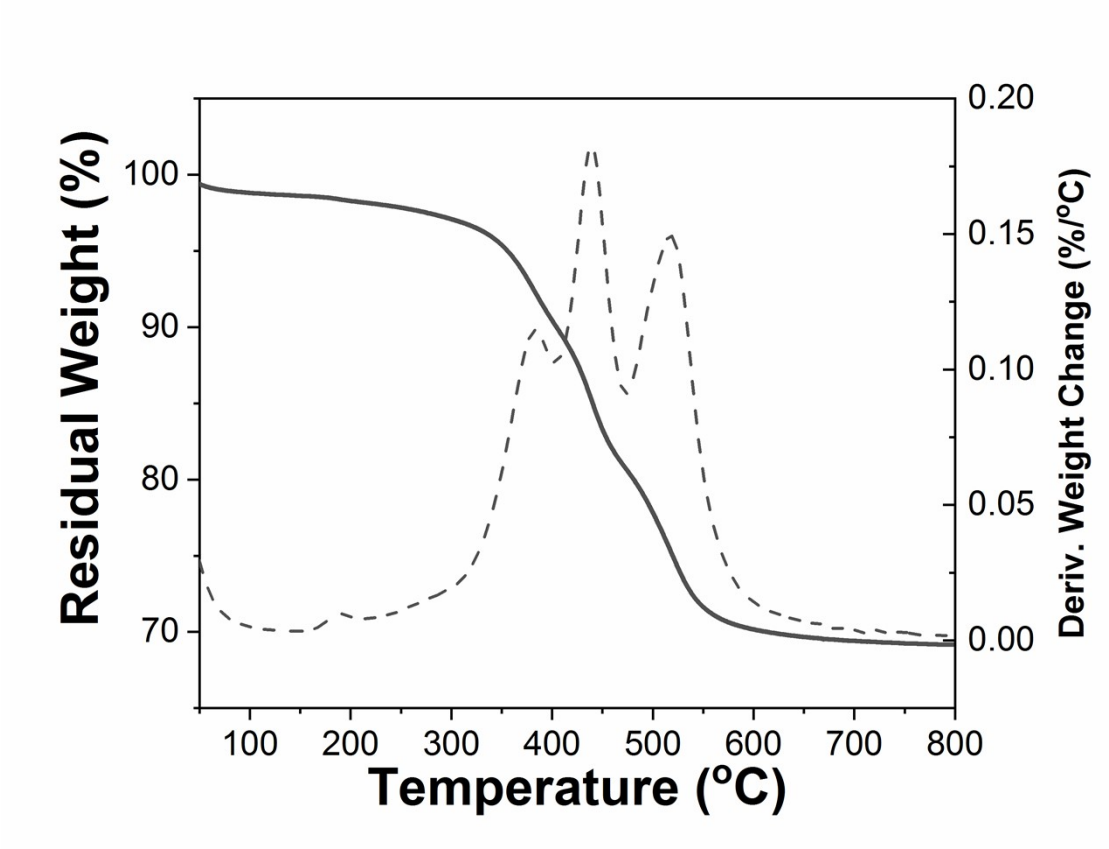


Figure S19. TG and DTG curves of HNTs-I-PHEMA (Case.No.8 in Tab.1)

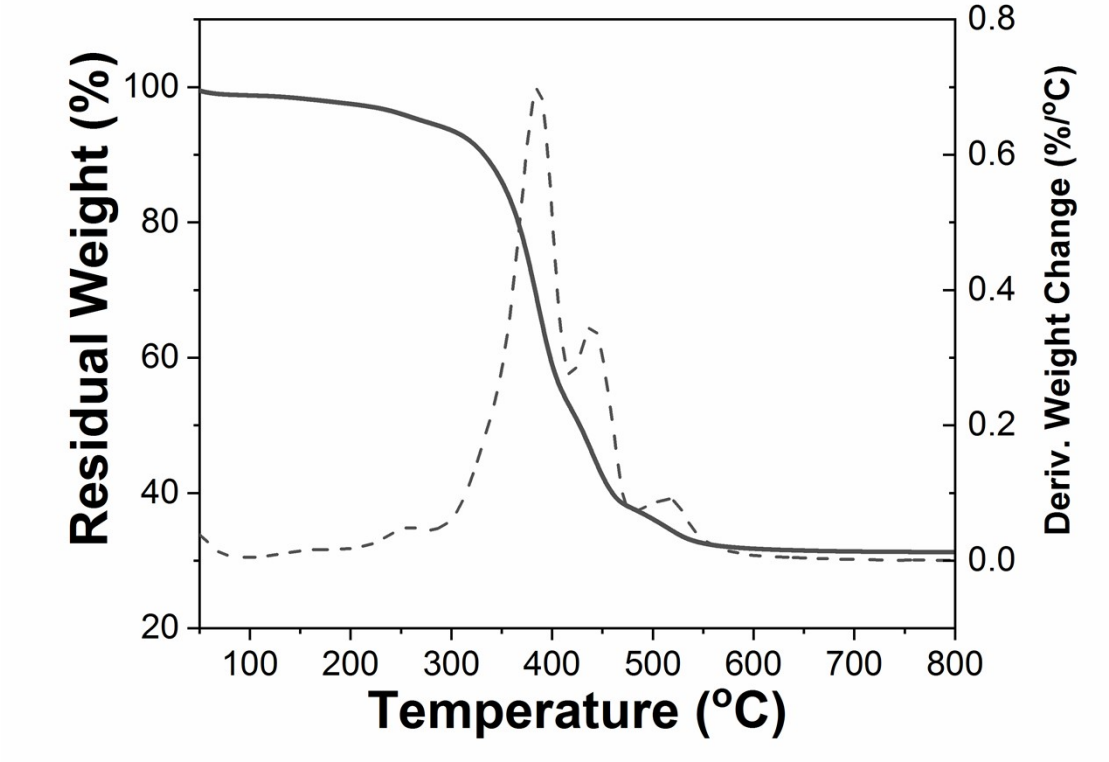


Figure S20. TG and DTG curves of HNTs-I-PHEMA (Case.No.9 in Tab.1)

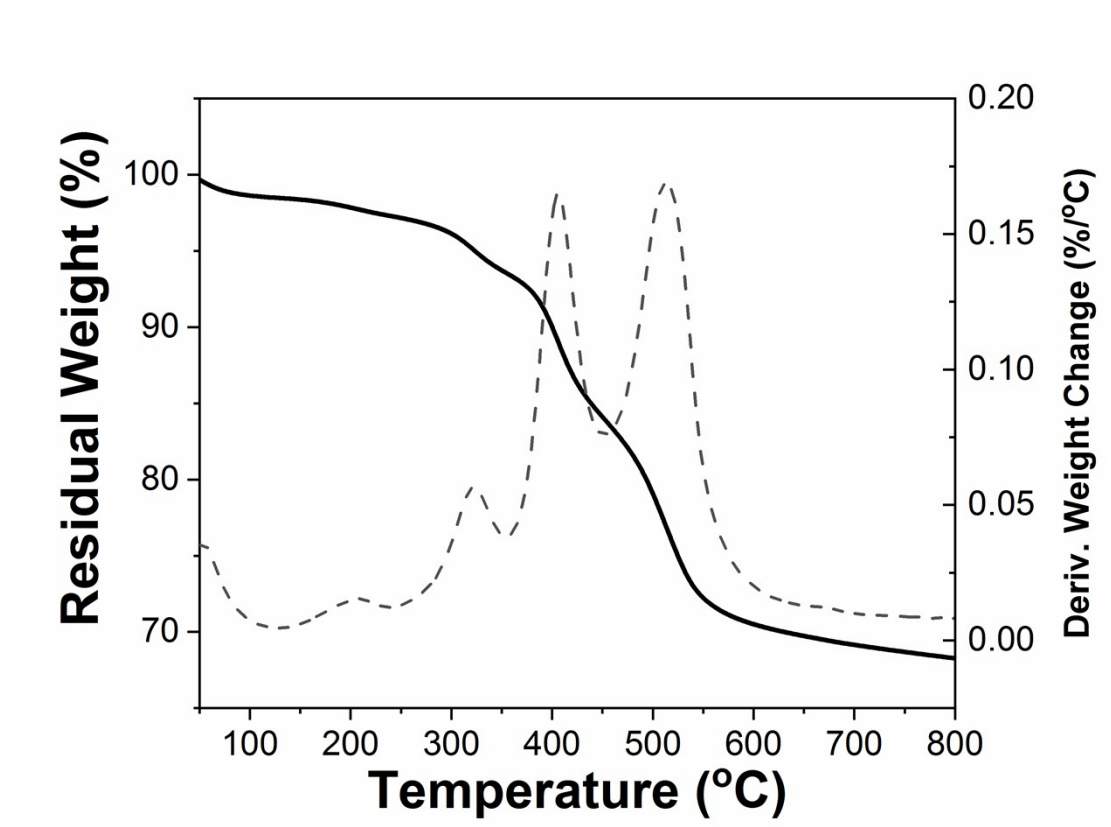


Figure S21. TG and DTG curves of HNTs-I-PAM (Case.No.10 in Tab.1)

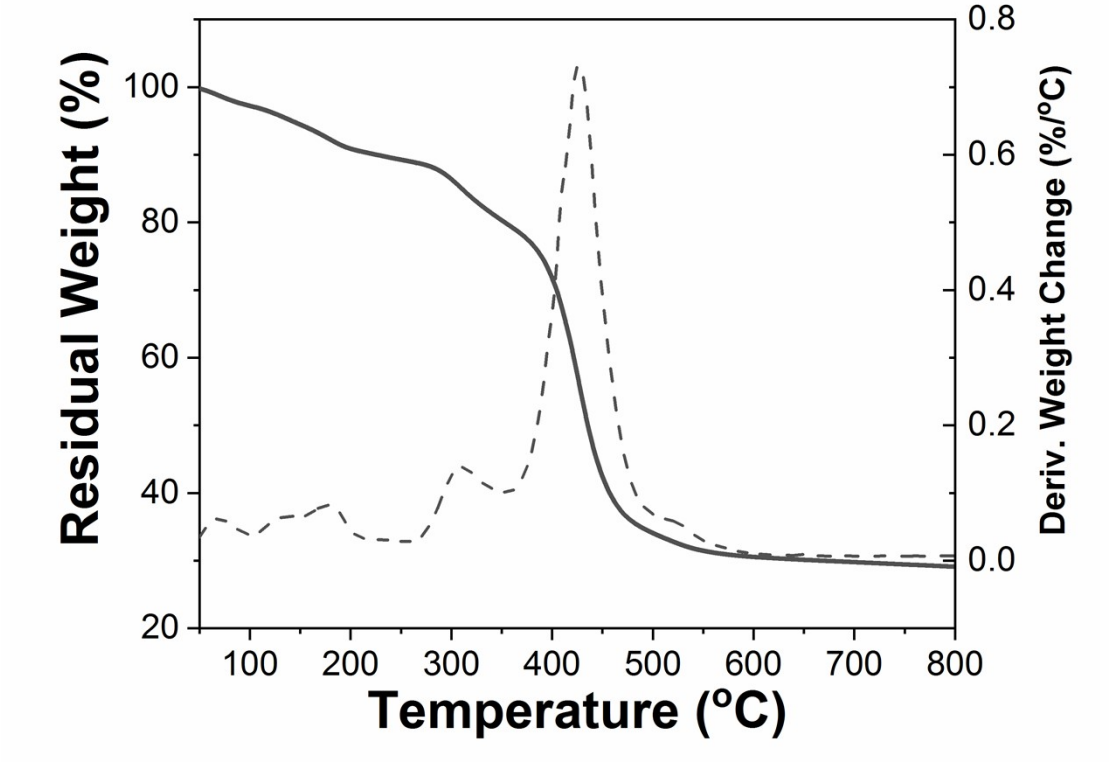


Figure S22. TG and DTG curves of HNTs-I-PAM (Case.No.11 in Tab.1)

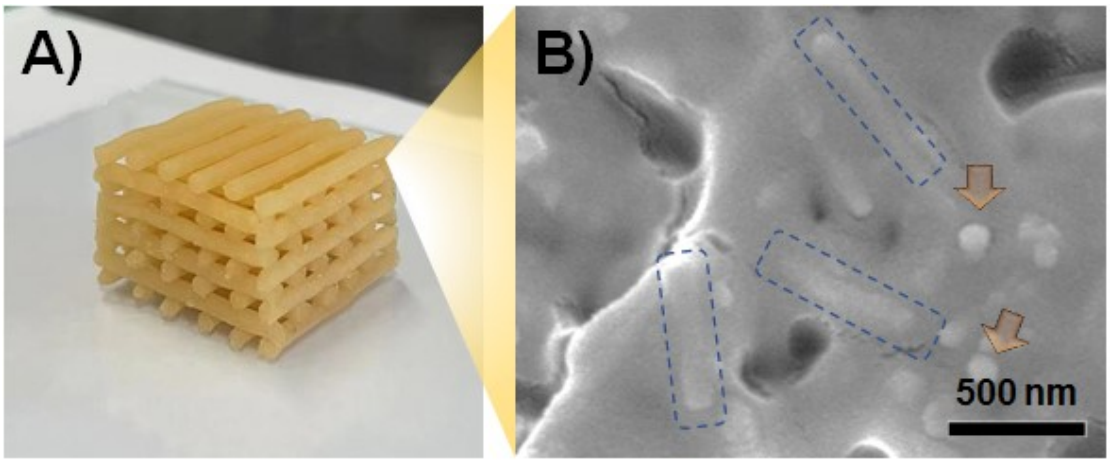


Figure S23. Photograph of the printed samples (A) and SEM image (B)

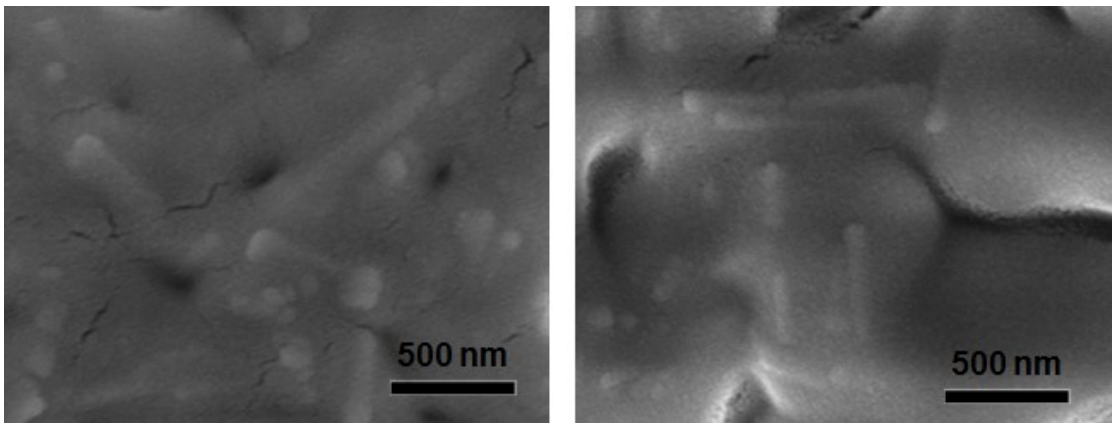


Figure S24. SEM images of printed samples

References

1. C. Cheng, Y. Gao, W. Song, Q. Zhao, H. Zhang and H. Zhang, *Chem. Eng. J.*, 2020, **380**, 122474.
2. Q. Zhao, H. Jiang, B. Tang, Y. Wu, X. Ba and H. Zhang, *ACS Appl. Nano Mater.*, 2021, **4**, 7435-7442.
3. M. Liu, Z. Jia, D. Jia and C. Zhou, *Prog. Polym. Sci.*, 2014, **39**, 1498-1525.