

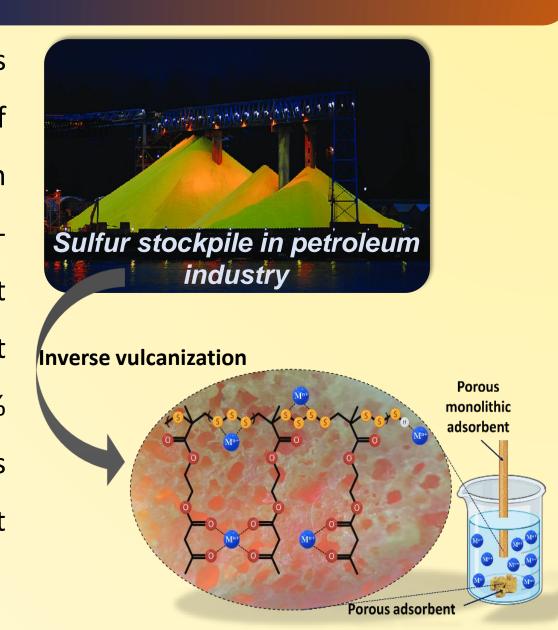
Inversely Vulcanized Porous Copolymer Monolith for Efficient Removal of Metal Ions from Water

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ABSTRACT

The world is witnessing a growing interest in using waste materials to reduce environmental burden, add product value and promote sustainability. Sulfur is the 10th most abundant element in the universe and more than 70 million tonnes of sulfur accumulate yearly, making it underutilized. The accumulation of large amounts of waste elemental sulfur is creating an environmental concern. Inverse vulcanization has been recently reported as a new copolymerization technique to convert highly crystalline elemental sulfur to a more useful polymeric form. In this study, we synthesized sulfur-based polymers bearing βdiketone functional groups via the inverse vulcanization between acetoacetoxy ethyl methacrylate (AAEMA) and sulfur. A porous variant of the adsorbent was fabricated using a facile template-assisted method employing NaCl as the porogen. Heavy metal adsorption studies conducted in a multi-element solution containing various metal ions demonstrated that the porous adsorbent exhibited remarkable heavy metal chelation properties, achieving 100% removal of Hg²⁺ and 72–96% removal of Cr³⁺, Pb²⁺, Co²⁺, Fe³⁺, Ni²⁺, Ag⁺, and Cu²⁺. A prototype of the identical porous adsorbent in monolithic form has been constructed. The porous monolith retains all the benefits of porous adsorbent in particulate form, while allowing the separation of the adsorbent from the treated water by simply lifting it as a single unit, eliminating the necessity for filtration, as is necessary with particulate adsorbents.



FT-IR spectra

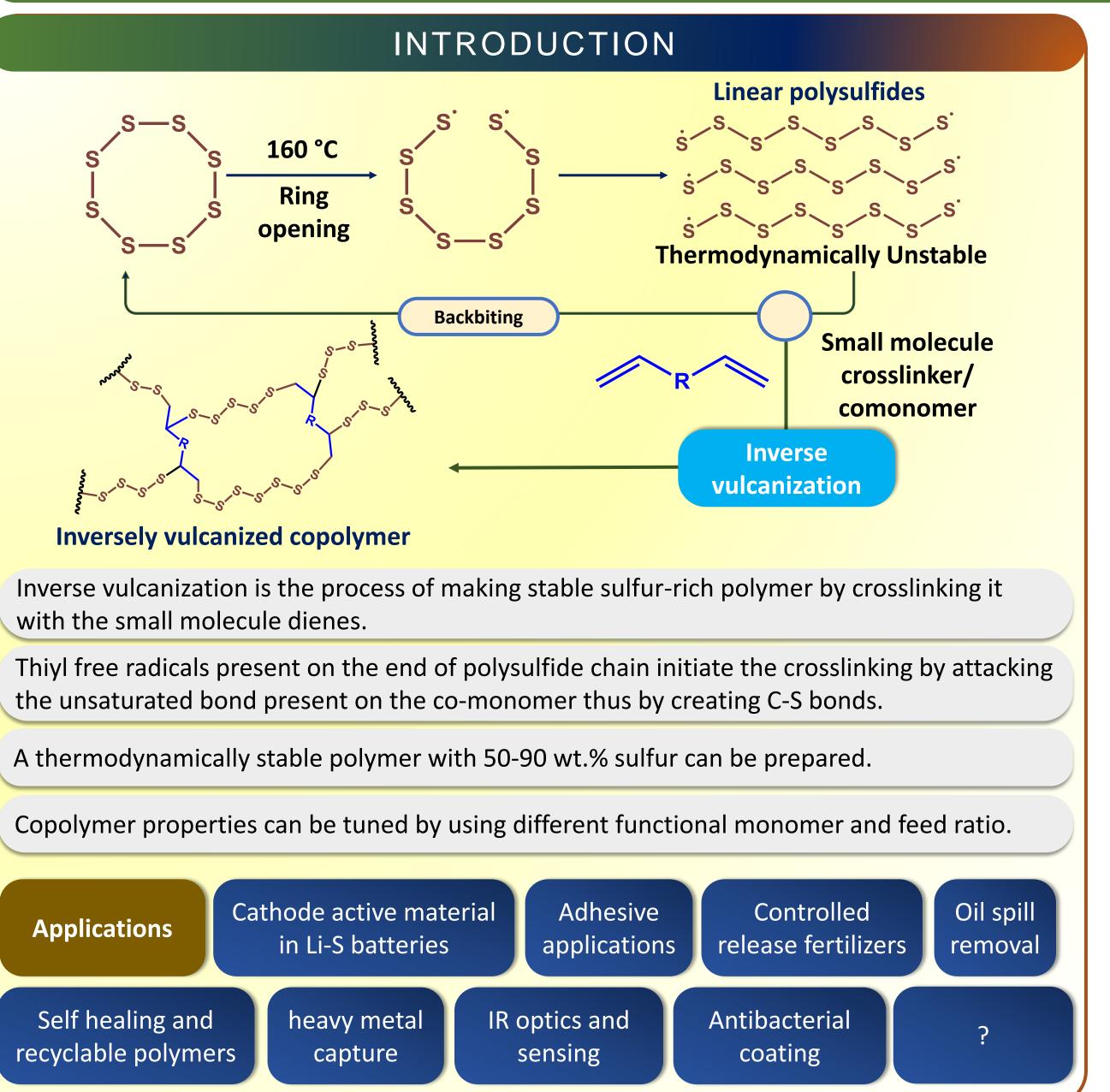
PAAEMA

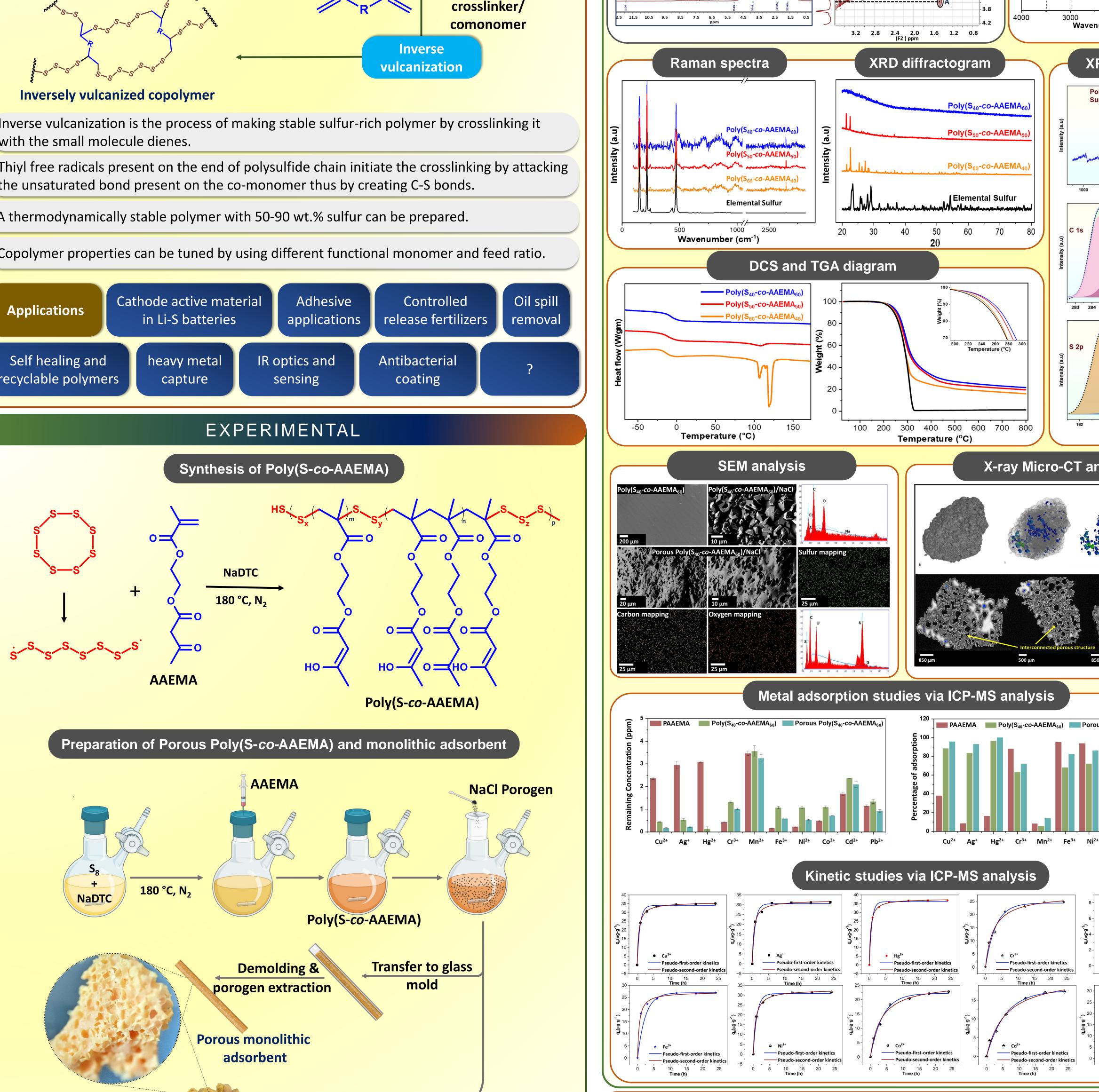
2.6

Poly(S₄₀-co-AAEMA₆₀)

Poly(S₅₀-co-AAEMA₅₀)

Poly(\$60-co-AAEMA40)





Porogen extraction

*1 wt.% of Sodium diethyl dithiocarbamate (NaDTC) is used in all compositions

AAEMA

60 wt.%

50 wt.%

40 wt.%

60 wt.%

100 wt.%

Sulfur

40 wt.%

50 wt.%

60 wt.%

40 wt.%

0 wt.%

Photographic images of the monolithic adsorbent

Porous adsorbent

Poly(S₄₀-co-AAEMA₆₀) *

 $Poly(S_{50}$ -co-AAEMA₅₀) *

 $Poly(S_{60}$ -co-AAEMA₄₀) *

Porous poly(S₆₀-co-AAEMA₄₀)*

Compositions:

Sample ID

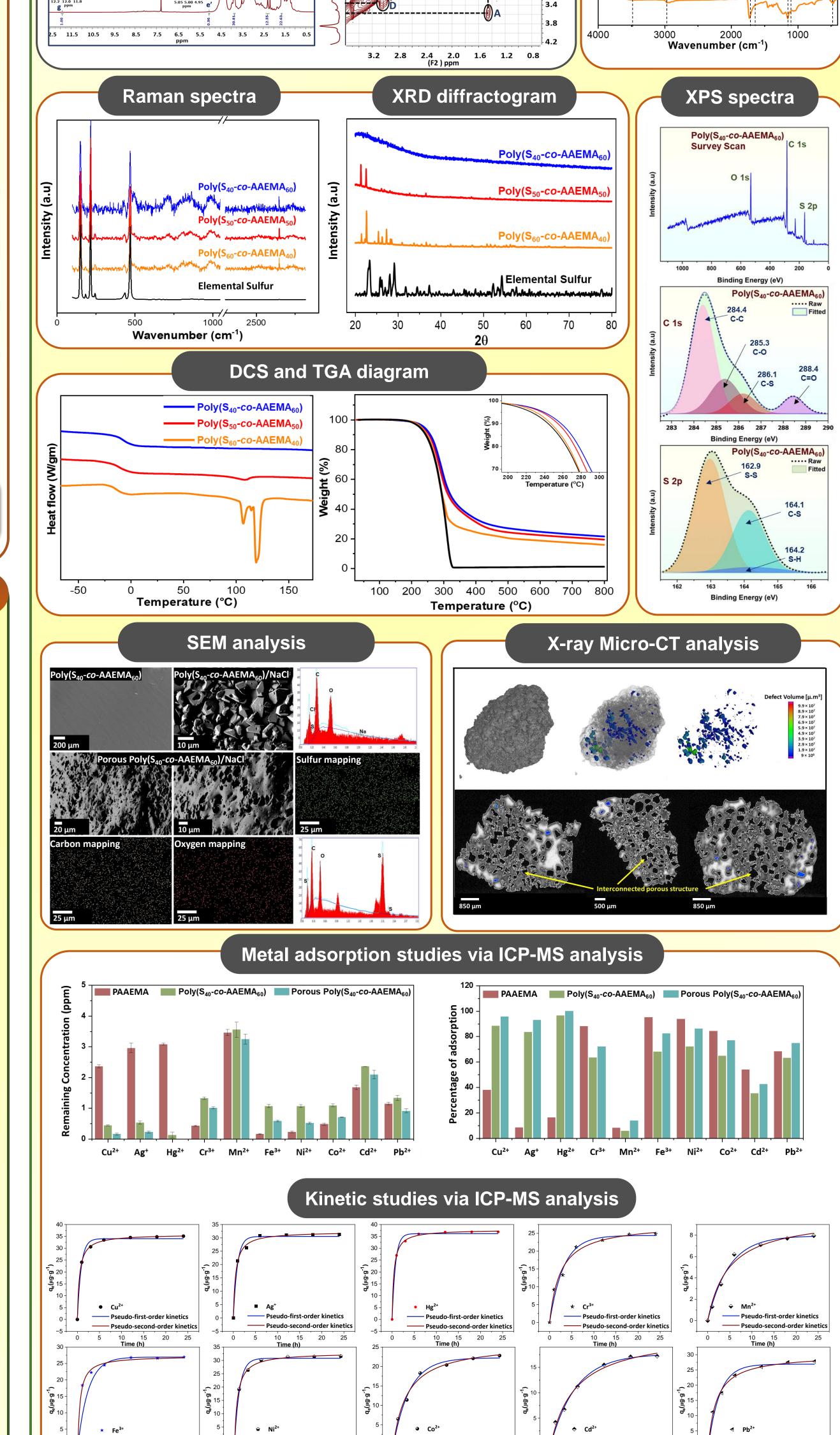
PAAEMA

(A)

(C)

(D)

(E)



RESULTS

¹H NMR of Poly(S₄₀-co-AAEMA₆₀)

CONCLUSION

- Porous polysulfide adsorbents bearing β-diketone functional groups were synthesized through inverse vulcanization between acetoacetoxy ethyl methacrylate and sulfur.
- The synergistic interplay between the thiol functional groups, polysulfide loops, and the strong binding affinity of the β-diketone moiety and hydroxyl group, coupled with the polymer's well-defined porous structure, collectively enhanced its adsorption capacity towards heavy metal ions.

REFERENCES

- [1] Chung, W.J., Griebel, J.J., Kim, E.T., Yoon, H., Simmonds, A.G., Ji, H.J., Dirlam, P.T., Glass, R.S., Wie, J.J., Nguyen, N.A. and Guralnick, B.W., 2013. The use of elemental sulfur as an alternative feedstock for polymeric materials Nat. Chem, 5(6), pp.518-524.
- [2] Alex, A., Kalita, U., Bhowmik, T., Singha, N.K. and Choudhury, S., 2025. Inversely Vulcanized Porous Copolymer Monolith for Efficient Removal of Metal Ions from Water. ACS Appl. Mater. Interfaces 2025, *17, 20, 30029–30043.*

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