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Designing 2,6-bis(1,2,3-triazol-4-yl) pyridine (BTP) Appended Self-healable Zn(II)-metallopolymers

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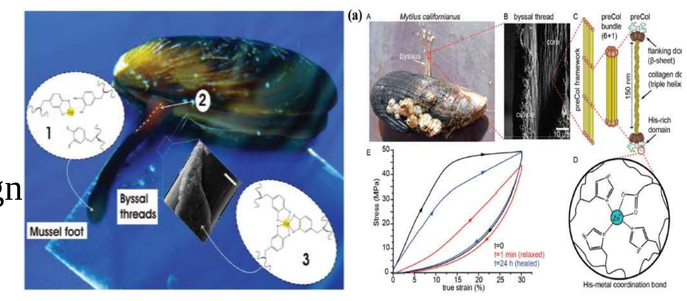
Abstract

Artificial self-healing materials enhance durability and longevity, drawing inspiration from mussel byssal threads. Here, a hexyl substituted vinyl functionalized 2,6-bis(1,2,3-triazol-4-yl)pyridine (BTP) monomer was synthesized and copolymerized with alkyl acrylates *via* RAFT polymerization. The resulting polymer was cross-linked with zinc metal ions to form a thin film that self-heals within 12 hours below 100 °C, with tunable properties based on the metal salt used. The metallopolymer also efficiently captures iodine, highlighting its potential for protective coatings, smart materials, and radioactive waste management.

Introduction

- Inspired by the autonomous repair in mussel byssal threads (natural phenomena), self-healing has been applied to metallopolymers for advanced use in electronics, coatings, and biomedical fields.[1]
- Intrinsic self-healing systems; rely on dynamic bonds (*e.g.* reversible covalent or noncovalent metal–ligand interactions) enables repeatable healing under mild conditions but requires more intricate design than single use extrinsic systems.[2]



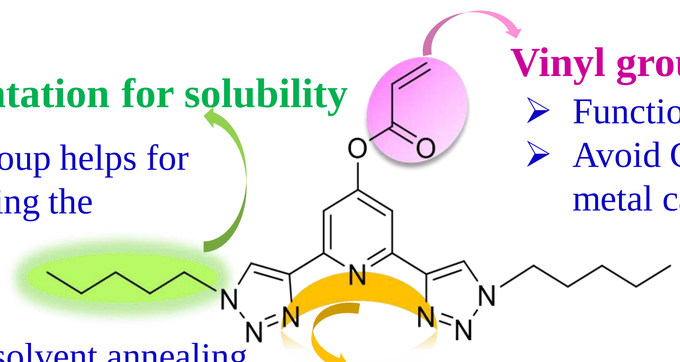
- Metal–ligand coordination, with its tunable stability and reversibility, provides a versatile platform for designing multifunctional self-healing polymers.[2]
- Integrating these features into polymeric thin films for applications such as iodine capture in nuclear waste management and environmental protection is highly promising,[3] as the rational design of such multifunctional systems remains largely unexplored.

Objective

- Strategically designing and synthesis of hexyl substituted vinyl functionalized 2,6-bis(1,2,3-triazol-4-yl) pyridine (HexVBTP) monomer.

Implementation for solubility

- Hexyl group helps for solubilizing the polymer
- Enables solvent annealing for improved application processability.



Vinyl group functionalization

- Functional group conversion
- Avoid C-C coupling using metal catalyst

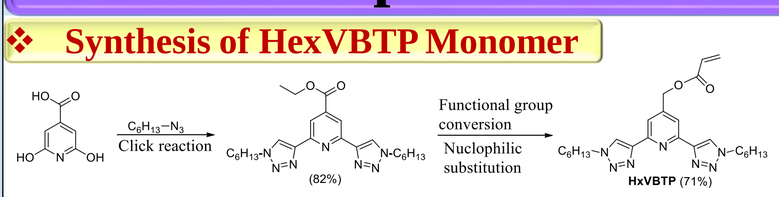
Chelating site for metal ion complexation

- Exclusive binding with metal ions
- Electron rich triazole nitrogens: advantageous for cooperative interaction with Lewis acid *i.e.* iodine

- Random copolymerization with alkyl acrylates via reversible addition fragmentation chain transfer (RAFT) polymerization to get a range of polymer.
- Crosslinking the polymers with targeted metal ion and systematic study of thermally induced self-healing and iodine capture.

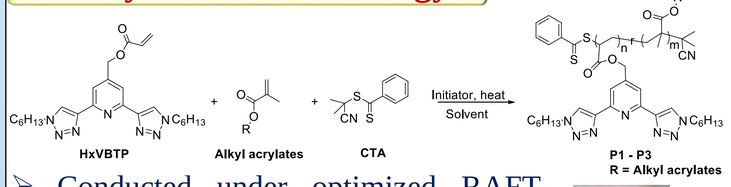
Experimental section

Synthesis of HexVBTP Monomer

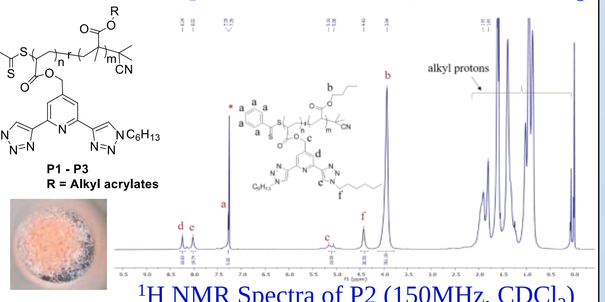


^{1}H NMR Spectra of HexVBTP (400MHz, $CDCl_3$)

Polymerization Strategy

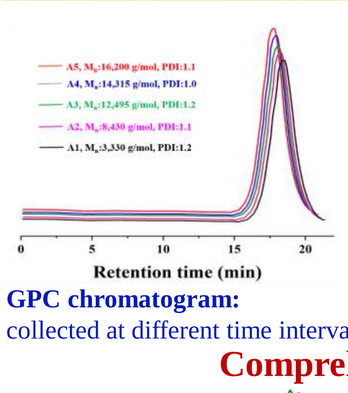


- Conducted under optimized RAFT polymerization conditions to obtain well-defined polymers

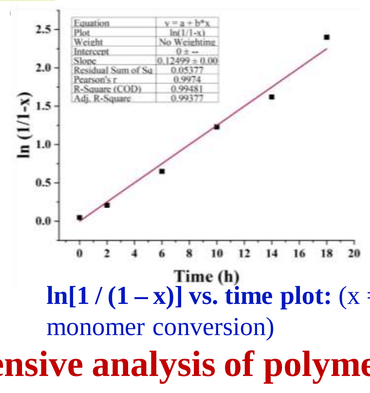


^{1}H NMR Spectra of P2 (150MHz, $CDCl_3$)

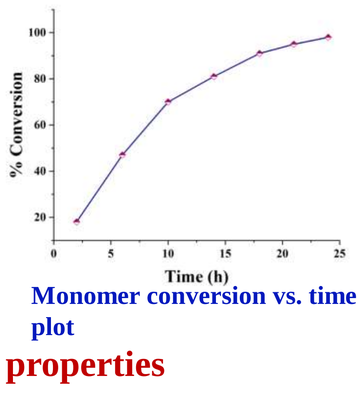
Polymerization kinetics



GPC chromatogram: collected at different time intervals

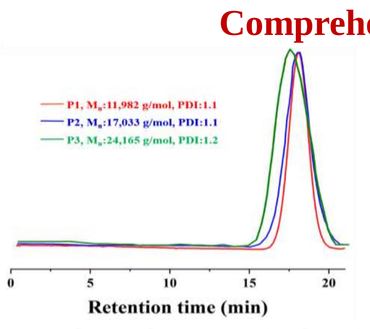


ln[1 / (1 – x)] vs. time plot: (x = monomer conversion)

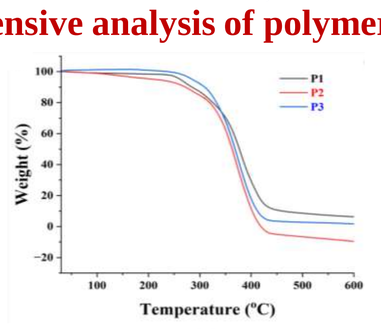


Monomer conversion vs. time plot

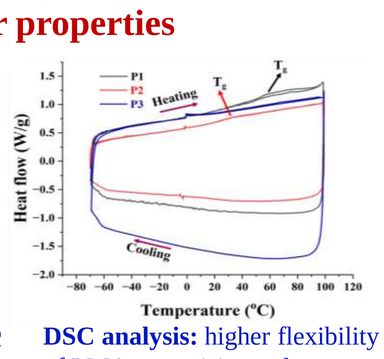
Comprehensive analysis of polymer properties



GPC data: Eluent THF (1ml/min)

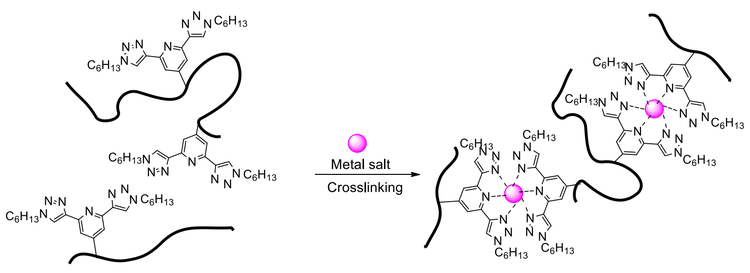


TGA curve: stable up to ~ 250 °C



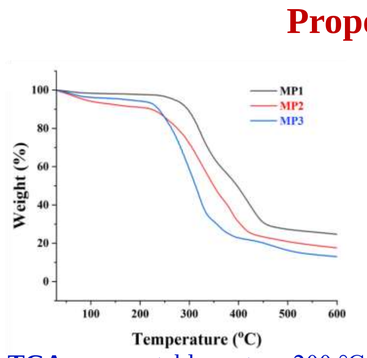
DSC analysis: higher flexibility of LMA comprising polymer

Cross-linking of polymers

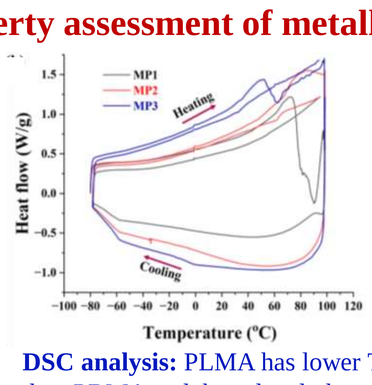


- Cross-linking of the btp-appended polymer using 1:2 metal ion:btp ratio.

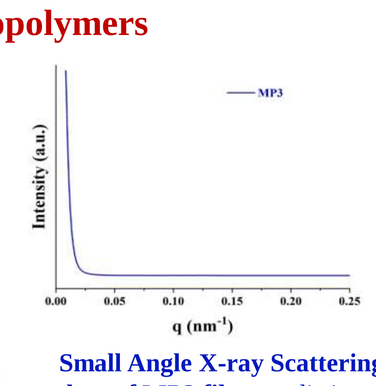
Property assessment of metallopolymers



TGA curve: stable up to ~ 200 °C



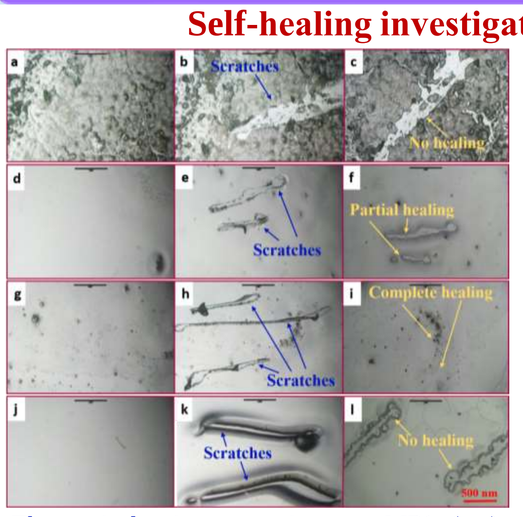
DSC analysis: PLMA has lower T_g than PBMA and broad endothermic peak at higher temperature



Small Angle X-ray Scattering data of MP3 film: no distinct scattering peaks

Results and Discussion

Self-healing investigation of metallopolymers' thin-film



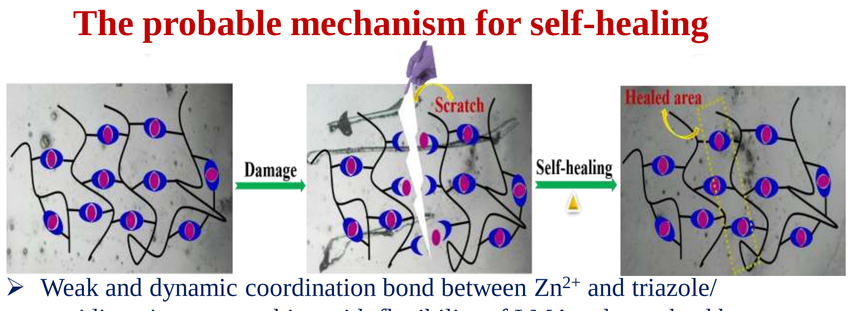
The optical microscopy images; MP1 (a-c), MP2 (d-f), MP3 (g-i), P3 (j-l) respectively

Polymer	Metallo polymer	Metal salt	Self-healing (temperature / time)	Polymer	Metallo polymer	Metal salt	Self-healing (temperature / time)
P1	MP1	$ZnCl_2.2H_2O$	No-healing	P3	MP11	$Zn(OTf)_2$	70°C/12 h
P2	MP2	$ZnCl_2.2H_2O$	120°C/18 h	P3	MP12	$Zn(OAc)_2.2H_2O$	No-healing
P3	MP3	$ZnCl_2.2H_2O$	70°C/12 h	P3	MP13	$ZnSO_4.7H_2O$	100°C/12 h
P2	MP4	$Zn(OTf)_2$	No-healing	P3	MP14	$FeCl_2.4H_2O$	No-healing
P2	MP5	$Zn(OAc)_2.2H_2O$	No-healing	P3	MP15	$NiCl_2.6H_2O$	No-healing
P2	MP6	$ZnSO_4.7H_2O$	120°C/20 h	P3	MP16	$CoCl_2.6H_2O$	No-healing
P2	MP7	$FeCl_2.4H_2O$	No-healing	P3	MP17	$Mn(OAc)_2.H_2O$	No-healing
P2	MP8	$NiCl_2.6H_2O$	No-healing	P1	MP18	$Zn(OTf)_2$	No-healing
P2	MP9	$CoCl_2.6H_2O$	No-healing	P1	MP19	$Zn(OAc)_2.2H_2O$	No-healing
P2	MP10	$Mn(OAc)_2.H_2O$	No-healing	P1	MP20	$ZnSO_4.7H_2O$	No-healing

Self-healing results overview for metallopolymers: MP1–MP20

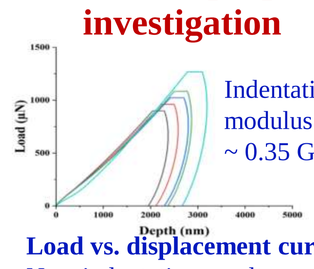
- **The best self-healing observed for MP3 thin-film**

The probable mechanism for self-healing



- Weak and dynamic coordination bond between Zn^{2+} and triazole/ pyridine nitrogen combine with flexibility of LMA polymer backbone

Mechanical property investigation

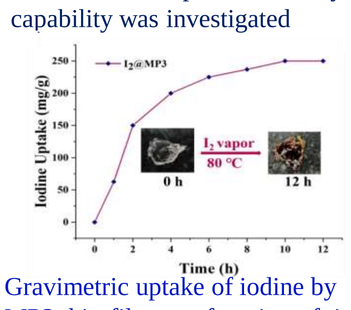


Indentation modulus: ~ 0.35 GPa

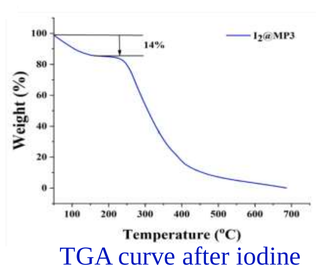
Load vs. displacement curve: Nanoindentation result

Iodine capture study

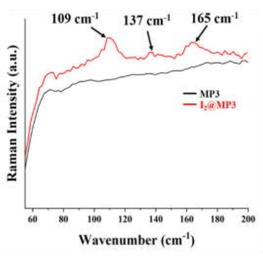
To enhance the practical utility of self-healing metallopolymers, the self-helable metallopolymers' iodine adsorption capability was investigated



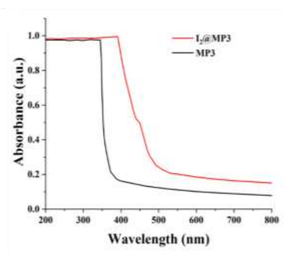
Gravimetric uptake of iodine by MP3 thin-film as a function of time



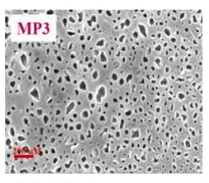
TGA curve after iodine adsorption



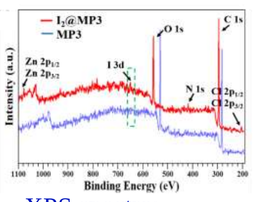
Raman spectra



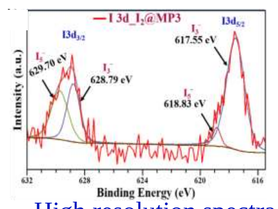
UV absorption spectra



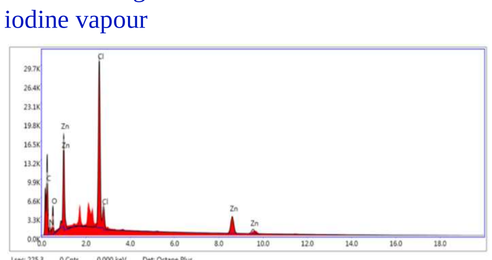
FESEM images of MP3 film before and after exposure to iodine vapour



XPS spectra: full survey scan

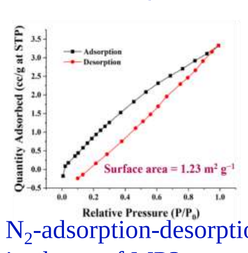


High resolution spectra for I 3d

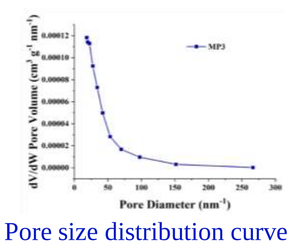


Uniform distribution of iodine along with other elements

EDX analysis of iodine captured MP3 thin-film



N_2-adsorption-desorption isotherm of MP3



Pore size distribution curve for MP3 using BJH method

References

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- Dzhardimalieva, G. I.; Yadav, B. C.; Singh, S.; Uflyand, *Dalt. Trans.* **2020,** *49* (10), 3042–3087
- Fajal, S.; W.; Torris, A.; Majumder, D.; Let, S.; Sen, A.; Kanheerampockil, F.; Shirolkar, M. M.; Ghosh, S. K. *Nat. Commun.* **2024**, *15* (1), 1278
- Mondal, C.; Behera, C. K.; Patra, S. K., Dual-Functional Zn(II)-Metallopolymers with Thermally Induced Self-Healing and Iodine Capture Capability (*Manuscript to be submitted*)

Conclusion

- Developed a dual-functional Zn(II)-coordinated btp-based self-healable metallopolymers thin-film coating.
- Combines autonomous self-healing with efficient iodine capture in a single material and those two functions operate independently, ensuring robust and versatile performance.
- We developed a thermally activated self-healing coating capable of toxic iodine capture. Promising for applications in protective films, environmental cleanup, and smart materials.
- Depth mechanistic studies of the healing process and design tuning to expand the functionality of the self-healable polymers are underway.

Acknowledgment

- IIT Kharagpur for funding and research facility
- CRF IIT Kharagpur
- SERB, India for project grant