Terpene-Based Thiol–Ene PolyHIPEs: Sustainable Routes to Tunable Porous Polymer Networks

Amadeja Koler[1], Peter Krajnc[1]
[1] Faculty of Chemistry and Chemical Engineering, University of Maribor, Maribor, Slovenia

In the pursuit of sustainable alternatives to fossil-derived polymers, terpenes have emerged as a promising class of renewable, bio-based monomers.[1,2] These naturally occurring hydrocarbons—found predominantly in plants, especially in essential oils—exhibit considerable structural diversity and functional group reactivity, making them attractive candidates for the synthesis of advanced polymeric materials.

In this study, porous polymer networks were synthesized by thiol–ene photopolymerization using terpene myrcene, a multifunctional thiol (trimethylolpropane tris(3-mercaptopropionate)) and ethylene glycol dimethacrylate (EGDMA). High internal phase emulsions (HIPEs)[3] were used as templates and allowed the formation of highly porous polymers (polyHIPEs[4,5]) with a porosity of up to 80%. By systematically varying the terpene content (9–40 mol%) and the ratio of thiol to alkene functional groups, the resulting polymer morphology could be precisely controlled. Lower terpene concentrations (10-20 mol%) in combination with an excess of alkene functional groups led to the formation of well-defined, open-cell polyHIPE structures with interconnected pores. In contrast, a higher terpene content (40 mol%) and a stoichiometric thiol:alkene ratio of 1:1 promoted the formation of bicontinuous morphologies.
The materials were characterized by scanning electron microscopy (SEM) for morphology analysis and elemental analysis to evaluate polymerization efficiency. The surface area was determined by nitrogen adsorption/desorption using the Brunauer–Emmett–Teller (BET) method.
A novel approach using thiol–ene polymerization for the synthesis of myrcene-based polyHIPE materials is presented, marking a significant departure from the conventional free-radical polymerization methods commonly used for polyHIPE synthesis. Thiolene polymerization is particularly advantageous for polyHIPEs as it offers superior structural uniformity, improved mechanical properties and the ability to precisely modulate the chemical and physical properties of the material. The results highlight the potential of terpene-based monomers in the development of tunable, porous polymeric materials and demonstrate their applicability in areas such as separation, catalysis and biomedical engineering.

Keywords: Thiol-ene polymerization, terpene, myrcene, polyHIPEs,

References

[1] F. Della Monica, A.W. Kleij, From terpenes to sustainable and functional polymers, *Polym. Chem.* **2020**, 11, 5109–5127.
[2] M.E.G. Mosquera, G. Jim, V. Tabernero, J. Vinueza-vaca, C. Garc, K. Kosalkov, A. Sola-landa, C. Acosta, R. Alonso, M.Á. Valera, Terpenes and Terpenoids : Building Blocks to Produce Biopolymers, *Sustain. Chem.* **2021**, 2, 467–492.
[3] N.R. Cameron, High internal phase emulsion templating as a route to well-defined porous polymers, *Polymer.* **2005**, 46, 1439–1449.
[4] I. Pulko, P. Krajnc, High Internal Phase Emulsion Templating – A Path To Hierarchically Porous Functional Polymers, *Macromol. Rapid Commun.* **2012**, 33, 1731–1746.
[5] I. Pulko, P. Krajnc, Porous Polymer Monoliths by Emulsion Templating, *Encycl. Polym. Sci. Technol.* **2017**, 1–28.