Bio-Based Hierarchically Porous Polymers from Terpenes and Terpenoid Acrylates via High Internal Phase Emulsion Templating

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The increasing demand for sustainable alternatives to fossil fuel-derived polymers has spurred interest in bio-based monomers, particularly terpenes and terpenoids, due to their natural abundance and inherent polymerisable functionalities [1],[2]. In this research, two complementary approaches were employed to develop hierarchically porous polymers (polyHIPEs) using terpene-based monomers via high internal phase emulsion (HIPE) templating. In the first part of the study, the terpenoids tetrahydrogeraniol, citronellol, and nopol were modified by using acryloyl chloride, resulting in the synthesis of terpenoid acrylates. These bio-derived acrylates served as the organic (monomer) phase in the formulation of HIPEs containing an 85% aqueous phase. The acrylate terpenoids in the organic phase were crosslinked with trimethylolpropane triacrylate (TMPTA) to form the polyHIPEs. A crosslinking degree of 5 and 10 mol% was used to investigate the feasibility of polyHIPE synthesis. While both crosslinking degrees facilitated the formation of polymers, only the 10 mol% systems exhibited the characteristic interconnected porous morphology. The primary pore diameters for tetrahydrogeraniol acrylate and citronellyl acrylate-based polyHIPEs were measured at 15.6 and 16.5 µm, respectively, whereas nopol acrylate-based polyHIPEs displayed a smaller average pore size of 5.6 µm. The second part of the study focused on the direct polymerization of the terpenes limonene, carvone, and myrcene, combined with multifunctional acrylate comonomers – TMPTA and pentaerythritol tetraacrylate (PETA). This strategy enabled the successful synthesis of poly(limonene-co-TMPTA), poly(limonene-co-PETA), poly(carvone-co-TMPTA), poly(carvone-co-PETA), poly(myrcene-co-TMPTA), and poly(myrcene-co-PETA) polyHIPEs. The terpene and acrylate ratios were varied to study the incorporation of the terpenes into the polyHIPE and the effects on the morphological properties. While the synthesis of terpene-based polyHIPEs was successful, the degree of limonene and carvone incorporation reduces when the content thereof in the HIPE mixture is increased. The obtained polyHIPEs exhibited primary pore sizes between 5.51 and 11.63 µm, and specific surface areas ranging from 2.7 $m^2\ g^{-1}$ to approximately 300 $m^2\ g^{-1}$. This combined study demonstrates the versatility of both terpenoid acrylates and unmodified terpenes as promising, renewable building blocks for the production of hierarchically porous polymers. Moreover, it highlights the potential of limonene and carvone in the synthesis of polyHIPEs, reinforcing the role of plant-derived monomers in the development of sustainable polymeric materials.

Keywords: Terpenes, Terpenoids, PolyHIPEs, Bio-sourced monomers, Porous polymers, High internal phase emulsions

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