



סמינר SEMINAR

The Influence of Polymerization Mechanism and Locus of Initiation upon Emulsion-Templated Porous Polymers

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PolyHIPEs are highly porous polymer monoliths synthesized through the polymerization of monomers in the external phases of high internal phase emulsions (HIPEs), emulsions with over 74% internal phase. Typically, polyHIPEs are crosslinked and synthesized using a conventional free radical polymerization (FRP) mechanism in surfactant-stabilized water-in-oil (w/o) HIPEs. When the initiator is dissolved in the internal aqueous phase a more closed-cell porous structure can result than when the initiator is dissolved, with the monomer, in the external organic phase. PolyHIPEs can also be synthesized using a “living” controlled radical polymerization (CRP) such as atom transfer radical polymerization (ATRP) or reversible addition-fragmentation chain transfer (RAFT) polymerization. The main advantage of CRPs is the narrow chain size distribution, for linear polymers, and the relatively homogeneous network structure, for crosslinked polymers.

The objectives of this research were to investigate the synthesis parameters such as the locus of initiation, the HIPE stabilization method, and the polymerization mechanism, all of which are known to affect the structure and properties of polyHIPEs, and to describe the synthesis-structure-property relationships. The polyHIPEs investigated were based on either styrene (St) or stearyl acrylate (A18) both crosslinked using divinylbenzene (DVB) as a crosslinking comonomer. The porous structures were characterized using scanning electron microscopy, the thermal properties and crystallinity using differential scanning calorimetry, the mechanical behavior using dynamic mechanical thermal analysis and uniaxial compression tests.

The polymerization mechanism had a profound effect upon the properties of the polyHIPEs. CRP reduced the void size to around 15 μm from around 35 μm for FRP. RAFT produced lower moduli and more elastomeric behaviors which could result from a more homogeneous network structure that imparts enhanced chain mobility. The existence of a more homogeneous network structure is also reflected in the tan peaks (narrower, higher peak values, and reductions of 30 °C in the peak temperatures, reflecting reductions in the T_{gs}). RAFT polymerized St-based polyHIPEs exhibited extraordinarily high solvent absorption (a toluene uptake of ~35 g/g compared to ~10 g/g for FRP) and RAFT polymerized A18-based polyHIPEs exhibited extraordinarily high crystallinities (e.g. ~50 % compared to ~25 % for FRP). PolyHIPEs based on nanoparticle-stabilized Pickering HIPEs (both FRP and RAFT), which had more closed-cell structures and larger voids, exhibited higher and narrower tan peak values and lower moduli, indicating a smaller extent of crosslinking and a higher chain mobility than in polyHIPEs from surfactant-stabilized HIPEs. The variation of the RAFT agent to initiator ratio was used fine-tune the macromolecular structure and achieve the desired mechanical properties. This research has demonstrated that RAFT polymerization can be used to achieve the same advantageous properties that can result from reducing the content of crosslinking comonomer, but without the associated negative impact upon the polyHIPE's mechanical integrity.

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