Initiator-Free Synthesis of Acrylic Acid-Based Hydrogels

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Polyacrylic acid (PAA)-based hydrogels are of growing interest for biomedical and pharmaceutical applications due to their high water absorption capacity and tuneable mechanical properties. Conventional synthesis typically employs a free-radical initiator, such as sodium persulfate, to trigger polymerization. However, concerns regarding residual initiators and chemical contaminants have motivated the exploration of cleaner synthesis pathways. In this work, a modified procedure is presented in which the hydrogel is synthesized without any added initiator, relying solely on thermal activation at 72 °C and N,N′-methylenebisacrylamide (MBA) as a crosslinker.

The synthesis was conducted in a calorimetrically controlled environment (MT EasyMax 102, equipped with a pH probe), where partially neutralized acrylic acid was reacted in the presence of MBA. Despite the absence of an external initiator, gelation successfully occurred. The resulting hydrogel was highly structured, with a dense network formed by short acrylic acid chains crosslinked by MBA. This structure resulted in extremely high viscosity and a swelling capacity (approximately ten times greater than that of hydrogels synthesized via initiated polymerization).

However, incomplete conversion of acrylic acid was observed under these conditions, necessitating post-synthesis dialysis to remove unreacted monomer. After purification, the hydrogel retained its integrity and exhibited rheological properties comparable to those of traditional hydrogels synthesized with an initiator—yet notably free of residual contaminants.

This initiator-free, thermally activated method offers a promising alternative for the production of clean, highly absorbent hydrogels suitable for sensitive applications such as topical drug delivery. Further optimization of reaction conditions is ongoing to improve monomer conversion while maintaining the advantageous structural and functional properties of the resulting material.