GRADIENT COPOLYMERIZATION-INDUCED SELF-ASSEMBLY: FROM MONOMERS TO NANOPARTICLES IN A SINGLE STEP

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Polymerization-induced self-assembly (PISA) has established itself as a versatile strategy for the one-pot fabrication of polymer nanoparticles, enabling high solid contents and minimizing the need for extensive post-polymerization processing.[1] Through the in situ generation of amphiphilic copolymers, PISA efficiently produces stable nanostructures with controllable morphologies and tailored properties.

In this work, we explore the integration of PISA with gradient copolymerization to achieve the single-step synthesis of amphiphilic nanoparticles. Leveraging monomers with contrasting reactivities and solubility profiles, we steer the formation of gradient copolymer architectures that spontaneously assemble into stable nanoparticle dispersions. Three systems are highlighted. First, an aqueous gradient PISA approach yields highly responsive ^{19}F MRI nanotracers from *N,N*-(2,2,2-trifluoroethyl)acrylamide and hydrophilic poly(ethylene glycol) methyl ether methacrylate, exhibiting enhanced relaxivity and strong potential for diagnostic imaging.[2] Second, a RAFT/MADIX-mediated statistical emulsion copolymerization of *N,N*-dimethylacrylamide and vinyl acetate results in surfactant-free latex nanoparticles, where the emulsion conditions significantly boost polymerization rates and impact morphology, leading to block-like structures despite a gradient-feed strategy. Finally, cationic ring-opening polymerization in dodecane enables the synthesis of poly(2-oxazoline) nanoparticles across both block and gradient configurations.[3] This CROPISA method also facilitates formulations suitable for applications such as Pickering emulsion stabilization. Collectively, these examples showcase the versatility of gradient copolymerization-induced self-assembly, offering efficient pathways to sophisticated polymer nanomaterials for a wide range of applications.

References:

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