

Hollow Polymeric Micro/Nanostructures - Synthesis, Morphology and Function

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The development of reliable synthesis routes to polymeric nanostructures of well-defined composition, morphology and function is of scientific importance and technological interest. The application and potential application of hollow polymeric micro- and nanostructures as nanoreactors, membranes and ultra-low dielectric constant and photonic materials, and in diagnostics, encapsulation, controlled release and other stimuli-responsive systems have been actively explored. The generation of functional hollow polymeric nanostructures, hollow nanospheres and nanotubes in particular, can be achieved through direct and template-directed synthesis, core-shell precursors, and self-assembly of copolymers and polymer conjugates, as well as from dendrimers. The ability to prepare precursor macromolecules of well-defined structure and architecture has been substantially enhanced by recent advances in controlled radical polymerizations and 'click' reactions.

Earlier interest of ours on polyimides were centered on the preparation of nanoporous polyimides ultra-low dielectric constant materials for microelectronics packaging and stimuli-responsive microporous membranes. Thermally-initiated controlled radical graft polymerization of thermolabile monomers from ozone-pretreated poly(amic acid)s or fluorinated poly(amic acid)s via a reversible addition-fragmentation chain-transfer (RAFT)-mediated process were carried out. Nanoporous ultra-low dielectric constant polyimide films were prepared by thermal imidization of the polyimide graft copolymers, followed by thermal decomposition of the side chains in air. The nanoporous polyimide films obtained from the RAFT-mediated graft copolymers had well-preserved polyimide backbones, porosity in the range of 5-20%, and pore size in the range of 30-50 nm [Figure 1].¹ Graft polymerization of stimuli-responsive monomers from fluorinated polyimides has also been carried out by the RAFT-mediated process. Microfiltration membranes can be fabricated from the polyimide comb copolymers by phase inversion in aqueous media. The surface composition, pore size, and morphology of the membrane, as well as flux/permeability of the membranes, can be controlled by the size and nature of the graft chains. A simple method for the chloromethylation of polyimides has also been developed for the atom transfer radical polymerization (ATRP) from polyimide backbones and surfaces.²

Combination of sol-gel reaction with distillation-precipitation polymerization, controlled radical polymerizations (ATRP and RAFT polymerization) and/or 'click' reactions (alkyne-azide and thiol-ene/yne/para-fluorine 'click' chemistry) allows the design and preparation of a range of functional hollow polymeric, inorganic and polymer-inorganic hybrid micro- and nanostructures.³ These micro- and nanostructures include stimuli-responsive and functional (i) hollow polymeric microspheres and concentric hollow silica microspheres, (ii) double-walled concentric hollow polymeric microspheres, (iii) concentric hollow nanospheres of mesoporous silica shell and titania core, (iv) core-double shell microspheres, (v) hybrid nanorattles of catalytic metal core and polymer shell, (vi) hairy hollow microspheres of fluorescent shell and polymer brushes, (vii) binary polymer brushes on silica@polymer hybrid nanospheres and hollow polymer nanospheres, (viii) hairy hybrid microrattles of metal nanocore with functional polymer shell and brushes [Figure 2] and (ix) jellyfish-shaped amphiphilic block-graft copolymer [Figure 3],⁴⁻⁶ as well as (x) a series of surface-functionalized and surface-functionalizable microporous membranes.⁷ Figure 4 illustrates schematically the preparation of surface-functionalized and surface-functionalizable microporous poly(vinylidene fluoride) (PVDF) membranes via combined 'grafting from' and 'grafting to' approaches.⁸

References

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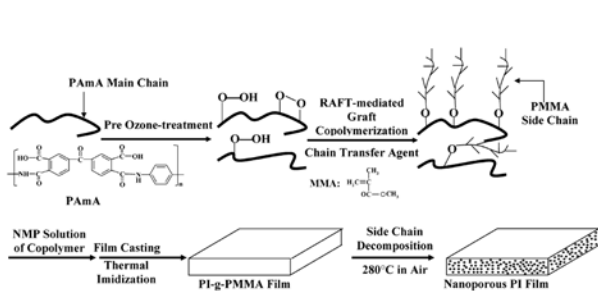


Figure 1. Thermally induced graft copolymerization of MMA from the ozone-preactivated PAmA backbone in the RAFT-mediated process and the preparation of nan porous PI film.

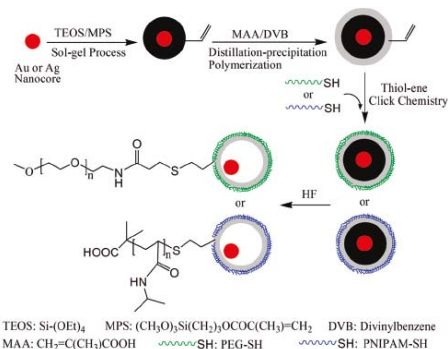


Figure 2. Synthesis of hairy metal@air@polymer hybrid microrattles with a metal nanocore, a cross-linked polymer shell, and functional polymers brushes on the exterior surface.

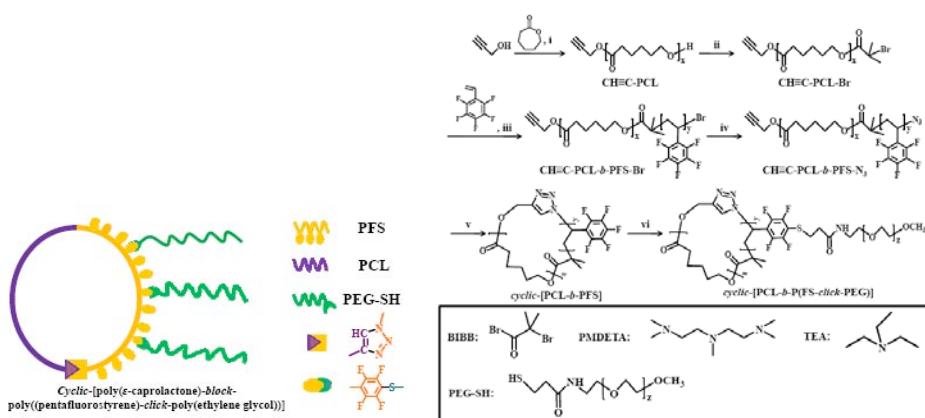


Figure 3. Synthetic route of the jellyfish-shaped *cyclic*-[poly(3-caprolactone)-*block*-poly((pentafluorostyrene)-*graft*-poly(ethylene glycol))], or *cyclic*-[PCL-*b*-P(FS-*g*-PEG)], copolymer.

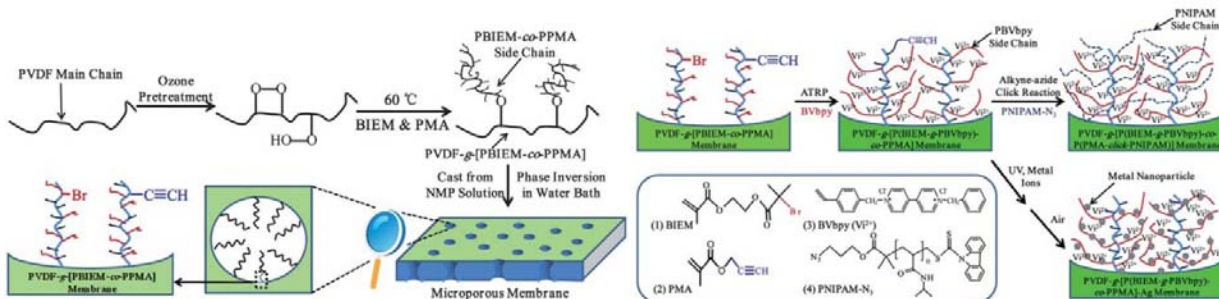


Figure 4. Preparation of PVDF-*g*-[PBIEM-*co*-PPMA] membrane with dual functionalities on the surface by phase inversion, preparation of the redox-sensitive PVDF-*g*-[P(BIEM-*g*-PBVbpy)-*co*-PPMA] membranes *via* surface-initiated ATRP of BVbpy from the PVDF-*g*-[PBIEM-*co*-PPMA] membrane, preparation of the redox- and temperature-sensitive PVDF-*g*-[P(BIEM-*g*-PBVbpy)-*co*-P(PMA-*click*-PNIPAM)] membrane *via* surface-initiated alkyne-azide click reaction of PNIPAM- N_3 on the PVDF-*g*-[P(BIEM-*g*-PBVbpy)-*co*-PPMA] membrane, and deposition of metal nanoparticles (Ag) on the PVDF-*g*-[P(BIEM-*g*-PBVbpy)-*co*-PPMA] membrane.