



Hollow polymeric nanostructures—Synthesis, morphology and function

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ABSTRACT

The development of reliable synthetic routes to polymeric nanostructures of well-defined composition, morphology and function is of scientific importance and technological interest. 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. The application and potential application of the hollow polymeric nanospheres and nanotubes as nanoreactors, and in diagnostics, encapsulation, controlled release, and other stimuli-responsive systems are also described.

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Abbreviations: ABS, poly(acrylonitrile-butadiene-styrene); AN, acrylonitrile; ATRP, atom transfer radical polymerization; BA, butyl acrylate; BDMA, *N,N*-dimethylbenzylamine; BIEE, 1,2-bis(2'-idoethoxy)ethane; BMAOE, 1,2-bis(methacryloyloxy) ethane; BzMA, benzyl methacrylate; CEMA, 2-cinnamoyl ethyl methacrylate; CPPy, acid-functionalized PPy; DdexMA, methacrylated *N,N*-diethylaminoethyl dextran; DMAEMA, 2-(dimethylamino)ethyl methacrylate; DMPVPML, bis(4-(dimethylamino)phenyl)(4-vinylphenyl)-methyl leucohydroxide; DPPC, 1,2-dipalmitoyl-sn-glycero-3-phosphocholine; DPTAP, dipalmitoyl-3-trimethylammonium-propane; DSM, dynamic swelling method; DTCM, 2-(*N,N*-diethyldithiocarbamyl)ethyl methacrylate; DVB, divinylbenzene; EGDEA, ethylene glycol diethacrylate; FDA, fluorescein diacetate; FET, field-effect transistor; FPEEK, poly(ether ethyl ketone); H-bonding, hydrogen bonding; HF, hydrofluoric acid; HMAAM, *n*-hydroxymethylacrylamide; Io, ionene; LbL, layer-by-layer; LCST, lower critical solution temperature; LFRP, living free radical polymerizations; MA, methyl acrylate; MAAC, methacrylic acid; MAzo4444, 4-butyloxy-2'-(4-(methacryloyloxy) butoxy)-4'-(4-butyloxy-benzoyloxy)azobenzene; MAH, maleic anhydride; MALOB, 1-methacryloyloxybutane; MBA, methylene bisacrylamide; MF, melamine formaldehyde; MHS, 1,1-dimethyl-2,2-dihexyldisilene; MMA, methyl methacrylate; MNDPAD, *N*-methyl-2-nitro-diphenylamine-4-diazo resin; MOPTMS, methacryloxypropyltrimethoxysilane; MPFR, *m*-methylphenol-formaldehyde resin; NCA, *N*-carboxyanhydride; NIPAm, *N*-isopropylacrylamide; NMRRP, nitroxide-mediated radical polymerization; oAdGP, 6-O-acryloyl- α -D-galactopyranose; P(TCE-10-HD), poly(2,2,2-trichloroethanol 10-hydroxyldecylate); PA444, poly((4'-acryloyl-oxybutyl)2,5-bis(4'-butyloxybenoyloxy)benzoate); PAAC, poly(acrylic acid); PAAE, poly(amic acid) ester; PAEMA, poly(2-aminoethyl methacrylate); PAH, poly(allylamine hydrochloride); PAMA, poly(alkyl methacrylate); PAMPS, poly(sodium 2-acrylamido-2-methylpropanesulfonate); PAN, polyacrylonitrile; PANi, polyaniline; PAPMAHC, poly(*n*-(3-aminopropyl)methacrylamide hydrochloride); PBA, poly(butyl acrylate); PBGLu, poly(γ -benzyl-L-glutamates); PBMA, poly(butyl methacrylate); PBzMA, poly(benzyl methacrylate); PCEMA, poly(2-cinnamoyl ethyl methacrylate); PCL, Poly(ϵ -caprolactone); PCIS, poly(4-chlorostyrene); PCMA, poly(cesium methacrylate); PDA, polydiacetylene; PDADMC, poly(diallyldimethylammonium chloride); PDEAEMA, poly(2-diethylamino)ethyl methacrylate; PDIPEMA, poly(2-diisopropylamino)ethyl methacrylate; PDMAA, poly(*N,N*-dimethylacrylamide); PDMAEMA, poly(2-dimethylamino)ethyl methacrylate; PDMS, polydimethylsiloxane; PDOPV, poly(dioctyloxyphenylenevinylene); PDPAEMA, poly(2-(diisopropylamino)ethyl methacrylate); PE, poly(ethylene); PEDOT, poly(3,4-ethylenedioxythiophene); PEI, polyethyleneimine; PEMA, poly(ethyl methacrylate); PEO, Poly(ethylene oxide);

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1. Introduction

Hollow polymeric nanostructures (HPNSs) have attracted considerable interest in recent years because of the new functionalities and unique physicochemical

properties anticipated from polymeric materials at the nanoscale. The development in HPNSs is reflected by the rapid increase in the number of scientific publications and patents in recent years. HPNSs in the size range of 1–1000 nm with spherical or cylindrical geometries

Abbreviations: PEOxM, poly(3-ethyl-3-oxetanemethanol); PEOz, poly(2-ethyl-2-oxazoline); PF, polyfluorene; PGeMA, poly(glycery methacrylate); PGlu, poly(glutamate); PGluA, poly(L-glutamic acid); PGMA, poly(glycidyl methacrylate); PHNSp, polymeric hollow nanospheres; PHNSs, polymeric hollow nanostructures; PI, polyisoprene; PIAT, polyisocyanopeptide; Plm, polyimide; Plo, Poly(ionene); PLeu, poly(L-leucine); PLGA, poly(lactide-co-glycolide); PLys, poly(L-lysine); PLysH, poly(L-lysine hydrochloride); PMA, poly(methyl acrylate); PMAAC, poly(methacrylic acid); PMAzo4444, poly(4-butyloxy-2'-(4-(methacryloyloxy) butoxy)-4'-(4-butyloxy-benoyloxy)azobenzene); PMAEPC, poly(2-(methacryloyloxy)ethyl phosphorycholine); PMAH, poly(maleic anhydride); PMF, poly(melamine formaldehyde); PMHS, poly(1,1-dimethyl-2,2-dihexyldisilene); PMMA, poly(methyl methacrylate); PMOPTMS, poly(methacryloxypropyltrimethoxysilane); PMOXA, poly(methyl oxazoline); PMPhAPHA, poly(6-[4-(methylphenyl-azo)phenoxy] hexylacrylate); PMVPI, poly(1-methyl-4-vinylpyridinium iodide); PNIPAm, poly(*N*-isopropylacrylamide); PNT, polymeric nanotubes; PoAdGP, poly(6-O-acryloyl- α -D-galactopyranose); POT, poly(o-toluidine); PPA-Ae, poly(4-ethynylbenzoyl-L-alanine methyl ester); PPFS, poly(pentafluorostyrene); PPhV, poly(*p*-phenylene vinylene); PPI, poly(propylene imine); PPO, poly(propylene oxide); PPQ, poly(phenyl quinoline); PPy, polypyrrole; PS, polystyrene; PSAAMOS, poly(sodium 2-acrylamido-2-methylpropanesulfonate); PSaMA, poly(stearyl methacrylate); PSMA, poly(soletamethacrylate) poly(solketal methacrylate); PSS, Poly(styrene sulfonate, sodium salt); PtBA, poly(*tert*-butyl acrylate); PTHF, poly(tetrahydrofuran); PVA, poly(vinyl alcohol); PVBA, poly(-vinyl benzaldehyde); PVBG, poly(6-O-(vinylbenzyl)-D-galactose); PVC, poly(vinyl chloride); PVDF, poly(vinylidene fluoride); PVP, poly(vinyl pyrrolidone); P4VP, poly(4-vinyl pyridine); PVph, poly(vinyl phenol); Py-EO12, *trans*-4-[2-[4-olig(oxyethylene)oxyphenyl]vinyl]pyridine; PYR, pyrene; RAFT, reversible addition-fragmentation chain transfer; SMA, soletamethacrylate; St, Styrene; Tba, *tert*-butyl acrylate; TEOS, tetraethoxysilicate; TESPMA, 3-(trimethoxysilyl)propyl methacrylate; TFA, trifluoroacetic; VAn, 4-vinylaniline; VBCB, 4-vinylbenzocyclobutene; vPLA, vinyl terminated polylactide; VTES, vinyltriethoxysilane; W/O/W, water/oil/water.

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