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Architecture, self-assembly and properties of well-defined hybrid polymers based on polyhedral oligomeric silsequioxane (POSS)

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ABSTRACT

Well-defined hybrid polymers based on polyhedral oligomeric silsequioxane (POSS) with a variety of architectures have been developed, including telechelic polymers, block copolymers and star-shaped polymers. The synthesis, self-assembly and properties of this kind of materials are reviewed. Well-defined POSS-containing hybrid polymers can be constructed by living polymerization techniques, such as ring-opening polymerization and living free-radical polymerization or the combination of living polymerization and coupling reactions, such as click chemistry and hydrosilylation. The self-assembly behavior of well-defined POSS-containing hybrid polymers is also described in detail. The POSS-containing hybrid polymers can self-assemble into nano-scaled aggregates in selective solvents, and form nanostructures in bulk. Some of the interesting self-assembly morphologies are remarkably different from those formed from the conventional purely organic amphiphilic polymers. Well-defined POSS-containing hybrid polymers have shown the unexpected properties, which lead to unlimited possibilities for promising applications, such as biomedicine, electronic, optical, magnetic nanodevices, sensors and stimulated catalysts. We highlight several recent examples of these applications.

Abbreviations: AFM, atomic force microscope; ATRP, atomic transfer radical polymerization; CDB, cumyl dithiobenzoate; CI-ROP, coordination/insertion ring-opening polymerization; CL, ε-caprolatone; CLSM, confocal laser scanning microscopy; CTA, chain transfer agent; CMC, critical micelle concentration; Cp-POSS, isocyanatopropyldimethylsilylcyclopentyl-POSS; DDAT, S-1-dodecyl-S′-α,α′-dimethyl-α″-acetic acid trithiocarbonate; DP, degree of polymerization; DOX, Doxorubicin; DVB, divinylbenzene; EB, ethidium bromide; EL, electroluminescence; FRET, Förster resonance energy transfer; Ib-POSS, isocyanatopropyldimethylsilylisobutyl-POSS; MA-POSS, POSS-containing methacrylate monomer; MEH-PPV, poly(2-methoxy-5-ethylhexyloxy-1,4-phenylenevinylene); NBETMS, 2-endo-3-exo-5-norbornene-2-3-dicaboxylic acid trimethyl ester; NBEPOSS, norbornene ethyl POSS monomer; NMRP, nitroxide-mediated radical polymerization; OFP, oligofluorene; PAA, poly(acrylic acid); PAS, poly(acetoxystyrene); P*t*BA, poly(*tert*-butyl acrylate); PBLG, poly(γ-benzyl-L-glutamate); PCL, poly(ε-caprolatone); PDMAEMA, poly(2-dimethylaminoethyl methacrylate); PDI, polydispersity index; PDLA, poly(D-lactide); PEG, poly(ethylene glycol); PEI, poly(ethylene imine); PEO, poly(ethylene oxide); PFO, poly(9-9-dihexyfluorenyl-2,7-diyl); PMA, poly(methacrylate); PMDETA, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine; PMMA, poly(methyl methacrylate); PNaPSS, poly(sodium 4-styrenesulfonate); PNIPAM, poly(*N*-isopropylacrylamide); PL, Photoluminescence; PLA, poly(lactic acid); PLLA, poly(L-lactide); POSS, polyhedral oligomeric silsesquioxane; POSS-PSS-POSS, POSS-containing poly(styrene-ran-sodium styrenesulfonate); POSS-Glu, POSS-containing poly(L-glutamic acid); PPO, poly(propylene oxide); PS, polystyrene; PU, polyurethane; P4VP, poly(4-vinylpyridine); RAFT, reversible addition-fragmentation chain transfer; ROMP, ring-opening metathesis polymerization; ROP, ring-opening polymerization; SBS, poly(styrene-butadiene-styrene); SEM, scanning electron microscope; $Sn(Oct)_2$, stannous 2-ethylhexanoate; TEM, transmission electron microscope; TSAXS, transmission small-angle X-ray scattering.

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Contents

1. Introduction

Considerable attention has concentrated on the preparation of organic/inorganic hybrid materials with excellent properties using nanoscale inorganically enhanced agents such as nanoparticles, clay, fullerene, carbon nanotubes, graphene and polyhedral oligomeric silsesquioxanes (POSS) [1–6]. POSS, a class of unique inorganic components with a definite nanostructure, can be introduced into polymer matrices to produce novel hybrid materials with advantageous properties [7–16]. POSS molecules have a cage-shaped three-dimensional structure with the formula $(RSiO_{1.5})_n$, $(n \geq 6)$ [17–23]. Among them, octa-silsesquioxanes ($R_8Si_8O_{12}$, T_8) have been mostly investigated; they consist of a rigid, cubic inorganic silica core with a 0.53 nm side length and eight corner organic groups. Thus, the POSS molecules demonstrate some unique characters in the construction of POSS-containing hybrid polymers, as compared to other inorganic agents. Firstly, most of other nanoscale inorganic agents have a size distribution, which often causes these inorganic agents could not to be well dispersed in hybrid polymers. Nonetheless, POSS molecules have a definite size and structure, and they can be well dispersed in hybrid polymers even on a molecular level. Secondly, the functional groups on the other inorganic nanoscale agents are ill-defined, and this means that we do the number of organic groups and their exact position on these agents. In contract, for POSS molecules, the number of organic groups is corresponding to the corner number. Moreover, these corner groups can be reactive or unreactive, which provide the POSS molecules with desired reactivity and solubility, and helps dispersing POSS molecules in hybrid polymers. For the typical POSS molecules ($R_8Si_8O_{12}$, T_8), the corner substituents can be same or different, which can be designed for the preparation of POSS-containing hybrid polymers. There are two main kinds of T_8 POSS molecules used in the preparation of POSS-containing hybrid polymers: T_8 POSS molecules bearing eight reactive or unreactive eight groups of the same kind, and those with one reactive group and seven unreactive groups (monofunctional POSS molecules). The synthesis of T_8

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