Division of Materials Chemistry
– Polymer Controlled Synthesis –

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Prof VOLLHARDT, K. Peter C. University of California, U.S.A., 20 May
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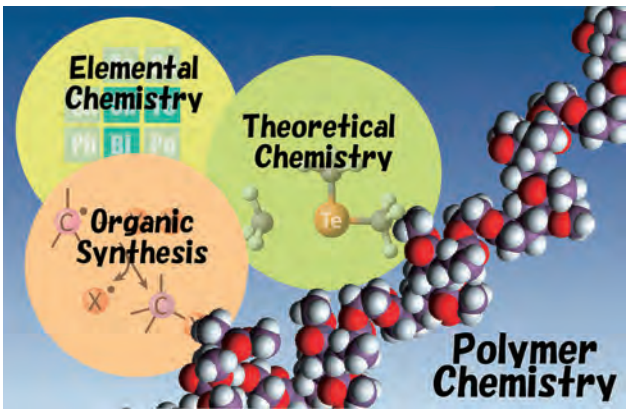
Scope of Research

Our research focuses on creation of new organic molecules which would become key reagents and materials for future science and technologies. Furthermore, we have been developing new organic and polymeric materials based on our tailor-made molecules. One such topic is the development of new living radical polymerization method utilizing heavier heteroatom compounds as controlling agents. The other topic is the synthesis of cycloparaphenylenes, hoop-shaped π-conjugated molecules, based on new synthetic strategy. We also study various polymer condensed states by both static and dynamic methods to understand the relation of physical properties and structures.



KEYWORDS

Organic Synthesis
Polymer Synthesis
Living Radical Polymerization
Polymer Properties
Conjugated π-Molecules

Selected Publications

Kayahara, E.; Iwamoto, T.; Takaya, H.; Suzuki, T.; Fujitsuka, M.; Majima, T.; Yasuda, N.; Matsuyama, N.; Seki, S.; Yamago, S., Synthesis and Physical Properties of a Ball-like Three-Dimensional π-Conjugated Molecule, *Nat. Commun.*, **4,** 2694 (2013).

Iwamoto, T.; Watanabe, Y.; Takaya, H.; Haino, T.; Yasuda, N.; Yamago, S., Size- and Orientation-Selective Encapsulation of C_{70} by Cycloparaphenylenes, *Chem. Eur. J.*, **19,** 14061-14068 (2013) (VIP article).

Yamago, S.; Yahata, Y.; Nakanishi, K.; Konishi, S.; Kayahara, E.; Nomura, A.; Goto, A.; Tsujii, Y., Synthesis of Concentrated Polymer Brushes via Surface-Initiated Organotellurium-Mediated Living Radical Polymerization (SI-TERP), *Macromolecules*, **46,** 6777-6785 (2013).

Nakamura, Y.; Arima, T.; Tomita, S.; Yamago, S., Photoinduced Swiching from Living Radical Polymerization to a Radical Coupling Reaction Mediated by Organotellurium Compounds, *J. Am. Chem. Soc.*, **134,** 5536-5539 (2012).

Tosaka, M.; Senoo, K.; Sato, K.; Noda, M.; Ohta, N., Detection of Fast and Slow Crystallization Processes in Instantaneously-Strained Samples of cis-1,4-Polyisoprene, *Polymer*, **53,** 864-872 (2012).

Synthesis and Physical Properties of a Ball-like Three-dimensional π-Conjugated Molecule

Curved π-conjugated molecules such as fullerenes and carbon nanotubes, which are characterized by the closed and three-dimensional (3D) structures, have been the subject of intensive research due to their potential applications in molecular electronics. However, basic molecular skeletons of 3D molecules are limited because of the lack of a rational and selective synthetic method by organic synthesis. We synthesized a 3D π-conjugated molecule based on the platinum-mediated assembly of four molecules of a stannylated trisubstituted benzene derivative forming a hexanuclear platinum complex with an octahedral shape, from which reductive elimination of platinum gave the target molecule. Since many supramolecular transition metal–ligand complexes with 3D cages and polyhedral structures have been synthesized by self-assembly of ligands and metals, the current assembly/reductive elimination strategy could provide a variety of new 3D π-conjugated molecules with different structures and topologies, which are challenging to obtain using conventional synthetic methods.

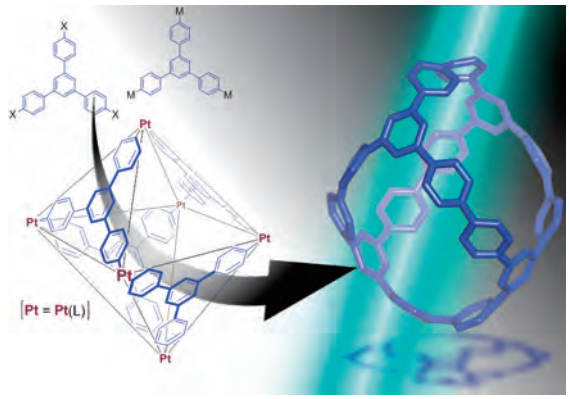


Figure 1. Synthesis of the 3D spherical π-conjugated molecule.

Synthesis of Concentrated Polymer Brushes via Surface-Initiated Organotellurium-Mediated Living Radical Polymerization

An organotellurium chain transfer agent (CTA) bearing a 2-methyltellanyl-2-methylpropionate group at one end and a triethoxysilyl group at the other was prepared and immobilized on the surface of a silicon wafer and silica nanoparticle (SiP). Surface-initiated organotellurium-mediated living radical polymerization from the immobilized CTA in the presence of nonimmobilized (free) organotellurium CTA was examined. Concentrated polymer brushes (CPBs) having surface occupancies above 0.1 were prepared by polymerization of various monomers, including styrene, methyl methacrylate, butyl acrylate, N-isopropyl acrylamide, N-vinyl pyrrolidone (NVP), and N-vinyl carbazole (NVC). All CPBs were formed in a controlled manner, with number-average molecular weights close to the theoretical values and low polydispersity indices (<1.41). Structurally well-controlled CPBs comprising unconjugated monomers, NVP and NVC, were prepared for the first time. Atomic force microscopy and transmission electron microscopy analyses of the CPBs revealed the highly stretched and anisotropic structure of the grafted polymer chain in a good solvent.

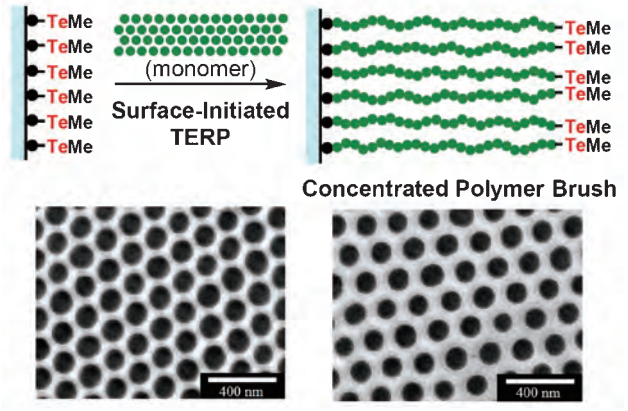


Figure 2. Surface-initiated TERP to obtain concentrated polymer brushes and TEM images of monolayers of the polystyrene-grafted silica particles.