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146. FLUORINATED HYDRAAMPHIPHILES: POLY(ETHYLENE OXIDE)-POLYLYSINE DENDRIMER HYBRIDS WITH MULTIPLE TERMINAL PERFLUOROOCYANOYL GROUPS. Toby M. Chapman, Eric J. Mahan, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260

Dendrimeric polylysine has been synthesized attached to a methylated poly(ethylene oxide) support. The terminal amines of the linear-dendrimeric hybrid can be acylated with pentafluorophenyl perfluorooctanoate giving a polymer which lowers water surface tension, demonstrates a critical micelle concentration, and solubilizes a water insoluble dye, orange OT at concentrations above the cmc. In comparing a generation 3 polymer with 8 perfluorooctanoyl groups to a generation 4 polymer with 16 terminal *t*-butyl groups, it is found that the former lowers surface tension to a greater extent, displays a smaller surface area at the air interface, and does not absorb as much of the azo dye.

147. COMBBURST POLYMERS: SYNTHESIS OF HIGH MOLECULAR WEIGHT WATER-SOLUBLE SYSTEMS. R. Yin, D. R. Swanson, and D. A. Tomalia, Michigan Molecular Institute, 1910 W. St. Andrews Rd., Midland, Michigan 48640

Well defined, water-soluble combburst polymers were prepared through a "graft upon graft" synthetic strategy. The living cationic polymerization of 2-ethyloxazoline (PEOX) was utilized to prepare both linear initiator cores and building blocks. The grafting reaction was achieved by termination of living PEOX chains with polyethyleimine (PEI) cores. Such a reaction was found to be dependent of PEOX chain length, initiator core size, grafting ratio, reaction time, and catalyst. Under optimized conditions, a series of combburst polymers with molecular weight up to  $10^7$  and polydispersity of 1.20 (G3) was synthesized. All the polymers were characterized by SEC-light scattering, NMR, and MS.

148. DEVELOPMENT OF ORGANOPHOSPHINE AND "MIXED" ORGANOPHOSPHINE-POLYAMIDOAMINE DENDRIMERS AS CATALYSTS FOR ELECTRO-CHEMICAL REDUCTION OF CO<sub>2</sub>. Alex Miedaner and Daniel L. DuBois, Basic Sciences Division, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado, 80401

By incorporating catalytically active organometallic and organophosphine complexes into dendrimers, it may be possible to create synthetic molecules that mimic enzymes in many important respects. Our laboratory has reported the synthesis and characterization of small organophosphine dendrimers containing up to 15 phosphorus atoms that catalyze the electrochemical reduction of CO<sub>2</sub> to CO. In this paper we describe attempts to extend this chemistry to polyamidoamine dendrimers containing [Pd(triphosphine)(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> complexes at their core. New triphosphine ligands with primary and secondary phosphine functional groups at the terminal and central phosphorus atoms, respectively, have been synthesized. Addition of the P-H bonds of these functional groups to allylamine substituted polyamidoamine dendrimers provide an entry into the desired class of compounds. The catalytic properties of these dendrimers will be discussed and compared to their mononuclear analogues.

149. POLYSTYRENE-POLY(PROPYLENE IMINE) DENDRIMER BLOCK COPOLYMERS: A NEW CLASS OF AMPHIPHILES. J.C.M. van Hest, C. Elissen-Román, M.W.P.L. Baars, D.A.P. Delnoye, M.H.P. van Genderen, E.W. Meijer, Laboratory of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

A new class of amphiphilic macromolecules has been synthesized by combining well-defined polystyrene (PS) with poly(propylene imine) dendrimers. Five different generations, from PS-*dendr*-NH<sub>2</sub> up to PS-*dendr*-(NH<sub>2</sub>)<sub>32</sub> were prepared in yields of 70 to 90%. Two head group modifications were performed, resulting in acid functionalized (PS-

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*dendr*-(COOH)<sub>x</sub> x=2-32) and fully quaternized (PS-*dendr*-(NMe<sub>3</sub>)<sub>x</sub> x=1-16) block copolymers in yields of 65 to 95%. Dynamic light scattering and transmission electron microscopy showed a generation dependent aggregation behavior for the PS-*dendr*-(NH<sub>2</sub>)<sub>x</sub> series, that was in qualitative agreement with the theory of Israclachvili. Amphiphilic behavior was studied at a toluene/water interface. PS-*dendr*-(NH<sub>2</sub>)<sub>x</sub> x=2-8 stabilized preferably toluene as continuous phase, PS-*dendr*-(NH<sub>2</sub>)<sub>16</sub> was equally capable of stabilizing toluene as well as water. pH-dependent amphiphilic behavior was observed for the PS-*dendr*-(COOH)<sub>x</sub> series, as well as an increased polarity of the PS-*dendr*-(NMe<sub>3</sub>)<sub>x</sub> series. These new amphiphilic block copolymers prove to be versatile structures of which amphiphilic behavior and type of aggregation can be controlled through head group variation; structures in between traditional organic surfactants and amphiphilic block copolymer, with the size of the latter and the shape of the first.

150. FORMATION OF METAL COLLOIDS IN BLOCK COPOLYMER MICELLES. M. Antonietti, E. Wenz, L. Bronstein\*, M. Seregina\*, Max Plank Institut für Kolloid- & Grenzflächenforschung, Kantstrasse 55, D-14513 Teltow-Seehof, Germany; \*Nesmeyanov Institute of Organoelement Compounds, 28 Vavilov Str., Moscow 117813, Russia

Metal colloids formation in block copolymer micelles with well chosen block length and chemical composition has been studied by the example of polystyrene/poly(4)vinylpyridine-block copolymers with varying chain lengths. In this case particle size can be controlled by the micelle size and the relative metal content. By FTIR data it was shown that dissolution of H<sub>2</sub>AuCl<sub>4</sub>·3H<sub>2</sub>O, AlCl<sub>3</sub>, Na<sub>2</sub>PdCl<sub>4</sub>, Pd(CH<sub>3</sub>COO)<sub>2</sub>, AgNO<sub>3</sub>, and AgClO<sub>4</sub> in micelles solutions leads to complexation of these salts with 4-vinylpyridine units. By the example of Au colloids it was found that size of colloid particles prepared by hydrazine reduction diminishes with decreasing of micelle size and loading of metal salt. SAXS data obtained for gold colloids in small micelles at molar ratio Au:N=1:9 after hydrazine reduction show the accumulation of spherical gold particles with a size about 10 nm and very narrow size distribution. The use of NaBH<sub>4</sub> and super-hydride as reducing agents leads to the formation of smaller particles. Pd colloids prepared in block copolymer micelles show catalytic activity and selectivity in hydrogenation of olefins and conjugated dienes.

151. SYNTHESIS AND INVESTIGATION OF THE THERMAL BEHAVIOR OF HIGH-LOADED ALN/POLYIMIDE NANOCOMPOSITES. Kenneth E. Gonsalves\*, Xiaohu Chen, Polymer Science Program at the Institute of Materials Science and Department of Chemistry, University of Connecticut, Storrs, CT 06269

Highly-loaded, fully consolidated aluminum nitride (AlN) / polyimide nanocomposites were prepared. The chemically synthesized nanostructured AlN powder was de-agglomerated and stabilized *in situ* during the formation of the ceramic/poly(amic acid) suspension in N-methylpyrrolidinone (NMP). After rapid precipitation from the suspension in a non-solvent, triethylamine, the ceramic bearing polymer was thermally cured. The fully dense nanocomposite samples were obtained via compression moulding. Preliminary characterization of the samples revealed a considerable increase in thermal conductivity and an obvious trend in reduction of the thermal expansion coefficient. The composite was also characterized by FTIR, X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

152. PHOTOCATALYSIS OF PHENOL AND SALICYLIC ACID BY NANOSTRUCTURED TITANIA POWDERS, G.P. Fotou and S.E. Pratsinis, Department of Chemical Engineering, University of Cincinnati, Cincinnati, OH 45221-0171

The photocatalytic destruction of phenol and salicylic acid was studied in aqueous suspensions of titania powders made in flame reactors. These powders were made in six hydrocarbon diffusion flames by hydrolysis and oxidation of TiCl<sub>4</sub> that resulted in powders of high specific surface area and high anatase content. The photoactivity of the flame-made titania powders was compared with