

132. AMPHIPHILIC BLOCKCOPOLYMERS BASED ON QUATERNIZED POLY(PROPYLENE IMINE) DENDRIMERS. C. Elissen-Román, J. C. M. van Hest, M. W. P. L. Baars, M. H. P. van Genderen, and E. W. Meijer. Laboratory of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

Quaternization of polystyrene-poly(propylene imine) dendrimer diblock copolymers yielded cationic superamphiphiles. The synthesis of quaternary ammonium salt-functionalized block copolymers, PS-dendr-(N(CH₃)₃)_n⁺, with n = 1, 2, 4, 8 and 16, and 1, 3, 7, 15 and 31 I⁻ counterions, is feasible in high yields. Critical association constants were determined for PS-dendr-(N(CH₃)₃)_n⁺, with n = 8 and 16, respectively. Π-A isotherm measurements were used to obtain information about the molecular area of the headgroup and orientational behaviour of the molecules at the air-water interface. The isotherms of the PS-dendr-(N(CH₃)₃)_n⁺, with n = 1, 2, 4, 8 and 16, indicated direct relation between the area per molecule and the generation reached on the dendrimer. The dimensions of the headgroup could only be obtained for PS-dendr-(N(CH₃)₃)_n⁺, with n = 8 and 16. For lower generations, PS-dendr-(N(CH₃)₃)_n⁺, with n = 1, 2 and 4, the isotherms were dominated by steric interactions between the polystyrene chains.

133. FRAGMENTATION STUDIES OF POLY(PROPYLENE IMINE) DENDRIMERS IN THE GAS-PHASE BY USING ELECTROSPRAY IONIZATION MASS SPECTROMETRY (ESI-MS). J. W. Weener, J. L. J. van Dongen, J. C. Hummelen, E. W. Meijer

Electrospray ionization mass spectrometry (ESI-MS) in combination with a simple statistical simulation program enabled us to fully characterize the commercially available poly(propylene imine) dendrimers, including their statistical errors. Fragmentation reactions of the poly(propylene imine) dendrimers were studied in detail in the gas-phase using ESI-MS. Collision activated dissociation (CAD) of the [M + H]⁺ ions from DAB-dendr-(NH₂)_n (n = 4, 8, 16) all followed the same mechanistic pathway involving a chain mechanism of nucleophilic displacement reactions. The chain starts at the diaminobutane (DAB) core, leading to a split dendrimer and proceeds outwards through the successive dendritic layers.

134. SYNTHESIS AND CHARACTERISATION OF POLY(PROPYLENE IMINE) DENDRIMERS WITH AN APOLAR PERIPHERY. M.W.P.L. Baars, and E.W. Meijer, Laboratory of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

The interesting (amphiphilic) properties of the inverted unimolecular dendritic micelles, obtained by the reaction of poly(propylene imine) dendrimers with acid functionalized alkyl chains, prompted us to investigate the structure-property relationship of poly(propylene imine) dendrimers functionalized with an apolar periphery. Dendrimers have been synthesized with variable substituents (rigid or flexible) and/or endgroup linkages (amides or urea). Hydrogen bonding interactions in the shell of these dendrimer series show distinct differences as is characterized in solution by ¹H-NMR and IR or in the solid phase by DSC. The substituent and endgroup-linkage play an important role in the host-guest interactions of dendrimers with UV-probes as is demonstrated by performing a series of extraction experiments. A new series of inverted unimolecular dendritic micelles has been synthesized with fluorinated alkyl chains displaying interesting and peculiar properties.