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Τίτλος

« **Synthesis and Characterization of Hyperbranched Polymers of 2- (Dimethylamino) Ethyl Methacrylate via Self Condensing Vinyl Copolymerization** »

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Abstract

We report the synthesis of randomly branched (arborescent) ionizable polymers by self – condensing vinyl copolymerization (SCVCP) of an acrylic inimer 2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate (MTSHEMA) with 2-(dimethylamino)ethyl methacrylate (DMAEMA) via group transfer polymerization (GTP). The influence of the comonomer ratio, $\gamma = [\text{DMAEMA}]/[\text{MTSHEMA}]$, and the monomer concentration in the polymerization on the polymer characteristic were investigated. In addition, we prepared hyperbranched polymers of a lower degree of branching by the slow addition of the comonomer mixture (inimer and monomer) to a monofunctional GTP initiator, 1-methoxy-1-(trimethylsilyloxy)-2-methyl-1-propene (MTS). Finally, the addition of 2-(trimethylsilyloxy)ethyl methacrylate (TMSHEMA) to living PDMAEMA hyperbranched precursors core yielded “hyperstar” polymers comprising a hyperbranched core and linear polymer chains in the shell.

The absolute molecular weights of the polymers were measured by GPC equipped with a refractive index, a viscosity and a low angle laser light scattering detectors. Depending on the comonomer ratio, $\gamma = [\text{DMAEMA}]/[\text{MTSHEMA}]$, and

the monomer concentration in the polymerization hyperbranched PDMAEMAs and hyperstar polymers with number-average molecular weights between 6,000 and 650,000 g mol^{-1} were obtained. The addition of a monofunctional initiator in the polymerization led to a considerable narrowing of the molecular weight distribution of the polymers, in particular for high MTS contents. The Mark-Houwink exponents of these hyperbranched polymers were significantly lower ($0.2 < \alpha < 0.5$) compared to that of a linear PDMAEMA ($\alpha = 0.6$) thus verifying the branched polymer structure. ^1H NMR spectroscopy indicated that very high comonomer conversions were obtained in most cases, however it could not be used to calculate the degree of branching of these polymers. The hydrodynamic size of the hyperbranched polymers in organic solvents were determined by dynamic light scattering while capillary viscosity measurements were used to calculate their intrinsic viscosities in organic media. The pH and temperature responsive behavior of the hyperbranched PDMAEMAs in aqueous solution were investigated by potentiometric titrations and dynamic light scattering respectively. Finally, melt rheology measurements were carried out in order to investigate the rheological response of the polymers. Dynamic spectra revealed that the hyperbranched polymers are not entangled and follow a dynamic scaling based on a Rouse-like behaviour.

Ο Πρόεδρος του Τμήματος

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