POLYMER GRAFT-MODIFIED CO_2-SWITCHABLE CELLULOSE NANOCRYSTALS PREPARED BY NIROXIDE-MEDIATED POLYMERIZATION AND THEIR USE AS PICKERING EMULSIFIERS

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We have studied solid-stabilized (Pickering), stimuli-responsive oil-in-water emulsions using polymer graft-modified CO_2-switchable cellulose nanocrystals (CNC). Following functionalization of the CNC surface with glycidyl methacrylate, CO_2-switchable poly(*N*,*N*-(diethylamino)ethyl methacrylate) (PDEAEMA) and poly(*N*-3-(dimethylamino) propyl methacrylamide) (PDMAPMAm) macroalkoxyamines with low dispersities, high livingness and chain end functionalities were grown through nitroxide-mediated polymerization (NMP) and grafted to the nanocrystals. The success of the grafting reactions was demonstrated by ^{13}C CP-MAS and FT-IR spectroscopy, as well as elemental and thermogravimetric analysis. The CO_2-responsiveness of the graft-modified CNC was demonstrated by zeta-potential measurements and reversible phase shuttling experiments in oil and water. The surface and interfacial properties of the graft-modified CNC were characterized by surface and interfacial tensiometer measurements. The stability of the solid-stabilized emulsions at diferent pH was investigated, and the resulting droplet size measured using optical microscopy. Depending on the pK_{aH} of the polymer grafted to the CNC and the polarity of the oil phase, the stability of the emulsions could be controlled by bubbling CO_2 and N_2, which led to protonation/deprotonation of the tertiary amino groups on the CNC surface. Various factors, including chain length of the grafted polymer, graft densities, total amount of CO_2-switchable groups on the CNC surface, and concentration of Pickering stabilizer and their effect on the properties of the emulsions were investigated.