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SYNTHESIS OF POLY-*N*-ISOPROPYLACRYLAMIDE (PNIPAAm) AND ACRYLIC PNIPAAm-COPOLYMERS BY NITROXIDE MEDIATED CONTROLLED FREE-RADICAL POLYMERIZATION

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Poly(*N*-Isopropylacrylamide) (PNIPAAm) is a very attractive polymeric material due to the thermosensitivity found in its aqueous solutions and cross-linked hydrogels. Its thermosensitivity is based on a “coil-to globule” transition at 32 °C turning the macromolecule from a hydrophilic to a hydrophobic structure at what is known as the lower critical solution temperature (LCST)¹. The temperature at which this transition takes place can be fine tuned by copolymerizing NIPAAm with hydrophilic² or hydrophobic^{3, 4} monomers, including monomers with ionizable acid^{4, 5} or basic⁶ groups. To our knowledge, a poorly addressed issue in the literature is the fact that most of this NIPAAm-polymers and copolymers are prepared by traditional free radical polymerization, which although being a very useful technique for polymerizing and copolymerizing a variety of functional monomers, lacks control of molecular weight, molecular weight distribution and composition of copolymers. With the introduction of controlled free radical polymerization techniques (CFRP) in recent years⁷, the preparation and study of well-controlled NIPAAm polymers and copolymers in different architectures is now possible. Initial attempts to obtain PNIPAAm by using this CFRP-techniques has however encountered some difficulties. For example, Matyjaszewski⁸ and Brittain⁹ reported by the use of atom transfer radical polymerization (ATRP) for the polymerization of a variety of acrylamides, that poor control over the polymerization was achieved due to the competition of the monomers with the ligands used for complexing the catalytic metal center (Copper I). Rizzardo et al.¹⁰ reported a successful synthesis of PNIPAAm by using the reversible addition-fragmentation technique (RAFT). They obtained PNIPAAm in molecular weights from 2 000 to 26 000 g mol⁻¹ with polydispersity indexes (PDI) from 1.11 to 1.27. However, for higher molecular weight samples the PDI increased to 1.46 - 1.54, close to the PDI's obtained for traditional free radical polymerization. In a recent study in the Hawker group¹¹, PNIPAAm-

macroinitiators were prepared by using nitroxide mediated controlled free radical polymerization (NOx-CFRP), which were successfully used to prepare block copolymers with polystyrene in different architectures. Although the PNIPAAm-macroinitiators prepared had only a moderate molecular weight (ca. 10 000 g mol⁻¹), the PDI of 1.07 showed the feasibility of NOx-CFRP for controlling PNIPAAm polymerization. We report here the preparation of PNIPAAm of different molecular weights by NOx-CFRP with good control and also the preparation of PNIPAAm, statistical and block, copolymers with *tert*-butylacrylate (tBA) as hydrophobic comonomer. In the PNIPAAm preparation, we observed a slight increase in the PDI from 1.15 to 1.21 to 1.36 by molecular weights of 11 800, 21 400 and 31 2000 g mol⁻¹ respectively. For the block copolymers we used two approaches, either first preparing a PNIPAAm-macromonomer and then growing a tBA block, or preparing first a tBA-macromonomer and growing then a NIPAAm block. Both approaches worked and we were able to obtain block copolymers with total molecular weights from 32 000 to 58 000 g mol⁻¹ varying the content on tBA from 3.6 up to 59.6 %. Through acidolysis using trifluoro acetic acid, the hydrophobic tBA sequences were converted into hydrophilic acrylic acid sequences, changing the behavior of the PNIPAAm-copolymers. In the conference we will report on the effects we observed in the LCST of PNIPAAm due to the controlled preparation on both polymers and copolymers.

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