

## **Synthesis of dual thermoresponsive ABA triblock copolymers by both living cationic vinyl polymerization and RAFT polymerization using a dicarboxylic RAFT agent**

### **Abstract**

To elucidate a difference of micelles formed from AB di- and ABA tri-block copolymers, PMOVE-PNIPAM-PMOVE triblock copolymers were synthesized by both living cationic polymerization of MOVE and RAFT polymerization of NIPAM using a dicarboxylic RAFT agent, where MOVE is 2-methoxyethyl vinyl ether, NIPAM is N-isopropylacrylamide. The ABA triblock copolymers consist of cationically polymerizable monomer (A), MOVE, and radically polymerizable monomer (B), NIPAM. The key to success in the triblock copolymerization is to utilize a dicarboxylic RAFT agent/SnBr<sub>4</sub> initiation system for living cationic polymerization. The cationic polymerization was simultaneously initiated from two protons per one dicarboxylic RAFT agent. After the cationic polymerization, the polymerization was quenched and then the RAFT carboxylate counter anion was concurrently recovered at ca. 86% efficiency, followed by the RAFT polymerization. The resulting PMOVE-PNIPAM-PMOVE triblock copolymers contain two thermoresponsive blocks. The resulting block copolymers reversibly formed or deformed micellar assemblies in water. When the chain length of the core-forming block, PNIPAM, is increased, larger micelles were invariably obtained. The triblock micellar size was larger than that of the corresponding diblock micelle. The micelles at the concentrated solution formed physical gel, and the minimum gelation concentration of the triblock micelles was lower than that of the corresponding diblock micelles.

### **Keywords**

Living cationic polymerization; Reversible addition fragmentation chain transfer (RAFT); Triblock copolymer