

Doctoral Dissertation Abstract

Major Materials Engineering

Course Applied Chemistry and Biotechnology

Name Akmal Hadi Bin Ma' Radzi

1. Dissertation Title (If in English, add the Japanese translation.)

Design of Various Functional Block Copolymers via Precision Radical and Cationic Polymerization (精密ラジカルまたはカチオン重合による機能性ブロックコポリマーの合成)

2. Abstract (Roughly 2,000 Japanese characters or 800 English words)

Since 1950, living polymerization is the most versatile method to prepare well-defined polymers with narrow molecular weight distributions (MWDs). A wide variety of polymer architectures such as block, graft and star copolymers can be constructed in a precise fashion which is considered impossible in conventional polymerization. The living vinyl polymerization can be divided into three types, i.e. anionic, cationic, and radical polymerization. In this doctoral thesis, controlled living radical polymerization and living cationic polymerization is focused because most various functional polymers were synthesized via these two methods.

In living radical polymerization, nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization are considered as the most efficient ways to produce well-defined polymers. As comparison, controlled living radical polymerization using a commercially available haloalkyl alcohol as chain transfer agent (CTA) was investigated. The living radical polymerization was conducted using methyl methacrylate (MMA) and styrene (St) initiated by 2,2'-azobisisobutyronitrile (AIBN) as an initiator at 60 °C. When the large amount of 2-bromoethanol for polymerization of MMA, controlled radical polymerization is proceeded. Even though the polymerization with 2-bromoethanol is not sufficient enough as the established systems, but it is commercially available and can be used without any further purification.

Major	Materials Engineering	Course	Applied Chemistry and Biotechnology	Name	Akmal Hadi Bin Ma' Radzi
<p>Mechanistic transformation between different polymerization modes were investigated in the next section. Following the previous study, poly(2-methoxyethyl vinyl ether-<i>block</i>-poly(<i>N</i>-isopropylacrylamide)-<i>block</i>-poly(2-methoxyethyl vinyl ether) (poly(MOVE)-<i>b</i>-poly(NIPAM)-<i>b</i>-poly(MOVE)) was synthesized via the combination of living cationic polymerization and RAFT polymerization using a dicarboxylic RAFT agent. The living cationic polymerization of MOVE proceeded smoothly under dicarboxylic RAFT agent/SnBr₄ initiation system and was simultaneously initiated from two protons per one dicarboxylic RAFT agent. The poly(MOVE) macro-CTA had number average α-end functionality, F_n of 86%. The RAFT polymerization was then conducted and the resulting triblock copolymers contain two thermoresponsive blocks which reversibly formed or deformed micellar assemblies in water.</p> <p>A novel vinyl ether-type RAFT agent, benzyl 2-(vinylloxy)ethyl carbonotrithioate (BVCT) was synthesized to prepare various block copolymers via the combination of living cationic polymerization of vinyl ethers and RAFT polymerization in the next section. The poly(vinyl ethers) was synthesized by living cationic polymerization under BVCT-trifluoroacetic acid (TFA)/EtAlCl₂/ethyl acetate initiating system. The resulting polymer had high number average α-end functionality (> 0.9) and therefore worked well as macromolecular chain transfer for RAFT polymerization. The RAFT polymerizations were conducted using AIBN in toluene at 70 °C. For example, a double thermoresponsive block copolymer (MOVE₆₁-<i>b</i>-NIPAM₁₅₀) was prepared via the combination of living cationic polymerization and RAFT polymerization. The block copolymer reversibly formed and deformed micellar assemblies above the phase separation temperature (T_{ps}) of poly(NIPAM) block in water. This BVCT also can be functioned as monomer. When BVCT was copolymerized with MOVE by living cationic polymerization, followed by graft copolymerization with NIPAM via RAFT polymerization, well-defined graft copolymers, (MOVE_{<i>n</i>}-<i>co</i>-BVCT_{<i>m</i>})-<i>g</i>-NIPAM_{<i>x</i>} ($n = 62-73$, $m = 1-9$, $x = 19-214$) were obtained. However, no micelle formed in water above T_{ps} of poly(NIPAM) graft chain unlike the case of block copolymers.</p> <p>As BVCT does not apply to non-conjugated monomer such as vinyl acetate (VAc), different types of novel xanthates containing a vinyl ether moiety, <i>S</i>-benzyl <i>O</i>-2-(vinylloxy)ethyl carbonodithioate (Xanthate 1) and <i>S</i>-1-(ethoxycarbonyl)ethyl <i>O</i>-2-(vinylloxy)ethyl carbonodithioate (Xanthate 2) were synthesized in the next section. For living cationic polymerization of IBVE and TBVE, the polymerizations</p>					

Major	Materials Engineering	Course	Applied Chemistry and Biotechnology	Name	Akmal Hadi Bin Ma' Radzi
<p>proceeded under Xanthate 1-HCl/SnCl₂/ethyl acetate and Xanthate 1 or 2-CF₃COOH/EtAlCl₂/ethyl acetate initiation system. Both systems show living polymerization nature because the calculated M_n of both polymers matches with the M_n polymerized assuming that one polymer chain form per one molecule of the Xanthates This is also estimated by the resulting poly(TBVE) which had a high number average α-end functionality (0.94). The RAFT/MADIX polymerization of VAc using AIBN at 60 °C was then conducted using either poly(IBVE) or poly(TBVE) macro-CTA.. However, poly(TBVE) macro-CTAs synthesized from the Xanthate 2 was able to polymerize VAc smoothly to prepare well-defined diblock copolymer, poly(TBVE)-<i>b</i>-poly(VAc). The resulting block copolymer was then hydrolyzed using KOH in methanol and followed by HBr gas bubbling. The resulting polymer is inherently stereoblock like copolymer, isotactic rich PVA-<i>b</i>-atactic PVA (iPVA-<i>b</i>-aPVA). From the DSC measurement, the stereoblock copolymer has one glass transition at 69.5 °C and two melting points according to iPVA and aPVA at 237.9 and 198.1 °C, respectively. Thus, it can be suggested that obtained PVA has two different geometries.</p>					
<p>...To prepare another shape that are high order structures, RAFT aqueous dispersion polymerization of 2-methoxyethyl acrylate (MEA) using PEO macro-CTA with different molecular weight were then conducted in the final section. First, trithiocarborate RAFT agent was prepared and the macro-CTA was synthesized by esterification with a commercial poly(ethylene oxide) monomethyl ether ($M_n = 350, 2000$ and 5000 gmol^{-1}). The obtained macromolecular RAFT agents acted as steric stabilizer which stabilized the dispersed particles during RAFT aqueous dispersion polymerization with water in 70 °C with 2-methoxyethyl acrylate (MEA). As these polymerizations proceeded, the solution viscosity was changed from transparent to opaque, indicating micellar solution characteristic and the number average molecular weight of the produced polymer is shifted to the higher molecular weight and then the nano-assemblies polymer was obtained. The RAFT aqueous dispersion polymerization produces a hydrophobic PMEA block, which let to in situ self-assembly to form well-defined sphere micelles, rod like micelles and vesicles. The final particle morphology was investigated by varying synthesis parameters such as the target DP of the hydrophilic group and the total solid concentration.</p>					