Polymerization of Vinyl Acetate in Supercritical CO₂ Using Poly(vinylacetate)-based MacroRAFT Agents

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Controlled living polymerization of vinyl acetate (VAc) by reversible addition-fragmentation chain-transfer (RAFT) was studied in supercritical carbon dioxide (scCO₂). Various poly(vinyl acetate) (PVAc) bearing xanthate groups were used as macroRAFT agents. Solubility of the RAFT agents in bare scCO₂ and monomer-scCO₂ mixture was investigated by cloud point measurement. Polymerization with an aid of the RAFT agents was carried out in scCO₂. Effect of reaction time, concentration of RAFT agent, and structure of RAFT agent on the yield, molecular weight, and polydispersity index (PDI) of PVAc were studied. As far as the result is concerned, the macroRAFT agents were well soluble in both scCO₂ and the mixture and higher solubility was found in the case of mixture as monomer played a role as cosolvent. Either molecular weight and PDI increased linearly with increasing yield. Increase in concentration of RAFT agent resulted in the decrease in the molecular weight and PDI. Effect of the molecular weight of RAFT agent was also investigated.