官能基シナジーを引き出す ビニルモノマーの設計と重合、機能

Polymerization and Function of Vinyl Monomers Designed for Functional Group Synergy

髙坂 泰弘

Abstract

This report reviews a strategy to design vinyl monomers using functional group synergy, which defined as intramolecular interaction between two or more functional group near polymerization points. One of the attractive motifs is α -functionalized acrylates, as the functionalized α -substituent can interact with vinyl and carbonyl groups by conjugation, hyperconjugation and intramolecular hydrogen bond. For example, α -arylacrylates undergoes alternating anionic copolymerization with methyl methacrylate; the alternating copolymers exhibited strong monomer emission, whereas the homopolymer, poly (α -arylacrylate)s exhibited excimer emission. α -(Halomethyl) acrylate undergoes nucleophilic conjugate substitution reaction in quantitative yield at room temperature even under air. This reaction was applied to monomer synthesis, end-functionalization, polycondensation and main chain scission reaction. This review also covers the design of recyclable vinyl polymer; a cyclic ketenacetal ester, dehydroaspirin, afforded the corresponding vinyl polymer by radical polymerization. The acid hydrolysis of the obtained vinyl polymer resulted in main chain scission with releasing the raw products of monomer, salicylic acid and acetic acid.

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1. はじめに

メタクリル酸メチル (MMA) と類似の重合性を示し、親水性を賦与したモノマーが必要な場合、エステル置換基にヒドロキシ基を導入したメタクリル酸 2-ヒドロキシエチル (HEMA)

や、アンモニウム塩を担持したメタクロイルコリンクロリドが思い浮かぶ。このように、機能性モノマーを設計する場合、一般にはビニルモノマーの重合点から遠い位置に、機能団を修飾する戦略が採用される。これは、重合点近傍に機能団を修飾すると、最悪の場合、モノマーの重合活性自体が失われることすらあるからである。例えば、アクリル酸メチル(MA)のα位にメチル基を置換した MMA は重合活性を示すが、イソプロピル基を置換した MIPA はラ

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