

論文内容要旨

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学位論文題目	Monomer sequence analysis of poly(methyl methacrylate-co-benzyl methacrylate)s prepared by various polymer reactions 種々の高分子反応で合成したメタクリル酸メチル-メタクリル酸ベンジル共重合体の連鎖解析		
内容要旨 <p>Control over monomer sequences in a polymeric chain is considered one of the last issues in polymer chemistry. Recently, a growing number of research groups have begun working toward various strategies to achieve control over monomer sequence distribution. Synthetic methods for sequence control can be categorized into four general categories: iterative, step growth, chain growth, and polymer reactions. In the iterative approach, each monomer is sequentially appended to the end of the chain using highly controlled microstructures; however, obtaining polymeric molecules with high molecular weights is not possible. In a step growth approach, such as click polymerization, detailed periodic polymers can be generated; however, this approach lacks control over polymer molecular weights and dispersity. Chain growth efficiently controls polymer molecular weights, but it does not provide a high level of control over sequence arrangement.</p> <p>In the polymer reaction approach, the main chain does not undergo cleavage or recombination; hence, the average degree of polymerization, degree of polymerization distribution, and stereoregularity of the original polymer are retained. This facilitates control over composition and sequence. In the case of more complex polymer systems or block copolymers, selective orthogonal deprotection depends on not only the nature of the protecting groups but also the architecture and chemical structure of their neighboring groups. Obtaining structural information on polymethacrylates is very complicated because of the resonance of copolymers, and these polymers often exhibit overlapped splitting when the chemical shifts of signals are sensitive to both configurational and</p>			

monomer sequences. To extract quantitative information regarding the microstructure of copolymers undergoing resonance, statistical (multivariate) analysis of the NMR spectra has recently been found to be beneficial. We have recently shown that multivariate analysis of NMR spectra is appropriate for the structural analysis of copolymers. For example, in one study, principal component analysis (PCA) was applied to ^{13}C NMR spectra of copolymers of MMA and TBMA with various chemical compositions. A PCA model was used to extract information regarding not only the chemical composition but also the monomer sequence, without assigning individual signals.

Here, we performed multivariate analysis on the ^{13}C NMR spectra of methacrylate copolymers synthesized through the partial chemical deprotection of poly(methyl methacrylate-benzyl methacrylate) (poly(MMA-co-BnMA)) via six routes to investigate the molecular structures of the resulting polymeric compounds. The benzyl groups were removed from poly(benzyl methacrylate) (PBnMA) through catalytic hydrogenation, acidic hydrolysis, basic hydrolysis, and transesterification. The copolymers of BnMA and methacrylic acid (MAA) were converted to poly(MMA-BnMA)s through methylation with diazomethane prior to the analysis. Furthermore, poly(MMA-BnMA)s were obtained from poly(MAA) through either benzylation–methylation or methylation–benzylation. Principal component analysis was performed on the ^{13}C NMR spectra of poly(MMA-BnMA)s containing various ratios of BnMA and MMA units. The results indicated that the monomer sequences of the copolymers synthesized through acidic hydrolysis and methylation–benzylation resembled those of radical copolymers (nearly random), whereas the monomer sequences of the copolymers synthesized through catalytic hydrogenation resembled the sequences of homopolymer blends (blocky). However, the sequences of the copolymers synthesized through basic hydrolysis and transesterification exhibited a relatively alternating tendency. Furthermore, the sequences of the copolymers derived from benzylation–methylation were suggested to exhibit a relatively blocky tendency.