SOLUBLE POLYMERS FROM DIACRYLIC MONOMER VIA ANIONIC POLYMERIZATION

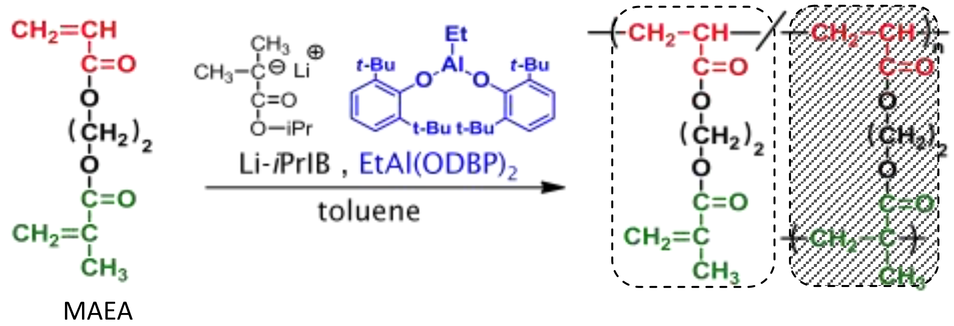
Tatsuki Kitayama, Takehiro Kitaura, Ayumi Hashimoto and Yasuyuki Ando

Department of Chemistry, Graduate School of Engineering Science, Osaka University
Toyonaka, Osaka, 560-8531, Japan

ABSTRACT

Anionic polymerization of carbonyl-containing polar vinyl monomers (acrylates and methacryltaes) has been often challenged by side reactions involving the carbonyl group, which deteriorate the control of the polymerization processes. Proper selection of initiators as well as additives has been proved effective to suppress such difficulties. We have developed a series of stereospecific living polymerizations of methacrylate that utilize additives such as trialkylaluminums [1], aluminum bisphenoxides [2], and lithium silanolates [3]. Some of these additives are also effective in monomer-selective living copolymerization of acrylate and methacrylate. For example, ethylaluminum bis(2,6-di-*tert*-butylphenoxide) [$\mathrm{EtAl(ODBP)_2}$], a bulky Lewis acid, is effective for living polymerization of primary alkyl acrylate including butyl acrylate (*n*BuA) and also for syndiotactic-specific polymerization of methyl methacrylate (MMA). Copolymerization of *n*BuA and MMA in toluene with *tert*-butyllithium with $\mathrm{EtAl(ODBP)_2}$ proceeds in a monomer-selective and living manner to afford a block-like copolymer, poly(*n*BuA)-*block*-PMMA, through preferential activation of *n*BuA with $\mathrm{EtAl(ODBP)_2}$.

Based on these results, polymerization of 2-(methacryloyloxy)ethyl acrylate (MAEA), possessing acrylate and methacrylate functionalities, was examined for anionic polymerization with $\mathrm{EtAl(ODBP)_2}$ in toluene at –78 ˚C. A soluble linear polymer with narrow molar mass distribution was obtained up to 90 % conversion, which consisted of an acrylate main-chain and methacrylate side groups. The results indicate that the polymerization proceeds acrylate-selective and living manner as in the case of the copolymerization of acrylate and methacrylate.



Statistical copolymerization of MAEA and alkyl acrylate under identical conditions afforded a random copolymer. Thus the reactive copolymers carrying prescribed number of methacrylate groups are readily obtainable by changing comonomer feed ratio. When polyacrylate anions formed under similar conditions was reacted with a small amount of MAEA, the acrylate-selective block polymerization took place first, followed by crosslinking reaction to form a star-branched polyacrylate. Thus the system is not only effective for reactive polymer syntheses but also for star polymer synthesis.

References

[1] Kitayama T, et al., *Makromol.Chem.Suppl.* (1989) 15, 167.
[2] Kitayama T, et al, *Tetrahedron* (1997) 53, 15263; Hirano T, et al., *Polym. J.* (1998) 30, 767.
[3] Kitaura, T., Kitayama, T. *Macromol. Rapid Commun*. 2007, 28, 1889.

[4] Kitayama T, et al., *Polym J.* (2000) 32, 796; Kitayama T, et al., *Polym. J.* (2002) **34**, 370.