

Synthesis of Polyethylene-*block*-Poly(ϵ -caprolactone) and Polyethylene-*block*-Poly(methyl methacrylate) from Hydroxy-terminated Polyethylenes

Manseong Jeon, Sang Youl Kim*

Department of Chemistry and School of Molecular Science (BK21), KAIST

373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea, e-mail: kimsy@kaist.ac.kr

Over the last two decades, the development of homogeneous catalysts has led to the production of functionalized polyolefins that had not been attainable with conventional Ziegler-Natta catalysts. In general, functionalized polyolefins can be prepared by 1) modification of preformed polyolefins, 2) direct copolymerization of olefins with a functional monomer (protected or non-protected) and 3) *in situ* chain transfer to chain transfer agent during polymerization. Among these methods, the *in situ* chain transfer method is a convenient way to make terminally functionalized polyolefins which can be further utilized in making the polymers with diverse structure such as block and graft copolymers.

The block copolymers consisting of two immiscible polymer chains have been known as a very effective compatibilizer in a polymer blend of two immiscible homopolymers. Block copolymers of polyolefins and vinyl monomers are particularly useful for blending of polyolefins that are not compatible with many other polymers.

In our previous study, we found that the chain transfer reaction of ethylene copolymerization with metallocene/methylaluminoxane (MAO) catalysts could be controlled through proper combination of metallocene catalysts and comonomers. Among several factors that affect the mode of chain transfer reactions, controlling steric bulkiness of the ligands is critical in homogeneous metallocene catalyzed polymerization. As steric bulkiness of the ligand increase, β -hydride elimination tends to decrease, because the steric repulsion between the bulky ligand and the axial polymer chain suppress the β -agostic interaction, a key step for β -H elimination. Consequently, the aluminum transfer reaction becomes the predominant chain transfer reaction.

In this study, we report the synthesis of hydroxy-terminated polyethylenes (PE-OH) through controlled chain transfer reaction and their transformation to polyethylene-*block*-poly(ϵ -caprolactone) and polyethylene-*block*-poly(methyl methacrylate).

Polymerization of ethylene was carried out in toluene with a catalyst having sterically hindered pentamethylcyclopentadienyl ligand, $\text{Cp}^*\text{ZrCl}_2/\text{MAO}$, and all the polymerization mixture were subjected to oxidative workup to convert the aluminum-terminated end groups to hydroxy groups. Oxidation of aluminum-terminated polyethylene was accomplished by bubbling dry oxygen into the polymerization solution (Scheme 1).

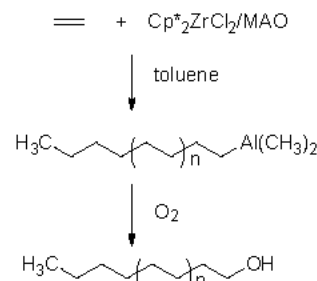
^1H and ^{13}C NMR spectra of the polymers obtained through the oxidative workup show the peaks corresponding to the hydroxyl methyl end groups, but there are no peaks of olefin end groups formed by β -H elimination. The resonances at 3.65 ppm in the ^1H NMR and at 62.97 ppm in the ^{13}C NMR are clear indication of the presence of a hydroxy methyl end group. The ratio of the hydroxy-terminated end group to the methyl end group was estimated by integration of ^1H NMR spectrum. It was found that the, however, ^1H NMR technique had some limitation to quantify the content of hydroxy methylene (triplet, 3.61 ppm) and methyl end group (triplet, 0.90 ppm) groups presumably due to the formation of micellar aggregation of hydrophilic -OH group in hydrophobic tetrachloroethane-*d*₂ solvent. The aggregation phenomenon was supported by variable temperature ^1H NMR experiment that showed the change of integration value of the hydroxy methyl group. As temperature increased, the integration ratio of $-\text{CH}_2\text{-OH}/-\text{CH}_2\text{-CH}_3$ increased. The ^1H NMR measurement at 120 °C reveals that at least more than 85% of the polymer chain has a hydroxy methyl end group.

Poly(ethylene-*b*-caprolactone) block copolymer was synthesized from PE-OH and ϵ -caprolactone by using stannous octoate as a catalyst for ring opening polymerization of ϵ -caprolactone. Structural analysis of the poly(ethylene-*b*-caprolactone) block copolymer with ^1H and ^{13}C NMR spectroscopy confirmed the formation of the block copolymer. In ^{13}C NMR spectrum, the carbonyl carbon of

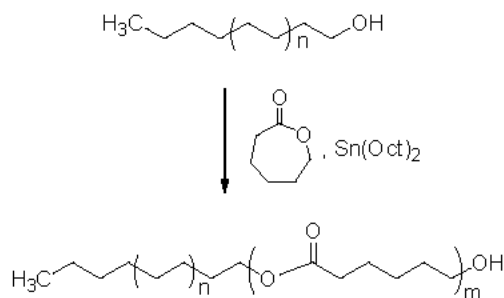
caprolactone unit appeared at 173.16 ppm. ^1H NMR spectrum also shows the methylene peaks of PE at 1.3 ppm as well as the peaks from the caprolactone unit at 4.1 [$-\text{CH}_2\text{-O}-$], 2.3 [$-\text{C}(\text{O})-\text{CH}_2-$], 1.7 and 1.4 [$-\text{CH}_2-\text{CH}_2-\text{CH}_2-$] ppm. DSC analysis of the block copolymer shows double melting points at 57.5 °C and 125.7 °C, which is typical in crystalline diblock copolymer. Melting point of polyethylene block, however, decreased compared to that of PE-OH presumably due to the hindered crystalline packing.

Polyethylene-*block*-PMMA was obtained by transforming the hydroxyl-terminated polyethylenes to macroinitiators for atom transfer radical polymerization (ATRP) and by reacting them with MMA. The block copolymers showed the number average molecular weight of 14000~23000 and polydispersity index around 1.4.

Scheme 1. Synthesis of Hydroxy-terminated Polyethylene



Scheme 2. Synthesis of Polyethylene-*block*-Polycaprolactone



Scheme 3. Synthesis of Polyethylene-*block*-PMMA

