Controlled Polymerization of Cyclic Esters

Andrzej Duda

Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, Sienkiewicza 112, Lodz, Poland

Ring-Opening Polymerization (ROP) of cyclic esters will be discussed, stressing that independently on the initiator/catalyst used, i.e.: covalent metal alkoxide [1], carboxylate [2, 3], or acetyloacetonate [3], polymerization proceeds on the alkoxide species. Preparative applications of the most often used catalysts: aluminum tris-isopropoxide and tin(II) bis-octoate will be presented in more detail, on the example of synthesis of linear and star-like poly(ε-caprolactone)s and polylactides [1-5] as well as poly[(R)-lactide]/poly[(S)-lactide] stereocomplexes [6, 7].

It will be also shown that initiation with aluminum alkoxides that bear bulky, bidendate phenolate-type ligands at the metal atom, results in an efficient suppression of both intra- and intermolecular transesterification [6, 8, 9]. The latter finding enabled preparation of the (*S,S*)-LA and ε-caprolactone (CL) di- and triblock copolymers via the poly(CL) (PCL) block growth initiation with the living poly[(*S,S*)-LA] (PLA*) [9]. In the previous attempts to prepare block copolymers this way only random copolyesters were obtained because the PLA* + CL cross-propagation rate was lower than that of the PLA-CL* + PLA transesterification.

Finally, it will be revealed that inversion of the initiator configuration may lead to a substantial change of the reactivity ratios [10]. It is a well-known fact that CL homopolymerization rate constant (k_{CC}) exceeds considerably that of (*S,S*)-LA homopolymerization (k_{LL}). For example, in polymerizations initiated with (*S*)-(+)-2,2'-[1,1'-binaphtyl-2,2'-diylbis-(nitrylomethylidyno)]-diphenolate aluminum isopropoxide (SBO_2Al-O^iPr): $k_{CC}/k_{LL} \approx 60$ (THF, 80 °C). However, the LA comonomer is consumed first from the CL/(*S,S*)-LA mixture. The corresponding reactivity ratios are equal to: $r_L = 322$ and $r_C = 19$. The observed phenomena can be explained assuming that the cross-propagation rate constant k_{LC} is relatively low. Change of the initiator configuration, from *S* to *R,* results in consumption of both comonomers with a comparable rate ($r_L = 1.5$ i $r_C = 1.9$).

Keywords: aliphatic polyesters; lactide; ε-caprolactone; living polymerization; star-shaped polymers; stereocomplexes; block copolymers; reactivity ratios; transesterification

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