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# Branched aliphatic polyesters by ring-opening (co)polymerization

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## ABSTRACT

The rapid development of biodegradable and biocompatible materials for biomedical applications is reflected in the search for new methods for aliphatic polyester modification applicable in this field. One possible approach is modification by changes to the polymer topology.

This review covers the main methods of synthesis of branched aliphatic biodegradable and biocompatible (co)polyesters, where the ring-opening polymerization (ROP) of cyclic esters or cyclic carbonates is the leading process. First, literature examples of ring-opening multibranching polymerization (ROMBP) of AB$_2$-type hydroxyl-substituted cyclic lactones, lactides and carbonates are cited followed by the presentation of the application of AB-type cyclic esters and additionally AB$_2$ cyclic ethers or esters as "branching monomers" for the synthesis of branched polyesters based on polycaprolactone (PCL), polylactide (PLA) and polyglycolide (PGA). In the following part, methods involving the combination of the ROP of AB-type cyclic esters and condensation processes leading to branched structures are summarized. Other related strategies leading to "dendri-star" or "core–shell" copolyesters are also discussed. Several examples of approaches to PCL and PLA graft copolymer syntheses are also shown. The advantages and disadvantages of the presented methodologies of branched polyester synthesis are highlighted. Finally, the influence of the branched structure on the properties of the presented class of polyesters, important from the application point of view, is considered.

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*Abbreviations:* bisMPA, 2,2-bis(hydroxymethyl) propionic acid; BHB, 2,2-bis(hydroxymethyl)butyric acid; $^{13}$C APT NMR, Attached-Proton-Test method of $^{13}$C NMR analysis; CALB, Candida antarctica Lipase B (lipasecatalyst); CGS-OBz, cyclo[Glc-Ser(OBz)] – cyclodepsipeptide; CL, ε-caprolactone; DBU, 1,8-diazabicycloundec-7-ene; DCC, dicyclohexylcarbodiimide; DMAP, 4-(dimethylamino)pyridine; DPTS, 4-(dimethylamino)pyridine 4-toluenesulfonate; DIAD, diisopropyl azodicarboxylate; DB, degree of branching; DI, dispersity index; DSC, Differential Scanning Calorimetry; EHDO, 5-ethyl-5-hydroxymethyl-1,3-dioxan-2-one; EHMOX, 3-ethyl-3-hydroxymethyl-oxetane; FT-IR, Fourier Transform Infrared Spectroscopy; GA, glycolide; GLY, glycidol; HEMA, hydroxyethyl methacrylate; 6HDON, 6-hydroxymethyl-1,4-dioxan-2-one; 5HDON, 5-hydroxymethyl-1,4-dioxane-2-one; 5HBDON, 5-(4-hydroxybutyl)-1,3-dioxan-2-one; HTHF, 2-hydroxymethyltetrahydrofuran; HMMOX, 3-hydroxymethyl-3-methyl-oxetane; LA, lactide; MALDI TOF MS, Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectroscopy; MMA, methyl methacrylate; OX, oxetane; PBA, poly(butylene adipate); PBS, poly(butylene succinate); PCL, poly(ε-caprolactone); PEG, poly(ethylene glycol); PEI, poly(ethylene imine); PET, poly(ethylene terephthalate); PES, poly(ethylene succinate); PGA, polyglycolide; PLA, polylactide; PMMA, poly(methyl methacrylate); PSt, polystyrene; PVA, poly(vinyl alcohol); ROP, ring-opening polymerization; ROMBP, ring-opening multibranching polymerization; SCVP, self-condensing vinyl polymerization; SMA, slow monomer addition; SEC, Size-Exclusion Chromatography; SMP, shape memory polymers; TMP, trimethylolpropane; TBD, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (); [η], intrinsic viscosity; Tg, glass temperature; TPP, triphenylphosphane; TBDMS, tert-butyldimethylsilyl; $T_{\mathrm{mH}}$, melting temperature of homopolymer; $T_{\mathrm{mS}}$, melting temperature of stereocomplex; $\Delta H_{\mathrm{m}}$, melting enthalpy; Xc, crystallinity; TGA, Thermogravimetric Analysis; $T_{\mathrm{trans}}$, switching temperature; VPO, vapor pressure osmometry.

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**Contents**

## 1. Introduction

Historically, aliphatic polyesters obtained by polycondensation were predominantly low molecular weight polymers with poor mechanical properties used as prepolymers e.g., in polyurethane synthesis or as additives, e.g., plasticizers [1–3]. The development of ring-opening polymerization (ROP) methods led to a new class of biodegradable and biocompatible polyesters like poly($\varepsilon$-caprolactone), polylactide and polyglycolide, which have found applications, often as sophisticated materials, in biomedicine as body implants, bioresorbable devices and surgical sutures, and drug delivery systems [4–11].

In recent years, ecological requirements have stimulated a renewed interest in aliphatic polyesters for applications such as degradable materials in packaging, disposables and agriculture as alternatives to commodity plastics [12–16,75]. As a result, new biodegradable condensation polyesters appeared [17–20]. Research has also been carried out with the aim of modifying polyesters synthesized via ROP. This can be achieved by very different ways, among them the design of polymer architectures, as the polymer topology can substantially influence its physical properties. Along with linear polymers, a variety of branched counterparts have been synthesized, among them star, hyperbranched, graft and dendri-graft polymers. Macromolecular engineering via controlled branching has become a goal of many research groups.

Branching can be achieved by applying different strategies and employing different methods of polymer synthesis. Branched polymers can be synthesized by both step-growth (polycondensation) and chain-growth (ROP) processes. In recent years, combinatorial chemistry has also been applied for this purpose.

The basic synthesis method for highly branched polymers is known from the studies of Flory in the early 1950s concerning the polycondensation of $AB_x$-type multifunctional monomers [21]. Highly branched structures can also be obtained by the chain polymerization of "latent" $AB_x$ monomers such as the self-condensing vinyl polymerization (SCVP) of $AB_x$ vinyl monomers (developed by Fréchet [22]) or by the ring-opening multibranching polymerization (ROMBP) of $AB_x$ cyclic monomers [23,24]. The name "hyperbranched polymers" was used for the first time by Kim and Webster in 1988 for hyperbranched polyphenylene [25].

The above general methods – the polycondensation of $AB_x$ monomers and ring-opening multibranching polymerization – are also the main methods of highly branched polyester synthesis.

Numerous diverse examples of the synthesis of branched aliphatic polyesters can be found in the literature, indicating the great interest in such products. They are also described in several reviews but only a few present selected branched polyesters synthesized by ring-opening polymerization (ROP) [26,27]. A significant part of the material presented in reviews on hyperbranched polymers [28–33] and aliphatic polyesters [14,34,35], where some chapters are devoted to branched polyesters, covers polyesters obtained by polycondensation processes of $AB_x$ monomers such as 2,2-bis(hydroxymethyl)propionic acid (bisMPA). The polycondensation of this hydroxy acid has been the subject of many articles and resulted in a commercial product, Boltorn$^{TM}$ (Perstorp), a densely branched dendritic polyester with multiple hydroxyl groups (polyol) and a molecular weight in the range of 1500–5300. Boltorn$^{TM}$ has found applications as an additive for polyurethane foams or a precursor oligomer for UV-curing coatings [29,36].

Several examples of copolymers of these dendritic condensation polyesters with polylactones obtained by the ring-opening polymerization of cyclic esters initiated from hydroxyl groups present in a hyperbranched core (leading to a core–shell structure) [14] and a few examples of dendrimer-like star polyesters [32] were also briefly discussed in the mentioned reviews. However, these examples are placed within a large body of information concerning