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# Branched polyesters: recent advances in synthesis and performance

Matthew G. McKee[b], Serkan Unal[a], Garth L. Wilkes[b], Timothy E. Long[a,*]

[a]*Department of Chemistry, Virginia Polytechnic Institute and State University, 124A Davidson Hall, Blacksburg, VA 24061, USA*
[b]*Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA*

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**Abstract**

The synthesis, characterization, physical properties, and applications of branched polyesters are discussed. This review describes recent efforts in the synthesis of statistically and tailored branched systems, and performance advantages compared to linear counterparts. In particular, an emphasis is placed on long-chain branching, where the branches are sufficiently long enough to form entanglements. Step-growth polymerization methodologies that employ various combinations of multi and mono-functional groups to achieve different levels of branching are reviewed in detail. The performance of branched polyesters, including behavior in dilute and semi-dilute solutions, and melt and solid-state properties are discussed. The implications of topological parameters including branch length, number of branches, and branching architecture on rheological performance are also reviewed. Although the majority of this review focuses on the synthesis and rheological behavior of branched polyesters, some discussion is devoted to the influence of branching on solid-state properties, sub-micron fiber formation, and controlled biodegradation for drug-delivery applications. Finally, a perspective of future directions in high performance applications for branched polyesters is provided.


*Keywords:* Branching; Polyesters; Rheology; Entanglements; Crystallization; Step-growth polymerization

**Contents**



* Corresponding author. Tel.: +1 540 231 2480; fax: +1 540 231 8517.
*E-mail address:* telong@vt.edu (T.E. Long).

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## 1. Scientific rationale and perspective

Branched polymers are characterized by the presence of branch points or the presence of more than two end groups and comprise a class of polymers between linear polymers and polymer networks [1]. Although undesirable branching can occur in many polymerization reactions, controlled branching is readily achieved. In fact, numerous studies on polymer structure-property relationships have shown that branched polymers display enhanced properties and performance for certain applications [2]. Long-chain branched polymers offer significantly different physical properties than linear polymers and polymer networks. For example, a low concentration of long chain branching in the polymer backbone influences melt rheology, mechanical behavior, and solution properties, while large degrees of branching readily affects crystallinity [3,4]. The strong influence of only one long chain branch per chain can be visualized by looking at Fig. 1. The 'slip-links' along the polymer backbone represent entanglements with other chains. The linear polymer is free to diffuse along a tube imposed by other chains, while it is obvious from Fig. 1b that the mobility of the long-chain branched polymer is restricted, and must diffuse through some other mechanism. Thus, it is not surprising that long-chain branched polymers exhibit very different properties where chain entanglements play a role.

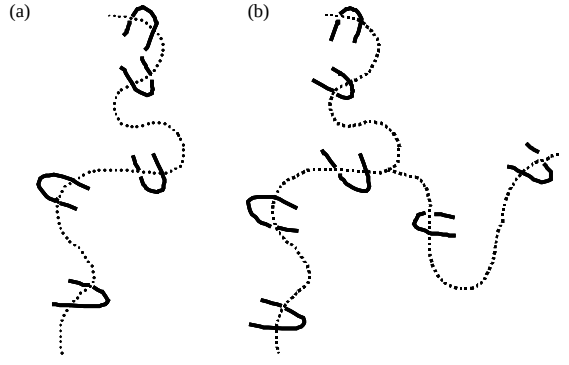


Fig. 1. Cartoon representing entangled linear chains (a), and long chain branched chains (b). The slip links represent entanglements due to other polymers.