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Feature article

# Recent advances in alternating copolymers: The synthesis, modification, and applications of precision polymers

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ABSTRACT

Alternating copolymers represent a special class of copolymers, in which the two comonomers copolymerize in a regular alternating sequence along the chain. Their interesting physical and chemical properties, as well as the underlying mechanism, have attracted significant attention in both academia and industry. The electron-donor benzylidene monomers – styrene and stilbene, readily form alternating copolymers with the electron-acceptor monomers – maleic anhydride and *N*-substituted maleimides. The rich chemistry of the substitution groups on these monomers offers enormous combinations for the synthesis of alternating copolymers for different applications. In this paper, we aim to provide a general overview of recent publications on the specific field of these benzylidene-containing alternating copolymers, and the emphasis is placed on the synthetic progress, structure-property relationships, and the applications of these copolymers.



**Contents**



## 1. Introduction

Copolymers are polymers synthesized from two or more species of monomers [1]. The study of copolymers could be traced back to the 1930s since synthetic rubber was invented and developed [2]. Ever since then, the research on copolymers has received considerable attention because an infinite variety of different copolymer composition could be synthesized and specific desired properties could be tailored by varying the species and composition of the comonomers. Based on different arrangements of the comonomers, the copolymers can be typically categorized as random or statistical copolymers, block or segmented copolymers, graft copolymers, alternating copolymers, periodic copolymers [3], while some new types of copolymers, such as gradient copolymers [4] and aperiodic copolymers [5] emerged in recent years (Fig. 1) [6–8].

In an alternating copolymer, the two comonomers arrange in a regular alternating sequence [1], and the alternating copolymerization is characterized by the product of the two monomer reactivity ratios as $r_1r_2 = 0$, in which $r_1$ and $r_2$ represent the ratio of the rate constant of homopropagation to the rate constant of cross-propagation of each reactive propagating species [9]. In other

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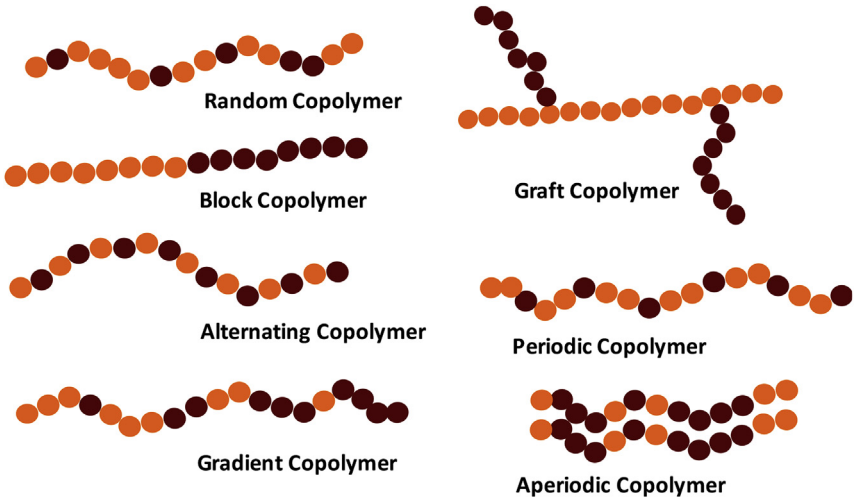


**Fig. 1.** Types of copolymers.

words, each of the propagating species prefers to add the other monomer rather than react with its own type of monomer. Perfect alternation happens when $r_1$ and $r_2$ are both equal to zero, where no dyads or homo-addition will be found in the copolymer, while such dyads can be found when both $r_1$ and $r_2$ are very small or one r is small and the other r is zero, where the copolymer shows alternating behavior but does not strictly alternate. The comonomer systems that can form alternating copolymers include electron donor-acceptor pairs, complexes formed with Lewis acids, Ziegler-Natta or metallocene catalyzed ethylene and cis-olefins, zwitterion intermediates, and etc. Although two difunctional monomers also polymerize alternatively in step growth, the polymers from step growth are not usually considered as alternating copolymers [10], and the two units are often seen as one repeat unit. Among all these systems, of special interests are in the radical polymerizable electron donor-acceptor pairs. The electron donor monomers, such as styrene, stilbene, vinyl ethers, dienes and *N*-vinylcarbazole, and electron acceptor monomers, such as maleic anhydride, *N*-substituted maleimides, dialkyl fumarates and fumaronitriles, provide numerous combinations and possibilities in achieving alternating copolymers of different properties and applications.

Several models have been proposed to explain the alternating behavior from a mechanistic point of view (Fig. 2). The earliest

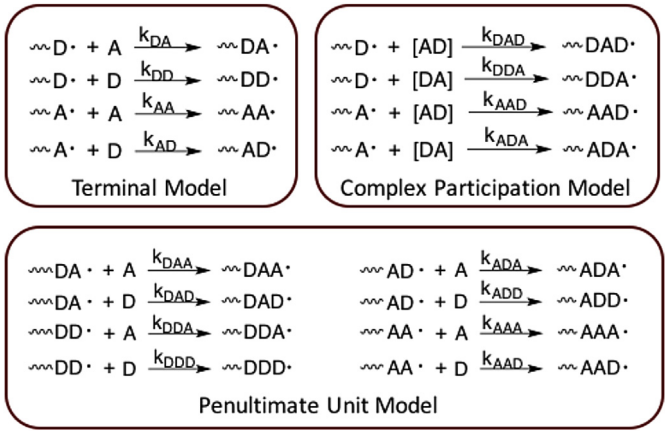


**Fig. 2.** Demonstration of three models of the mechanism of alternating copolymerization, D and A represent donor and acceptor monomers, respectively.

Mayo-Lewis model suggested that the rate constant of the propagation of the polymer chain relates to the terminal radical and the incoming monomer (thus it's also referred as the terminal model) [11]. The terminal model could be used to describe the copolymer composition as a function of monomer feed composition, but fails to explain the relationship of rate constant versus monomer feed composition [12]. However, this relationship could be explained well using the penultimate unit model, which suggests that the rate of propagation of the polymer chain does not only rely on the terminal radical, but also on the penultimate monomer unit [12–15]. One plausible interpretation from the theoretical calculations was that the transition state of the propagation can be represented by three hindered rotors, and one of the rotors is greatly affected by the penultimate unit [16]. Another well-known model, the complex participation model suggests that the charge-transfer complex, which is formed *via* the interaction between the electron donor monomer and the electron acceptor monomer pairs, participates in the copolymerization [17,18]. The existence of the charge-transfer complexes have been confirmed by spectroscopic evidence [18–21], but it is still questionable whether the complexes are actually added to the propagating radicals, or the complexes dissociate upon the polymerization and only one monomer is added to the propagating chain each time [22–24]. Generally speaking, there still remains a debate over the exact mechanism of the alternating behavior, and efforts are continuously made to study the mechanistic steps behind alternating copolymerization.

Examination of the literature shows that there is a lack of review articles on alternating copolymers since 2000. Cowie's book on alternating copolymers was published in 1985 [10], and a few reviews focusing on the mechanisms of alternating copolymerization [15,25,26] or specific applications of some alternating copolymers [27] were reported. However, much progress has been made on the synthetic techniques, mechanistic studies, property evaluation and applications. In this review, we specifically focus on the alternating copolymers that were formed by benzylidene monomers styrene or stilbene with maleic anhydride or *N*-substituted maleimides. The detailed synthetic pathways, the miscellaneous modifications, fundamental structure property measurements, and various applications of the alternating copolymers of styrene or stilbene with maleic anhydride or maleimides monomers will be discussed in this paper.