



Feature Article

Molecular engineering of branched polymers through 1,1-diphenyl-ethylene chemistry and anionic polymerization



Linxiang Hong, Shaohui Yang, Junpo He*

State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Polymers and Polymer Composite Materials,
Department of Macromolecular Science, Fudan University, Shanghai 200433, China

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ABSTRACT

In this feature article, we describe the synthetic work in our laboratory on branched polymers through anionic polymerization reaction based on selective addition of organolithium toward a bifunctional 1,1-diphenylethylene derivative, 1,3-bis(1-phenylvinyl)benzene (MDDPE). Exclusive monoaddition was achieved using equal molar ratio of organolithium and MDDPE in THF, in which the solvent polarity played a decisive role for the addition behavior. The monoaddition was used in the synthesis of ABC- and ABCD-type miktoarm star polymers through successive reactions on the double bonds of MDDPE. The monoadduct, either with butyllithium or polymeric lithium, was also utilized as inimer or macroinimer to synthesize hyperbranched polymers, hyperbranched block copolymers or terpolymers, respectively, through self-condensing vinyl copolymerization (SCVCP) with vinyl monomer. A very specific application of the anionic inimer is the development of a continuous process for the synthesis of living dendrimer-like polymers. By this approach, dendrimer-like polystyrene of 5th generation can be synthesized within 12 h. Functionalization and copolymerization were also possible on the basis of living dendrimer-like polymers. We also developed another facile method for the synthesis dendrimer-like polymers using anionic “grafting-to” reaction. Dendritic products with extremely large molecular weights were obtained. In addition, the anionic “grafting-to” reaction was used in the synthesis of graft polymers with “V-shaped”, “Y-shaped”, “comb-on-comb” and dendritic side chains.

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* Corresponding author.

E-mail address: jphe@fudan.edu.cn (J. He).

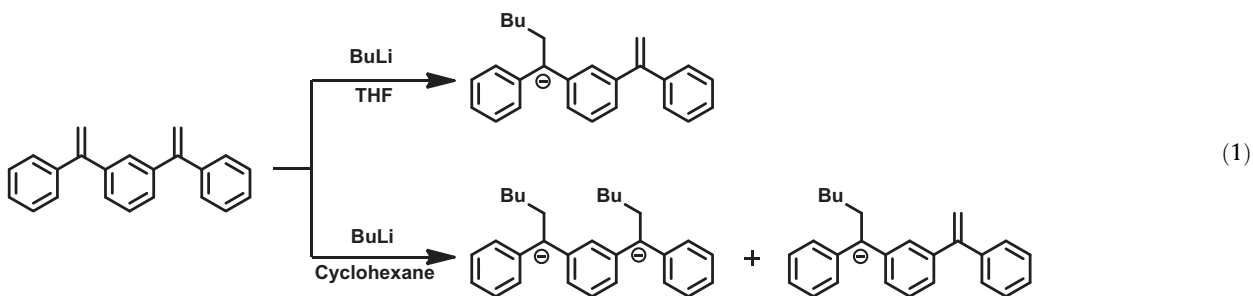
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1. Introduction

The chemistry of 1,1-diphenylethylene (DPE) with carbanion is widely applied in polymer synthesis through anionic polymerization [1]. DPE reacts readily with alkyllithium at stoichiometric condition, resulting in 1,1-diphenylalkyllithium with attenuated reactivity due to delocalization effect and the steric hindrance of the two phenyl rings. This reaction has therefore been used to make model initiator, macromonomer, end-functionalized polymers with orthogonal functionalities, block copolymers, as well as polymers with various architectures [2,3].

Bifunctional DPE derivatives, 1,3-bis(1-phenylethenyl)benzene (MDDPE) and 1,4-bis(1-phenylethenyl)benzene (PDDPE), can serve as precursors for dilithium initiators

first vinyl group had reacted with alkyllithium, the second vinyl group showed similar or even higher reactivity in MDDPE, but reduced reactivity in PDDPE, respectively [11,12]. This is because the latter can delocalize the negative charge into *para*-positioned double bond, while the former cannot delocalize the negative charge into *meta*-positioned double bond. Therefore, the reactivities of the two double bonds of MDDPE are nearly equivalent, while the reactivity of the second double bond of PDDPE is remarkably reduced. A more important factor that determines the addition behavior is the reaction medium polarity. Nonpolar solvent such as cyclohexane favors diadduct, while polar solvent such as THF results in monoadduct even at equal molar ratio of MDDPE to organolithium [13].



and linking molecules for the synthesis of block and star-like polymers via anionic polymerization [4–10]. These capabilities closely relate to their addition reaction behavior with carbanion. It was reported that, once the

We revisited the addition reaction between MDDPE and *sec*-butyllithium (*sec*-BuLi) and analyzed the product distribution systematically with varying the molar ratio of the reactants [14–16]. As shown in Fig. 1, the product of

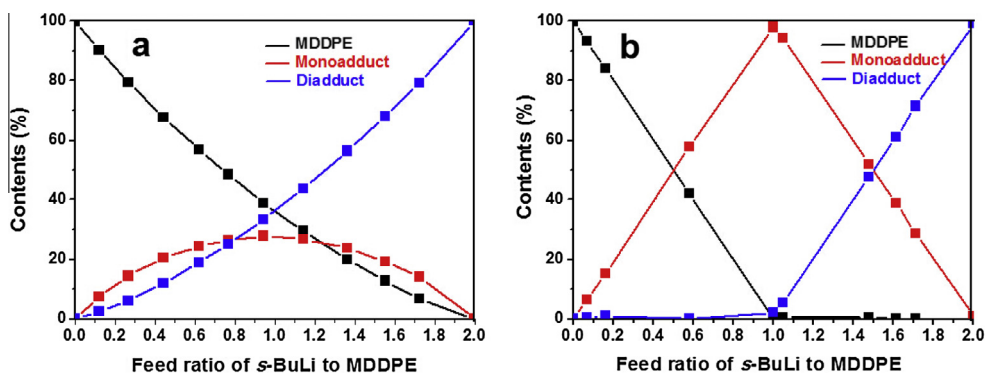


Fig. 1. Product distribution of the addition reaction at various feed ratio of *sec*-BuLi/MDDPE in (a) cyclohexane at 45 °C and (b) in THF at ca. -80 °C. The lines are drawn for guiding the eyes. Reproduced from Ref. [16] with permission from ACS.

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