



Feature article

Reorganizable and stimuli-responsive polymers based on dynamic carbon–carbon linkages in diarylbibenzofuranones

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ABSTRACT

The incorporation of dynamic bonds into polymer structures has endowed polymers with structurally reorganizable properties and stimuli-responsiveness. Their macroscopic responses are directly attributed to the nature of each dynamic bond. In this paper, we review the unique chemistry of diarylbibenzofuranone-based dynamic carbon–carbon covalent linkages that are under continuous equilibrium between dissociation and recombination at room temperature without any external stimulus, in polymers. Such polymers with the dynamic C–C bonds can show fascinating functions in response to mild stimuli as represented by self-healing and reversible stress-detection, although the continuous equilibrium should be regulated properly for each desired outcome by rational macromolecular design. This review highlights the potential of the dynamic C–C covalent chemistry for polymeric materials, particularly those used in the biomedical field because of its dynamic nature under mild conditions, and describes how to fully utilize it.

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1. Introduction

Throughout the history of polymeric materials, polymers have been designed to “passively” endure external factors such as light, heat, mechanical stress, and chemicals, which can degrade their material properties. For this purpose, irreversible, strong covalent bonds and interactions, rigid chains, crystalline structures, and polymer additives have been typically used to prevent bond cleavage. In the last two decades, however, some polymers have been synthesized that have a dynamic nature in response to external stimuli based on dynamic chemistries, where specific bonds (or interactions) can be cleaved (dissociated) and reformed (associated) under certain environmental conditions. This “active” mode has endowed polymers with structurally reorganizable properties and stimuli-responsiveness [1–4]. A variety of dynamic polymeric materials with fascinating properties have been developed, e.g., controlled drug delivery systems [5], self-healing polymers [6,7], stress-reporting polymers [8,9], and adaptable surfaces [10,11]. Such macroscopic responses are directly attributed to the nature of each dynamic bond at the molecular level; therefore, one can tune the dynamic properties of polymers by careful selection of the dynamic bonds.

Dynamic bonds can be defined as bonds or interactions that can undergo selective, reversible cleavage and reformation under equilibrium conditions upon exposure to certain environmental factors. Such bonds can be classified into two systems according to their underlying chemistries [12]: supramolecular chemistry [13] or dynamic covalent chemistry [14]. Both chemistries have been utilized in the fields of organic synthesis and drug discovery based on a concept of dynamic combinatorial chemistry [5,15]. Many bonds and interactions are known to form thermodynamically stable products under certain environmental conditions without any irreversible side reactions. Although the two chemistries share several principal features, generally, supramolecular interactions, where molecular shape and polarity are the dominant factors, are in continuous equilibrium under ambient conditions, whereas dynamic covalent bonds require external stimuli to undergo reversible chemical reactions.

This review focuses on the unique chemistry of dynamic carbon–carbon covalent linkages that are under continuous equilibrium at room temperature without exposure to any external stimulus. These anomalous bonds in dynamic covalent chemistry allow the structural reorganization and stimuli-responsiveness of polymers under mild conditions, resulting in macroscopic functions such as self-healing and reversible stress-detection. This review is not intended to be all-encompassing but instead highlights some recent examples that illustrate the potential of this unique chemistry for polymeric materials.

1.1. Dynamic covalent chemistry

In 2002, the concept of “dynamic covalent chemistry” was proposed by Rowan et al., where certain covalent bonds equilibrate between cleavage and recombination without any by-products, and rather than affording kinetically favorable species, thermodynamically stable species are formed under certain environmental conditions, despite the high stability under usual conditions [14]. Since then, various kinds of molecules with such covalent bonds have been recognized as dynamic covalent linkages. Several types of reactions have been used in organic synthesis, as well as in polymer chemistry: (i) reversible condensation reactions including boronate ester linkages [16,17], imine bonds [18,19], acylhydrazone bonds [20], and hemiaminal linkages [21]; (ii) reversible addition reactions as represented by some Diels–Alder/retro-Diels–Alder reactions [22]; (iii) chain exchangeable reactions such as

transesterification [23], olefin [24] and disulfide [25,26] metathesis, and siloxane chemistry [27]; (iv) radical transfer and crossover reactions involving disulfide bonds [28] and related sulfur-containing linkages [29,30]; and (v) homolytic bond cleavage and reformation, as typified by alkoxyamine linkages [31] and sulfanyl dimers [32]. These dynamic covalent systems can show their dynamic nature only under limited conditions; that is, under suitable equilibrium conditions realized by external stimulation such as heating. There are few systems that are in equilibrium at room temperature without stimulation, except for some modifications of existing systems [33–38].

1.2. Dynamic carbon–carbon linkages

Generally, carbon–carbon covalent bonds are regarded as being strong, irreversible, and static. For example, the C–C bond in ethane has a bond dissociation energy of 90 kcal/mol [39], which is much higher than those of dynamic supramolecular interactions represented by hydrogen bonds (ca. 7 kcal/mol) [40]. However, modification around the C–C bond including the introduction of steric hindrance, electronic effects, and resonance stabilization can lower the dissociation energy. One extreme example is the central C–C bond in diarylbibenzofuranone (DABBF) (Fig. 1). The modification around the central C–C bond lowers the dissociation energy to 20–25 kcal/mol [41,42] and stabilizes the radicals generated from C–C bond cleavage, enhancing the tolerance toward oxygen [43–45] even though usual carbon-centered radicals are unstable and highly reactive to oxygen. Because of these effects, the bonds can undergo selective, reversible cleavage and reformation with no irreversible side reactions under equilibrium conditions even at room temperature in air, while the ratio of dissociated species is significantly lower, less than 0.01%, in solution [41,42]. In addition to these unique features, the generated radicals are blue, which promises stimuli-responsive color changes [46]. Therefore, polymers with DABBF linkages can show dynamic behavior on exposure to mild stimuli or without any stimulus, as can supramolecular

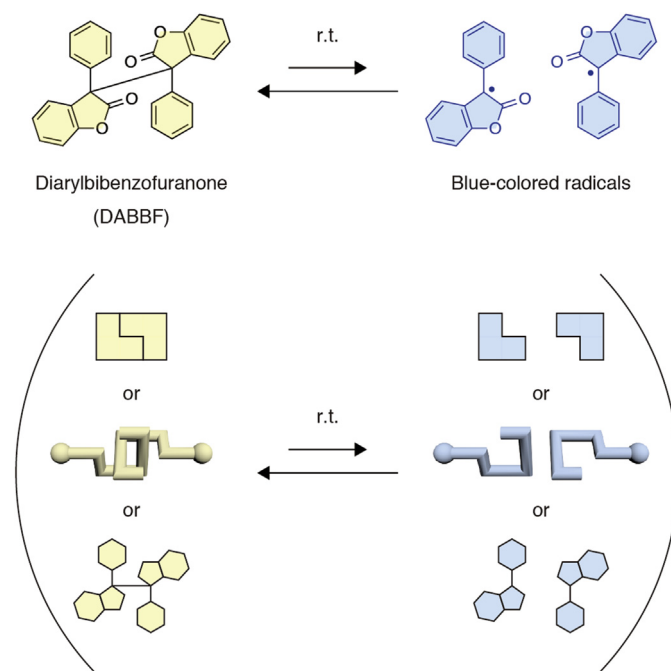


Fig. 1. Chemical structure and equilibrium of DABBF with corresponding stable blue radicals. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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