



Review

Let spiropyran help polymers feel force!

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ABSTRACT

Mechanoresponsive polymers have garnered significant attention in recent years, due to their great potential application in stress/strain sensing and damage warning. Several reviews of mechanochemistry have been published recently. In this review, we mainly focus on the most established mechanophore, spiropyran (SP), from an engineering perspective. We present a workflow for SP mechanochemistry, applications in various polymeric systems and impacting factors, as well as characterization techniques. Current limitations and future research directions are briefly highlighted in the end. This review aims to offer deep insight into polymer mechanochemistry and provide approaches to study other mechanophores using the example of SP mechanochemistry in polymers.

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1. Introduction

Recent decades have witnessed a growing interest in smart materials that are responsive to external stimuli, such as pH [1], temperature [2], light [3], ultrasound [4], redox agent [5], and voltage [6]. Among all fascinating responsiveness, mechanoresponsive polymers are of particular interest and importance due to their potential applications in stress/strain sensing and damage reporting. The most prevalent approach to design a mechanoresponsive polymer is to incorporate “mechanophore”, which contains mechanically labile bonds that are subjective to change under the influence of exogenous forces [7]. Based on different mechanoresponsiveness, mechanophores fall into several categories, such as mechanoluminescence [8], mechanochromism (optical changes under mechanical loadings) [9], mechanocatalysis [10], damage-healing [11], polymer remodeling [11], small molecule release [12].

So far there have been a variety of reviews covering various mechanochemistry, design principles of mechanoresponsive polymers and mechanoactivation approaches [13–17]. In this review, we mainly focus on spiropyran (SP) mechanochemistry, the most established and intensively studied among all mechanophores. When force is transmitted to the labile spiro C–O bond, the colorless SP form is mechanically activated to a colorful merocyanine (MC) form. SP motif is a model mechanophore in fundamental studies of the mechanoactivation behaviors in polymers. Because it is not only easy to be incorporated into polymer backbones or networks, but also capable of changing color and fluorescence upon mechanical loading, which is easy and direct to be detected. Therefore, gaining a deep and comprehensive knowledge of SP mechanochemistry is of great significance in the exploration of mechanochemistry in general.

Herein, this review is mainly focused on spiropyran mechanochemistry and its application in polymers. The remainder of this review is divided into five main sections: (1) to introduce spiropyran mechanochemistry; (2) to discuss applications of spiropyran mechanochemistry in polymer systems; (3) to systematically investigate impacting factors of spiropyran mechanoactivity (i.e. forward reaction of SP-to-MC and reversion of MC-to-SP); (4) to summarize characterization approaches; (5) to give a summary and a future perspective in terms of tackling the existing challenges of SP mechanochemistry.

2. Spiropyran mechanochemistry

2.1. SP mechanophore

When the C–O bond is cleaved by mechanical force, SP is activated to MC [18]. The closed SP is colorless/yellow and non-fluorescent, whereas the open MC form is blue/red/purple and fluorescent, as shown in Fig. 1a. Since the spiro C–O is the determining point for SP mechanoactivation, the attachment points on SP molecule should be on the opposing sides of the spiro junction so that the force can be effectively transmitted across the labile

bond to rupture it [9]. Based on this designing principle of active SP mechanophores, three types of SP mechanophores, as shown in Fig. 1b, have been reported and intensively studied in literature so far. Being “super smart”, SP1 and SP2 are sensitive to both UV light and mechanical force. However, it is not always advantageous to be super smart, since either UV irradiation or mechanical activation can result in the ring-opening of SP for outdoor materials. Compared to SP1 and SP2, SP3 exhibit advantages in damage sensing in outdoor materials since it is sensitive to mechanical force but not to UV irradiation due to the absence of electron withdrawing nitro group [19,20]. Moreover, SP3 appears to be more thermally stable (no SP-to-MC transition at high-temperature processing) than SP1 and SP2, which is advantageous in polymer processing [21]. Last but not least, the reversion of MC-to-SP is faster in SP3 than in SP1 and SP2 [20]. Hence, SP1 and SP2 can be used to give longer visual color warning, whereas SP3 is applicable for real-time stress sensing.

SP mechanophores are usually obtained by boiling salicylaldehyde (e.g. compound 2, 4, 5) and indole (compound 1, 3) in presence of piperidine or pyridine. Dihydroxyl group-containing SP mechanophores are easy to be prepared and thus used as precursor, which can be further functionalized into various groups, such as α -bromoisobutyryl group, methylacryloyl ester group, and bis-alkene group, to be covalently attached to different polymer systems. Fig. 2a–c shows the detailed synthetic route of three types of hydroxyl group-containing SP [9,19,22]. The most critical principle to design and prepare an effective HO-SP-OH mechanophore is to have the hydroxyl groups on the opposing sides of spiro junction, which requires both indole and salicylaldehyde contain hydroxyl group or hydroxyl group precursor.

2.2. SP mechanophore in polymers

To incorporate SP mechanophore into various polymer systems via different chemistries and mechanisms, SP molecule has been functionalized with different functional groups, such as hydroxyl group, α -bromoisobutyryl group, methylacryloyl ester group, and bis-alkene group, as shown in Fig. 1b. Generally, SP moiety is covalently incorporated into polymers as initiator, cross-linker or monomer.

2.2.1. Initiator

Hydroxyl-containing SP was used as initiator for ring opening polymerization (ROP) of caprolactone (CL) [22]. Functionalized with α -bromoisobutyryl group, SP was applied as atom-transfer radical-polymerization (ATRP) initiator for various polymer systems, including polyacrylates and block copolymers [9,23,24].

2.2.2. Monomer

Diol SP can also be employed as a monomer in step growth polymerization to obtain polyurethane (PU). The step growth polymerization enables controlling mechanophore concentration independently of molecular weight or cross-linking density [25].

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