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Mechanochromic Polymers that Turn Green upon the Dissociation of Diarylbibenzothiophenonyl: The Missing Piece toward Rainbow Mechanochromism

(a) DABBF

Kuniaki Ishizuki, Hironori Oka, Daisuke Aoki, Raita Goseki, and Hideyuki Otsuka*^[a]

Abstract: Mechanochromic polymers, i.e., polymers sensitive to mechanical impact, promise great potential for applications in damage sensors. In particular, radical-type mechanochromic polymers, which produce colored radical species in response to mechanical stress, may enable not only the visualization of mechanical stress, but also its quantitative evaluation by electron paramagnetic resonance analysis. In this work, a radical-type mechanochromic polymer that exhibits a color change from white to green upon dissociation of a diarylbibenzothiophenonyl moiety at the mid-point of a polystyrene chain is presented, and its mechanochromic behavior examined. Mechanochromic materials that show a variety of colors ('rainbow colors') in response to mechanical stress were prepared by simply mixing radical-type mechanochromic polymers of primary colors.

Mechanoresponsive materials have recently received increasing interest.^[1-4] In particular, mechanochromic polymers, which exhibit color changes upon exposure to mechanical stress, have attracted much attention in the field of materials science, as they are able to detect damage in materials, thus potentially preventing serious accidents by providing the chance to easily identify damaged parts and replace or repair them.[4-18] The main strategy for the design of mechanochromic polymers involves the incorporation of mechanochromophores, i.e., optically mechanoresponsive moieties, into polymer chains. A variety of mechanochromic polymers have been developed since Sottos and co-workers reported the first mechanochromic spiropyran unit embedded in poly(methyl acrylate), which endows this commodity plastic with mechanochromic properties.^[4] However, the combinatorial generation of color in mechanochromism remains challenging, as the number of molecules able to act as mechanochromophores is still limited. If color-controlled mechanochromism could be realized, it would be possible to detect damage and even recognize both the type and intensity of the mechanical stimulus via differences in the resulting colors.^[19-22] Since such a mechanoresponsive behavior is mainly limited to small molecules, the development of macromolecules, e.g., polymers, with mechanochromic properties is highly desirable, as it would allow the facile design

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Figure 1. Chemical structures of (a) DABBF, (b) TASN, and (c) DABBT before and after applying mechanical stress.

of materials with properties fit for that purpose. Herein, we report preliminarily work on the combinatorial generation of color with mechanochromic polymers by mixing three different mechanochromic polymers that exhibit differently colored radicals in response to mechanical stimuli of similar magnitude. The ultimate advantage of radical-type mechanochromic polymers is not only the qualitative visualization of the mechanical stress, but also its quantitative evaluation by electron paramagnetic resonance (EPR) spectroscopy, both in solution and the solid state. We have already reported two mechanochromic polymers radical-type that bear diarylbibenzofuranone (DABBF) or tetraarylsuccinonitrile (TASN) moieties (Figure 1a, b).^[7,23–27] Homolytic cleavage of the central carbon-carbon bond in the DABBF and TASN units in response to mechanical stress affords arylbenzofuranone (blue) and diarylacetonitrile radicals (pink), respectively. In these molecular systems, the regeneration of the carbon-carbon bonds via coupling reactions of the generated radicals has also been confirmed. Remarkably, the mechanoresponsiveness of the DABBF and TASN mechanochromophores was strongly enhanced after the incorporation in polymer chains. Since the two radical-type mechanochromophores display different colors, we envisioned that the development of a green radical-type mechanochromophore would complete the set of three primary colors, which would allow a subsequent development of rainbow mechanochromism. Maeda et al. have reported that the arylbenzothiophenonyl (ABT) radical, generated from diarylbibenzothiophenonyl (DABBT; Figure 1c) by homolytic

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cleavage in response to mechanical stress, exhibits green color $^{[2\bar{8},29]}$ We thus focused on the DABBT skeleton and designed DABBT derivatives for the insertion in a polymer chain. Since the responsiveness of mechanochromophores can be amplified upon incorporation in a polymer chain, a DABBTcentered polymer seemed an appropriate prospective for a mechanochromic material exhibiting green color upon exposure to mechanical stress. In this work, DABBT was employed as the mechanochromophore for a green-colored mechanochromic polymer, given that this color represents the missing piece toward the development of rainbow mechanochromism. A rational combination of such colored radical-based mechanochromic polymers, all of which are sufficiently stable in air to be easily handled, could potentially allow the control of the mechanochromism, the generation of a spectrum of colors, and a quantitative evaluation of mechanical stress.

To incorporate the DABBT skeleton into a polymer chain. a DABBT derivative with two hydroxy groups (DABBT-diol; Scheme 1) was designed and synthesized in eight steps from ethyl-2-(4-methoxyphenyl)acetate (Scheme S1). The product was fully characterized by ¹H NMR, ¹³C NMR, and IR spectroscopy, as well as mass spectrometry measurements, the results of which support the successful synthesis of DABBT-diol (Figures S19-S21). To investigate whether DABBT-diol could act as a green mechanophore, shear forces were applied to DABBT-diol at room temperature in air. The pale-yellow DABBT-diol powder turned to yellow/green after grinding (Figure 2a). EPR studies of the powder before and after grinding in a ball mill (30 Hz, 20 min) revealed a strong signal after grinding, while only a weak signal was observed before grinding (Figure 2c). The g value (2.005) confirmed that DABBT-diol undergoes, in response to the shear forces, a homolytic bond cleavage under concomitant formation of green radicals. To obtain further insight into the dissociation behavior of DABBTdiol, variable-temperature EPR and UV-vis spectroscopy measurements were carried out in solution. Based on the results of the EPR analysis and a van't Hoff plot (Figure S30-S32), the bond dissociation energy of the central C-C bond in DABBTdiol (87.9-92.0 kJ/mol) was estimated to be very similar to those of DABBF (85.4-104.8 kJ/mol)[27] and TASN (92.9 kJ/mol).^[25] High-temperature (70 °C) UV-vis measurements of a 1,4-dioxane solution of DABBT-diol revealed an absorption maximum at 452 nm, whose complementary color is green, demonstrating good correlation with the observed mechanochromism in the bulk. On the other hand, DABBF and TASN derivatives display absorption maxima at 640 and 543 nm, whose complementary colors are blue and pink, respectively (Figure S33).

Prior to the incorporation of **DABBT-diol** into a polymer chain, two ethynyl groups were added to **DABBT-diol** by reaction with 5-hexynoyl chloride to afford **DABBT-dialkyne**. Since mechanochromic polymers with relatively high glass transition temperatures (T_g) prevent the recombination of the activated radicals obtained upon cleavage of the mechanochromophore, polystyrene was selected as the matrix polymer to which the DABBT skeleton was attached.^[25,26] In the presence of CuBr as a catalyst, a click reaction of azideterminated polystyrene ($M_n = 6$ kDa, PDI = 1.18) and **DABBTdialkyne** afforded the corresponding linear polymer with a DABBT unit in the middle of the chain as a white powder (**PS-DABBT-PS**; Scheme 1). **PS-DABBT-PS** was characterized by ¹H NMR spectroscopy and gel permeation chromatography



Scheme 1. Synthesis of DABBT-dialkyne and PS-DABBT-PS.



Figure 2. (a) DABBT-diol and (b) PS-DABBT-PS before and after grinding. (c) EPR spectra of DABBT-diol and PS-DABBT-PS before and after grinding.

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(GPC). The ¹H NMR spectrum of **PS-DABBT-PS** (Figure S27) exhibits the characteristic signals of the DABBT skeleton, while the GPC profile shows a unimodal peak, whose molecular weight is approximately twice that of the precursor (the azideterminated polystyrene; Figure S28), indicating the successful synthesis of **PS-DABBT-PS** (M_n = 11 kDa, PDI = 1.13). The mechanochromic properties of **PS-DABBT-PS** were preliminarily evaluated by a grinding test (30 Hz, 20 min). After grinding, a color change from white to green was clearly observed (Figure 2b). The incorporation of polystyrene did not only result in a color change of the corresponding DABBT derivative from yellow to white before grinding, but also from yellow/green to bright green after grinding. Although the green color of the ground polymer was stable even after one day, the color immediately vanished and returned to white upon heating beyond the T_g of **PS-DABBT-PS** (90 °C) (Figures S29 and S34), or upon addition of a good solvent such as THF, which increases the molecular mobility. An EPR analysis of PS-DABBT-PS showed that the radical content increased with grinding ($g \approx 2.005$) in a similar fashion to that of ground DABBT-diol (Figure 2c). These results clearly confirm the mechanical selective scission of the central C-C bond of the DABBT unit at the center of the polymer chain. The dissociation ratio of DABBT in PS-DABBT-PS after grinding (~8.2%) was estimated to be more than 40 times that of **DABBT-diol** (0.2%). clearly demonstrating the enhancement of the mechanochromic properties after incorporation into the polymer chains.^[30-33] In general, PS-DABBT-PS was found to exhibit a behavior that is similar to that of other mechanochromic polymers bearing DABBF and TASN units as mechanochromophores.^[25,26]

Polystyrene-based mechanochromic polymers bearing TASN and DABBF units that connect their polymer chains (PS-**DABBF-PS**: *M*_n = 11 kDa, PDI = 1.14; **PS-TASN-PS**: *M*_n = 12 kDa, PDI = 1.10) were synthesized in a similar manner using the corresponding TASN and DABBF derivatives.^[25,26] The three radical-type mechanochromic polymers, PS-DABBT-PS, PS-DABBF-PS, and PS-TASN-PS were mixed and ground by ball milling (30 Hz, 5 min). As shown in Figure 3, the mixture containing PS-DABBT-PS and PS-DABBF-PS (1:1, w/w) exhibited a color change from white to dark green after grinding, which is a color that is different to those of the individual polymers. This color change can be explained by the fact that the individual polymers in the mixture absorb light of different wavelengths and reflect or transmit other colors, as observed in the case of colored paint. Similarly, the mixture of PS-DABBT-PS and PS-TASN-PS (1:1, w/w) underwent a color change from white to orange, while a mixture of PS-DABBF-PS and PS-TASN-PS (1:1, w/w) exhibited a color change from white to purple. Furthermore, the color of a mixture of all three polymers (1:1:1, w/w/w) changed after grinding from white to beige, the analogue of black when working with colored paint. These color grinding changes were also observed after the mechanochromophores themselves, i.e., the DABBT, DABBF, and TASN derivatives without the polymer chains, showing the corresponding color changes derived from the dissociation of the mechanochromophores after grinding under similar conditions. Such a rainbow mechanochromism may potentially be applied to a wide variety of polymeric materials.

In conclusion, a novel mechanochromic polymer that exhibits the green color of ABT radicals in response to shear forces was successfully synthesized from DABBT. The mechanochromic properties of DABBT were amplified upon



Figure 3. Photographs of PS mixtures containing DABBF, TASN, and DABBT before (top) and after (bottom) grinding.

incorporation of polymer chains with a relatively high T_{g} . Rational combinations with other mechanochromic polymers showed different colors in response to similar shear forces, and thus allowed the development of rainbow mechanochromism by simply mixing these polymers. Since the mechanochromophores can be inserted in different polymer chains, we intend to report in the near future the application of such high-performance materials with rainbow mechanochromism and defined mechanical properties in damage sensors able to discriminate

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both the type and intensity of mechanical stimuli by the resulting color.

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Keywords: polymer reactions • chromism • mechanochemistry • mechanochromism • radical

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Rainbow mechanochromism: A mechanochromic polymer that exhibits green color upon the dissociation of а diarylbibenzothiophenonyl unit at the mid-point of its polymer chain is presented. Rainbow mechanochromism was achieved by mixing three different radical-type mechanochromic polymers that exhibit blue, pink, and green color upon exposure to shear forces.



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