Mechanochemical Oxidative Cleavage of 1,1-Diarylethylene Derivatives Using Polymeric Mechanoradicals

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Polymer chains with molecular weights above a certain threshold undergo homolytic cleavage under mechanical stimuli, producing active radical species called mechanoradicals. While their use in polymer functionalization has been reported,[1] their application as radical sources in small-molecule organic reactions remains largely unexplored.[2]

1,1-Diarylethylene (DAE) undergoes oxidative cleavage catalyzed by azobisisobutyronitrile-derived carbon radicals in solution under an oxygen atmosphere, forming 1,1-diaryl ketones (DAK).[3] In this study, we investigated the oxidative cleavage of DAE derivatives under solid-state conditions using polymer chains as radical sources (**Fig. 1**).

DAE derivatives with various substituents were ground in the presence of a common polymer using a ball mill. ^{1}H NMR confirmed the formation of the corresponding 1,1-diaryl ketones for all derivatives, while the electron-poor derivatives also afforded 1,1-diaryloxiranes (**Fig. 1b**). Solid-state electron paramagnetic resonance (EPR) revealed the formation of oxyradicals (**Fig. 1c**), suggesting oxidation of the formed DAE-derived carbon radicals.

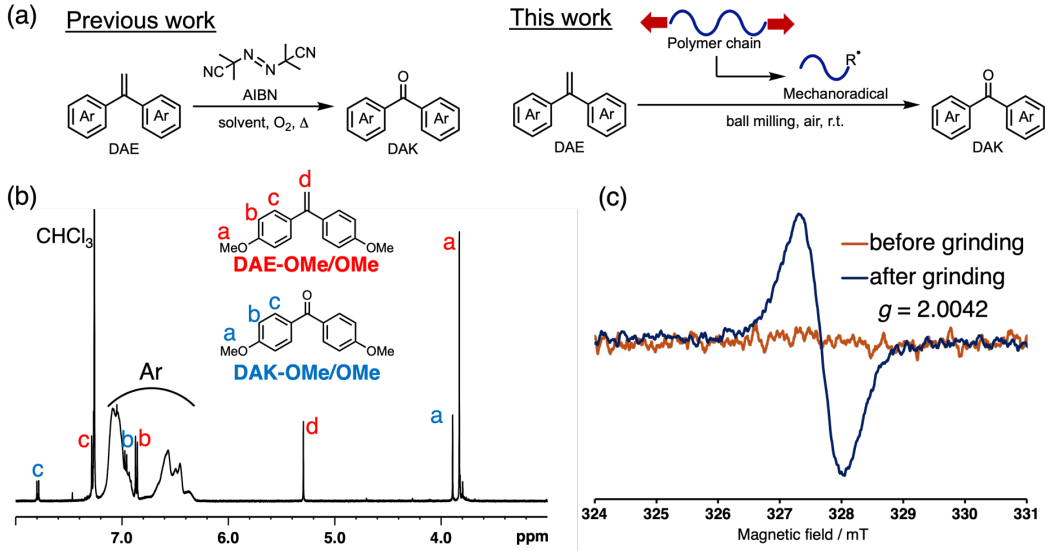

Fig. 1. (a) Conceptual illustration of previous work and this work. (b) ^{1}H NMR spectrum of the ground mixture of **DAE-OMe/OMe** and polystyrene ($CDCl_3$, 500 MHz). (c) ESR spectra of the mixture of **DAE-OMe/OMe** and polystyrene before and after grinding.

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