Synthesis of Functional Peroxide Mechanophores and Their Application to Mechanoresponsive Polymer Networks That Release Fluorescent Molecules

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For a long time, organic peroxides have been considered as unstable species and applied as radical generators or bleaching agents. Nevertheless, we found that bis(9-methyl-9-fluorenyl) peroxide derivatives (**BMPF**) were a class of stable compounds at room and even elevated temperatures. Furthermore, **BMPF** underwent chemical reactions in response to mechanical force and thus exhibited mechanochromic properties. Study on the model compound revealed the mechanism of the mechanochemical reaction in which 9-fluorenone, a fluorescent molecule, was released via the homolytic cleavage of peroxide bond, followed by β-scission[1] of the resulting oxygen radical. Since the mechanochemical properties of organic peroxide have rarely been documented hitherto, herein, we report our findings in exploring the mechanochemical properties of **BMPF**.[2]

Namely, **BMPF** was introduced as cross-linking units into both glassy and elastomeric network polymers. Grinding test to the glassy network polymer resulted in mechanochromic phenomena (Fig. 1B, upper) derived from the releasing of 9-fluorenone from the network polymer (Fig. 1A), which was consistent with the proposed mechanism in the model study. On the other hand, the elastomeric network showed mechanochromic behaviors under compressive force. A well-controlled fluorescent pattern could be printed by compressing the elastomer with an H-shaped metal stamp (Fig. 1B, lower). Besides, the network polymer exhibited satisfying stability at elevated temperatures up to 100 °C without stress relaxation or optical change. These results suggested that **BMPF** is a potential candidate as a novel peroxide-based mechanochromophore.

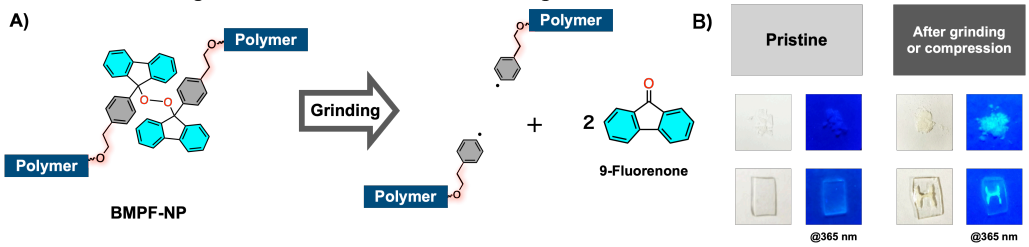

Fig. 1 (A) Releasing of 9-fluorenone from network polymer cross-linked by BMPF units, (B) Mechanochromic phenomena of BMPF cross-linked polymers.

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