論文 / 著書情報
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Title(English)	Theoretical and Experimental Studies on the Design of Stable Radical-type Mechanochromophores
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論 文 要 旨

THESIS SUMMARY

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要旨（英文800語程度）
Thesis Summary（approx.800 English Words ）

Mechanochromophores are the basic molecular units that exhibit optical changes upon the application of mechanical force, which could be utilized for damage reporting, life prediction, etc. The interesting properties of mechanochromophores are facilitated by the cleavages of semi-stable bonds in response to mechanical stimuli. Among various mechanochromophores, radical-type mechanochromophores, which undergo homolytic carbon-carbon bond cleavages and generate corresponding radicals in response to mechanical force, are especially of scientific and practical significance because the generation of radicals would not only result in color change, but also allow quantitative analyses via electron paramagnetic resonance (EPR) spectroscopy.

Nevertheless, the poor thermal stability of common radical-type mechanochromophores has long been a limitation for the further development of radical-type mechanochromophores. In detail, most of the radical-type mechanochromophores are in equilibriums with corresponding radicals even at mild temperature, which makes it impossible to integrate such mechanochromophores into polymers via the mostly used free radical polymerization. On the other hand, the poor thermal stabilities also result in unspecific response to mechanical force because heat could work as an interference. Due to the limited examples of thermally stable radical-type mechanochromophores, the methodology to design such a mechanochromophore had remained unexplored. This dissertation aims to solve these issues in order to expand the versatilities of radical-type mechanochromophores. For that purpose, a variety of carbon-centered radicals were synthesized and the characterizations of their reactivities were carried out.

In Chapter 2, bis[9-(4-methyl)phenyl-9-fluorenyl] peroxide (BMPF) was accidentally obtained as the degradation product of 4-methylphenyl-9-fluorenyl radical. Interestingly, the BMPF unit exhibited mechanochromic properties that had never been reported so far. Motivated by the extensive research interest in organic peroxides as well as the novelty to design mechanochemical motifs based on organic peroxides, the mechanochemical reaction of BMPF was characterized and the results suggested the mechanism of the mechanochemical reaction was similar to the mechanism of the thermolysis of organic peroxides. Furthermore, the network polymers with BMPF cross-linking points were synthesized. The clarified reaction mechanism was utilized to render the network polymers with interesting mechanochemical reactivities, such as mechanochromic behaviors and fluorescent molecule releasing. Moreover, unlike common organic peroxides that are usually unstable, the BMPF motif exhibited good reaction compatibility and satisfying thermal stability that could tolerate high temperatures up to 110 °C. These findings suggested the novel organic peroxide-based mechanophore BMPF had great versatility. The discoveries in this chapter had a great novelty as one of the few reports regarding organic peroxide mechanophores and the first report on a system that could release small molecules based on the mechanochemistry of an organic peroxide.

In Chapter 3, to investigate the relationship between chemical structures and stabilities of organic radicals from a quantitative perspective, 19 radical dimers of organic radicals from 3 major categories were synthesized and their stabilities with respect to the two major degradation pathways of organic radicals, namely dimerization and aerobic peroxidation, were carefully examined. The experimental observations were further compared with radical stabilization energy (RSE) and singly occupied molecular orbital (SOMO) energy derived from the quantum chemical calculation. The results revealed that with the increasing electron abundance of radical centers, the dissociation constants of radical dimers derived from the experiment became larger while the computational RSE became deeper, as well as the first-order rate constants of aerobic peroxidation derived from the experiment became higher while the computational SOMO became larger. In particular, an approximately linear relationship between RSE values and the natural logarithms of dimer-radical dissociation constants, and a strong correlation between SOMO energies and the first-order rate constants of aerobic peroxidation were observed. These findings could be applied to design organic radicals with designated stabilities.

The conclusion of Chapter 3 suggested the electron-deficient design of an organic radical would result in the high thermal stability of the corresponding dimer. Based on this inference, a series of novel radical-type mechanochromophores with electron-deficient skeletons were designed and synthesized as thermally stable radical-type mechanochromophores in Chapter 4. These mechanochromophores were firstly characterized with respect to their thermal stabilities and reaction tolerances in free radical reactions. The results suggested they had satisfying thermal stabilities and hardly dissociated into radicals so that they could remain intact in radical reactions at mild temperature. Next, these mechanochromophores were integrated into network polymers as the cross-linking points via radical polymerizations at room temperature. The resulting polymers exhibited mechanochemical reactions to generate colored radicals, inducing multi-color mechanochromism, which was the coloration of pink, green, or blue, upon compression or stretching. The stress relaxation behaviors of these polymers were found to be related to the thermal stabilities of their cross-linking units. These findings not only verified the conclusion of Chapter 3, but also greatly expanded the versatilities of radical-type mechanochromophores.

In summary, novel thermally stable radical-type mechanochromophores and the guideline to design them were shown in this dissertation. The results are expected to contribute to the field of organic chemistry, polymer chemistry, material science, etc.