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Force-Triggered Radical-Type and Ratiometric Mechano-Fluorescence of Polyurethane Elastomers Containing Innovatively Modified [c2] Daisy Chain Molecules with Promoted Stretchabilities and Toughnesses

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The introductions of [c2] daisy chain rotaxanes with extended/contracted conformations and different polymerization active sites into mechano-fluorophoric polyurethane (PU) networks were carried out via the step-growth polymerizations to gain PU films with interesting mechanical and optical properties upon stretching. As expected, the distinctive stretchabilities and toughnesses of PU films containing [c2] daisy chains with long-range slipping motions of mechanically interlocked molecules (MIMs) were noticeably enhanced, the obtained PU films presented great stretchabilities and toughnesses. Moreover, the attractive ratiometric fluorescent behaviors (Figure 1) with the energy transfer efficiency of ca. 27.8% between blue-emissive tetraphenylethylene (TPE) and yellow-emissive diaryl acetonitrile radical species (DAAN·) could be observed by stretching due to the combination of [c2] daisy chain rotaxanes into PU backbones to offer the reversible dual fluorescent switching upon stretching and relaxation processes [1, 2]. Furthermore, the stretching deformation of PU films could be studied by small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) techniques to prove correlated morphological characteristics of stretching states in the oriented [c2] daisy chain-based PU films. Besides, the important shape recovery and reversible ratiometric mechano-fluorescent switching characteristics of [c2] daisy chain-based PU films could be obtained by heating, demonstrating practical applications of designed daisy chain-based PU films with impressive mechanical and optical properties in advanced materials.

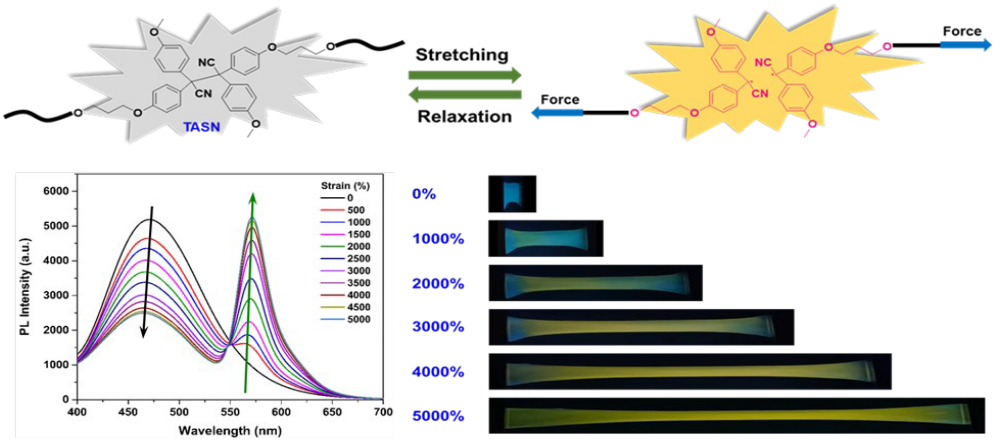

Figure 1. PL spectra of polyurethane (PU) films with different stretching ratios of 0-5000% strains (λ_{ex} = 365 nm).

[1] Khang, T. M., Huang, R., Khan, A., Chuang, W. T., Nhien, P. Q., Cuc, T. T. K., Hue, B. T. B., Wei, K. H., Li, Y. K., Lin, H. C. (2022). *ACS Mater. Lett.* **4**, 2537.

[2] Cuc, T. T. K., Hung, C. H., Wu, T. C., Nhien, P. Q., Khang, T. M., Hue, B. T. B., Chuang, W. T., Lin, H. C. (2024). *Chem. Eng. J.*, **485**, 149694.

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