

Visualization of Polymer Crystallization and Neck-initiation in Uniaxial Tensile Deformation by Using Fluorescent Mechanochromophore

(¹Department of Chemical Science and Engineering, Tokyo Institute of Technology, ²Department of Life Science and Technology, Tokyo Institute of Technology, ³RIKEN)

○Sota Kato,¹ Daisuke Aoki,¹ Kazusato Oikawa,² Kousuke Tsuchiya,² Naohiko Shimada,³ Atsushi Maruyama,³ Keiji Numata,² and Hideyuki Otsuka¹

Keywords: Spherulites, Confocal laser scanning microscopy, Electron paramagnetic resonance measurement, Necking, Tie molecule

The growth process of lamellar crystals and the effects of the crystallization process on the mechanical properties have been studied. Herein, we propose the strategy for visualizing the polymer crystallization or neck-initiation in uniaxial tensile deformation with quantitative evaluation of mechanical stress by using a mechanochromic probe, called tetraarylsuccinonitrile (TASN, **Fig. 1a**),^[1-4] generating radicals with yellow fluorescence triggered by homolytic cleavage at the central C–C bond in response to mechanical stress. In this work, poly(ϵ -caprolactone)s (PCLs) with TASN in the center of the structure are synthesized by ring-opening polymerization initiated by TASN derivatives. Their primary structures are selected as linear or star, named as **L-PCL** or **S-PCL** (**Fig. 1a**).

The visualization of the polymer crystallization or neck-initiation in uniaxial tensile deformation was studied by confocal fluorescence microscope observations. As shown in **Fig. 1b**, spherulites of **L-PCL** grew from the amorphous part from the beginning of isothermal crystallization. As shown in **Fig. 1c**, spherulites of **S-PCL** were oriented to stretched direction and emit yellow fluorescence in uniaxial tensile tests. Through electron paramagnetic resonance (EPR) measurements in isothermal crystallization or uniaxial tensile deformation, the dissociation ratio of TASN moiety was increased as the molecular weight or the number of arm-PCLs increased. It could indicate (1) an increase of TASN moiety as the tie molecule with increasing molecular weight and (2) a large difference in the number of ‘active’ TASN moiety due to the difference in the formation of lamellar layers.

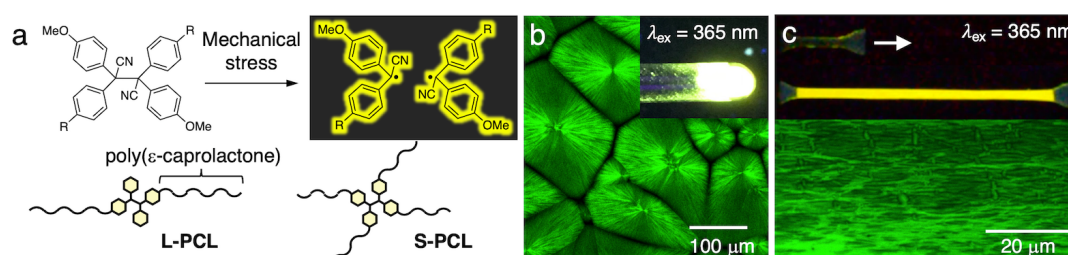


Fig 1. a) Chemical structure of tetraarylsuccinonitrile (TASN) derivative and schematic image of TASN-containing linear polycaprolactone (**L-PCL**) and star polycaprolactone (**S-PCL**). b) Microscopic image of **L-PCL** after isothermal crystallization.^[5] c) Microscopic image of **S-PCL** after uniaxial tensile test.

[1] H. Otsuka *et al.*, *Chem. Commun.* **2017**, 53, 11885. [2] S. Kato, K. Ishizuki, D. Aoki, R. Goseki, H. Otsuka, *ACS Macro Lett.* **2018**, 7, 1087. [3] S. Kato, D. Aoki, H. Otsuka, *Polym. Chem.* **2019**, 10, 2636. [4] S. Kato, D. Aoki, H. Otsuka, *ACS Appl. Polym. Mater.*, **2021**, 3, in press. [5] S. Kato, S. Furukawa, D. Aoki, R. Goseki, K. Oikawa, K. Tsuchiya, N. Shimada, A. Maruyama, K. Numata, H. Otsuka, *Nat. Commun.*, **2021**, 12, 126.