

Mechanical properties and structures under the deformation of thiophene copolymers with cyclic siloxane units

Polymer-based electronic devices have attractive features such as low fabrication cost, low weight, and diverse form design. Controlling the mechanical modulus and elongation at break expands the utility of conjugated polymers when developing flexible and stretchable devices. Flexibility and stretchability are achieved in wearable devices that follow the stretching of the human skin with a low mechanical modulus, high elongation, and elastic recovery. However, because conjugated polymers consist of rigid aromatic rings, their fragility is a challenge. Researchers have focused on achieving flexibility in conjugated polymers using various approaches; for example, composites of rubber components and block copolymers with flexible segments have been proposed.

Although polythiophenes have garnered significant attention as semiconductive materials for hole transport, polythiophenes without side chains lack solubility in conventional organic solvents as well as processability using painting and heat-melting methods. Substitution of alkyl side chains into thiophene rings has been suggested in order to improve their solubility and processability, as well as to achieve higher electronic conductivities through self-assembly and crystallization involving side chains. Thus, we focused on the effects of polythiophene side chains and introduced flexible dimethylsiloxane groups into these side chains. We previously reported the flexibility of polythiophenes with disiloxane side chains [1].

Herein, we focus on random copolymers with 3-dodecyl-thiophene (3DDT) and thiophenes, including cyclic siloxanes, as flexible side chains (3CSiT or

3tetraCSiT), as shown in Fig. 1 [2]. Self-standing P(3DDT-3CSiT) films were prepared via the formation of cross-links. P(3DDT-3CSiT) films containing the acid generator TsOCH were prepared using a casting method. Acid_anneal and Acid_melt films were prepared under different thermal heating conditions. In contrast, the Melt_tetra films inherently possessed cross-linking points without any thermal treatment because the four-armed cross-linker unit 3tetraCSiT was involved in the polymerization process. A Melt_tetra film was also prepared by hot-pressing owing to the low solubility of P(3DDT-3tetraCSiT) in organic solvents. To compare the structural and mechanical properties, a Noacid film without the acid generator was also prepared.

The mechanical properties of the prepared polythiophene films were investigated via tensile tests. The strain-stress curves are shown in Fig. 2. Compared to P3DDT without cyclic siloxane moieties, the Young's modulus and tensile strength of the Noacid film decreased, whereas its strain at break reached 300%. The Noacid film exhibited crystallinity similar to that of P3DDT. Therefore, the higher strain at break can be attributed to the flexible cyclic siloxane side chains. Moreover, the formation of crosslinkers in the Acid_melt and Acid_anneal films provided larger modulus and lower strain at break than those of the Noacid films. The difference in crystallinity between the Acid_melt and Acid_anneal films caused the slightly larger modulus for the Acid_anneal films than for the Acid_melt films. The mechanical properties of the Melt_tetra film were similar to those of the Acid_anneal

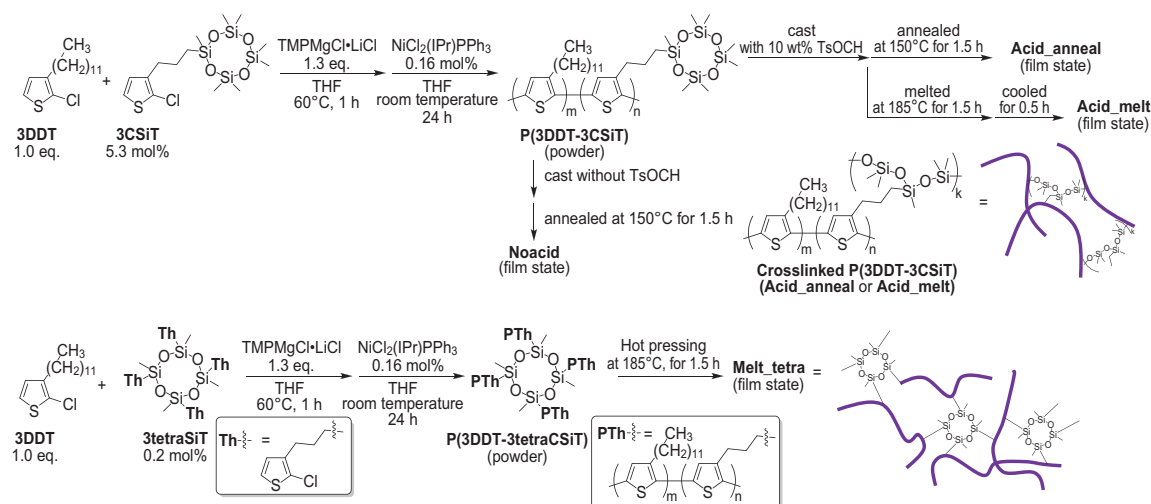


Fig. 1. Scheme of crosslinked polythiophenes syntheses.

and Acid_melt films due to the crosslinking of the tetra-substituted cyclic siloxane in the Melt_tetra film.

Cyclic tensile tests were performed to evaluate the elastic recovery of the cross-linked polythiophenes. The strain recovery ratio (R_{50}) was calculated from the strain values before and after unloading. The R_{50} values of the Noacid, Acid_anneal, and Acid_melt films were 80%, 87%, and 91%, respectively. The Acid_melt film exhibited the largest elastic recovery ratio because of its cross-linking and low crystallinity. The Acid_anneal film had a lower crystallinity than did the Acid_melt film, which enhances plastic deformation. In contrast, R_{50} for the Melt_tetra film was 84%, which was higher than that of the Noacid film and lower than those of the Acid_anneal and Acid_melt films.

Next, we focused on the effects of cross-linking on elastic recovery and structural deformation and performed X-ray diffraction measurements under cyclic tensile deformation using SPring-8 BL03XU [3]. The changes in the degree of crystallite orientation under loading and after unloading were analyzed using the diffraction of the (100) plane, as shown in Fig. 3. These measurements were performed for the Noacid, Acid_anneal, and Melt_tetra films because their crystallinities were sufficient to evaluate the crystallite orientation under deformation. For the films without stress, the diffraction of the (100) plane was observed as Debye-Scherrer rings at 0 MPa, as shown in Fig. 3(c). Thus, before stress was applied, the crystallites were randomly oriented. As the stress increased, the diffraction ring gradually changed to an arc in the meridian direction. Changes in the Hermann orientation degrees of the films are shown in Fig. 3(b). The crystallite orientation of the Noacid film increased when the loading strain was greater than 50% and decreased after unloading. However, for strains of less than 50%, the orientation gradually increased through repeated loading and unloading. The degree of orientation did not decrease after unloading. These results suggest that when the Noacid film was drawn, the film involved necking, and yielding deformations occurred under strains less than 50%. In addition, after the necking was completed, the film was drawn

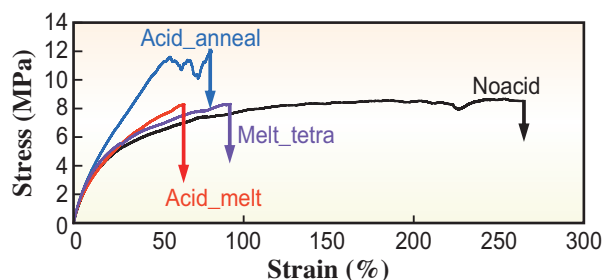


Fig. 2. Stress-strain curves of synthesized thiophene copolymers.

homogeneously after elongation at a strain greater than 50%. Therefore, the correlation between the strain and the orientation degree of the Noacid film was linear at strain values larger than 50%. The orientation degrees of the Acid_anneal film with high crystallinity and cross-links exhibited the highest repeatability with loading strains, as shown in Fig. 3. For the Melt_tetra film, the orientation degree of the crystallites exhibited higher repeatability when the strain was less than 40% compared with that of the Noacid film. However, the orientation degrees at strains greater than 40% were dispersed because of localized deformation under loading strain. These results coincide with the degree of cross-linking of the tetra-substituted cyclic siloxane moieties.

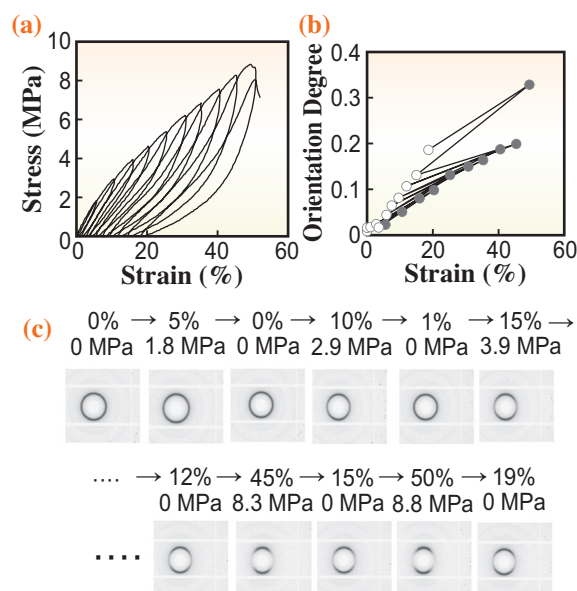


Fig. 3. (a) Stress-strain curves, (b) orientation degrees, (c) 2D X-ray diffraction images of Acid_anneal in *in situ* X-ray diffraction pattern measurements under cyclic tensile tests.

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References

- [1] J. Shen *et al.*: *Macromol. Chem. Phys.* **218** (2017) 1700197.
- [2] T. Matsumoto, M. Kashimoto, C. Kubota, S. Horike, K. Ishida, A. Mori and T. Nishino: *Polym. Chem.* **13** (2022) 5536.
- [3] H. Masunaga *et al.*: *Polym. J.* **43** (2011) 471.