



Structural deformation of elastic polythiophene with disiloxane moieties under stretching

Shen, Jian

Kashimoto, Masaki

Matsumoto, Takuya

Mori, Atsunori

Nishino, Takashi

(Citation)

Polymer Journal, 52(11):1273-1278

(Issue Date)

2020-11

(Resource Type)

journal article

(Version)

Accepted Manuscript

(Rights)

© 2020, The Society of Polymer Science, Japan

(URL)

<https://hdl.handle.net/20.500.14094/90009476>



Structural Deformation of Elastic Polythiophene with Disiloxane Moieties under Stretching

*Jian Shen^a, Masaki Kashimoto^a, Takuya Matsumoto^a, Atsunori Mori^a and Takashi Nishino^{*a}*

^aDepartment of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, Rokko, Nada, Kobe, 657-8501, Japan

Key Word

polythiophene derivatives, X-ray diffraction, semiconductive elastomer, fourier transform infrared spectrometer, *in situ* measurements

ABSTRACT

For the developments of wearable and stretchable devices, the insights on the mechanical properties and structural deformation of functional conjugated polymers are required. Especially, polythiophene has received much attention as a typical hole transfer material in electronic devices. However, the widely accepted polythiophenes were brittle because of the rigid chemical structure of thiophene rings. We have reported on the synthesis and flexible properties of polythiophene with disiloxane groups in side chains, and it was revealed that the polythiophene possessed larger elongation at breaking than 200% at room temperature. In this study, we investigated on the deformation process of the polythiophene with *in situ* measurements under stretching using X-ray diffraction at synchrotron radiation and polarized infrared spectroscopy. In the X-ray diffraction measurements, the orientation of crystallites occurred after yielding, while relative intensities of polarized infrared absorption bands were gradually increased once stretching. From these results, at the first of the deformation, the polythiophene chains in the amorphous region were aligned and then the whole bulks of the polythiophene including crystallites and amorphous were oriented after yielding. We succeeded in trace of structural deformation of the polythiophene under stretching.

Introduction

For these decades, electronic devices and their technologies have been remarkably developed. The types of the devices are diversified such as photovoltaic cells,¹⁻³ semi-conductive transistors,⁴⁻⁶ light-emitting diodes,⁷⁻⁹ biosensors,^{10,11} capacitors,¹²⁻¹⁴ memories¹⁵⁻¹⁸ and so on. In particular, portable devices (e-books, smartphones and tablets) are progressing rapidly from the perspective of their size, weight and performance.^{19,20} In future, for the further advance of Internet-of-things (IoT), higher-potential consumer electronics including those portable devices as well as wearable sensors, biomedical chips and flexible displays, are desired.^{10,11,19-22} In these electronic products, it is required that the fabrication cost, the weight, and the electricity power consumption of their electronic devices should be reduced. Therefore, the electronic properties of various organic- or inorganic-based materials have been investigated. In addition, the flexible, stretchable and bendable properties are indispensable in those advanced electronics. Compared with metal- or metal oxide-based materials, polymers are promising materials in the flexible, stretchable and bendable devices.

In reported flexible devices, micro patterning of their electrodes composed of inorganic materials²³⁻²⁵ and conventional elastomers including conductive inorganic fillers has been suggested.²⁶⁻³¹ For the fabrication of these devices, customization of the electrodes and another process of compositing with polymer and conductive fillers are required. Large mechanical deformation interrupts the electric performance of these customized devices by stress concentration to patterned electrodes and disconnection of conductive path. Therefore, fabrication of devices with elastic semi-conductive polymers is a preferable approach to bendable and stretchable devices with high durability toward mechanical deformation.³² The electrodes or

charge transport layers with single components of elastic materials lead to inherent improvements of mechanical brittleness in those devices.

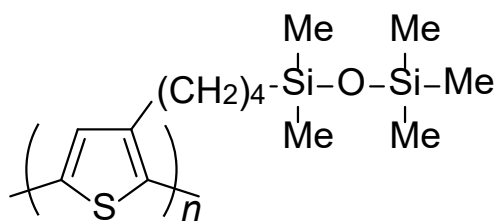


Fig.1 Chemical structure of P3SiT.

Conjugated polymers attract much attention as semi-conductive materials in flexible devices. However, conjugated polymers, with aromatic ring are rigid compared with conventional plastics. For deforming motions of wearable and comfortable devices such as bending and stretching, it is desired that the conjugated polymers are tougher and more elastic in their mechanical properties.^{33,34} In our previous work, we synthesized polythiophene with disiloxane moieties in side chains (P3SiT), as shown in Fig. 1, and investigated on its structure and mechanical and electric properties.^{35–37} The obtained P3SiT showed not only low Young's modulus (<50 MPa) and large elongation at break (>200 %), but also high electronic conductivity similar to P3HT. Higashihara *et. al.* have also reported on the polythiophenes with siloxane moieties and polythiophene-based *block-co*-polymers.^{38–40} Moreover, it is reported that siloxane moieties in side chains of conjugated *co*-polymers with diketopyrrolopyrrole and polythiophene units in their main chains also improved their mechanical properties as well as electronic performances.^{41,42} Their thiophene polymers with siloxane moieties were promising materials for flexible devices.

We have revealed that the electronic conductivity of P3HT in parallel to drawn direction increased with the crystallite orientation through drawing. The structure of P3SiT is one of the significant factors for the electrical and elastic performance. Herein, we evaluated the effect of tensile deformation on the orientation of crystallites and molecular chains. Synchrotron 2D X-ray

diffraction images and polarized Fourier transform infrared spectroscopy (FT-IR) of P3SiT were measured *in situ* under tensile tests. These results would provide significant insights on the molecular behavior under deformation of flexible and stretchable devices.

Experiments

Materials

P3SiT was synthesized in our reported method,^{35–37} as shown in Scheme S1 in the Supplementary Information. The number-average molecular weight and its distribution were 100k and 1.30, respectively. The characterization were performed with ¹H NMR (ECZ400, JEOL) in *d*-chloroform and gel permeation chromatography with chloroform as eluent solvents (G CBM-20A, Shimadzu) as shown in Figure S1 and S2 in the Supplementary Information. The molecular weight of P3SiT was estimated by standard polystyrene.

X-ray diffraction measurements under tensile tests

Crystallite orientation of the drawn film was investigated by X-ray diffraction photographs taken at SPring-8 BL03XU⁴³ (wavelength: 0.60 Å). A detector (Pilatus3 1M, Dectris) was employed. In the *in-situ* measurements under tensile tests, the diffraction patterns were measured at every 10% of sample strain during increasing tensile deformation. For the *in situ* tensile tests, P3SiT films with 80 μm thickness were cast and trimmed with 30 mm x 5 mm. A tensile machine (TST-350 Tensile Testing System, LINKAM SCIENTIFIC) was employed. The tensile rate was 5 mm/min. The initial length was 20 mm. The degree of the crystallite orientation π was defined with equation (1).

$$\pi = 100 \times (180 - H^\circ)/180 \quad (1)$$

where H° is the half-width of the intensity distribution curve for the diffraction lattice of the assembled side chains of P3SiT along the Debye–Scherrer ring.

FT-IR measurements under tensile tests

IR absorption measurements were performed with FT-IR microscope (AIM-9000 Infrared Microscope, Shimadzu. Co. Ltd.) using polarizing elements (Infrared Polarizer, Shimadzu. Co.

Ltd.). In the *in-situ* measurements under tensile tests, an IR spectrum was obtained every 10% of sample strain. For the *in situ* tensile tests, P3SiT films with 80 μm of thickness were casted and trimmed with 20 mm x 5 mm. A tensile machine (STJ-0116-M Micro Vice Holdr, S.T.JAPAN INC.) was also employed in this measurement. The tensile test was controlled by manual operation. The initial length was 10 mm and the tensile rate was around 5 mm/min. The orientation behaviors were evaluated from ratios of the absorbance bands of polarized FT-IR spectra with parallel and perpendicular (0° and 90°) to the drawn direction A_0/A_{90} .

Results and Discussion

P3SiT was prepared using nickel catalyst through Kumada coupling polymerization in the literature method.³⁵ The regioregularity of P3SiT was more than 99%. The molecular weights and amounts were large enough for solvent-casting flat film preparation and tensile tests. In our previous work, this P3SiT possessed larger elongation at break than 200%, and the elongation was nearly 20 times larger than P3HT,³⁶ as shown in Fig. S1 in the Supplementary Information. Therefore, it is possible to evaluate structural change under mechanical deformation.

Before *in situ* X-ray diffraction measurements under tensile tests, the structure of P3SiT with undrawn and 3-times drawn were investigated. Fig. S5 in the Supplementary Information shows their X-ray diffraction photographs. In the undrawn films, two Debye-Scherrer rings were observed, whereas the drawn P3SiT samples showed orientation pattern. These equatorial reflections were originated from the diffraction lattice of the assembled side chains.³⁶ The crystallite orientation in the drawn P3SiT film, which was evaluated using the equatorial π - π stacking reflection ($2\theta = 4.31^\circ$), was 0.80.

We performed *in situ* X-ray diffraction measurements under tensile tests with synchrotron radiation at SPring-8 BL03XU. Fig. 2 shows stress-strain curve and strain-crystallite orientation curve of P3SiT and X-ray diffraction patterns at various tensile strains. The mechanical yielding of P3SiT was observed at 14% strain. The tensile strength were increasing with the strain linearly before achieving to the yielding point. After yielding, the strain-stress curve was almost plateau and the stress was gradually increased again at the larger strain. In contrast, at lower strain than 40%, the crystallite orientation was not observed at all. After yielding, the orientation was increased abruptly at 40% strain and reached more than 0.60. In the cyclic test of P3SiT, permanent set was observed at larger than 50% strain. This result was coincidence to the crystallite orientation

behavior in the *in situ* X-ray diffraction measurements. The orientation also increased slowly at larger elongation (<40%) and reached a steady value, approximately 0.80 at tensile strain up to 140%. This sample was not broken even at larger than 250%.

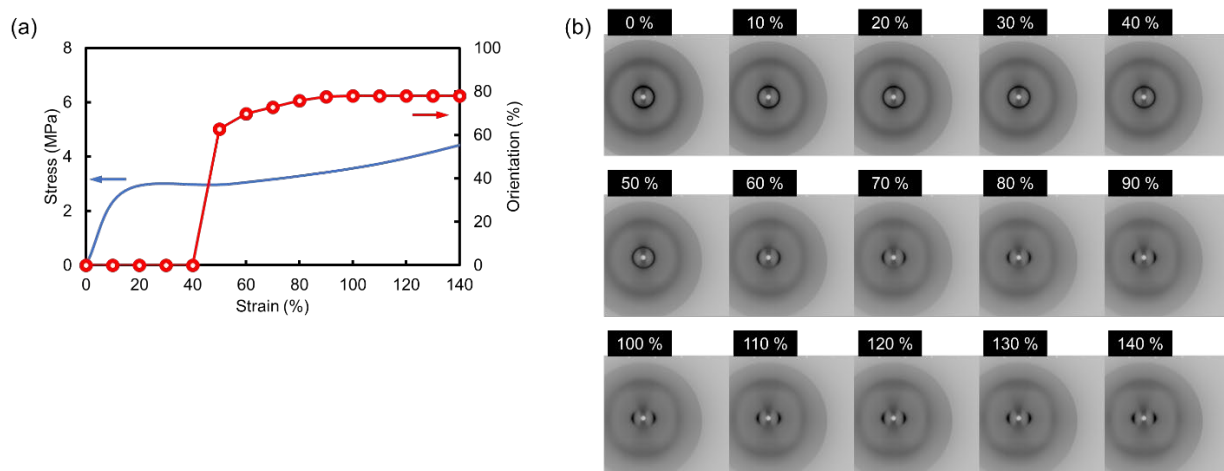


Fig. 2 (a) *In situ* stress-strain and strain-orientation curves. (b) *In situ* 2D XRD patterns at various strains.

In the X-ray diffraction measurements, only the crystalline regions of the samples were evaluated. The whole of the sample including crystalline and amorphous regions were investigated with FT-IR measurements. Before *in situ* FT-IR absorption measurements under tensile tests, undrawn and drawn P3SiT films were evaluated.

Fig. S8 in the Supplementary Information shows FT-IR spectra of undrawn P3SiT films. The absorption bands were observed at 3049 cm^{-1} , 2854 cm^{-1} , 1508 cm^{-1} , 1448 cm^{-1} and 1259 cm^{-1} , and they were originated from stretching vibration of C–H in thiophene rings, stretching vibration of $-\text{CH}_2$, asymmetric stretching vibration of C=C, symmetric stretching vibration of C=C and deformation vibration in Si–CH₃, respectively.^{44–47} In addition, for the investigation on the orientation of molecular chains of 3 times drawn P3SiT film, the polarized FT-IR measurements

were performed with every 15°. In Fig. 3a, the FT-IR spectra of 3-times drawn P3SiT with polarization of 0° and 90° were shown. We focused on the absorption bands observed at 3049 cm⁻¹, 2854 cm⁻¹ and 1508 cm⁻¹. Fig. 3b shows dependence of the polarizer angles on their absorption band intensities. At 0° of the polarizer angles, the band intensities originated from stretching vibration of C–H at 3049 cm⁻¹ and C=C at 1508 cm⁻¹ showed significant reduction to minimum, while both the band intensities were maximum at 90° of the polarizer angles. Anisotropy in both angles were apparent by the difference in intensity of IR absorbance between the parallel and perpendicularly polarized spectra. These indicated that the C–H and C=C bonds in thiophene rings of P3SiT was aligned to the perpendicular to the drawn direction. In contrast, the intensities of the bands at 2854 cm⁻¹ remained constant regardless of the polarizer angles. These suggested that the drawing provided the orientation of only the main chain, not side chain, of P3SiT. In the *in situ* measurements under stretching, we evaluated with the relative intensity between these absorption bands.

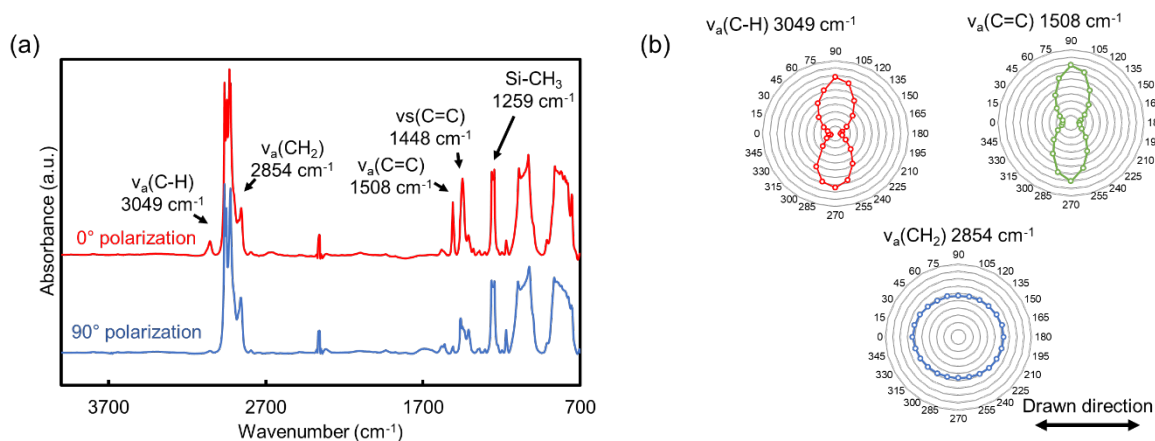


Fig. 3 (a) FT-IR spectra of 3-times drawn P3SiT with polarization of 0° and 90° and (b) dichroic profiles of polarized FT-IR of 3-times drawn P3SiT.

In situ FT-IR absorption measurements were performed under tensile tests. All the IR measurements were performed under strain from 0% to 140% and the relationship between strain and relative intensities of absorption bands at 3049 cm^{-1} , 2854 cm^{-1} and 1508 cm^{-1} of polarized FT-IR measurements are shown in Fig. 4. For the evaluation of the depolarization under stretching, we focused on the IR spectra with polarized angles parallel and perpendicular (0° and 90°) to the drawn direction and employed their intensity ratios of stretching vibration originated from C–H and C=C bonds at 3049 cm^{-1} and 1508 cm^{-1} , respectively. Both the intensity ratio of P3SiT film before elongation was 1.0, which means that the film possessed no anisotropy. As the film was strained, the intensity ratios were then steadily increased and were finally come up to 4.5 and 3.5 at tensile strain of 140%, respectively. On the other hands, the intensity ratio of the stretching vibration of $-\text{CH}_2$ at 2854 cm^{-1} maintained constant, around 1.0. These results indicated that the main chain was oriented along the strain direction, not the side chains. The flexible and long side chains of disiloxane would prevent these oriented-assembly and these factors could inhibit spectroscopically the alignments of the side chains under stretching. These corresponded to the polarized FT-IR measurements of the drawn-annealed P3SiT film. The increases of the intensity ratios was associated linearly with the tensile strain.

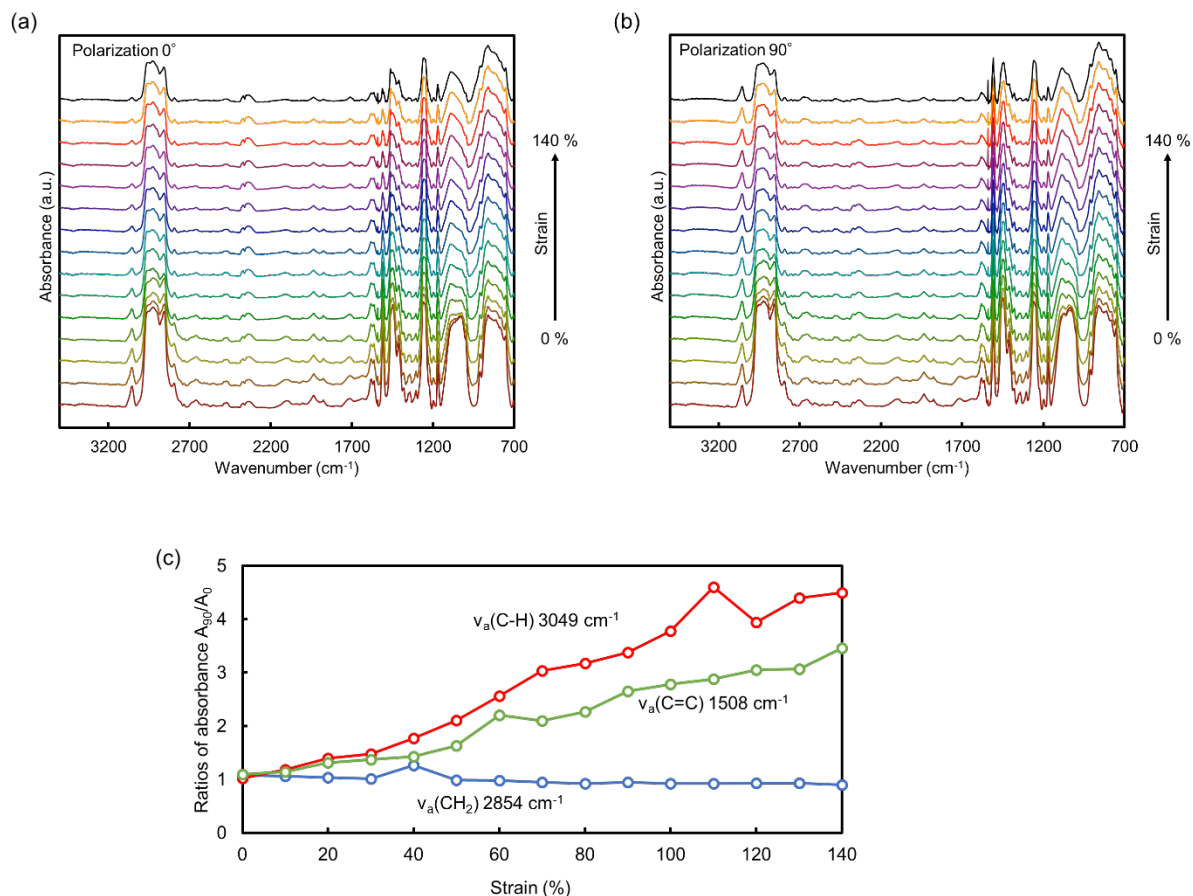


Fig. 4 (a), (b) *In situ* FT-IR spectra of P3SiT under strain from 0% to 140%. (c) Relationship between strain and relative absorption intensities of *In situ* polarized FT-IR.

In both the results of X-ray diffraction and FT-IR *in situ* measurements under tensile strain, the orientation of P3SiT main chains were observed, while the changing processes of both the measurement results under straining were different. The orientation of P3SiT crystallites kept isotropic state before yielding points under strain process. After the yielding point, the anisotropy of crystallites was increased abruptly. At higher strain, the crystallite orientation was increased and saturated gradually. On the other hand, in the FT-IR measurements, the molecular orientation was increased as the P3SiT film was strained even at lower strain region. The difference of the orientation behaviors between X-ray diffraction and FT-IR was attributed to the difference of the

measurement subjects between their measurement mechanisms. In the X-ray diffraction measurements, only the crystalline regions of P3SiT were evaluated, whereas the FT-IR measurement provided the structural conformation of the whole bulk including the crystallites and amorphous regions. It is revealed that, at the lower strain before yielding, the P3SiT molecules in amorphous region were aligned, and then the alignment of the crystalline regions was started abruptly after yielding point. Therefore, before the yielding point was reached, the elastic recovery was observed because the structure of the crystallites had not changed, while the permanent distortion was caused by the alignment of the crystallites after yielding.

CONCLUSIONS

We performed the evaluation of the structural change of elastic polythiophene with disiloxane side chains under *in situ* strain. In both the measurements of X-ray diffraction and polarized FT-IR absorption, it was observed that the drawn and annealed P3SiT film possessed anisotropic structure. We focused on the anisotropic X-ray diffraction streaks and absorption bands, and the structural changes were investigated *in situ* under tensile strain of P3SiT. These measurements concluded that only the soft amorphous region was oriented before yielding, whereas the alignment of the rigid crystalline regions was observed after yielding. The bulk deformation behavior of elastic conjugated polythiophene corresponded to the changes of their micro and molecular structure.

ASSOCIATED CONTENT

Supplementary Information.

The Supplementary Information includes synthesis scheme, NMR chart, GPC chart, strain–stress curves, curve of tensile cyclic tests, X-ray diffraction photographs and profiles, FT-IR spectrum, and electrical resistivity. This material is available free of charge via the Internet at <http://>

AUTHOR INFORMATION

Corresponding Author

*(T.N.) E-mail: tnishino@kobe-u.ac.jp

Funding Sources

This work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas “New Polymeric Materials Based on Element-Blocks (No. 2401)” (MEXT/JSPS KAKENHI Grant Number JP 24102009) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Acknowledgments

The synchrotron radiation experiments were performed at the BL03XU of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2017A7209, 2017B7261, 2018A7211, 2018B7261, 2019A7209, and 2019B7259)

Notes

The authors declare no competing financial interest.

REFERENCES

- 1 P. Docampo, J. M. Ball, M. Darwich, G. E. Eperon and H. J. Snaith, Efficient organometal trihalide perovskite planar-heterojunction solar cells on flexible polymer substrates, *Nat. Commun.*, 2013, **4**, 2761.
- 2 Y. Li, Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward Suitable Electronic Energy Levels and Broad Absorption, *Acc. Chem. Res.*, 2012, **45**, 723–733.
- 3 G. Li, R. Zhu and Y. Yang, Polymer solar cells, *Nat Phot.*, 2012, **6**, 153–161.
- 4 S. R. Forrest, The path to ubiquitous and low-cost organic electronic appliances on plastic, *Nature*, 2004, **428**, 911–918.
- 5 H. Sirringhaus, Device Physics of Solution-Processed Organic Field-Effect Transistors, *Adv. Mater.*, 2005, **17**, 2411–2425.
- 6 D.-H. Kim, J.-H. Ahn, W. M. Choi, H.-S. Kim, T.-H. Kim, J. Song, Y. Y. Huang, Z. Liu, C. Lu and J. A. Rogers, Stretchable and Foldable Silicon Integrated Circuits, *Science*, 2008, **320**, 507 LP – 511.
- 7 T.-H. Han, Y. Lee, M.-R. Choi, S.-H. Woo, S.-H. Bae, B. H. Hong, J.-H. Ahn and T.-W. Lee, Extremely efficient flexible organic light-emitting diodes with modified graphene anode, *Nat. Photonics*, 2012, **6**, 105.

- 8 X. Dai, Z. Zhang, Y. Jin, Y. Niu, H. Cao, X. Liang, L. Chen, J. Wang and X. Peng, Solution-processed, high-performance light-emitting diodes based on quantum dots, *Nature*, 2014, **515**, 96.
- 9 Q. Cao and J. A. Rogers, Ultrathin Films of Single-Walled Carbon Nanotubes for Electronics and Sensors: A Review of Fundamental and Applied Aspects, *Adv. Mater.*, 2009, **21**, 29–53.
- 10 N. K. Guimard, N. Gomez and C. E. Schmidt, Conducting polymers in biomedical engineering, *Prog. Polym. Sci.*, 2007, **32**, 876–921.
- 11 H. Kudo, T. Sawada, E. Kazawa, H. Yoshida, Y. Iwasaki and K. Mitsubayashi, A flexible and wearable glucose sensor based on functional polymers with Soft-MEMS techniques, *Biosens. Bioelectron.*, 2006, **22**, 558–562.
- 12 Z.-M. Dang, J.-K. Yuan, S.-H. Yao and R.-J. Liao, Flexible Nanodielectric Materials with High Permittivity for Power Energy Storage, *Adv. Mater.*, 2013, **25**, 6334–6365.
- 13 C. Meng, C. Liu, L. Chen, C. Hu and S. Fan, Highly Flexible and All-Solid-State Paperlike Polymer Supercapacitors, *Nano Lett.*, 2010, **10**, 4025–4031.
- 14 P. Simon and Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mater.*, 2008, **7**, 845.
- 15 M. Sup Choi, G.-H. Lee, Y.-J. Yu, D.-Y. Lee, S. Hwan Lee, P. Kim, J. Hone and W. Jong Yoo, Controlled charge trapping by molybdenum disulphide and graphene in ultrathin heterostructured memory devices, *Nat. Commun.*, 2013, **4**, 1624.

- 16 S. Bertolazzi, D. Krasnozhan and A. Kis, Nonvolatile Memory Cells Based on MoS₂/Graphene Heterostructures, *ACS Nano*, 2013, **7**, 3246–3252.
- 17 T. Sekitani, T. Yokota, U. Zschieschang, H. Klauk, S. Bauer, K. Takeuchi, M. Takamiya, T. Sakurai and T. Someya, Organic Nonvolatile Memory Transistors for Flexible Sensor Arrays, *Science*, 2009, **326**, 1516 LP – 1519.
- 18 S. C. B. Mannsfeld, B. C.-K. Tee, R. M. Stoltenberg, C. V. H.-H. Chen, S. Barman, B. V. O. Muir, A. N. Sokolov, C. Reese and Z. Bao, Highly sensitive flexible pressure sensors with microstructured rubber dielectric layers, *Nat. Mater.*, 2010, **9**, 859.
- 19 M.-C. Choi, Y. Kim and C.-S. Ha, Polymers for flexible displays: From material selection to device applications, *Prog. Polym. Sci.*, 2008, **33**, 581–630.
- 20 S. Patel, H. Park, P. Bonato, L. Chan and M. Rodgers, A review of wearable sensors and systems with application in rehabilitation, *J. Neuroeng. Rehabil.*, 2012, **9**, 21.
- 21 S. Vashi, J. Ram, J. Modi, S. Verma and C. Prakash, in *2017 International Conference on I-SMAC (IoT in Social, Mobile, Analytics and Cloud) (I-SMAC)*, 2017, pp. 492–496.
- 22 J. Gubbi, R. Buyya, S. Marusic and M. Palaniswami, Internet of Things (IoT): A vision, architectural elements, and future directions, *Futur. Gener. Comput. Syst.*, 2013, **29**, 1645–1660.
- 23 K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi and B. H. Hong, Large-scale pattern growth of graphene films for stretchable transparent electrodes, *Nature*, 2009, **457**, 706.

- 24 J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan and X. W. (David) Lou, Recent Advances in Metal Oxide-based Electrode Architecture Design for Electrochemical Energy Storage, *Adv. Mater.*, 2012, **24**, 5166–5180.
- 25 S. Gong, W. Schwalb, Y. Wang, Y. Chen, Y. Tang, J. Si, B. Shirinzadeh and W. Cheng, A wearable and highly sensitive pressure sensor with ultrathin gold nanowires, *Nat. Commun.*, 2014, **5**, 3132.
- 26 M. Park, J. Im, M. Shin, Y. Min, J. Park, H. Cho, S. Park, M.-B. Shim, S. Jeon, D.-Y. Chung, J. Bae, J. Park, U. Jeong and K. Kim, Highly stretchable electric circuits from a composite material of silver nanoparticles and elastomeric fibres, *Nat Nano*, 2012, **7**, 803–809.
- 27 H. Koerner, G. Price, N. A. Pearce, M. Alexander and R. A. Vaia, Remotely actuated polymer nanocomposites—stress-recovery of carbon-nanotube-filled thermoplastic elastomers, *Nat. Mater.*, 2004, **3**, 115–120.
- 28 J. Cao, C. Lu, J. Zhuang, M. Liu, X. Zhang, Y. Yu and Q. Tao, Multiple Hydrogen Bonding Enables the Self-Healing of Sensors for Human–Machine Interactions, *Angew. Chem. Int. Ed.*, 2017, **56**, 8795–8800.
- 29 D. S. Gray, J. Tien and C. S. Chen, High-Conductivity Elastomeric Electronics, *Adv. Mater.*, 2004, **16**, 393–397.
- 30 S. Rosset and H. R. Shea, Flexible and stretchable electrodes for dielectric elastomer actuators, *Appl. Phys. A*, 2013, **110**, 281–307.

- 31 S. P. Lacour, S. Benmerah, E. Tarte, J. FitzGerald, J. Serra, S. McMahon, J. Fawcett, O. Graudejus, Z. Yu and B. Morrison, Flexible and stretchable micro-electrodes for in vitro and in vivo neural interfaces, *Med. Biol. Eng. Comput.*, 2010, **48**, 945–954.
- 32 C.-L. Choong, M.-B. Shim, B.-S. Lee, S. Jeon, D.-S. Ko, T.-H. Kang, J. Bae, S. H. Lee, K.-E. Byun, J. Im, Y. J. Jeong, C. E. Park, J.-J. Park and U.-I. Chung, Highly Stretchable Resistive Pressure Sensors Using a Conductive Elastomeric Composite on a Micropylramid Array, *Adv. Mater.*, 2014, **26**, 3451–3458.
- 33 G.-J. N. Wang, A. Gasperini and Z. Bao, Stretchable Polymer Semiconductors for Plastic Electronics, *Adv. Electron. Mater.*, 2018, **4**, 1700429.
- 34 S. E. Root, S. Savagatrup, A. D. Printz, D. Rodriquez and D. J. Lipomi, Mechanical Properties of Organic Semiconductors for Stretchable, Highly Flexible, and Mechanically Robust Electronics, *Chem. Rev.*, 2017, **117**, 6467–6499.
- 35 K. Fujita, Y. Sumino, K. Ide, S. Tamba, K. Shono, J. Shen, T. Nishino, A. Mori and T. Yasuda, Synthesis of Poly(3-substituted thiophene)s of Remarkably High Solubility in Hydrocarbon via Nickel-Catalyzed Deprotonative Cross-Coupling Polycondensation, *Macromolecules*, 2016, **49**, 1259–1269.
- 36 J. Shen, K. Fujita, MatsumotoTakuya, C. Hongo, M. Misaki, K. Ishida, A. Mori and T. Nishino, Mechanical, Thermal, and Electrical Properties of Flexible Polythiophene with Disiloxane Side Chains, *Macromol. Chem. Phys.*, 2017, **218**, 1700197.

- 37 J. Shen, I. Sugimoto, T. Matsumoto, S. Horike, Y. Koshihara, K. Ishida, A. Mori and T. Nishino, Fabrication and characterization of elastomeric semiconductive thiophene polymers by peroxide crosslinking, *Polym. J.*, 2019, **51**, 257–263.
- 38 T. Higashihara, S. Fukuta, Y. Ochiai, T. Sekine, K. Chino, T. Koganezawa and I. Osaka, Synthesis and Deformable Hierarchical Nanostructure of Intrinsically Stretchable ABA Triblock Copolymer Composed of Poly(3-hexylthiophene) and Polyisobutylene Segments, *ACS Appl. Polym. Mater.*, 2019, **1**, 315–320.
- 39 T. Higashihara, S. Ito, S. Fukuta, S. Miyane, Y. Ochiai, T. Ishizone, M. Ueda and A. Hirao, Synthesis and Characterization of Multicomponent ABC- and ABCD-Type Miktoarm Star-Branched Polymers Containing a Poly(3-hexylthiophene) Segment, *ACS Macro Lett.*, 2016, **5**, 631–635.
- 40 S. Miyane, H.-F. Wen, W.-C. Chen and T. Higashihara, Synthesis of block copolymers comprised of poly(3-hexylthiophene) segment with trisiloxane side chains and their application to organic thin film transistor, *J. Polym. Sci. Part A Polym. Chem.*, 2018, **56**, 1787–1794.
- 41 J. Mei, D. H. Kim, A. L. Ayzner, M. F. Toney and Z. Bao, Siloxane-Terminated Solubilizing Side Chains: Bringing Conjugated Polymer Backbones Closer and Boosting Hole Mobilities in Thin-Film Transistors, *J. Am. Chem. Soc.*, 2011, **133**, 20130–20133.
- 42 A. R. Han, J. Lee, H. R. Lee, J. Lee, S. H. Kang, H. Ahn, T. J. Shin, J. H. Oh and C. Yang, Siloxane Side Chains: A Universal Tool for Practical Applications of Organic Field-Effect Transistors, *Macromolecules*, 2016, **49**, 3739–3748.

- 43 H. Masunaga, H. Ogawa, T. Takano, S. Sasaki, S. Goto, T. Tanaka, T. Seike, S. Takahashi, K. Takeshita, N. Nariyama, H. Ohashi, T. Ohata, Y. Furukawa, T. Matsushita, Y. Ishizawa, N. Yagi, M. Takata, H. Kitamura, K. Sakurai, K. Tashiro, A. Takahara, Y. Amamiya, K. Horie, M. Takenaka, T. Kanaya, H. Jinnai, H. Okuda, I. Akiba, I. Takahashi, K. Yamamoto, M. Hikosaka, S. Sakurai, Y. Shinohara, A. Okada and Y. Sugihara, Multipurpose soft-material SAXS/WAXS/GISAXS beamline at SPring-8, *Polym. J.*, 2011, **43**, 471–477.
- 44 S. Hotta, W. Shimotsuma and M. Taketani, Fourier transform infrared study of electrochemically prepared polythienylene films with varying doping levels, *Synth. Met.*, 1984, **10**, 85–94.
- 45 S. Hotta, M. Soga and N. Sonoda, Infrared dichroic studies of polythiophenes, *J. Phys. Chem.*, 1989, **93**, 4994–4998.
- 46 L. M. Johnson, L. Gao, C. W. Shields IV, M. Smith, K. Efimenko, K. Cushing, J. Genzer and G. P. López, Elastomeric microparticles for acoustic mediated bioseparations, *J. Nanobiotechnology*, 2013, **11**, 22.
- 47 A. C. M. Kuo, in *Polymer Data Handbook*, ed. James E. Mark, OXFORD UNIVERSITY PRESS, 1999, pp. 411–435.

