Research Article Adv. Mater. Lett. 2015, **6**(2), 99-103 ADVANCED MATERIALS Letters

www.amlett.com, www.vbripress.com/aml, DOI: 10.5185/amlett.2015.5720

Formation of nanowires from pentacene derivatives by single-particle triggered linear polymerization

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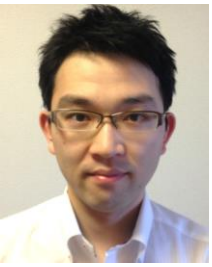
Received: 28 September 2014, Revised: 17 November 2014 and Accepted: 26 December 2014

ABSTRACT

The present paper highlights the development of organic nanowires from small-molecular organic compounds through intra-track chemical reactions by using ion beams. Thin films of pentacene derivatives, 6,13-bis(triethylsilylethynyl)pentacene (TES-Pn) and 6,13-bis((triisopropylsilyl)ethynyl)pentacene (TIPS-Pn), were subjected to high-energy particle irradiation at a fluence of 10^8–10^{10} cm^{-2} and thereafter developed by organic solvents. This method, referred as Single-particle Triggered Linear Polymerization (STLiP), afforded the isolation of wire-shaped nanomaterials on a substrate that were visualized by atomic force microscopy and scanning electron microscopy. These derivatives exhibited high enough propagation and cross-linking reaction efficiencies (G) as $G_{\text{TES-Pn}}$ of > 7 and $G_{\text{TIPS-Pn}}$ of > 5 (100 eV)$^{-1}$, whose values are significantly larger than those observed for previously studied simple cross-linking reactions observed in other polymeric materials, being apparently in the G-value range of chain reactions. On the other hand, the pristine pentacene and derivative without (trialkylsilyl)ethynyl moiety did not give any nanowires. Considering these observations, highly efficient intra-track propagation/polymerization/cross-linking reactions would take place due to the introduction of (trialkylsilyl)ethynyl groups, resulting in the formation of one-dimensional nanostructures based on small molecules. The STLiP technique serves as a versatile and easy nanofabrication tool for small molecular materials and the resultant nanowires with high functional density are potentially usable as optical, electronic, and sensor materials. Copyright © 2015 VBRI press.

Keywords: Nanowire; pentacene; ion beam; ion track; organic materials.



Tsuneaki Sakurai received his PhD degree in 2012 from the University of Tokyo, Japan under the supervision of Prof. Dr. Takuzo Aida. He worked as a postdoctoral research fellow under Prof. Dr. Shu Seki at Osaka University. In 2014, he became assistant professor. His research interest includes development of functional soft materials from π-electronic systems through self-assembly and ion beam-based top-down technologies and evaluation of charge carrier mobilities by microwave-based techniques.

Shu Seki graduated from the University of Tokyo in 1993, and received his PhD degree in 2001 from Osaka University. He joined Argonne National Laboratory, USA in 1993, and Delft University of Technology in 2001. He was appointed as Professor of Applied Chemistry, Graduate School of Engineering, Osaka University in 2009. His research is primarily focused on the physical chemistry of condensed matters, functional organic materials and nanomaterials.

Introduction

Well-defined nano-sized objects **[1, 2]** have attracted increasing attentions due to the recent advances in materials science and nanotechnology. In particular, one-dimensional (1D) nanostructures from π-conjugated molecules serve as promising materials for optical and electronic applications **[3-8]** such as chemical sensors, memory devices, organic photovoltaic cells (OPVC), and organic field-effect transistors (OFET). Because organic materials are soft and finely tunable by molecular design, most of these nanostructures are constructed by bottom-up self-assembly approaches with non-covalent interactions of the elaborately-designed π-conjugated molecules or polymers **[9-11]**. On the other hand, top-down technologies to access such 1D nanostructures are attractive in view of generality and versatility but have been still limited **[12-14]**. As a unique top-down technology using swift heavy ions, we have succeeded in the development of 1D nanostructure by employing cross-linking reactions of macromolecules in the film state. This method is named “single particle nano-fabrication technique (SPNT)” **[15]**. In SPNT, the MeV-order swift heavy ions, irradiated to the target polymer films non-homogeneously produce the reactive intermediates—ion radicals, neutral radicals, *etc*.––along their trajectories called ion tracks. Because of effective and high-density formation of neutral radical species generated in radiation cross-linking type polymers **[16-17]**, they induce the recombination reactions within the ion track, forming wire-shaped insoluble nanogels with fairly controlled sizes (**Fig. 1**). The obtained nanowires are isolated by development process, where the non-irradiated area in the film is washed away by organic solvents. Although SPNT has been utilized so far for various type of synthetic polymers **[18-21]** and biomacromolecules **[22]**, however, there is only one example that nanowires are available from small-molecular materials by analogous means of SPNT **[23]**, where high reactivity of fullerene derivatives upon ion beam irradiation **[24]** was utilized. In order to further investigate the applicability of the high energy particle technique, here we report the nanowire formation via polymerization/crosslinking reactions of pentacene derivatives, one of the representative semiconducting small molecules, and classified as Single Particle Linear Polymerization (STLiP) technique that these molecules showed high efficiencies of both propagation **[25, 26]** and cross-linking reactions along the linear trajectories of a heavy ion particle.

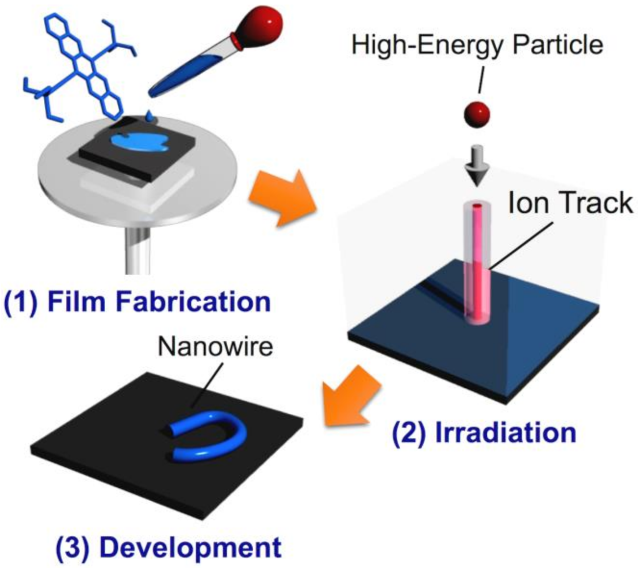
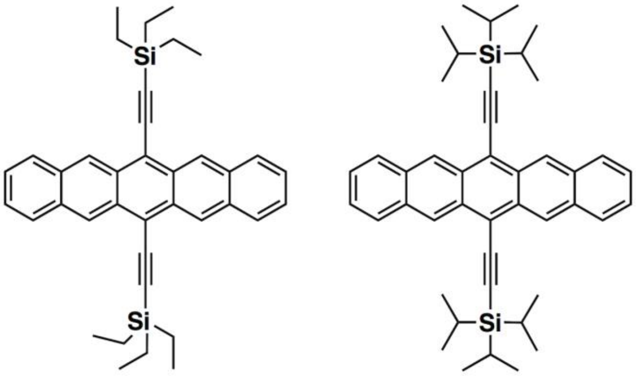


Fig. 1. Schematic illustrations of nanowire fabrication process from soluble pentacene derivatives.

Pentacene is one of the most intensively studied organic semiconducting motifs and often used as an OFET active layer because of its high hole mobility **[27, 28]**. Nevertheless, pentacene is sensitive to oxygen and in fact unstable under ambient condition. To improve the stability and solubility of pentacene, silylethyne substituted pentacenes were reported and proved their excellent carrier transporting performance **[29, 30]**. In this study, considering the easy isolation by the development procedure in STLiP, we fabricated thin films of soluble pentacenes, 6,13-bis((triethylsilyl)ethynyl)pentacene (TES-Pn) and 6,13-bis((triisopropylsilyl)ethynyl)pentacene (TIPS-Pn) (**Fig. 2**), and develop them in organic solvent after irradiation of swift heavy ions. Advancement of initiation and propagation of the polymerization reactions as well as the cross-linking reactions were quantitatively discussed in terms of simple model of radial energy distribution in an ion track. The detailed experimental method and observation results are discussed in the following sections.



TES-Pn **TIPS-Pn**

Fig. 2. Chemical structures of 6,13-bis((triethylsilyl)ethynyl)pentacene (**TES-Pn**) and 6,13-bis((triisopropylsilyl)ethynyl)pentacene (**TIPS-Pn**).

Experimental

Materials

6,13-Bis((triethylsilyl)ethynyl)pentacene (≥99%), 6,13-bis((triisopropylsilyl)ethynyl)pentacene (≥99%), and pentacene-*N*-sulfinyl-*tert*-butylcarbamate (99%) were purchased from Sigma-Aldrich Chemical Co. and used as received. All other reagents and solvents were purchased from Wako Chemical Co. and used without further purification. Si substrate was cut about the size of ~1.5 × 1.5 cm, sonicated in isopropanol, dried, and treated with UV-O$_3$ prior to the use. Pentacene derivatives were dissolved 5–10 wt% in THF, and the solution was spin-coated or drop-cast on the Si substrate to provide thin films. A pentacene film was prepared UV irradiation under acid generator and heating of pentacene-*N*-sulfinyl-*tert*-butylcarbamate according to a reported procedure. The thickness of the films was evaluated by a Veeco Instruments Inc. model Dektak 150 surface profiler.

Method

MeV order charged particles were generated from a cyclotron accelerator at Japan Atomic Energy Agency, Takasaki Advanced Radiation Research Institute. The prepared thin films of TES-Pn and TIPS-Pn were exposed to a 490 MeV ^{192}Os^{30+} ion beam in a vacuum chamber ($< 1 \times 10^{-4}$ Pa). The number of incident particles was controlled at 10^8–10^{10} particles cm^{-2} to prevent overlapping of the particle trajectories. Then, the irradiated films were developed directly in hexane for 10–60 s. The sizes and shapes of the nanostructures were observed using a Seiko Instruments Inc. model SPI-4000 atomic force microscope (AFM) and JEOL Ltd. model JSM-7001F scanning electron microscope (SEM). The loss of kinetic energy of ions due to penetration through the pentacene films was estimated using the SRIM 2010 calculation code.

Results and discussion

Ion-beam irradiation of thin films of organic compounds is shown to cause propagation/cross-linking reactions, leading to the formation of a 1D-organogel along the ion tracks. The key point is the remarkable difference in solubility between irradiated and non-irradiated area, which enable the easy isolation of the resultant nanowire objects by development solvents. In principle, the initial nanowire structures stand on a substrate. However, due to the interfacial surface tensions by organic solvent, observed nanowires usually lie down to the substrate and are observed as a 2D-image (**Fig. 1**). Prior to the experiments, we performed simulation of ion track within pentacene materials. For example, as shown in **Fig. 3**, 490 MeV $^{192}\text{Os}^{30+}$ particles can linearly pass through a 5-μm thick TIPS-Pn (ρ ~ 1.1 g cm^{-3}) on a 5-μm thick Si (ρ ~ 2.3 g cm^{-3}). Because of the large difference between the linear energy transfers (LETs) of TIPS-Pn and the Si wafer, the primary charged particles and secondary electrons preferentially induce the formation of dense reactive species at the pentacene/Si interface, leading to the heterogeneous covalent-bond formation. Along with that, the termini of the obtained nanowires become permanently bound to the surface of the Si wafer via Si–C or Si–O–C bonds, preventing the nanowires from being washed away by the developer.

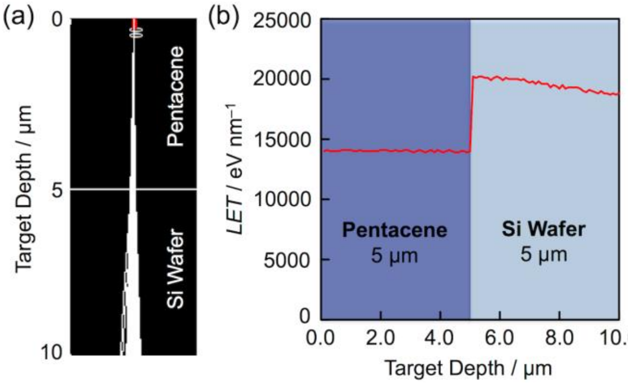


Fig. 3. (**a**) Ion track image of 5-μm thick pentacene (ρ ~ 1.1 g cm^{-3}) film coated on 5-μm thick Si-wafer (ρ ~ 2.3 g cm^{-3}) upon 490 MeV $^{192}\text{Os}^{30+}$ particles irradiation and (**b**) Calculated LET value as a function of target depth. Calculation was carried out using SRIM 2010 calculation code.

When the soluble pentacene films were exposed to 490 MeV $^{192}\text{Os}^{30+}$ particles at the fluence of 5.0×10^8–1.0×10^9 ions/cm^2 followed by the development in hexane, nanowire objects were visualized in AFM (**Fig. 4**). By carefully looking at the images, partial fragmentation of the nanowires was confirmed. Nevertheless, even for the thick (> 1 μm) films prepared by drop-cast method, nanowires with ultrahigh aspect ratio were observed. Compared to our previous reports **[18-23]**, the obtained nanowires look flexible, while their diameters appeared small. Due to such flexibility, network structures of nanowires may be formed, which is more obvious in SEM images (**Fig. 5**). It is considered that these network structures were resulted from the entanglement of the formed nanowires one another. In contrast, irradiation to pristine pentacene films did not afford any nanowire. These results indicate that silylethyne moieties in the pentacene derivatives give the high reaction efficiency and/or significant difference in solubility. In regard to this possibility, we have already reported that introduction of terminal alkyne groups into the polystyrene backbone provides efficient cross-linking reactions in SPNT **[21]**. Therefore, we consider that alkyne groups would increase the reactivity upon swift heavy ion irradiations.

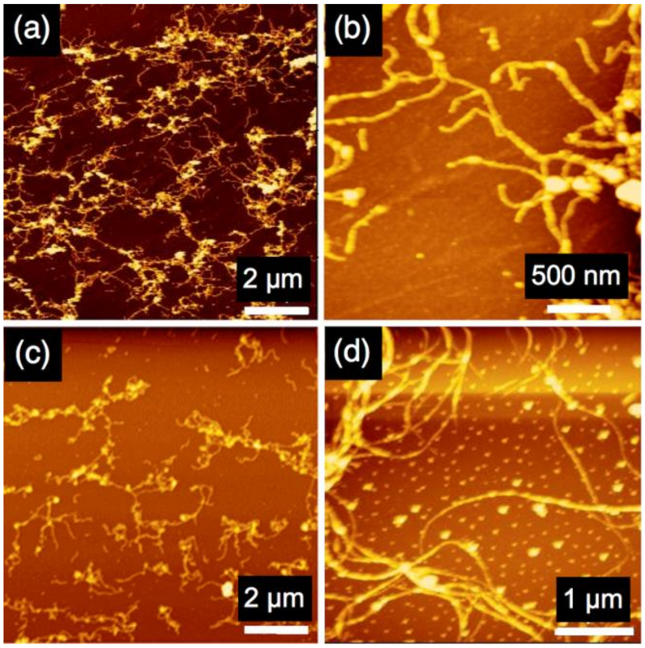


Fig. 4. AFM topographic images of nanowires isolated via development of (**a, b**) TES-Pn and (**c, d**) TIPS-Pn drop-cast films with *n*-hexane after irradiation with 490 MeV $^{192}\text{Os}^{30+}$ particles at the fluence of 1.0×10^9 and 5.0×10^8 ions cm^{-2} for (**a**) and (**b–d**), respectively.

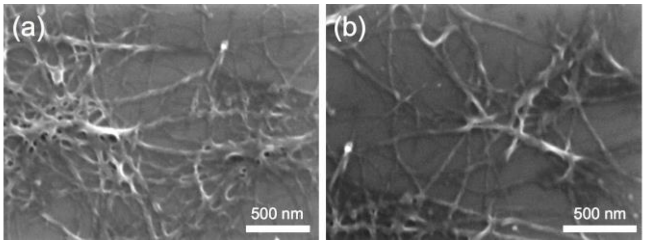


Fig. 5. SEM images of nanowires isolated via development of **TIPS-Pn** drop-cast film with *n*-hexane after irradiation with 490 MeV $^{192}\text{Os}^{30+}$ particles at the fluence of 1.0×10^{10} ions cm^{-2}.

The radius of nanowire was evaluated by the cross-sectional profile in AFM. After the development process, the cross-section of nanowires on the substrate was elliptically deformed as a consequence of adsorption forces. Taking into account this issue, the radius of nanowire is calculated by applying the ellipse model to cross-section of nanowire (**Fig. 6d**). The values of r_x and r_y are defined as the half-width and half-height of at half-maximum of the cross-section of nanowires, respectively. **Fig. 6c** shows the cross-sectional profile of the nanowire based on TES-Pn. The profile was measured on the line in **Fig. 6b**. The radii of the nanowires from TES-Pn and TIPS-Pn are calculated as 4.5 and 4.2 nm, respectively.

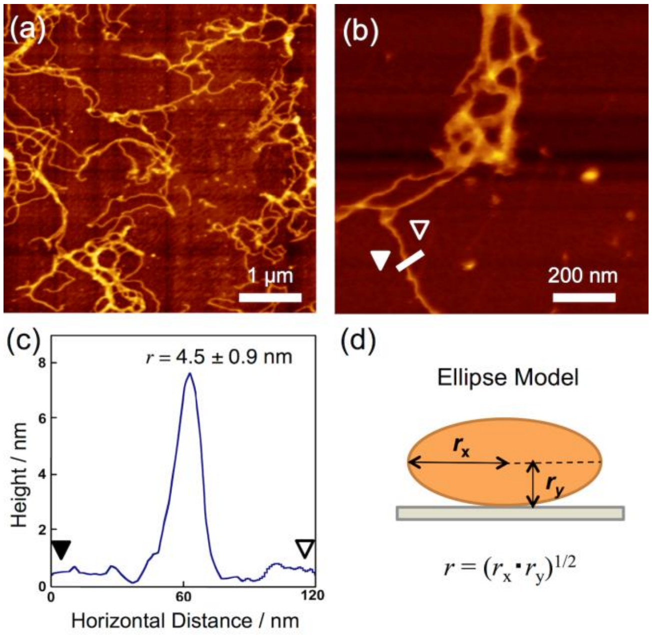


Fig. 6. (**a, b**) AFM topographic images of nanowires isolated via development of 1.7-μm thick TES-Pn film with n-hexane after irradiation with 490 MeV $^{192}Os^{30+}$ particles at the fluence of 5.0 × 10^8 ions cm^{-2}. (**c**) Cross-sectional profiles of the nanowires on Si substrate based on TES-pentacene produced by STLiP. The profile was measured at the position indicated by lines in (**b**). (**d**) Schematic illustration of nanowire radius using ellipse model.

To investigate the reactivity of silylethyne substituted pentacene, the overall propagation/crosslinking efficiency *G* was evaluated. The value of *G* is defined as the number of reactions of the resulting polymer propagation and/or crosslinking in the isolated nanostructures per 100 eV of absorbed dose. Considering the energy distribution in an ion track, the size of the nanowire was well interpreted by the theoretical model. *G* is expressed as:

$$G = \frac{400\pi\rho N_A \cdot r^2}{LET \cdot M} \ln\left(\frac{e^{1/2} r_p}{r_c}\right) \quad (1),$$

where the value of ρ is the density of the material, N_A is Avogadro's number, *r* is the radius of the nanowire, *LET* is the linear energy transfer, *M* is the molecular weight, r_c and r_p are the radii of the core and penumbra areas, and *e* is the elementary charge, respectively **[31-32]**. As demonstrated in the **Fig. 3** of Monte-Carlo simulation of energy deposition for the present 490 MeV $^{192}Os^{30+}$ particle, electronic stopping is far higher than the nuclear one, with relatively the larger value of r_p as 340 nm than r_c of 0.75 nm. The observed values of nanowire radii in the present case are far larger than r_c, and in the range of penumbra, where knocked-on secondary electrons by the an incident Os particle release their kinetic energy via in elastic corrosions. This is also suggestive that rather simple radiation chemical processes are taking place in the outer parts of the nanowires without drastic chemical transformations.

This theoretical modeling of the nanowire sizes afford the estimation of the cross-linking efficiencies for TES and TIPS-pentacene as $G_{\text{TES-Pn}} > 7$ and $G_{\text{TIPS-Pn}} > 5$ (100 eV)$^{-1}$ that are extremely high values compared with those observed for the other polymeric materials, and apparently suggestive of the strong contribution of chain reactions for the formation of nanostructures via gelation of the organic molecules. In general, deprotection of trialkylsilyl groups is performed with acids, bases, or fluorides. The relative stability of trialkylsilyl protection can be tuned by changing the volume of substituents **[33]**. TIPS group indicates higher resistance to these conditions than TES group. Therefore, it is expected that TIPS group control the generation of radical intermediates and promotion of the polymerization/crosslinking reactions.

Conclusion

We propose the new concept of nanofabrication classified as Single-particle Triggered Linear Polymerization (STLiP) in the present study, and the direct formation of nanowires from pentacene derivatives was demonstrated. This one-dimensional gelation event was triggered by the effective initiation/propagation reaction of intra-track polymerization as well as crosslinking along the trajectories of incident high-energy charged particles. Although the size of molecules is much smaller than polymeric materials, the pentacene derivatives carrying silylethyne groups gave flexible nanowires in STLiP that were strongly entangled into network structures. Based on our observations, the silylethyne groups provide appropriate solubility and increased overall reaction efficiencies of propagation and crosslinking reactions upon irradiation of swift heave ions. Considering the prominent semiconducting property of pentacene and observed unique network structures, together with potential universality of our technique to other small molecular systems, we believe that nanowires by STLiP encourage the development of future electronic devices.

Acknowledgements

This work was supported by Funding Program for Next-Generation World-Leading Researches (NEXT Program) and KAKENHI from JSPS. A.A. and T.S. thank the Japan Society for the Promotion of Science for a Young Scientist Fellowship.

Reference

1. Sanchez, C.; Belleville, P.; Popall, M.; Nicole, L; *Chem. Soc. Rev.*, **2011**, *40*, 696.
   DOI: 10.1039/c0cs00136h
2. Long, Y.-Z.; Yu, M.; Sun, B.; Gu, C.-Z.; Fan, Z.; *Chem. Soc. Rev.*, **2012**, *41*, 4560.
   DOI: 10.1039/c2cs15335a
3. Zhao, Y. S.; Fu, H.; Peng, A.; Ma, Y.; Xiao, D.; Yao, J.; *Adv. Mater.*, 2008, *20*, 2859.
   DOI: 10.1002/adma.200800604
4. Zhao, Y. S.; Fu, H. B.; Hu, F. Q.; Peng, A. D.; Yang, W. S.; Yao, J. N.; *Adv. Mater.*, **2008**, *20*, 79.
   DOI: 10.1002/adma.200700542
5. Bruce, P. G.; Scrosati, B.; Tarascon, J.-M.; *Angew. Chem. Int. Ed.*, **2008**, *47*, 2930.
   DOI: 10.1002/anie.200702505
6. Kim, F. S.; Ren, G.; Jenekhe, S. A.; *Chem. Mater.*, **2011**, *23*, 682.
   DOI: 10.1021/cm102772x

7. Chen, X.; Wong, C. K. Y.; Yuan, C. A.; Zhang, G.; *Sensors and Actuators B: Chemical*, **2013**, *177*, 178.
   DOI: 10.1016/j.snb.2012.10.134
8. Hochbaum, A. I.; Yang, P.; *Chem. Rev.*, **2010**, *110*, 527.
   DOI: 10.1021/cr900075v
9. Zang, L.; Che, Y.; Moore, J. S.; *Acc. Chem. Res.*, **2008**, *41*, 1596.
   DOI: 10.1021/ar800030w
10. Lee, C. C.; Grenier, C.; Meijer, E. W.; Schenning, A. P. H. J.; *Chem. Soc. Rev.*, **2009**, *38*, 671.
    DOI: 10.1039/b800407m
11. Giansante, C.; Raffy, G.; Schäfer, C.; Rahma, H.; Kao, M.-T.; Olive, A. G. L.; Del Guerzo, A.; *J. Am. Chem. Soc.*, **2011**, *133*, 316.
    DOI: 10.1021/ja106807u
12. Greiner, A.; Wendorff, J. H.; *Angew. Chem. Int. Ed.*, **2007**, *46*, 5670.
    DOI: 10.1002/anie.200604646
13. Cho, H.; Min, S.-Y.; Lee, T.-W. *Macromol. Mater. Eng.*, **2013**, *298*, 475.
    DOI: 10.1002/mame.201200364
14. Min, S.-Y.; Kim, T.-S.; Kim, B. J.; Cho, H.; Noh, Y.-Y.; Yang, H.; Cho, J. H.; Lee, T.-W.; *Nature Commun.*, **2013**, *4*, 1773.
    DOI: 10.1038/ncomms2785
15. Seki, S.; Maeda, K.; Tagawa, S.; Kudoh, H.; Sugimoto, M.; Morita, Y.; Shibata, H; *Adv. Mater.* **2001**, *13*, 1663.
    DOI: 10.1002/1521-4095(200111)13:22<1663::AID-ADMA1663>3.0.CO;2-8
16. Miller, A. A.; Lawton, E. J.; Balwit, J. S.; *J. Poly. Sci.*, **1954**, *14*, 503.
    DOI: 10.1002/pol.1954.120147711
17. Thomas, J. K.; *Nucl. Instr. and Meth. B* **2007**, *265*, 1.
    DOI: 10.1016/j.nimb.2007.08.021
18. Seki, S.; Tsukuda, S.; Maeda, K.; Tagawa, S.; Shibata, H.; Sugimoto, M.; Jimbo, K.; Hashitomi, I.; Kohyama, A.; *Macromolecules*, **2005**, *38*, 10164.
    DOI: 10.1021/ma051821x
19. Tsukuda, S.; Seki, S.; Sugimoto, M.; Tagawa, S; *J. Phys. Chem. B*, **2006**, *110*, 19319.
    DOI: 10.1021/jp0640981
20. Seki, S.; Saeki, A.; Choi, W.; Maeyoshi, Y.; Omichi, M.; Asano, A.; Enomoto, K.; Vijayakumar, C.; Sugimoto, M.; Tsukuda, S.; Tanaka, S.; *J. Phys. Chem. B*, **2012**, *116*, 12857.
    DOI: 10.1021/jp3069249
21. Asano, A.; Omichi, M.; Tsukuda, S.; Takano, K.; Sugimoto, M.; Saeki, A.; Seki, S.; *J. Phys. Chem C*, **2012**, *116*, 17274.
    DOI: 10.1021/jp3046406
22. Omichi, M.; Asano, A.; Tsukuda, S.; Takano, K.; Sugimoto, M.; Saeki, A.; Sakamaki, D.; Onoda, A.; Hayashi, T.; Seki, S.; *Nature Commun.*, **2014**, *5*, 3718.
    DOI: 10.1038/ncomms4718
23. Maeyoshi, Y.; Saeki, A.; Suwa, S.; Omichi, M.; Marui, H.; Asano, A.; Tsukuda, S.; Sugimoto, M.; Kishimura, A.; Kataoka, K.; Seki, S.; *Sci. Rep.*, **2012**, *2*, 600.
    DOI: 10.1038/srep00600
24. Kumar, A.; Avasthi, D. K.; Tripathi, A.; Kabiraj, D.; Singh, F.; Pivin, J. C.; *J. Appl. Phys.*, **2007**, *101*, 014308.
    DOI: 10.1063/1.2404794
25. Kitamura, A.; Hamamoto, S.; Taniike, A.; Ohtani, Y.; Kubota, N.; Furuyama, Y.; *Radiat. Phys. Chem.*, **2004**, *69*, 171.
    DOI: 10.1016/S0969-806X(03)00439-0
26. Cataldo, F.; Strazzulla, G.; Iglesias-Groth, S.; *Radiat. Phys. Chem.*, **2009**, *78*, 244.
    DOI:10.1016/j.radphyschem.2009.01.004
27. Butko, V. Y.; Chi, X.; Lang, D. V.; Ramirez, A. P.; *Appl. Phys. Lett.*, **2003**, *83*, 4773.
    DOI: 10.1063/1.1631736
28. Chao, T.-H.; Chang, M.-J.; Watanabe, M.; Luo, M.-H.; Chang, Y. J.; Fang, T.-C.; Chen, K.-Y.; Chow, T. J.; *Chem. Commun.* **2012**, *48*, 6148.
    DOI: 10.1039/c2cc31754k
29. Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R.; *J. Am. Chem. Soc.*, **2001**, *123*, 9482.
    DOI: 10.1021/ja0162459
30. Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N.; *J. Am. Chem. Soc.*, **2005**, *127*, 4986.
    DOI: 10.1021/ja042353u
31. Seki, S.; Tsukuda, S.; Maeda, K.; Matsui, Y.; Saeki, A.; Tagawa, S.; *Phys. Rev. B*, **2004**, *70*, 144203.
    DOI: 10.1103/PhysRevB.70.144203
32. Seki, S.; Tsukuda, S.; Tagawa, S.; Sugimoto, M.; *Macromolecules*, **2006**, *39*, 7446.
    DOI: 10.1021/ma0612172
33. Nelson, T. D.; Crouch, R. D.; *Synthesis*, **1996**, 1031.
    DOI: 10.1055/s-1996-4350