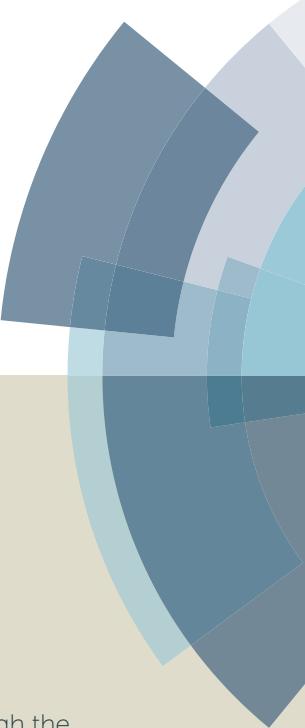


Polymer Chemistry

Accepted Manuscript



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ARTICLE

Linear-selective Cross-coupling Polymerization of Branched Oligothiophene by Deprotonative Metalation and Cross-coupling

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Kohei Murakami, Shota Tanaka and Atsunori Mori*

Brominated oligothiophene with a branched structure was subjected to deprotonative metalation with the bulky magnesium amide chloromagnesium 2,2,6,6-tetramethylpiperidine-2-yl lithium chloride salt (TMPMgCl₂·LiCl), which is recognized as Knochel-Hauser base. The thus metalated oligothiophene was polymerized in the presence of a nickel(II) NHC (*N*-heterocyclic carbene) complex to afford polymers of M_n of 4400 to 44000, which correspond well to the monomer feed/catalyst loading ratio. Analysis by MALDI-TOF MS suggests formation of a linear polymer with oligothiophene as the monomer. Polymerization of 7-mer (**7T-Br**₄) also affords polythiophene of a similar structure.

Polythiophenes obtained by transition-metal-catalyzed cross coupling polymerization are of great interest in materials science as well as polymer synthesis.^{1,2} Regioregular head-to-tail-type poly(3-hexylthiophene) (HT-P3HT) shows particularly interesting properties as materials and is employed in a wide range of optoelectronic devices such as photovoltaic cells,³ organic semiconductors,⁴ and conductive thin films.⁵ Oligo and polythiophenes with branched structures also attract attention and a wide range of such compounds have been designed and synthesized to date.⁶ We recently described the highly efficient preparation of oligothiophene dendrimers in a stepwise manner, in which extension of each generation is concisely achieved in a single step.⁷ Several branched oligothiophenes such as **3T**, **7T** were shown to be prepared with high efficiencies. It was also shown that such dendrimers were regioselectively halogenated to afford multiply halogenated branched oligomers. (Chart 1)

Department of Chemical Science and Engineering, Kobe University, 1-I Rokkodai, Nada, Kobe 657-8501, Japan

E-mail: amori@kobe-u.ac.jp

† Electronic Supplementary Information (ESI) available: Synthetic procedures and characterisation data. See DOI: 10.1039/b000000x/

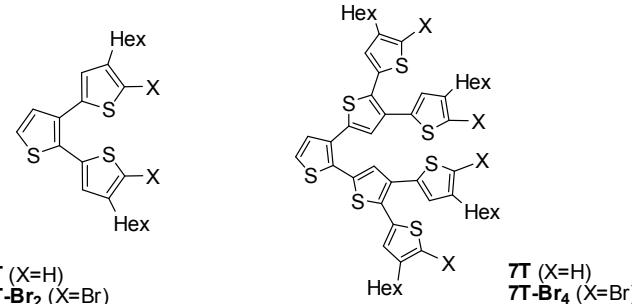


Chart 1 Oligothiophene dendrimers

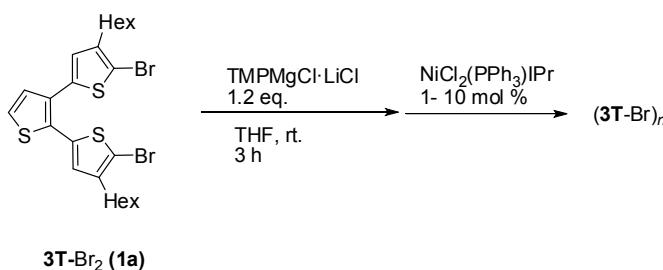
Our interest turned to cross coupling polymerization of the thus formed branched halo thiophenes, in which preference for linear⁸ or divergent propagation⁹ would be of particular interest. Herein, we report that deprotonative polymerization of multiply brominated oligothiophene dendrimers furnishes linear polymers and the remaining carbon-bromine bond in the polymer side chains can be successfully transformed.

Preparation of monomer precursor (**1a**) was performed according to our previously reported method that described the nickel catalyzed cross coupling reaction of 2,3-dibromothiophene with regioselectively metalated 3-hexylthiophene.⁷ The obtained branched terthiophene **3T** was selectively brominated by careful treatment with two equivalents of *N*-bromosuccinimide. Polymerization of **1a** was carried out with 1.2 equivalents of Knochel-Hauser base (chloromagnesium 2,2,6,6-tetramethylpiperidine lithium

ARTICLE

Journal Name

chloride salt: $\text{TMPCMgCl}\cdot\text{LiCl}$ ¹⁰ at room temperature for 3 h followed by addition of a nickel catalyst.¹¹



Scheme 1 Polymerization of **3T-Br₂ (1a)** with $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$

When the reaction of **1a** was carried out with 1.0 mol % nickel *N*-heterocyclic carbene (NHC) complex $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$ (*IPr*: *N,N'*-(2,6-diisopropylphenyl)imidazolium) in THF as shown in Scheme 1, rapid polymerization took place and the color change of the solution turned dark orange after stirring for 2 h. Termination of the polymerization with HClaq/MeOH resulted in formation of crude polymer solid. The obtained polymer was found to be highly soluble in organic solvents and SEC analysis showed $M_n = 44000$ (PDI = 1.30). The reaction was carried out under several conditions as summarized in Table 1, revealing that increasing the loading of catalyst (1-10 mol %) afforded polymers with lower molecular weight (entry 1-6). MALDI-TOF mass spectrometry (MS) of the polymer of entry 6 ($M_n = 4350$ by SEC) revealed a repeating unit of $M/Z = 493.06$ as shown in Fig. 1, suggesting the structure of $(3\text{T-Br})_n$ and end groups composed of H/H (minor) and H/Br (major). The average molecular weight corresponded reasonably well with the monomer feed/ catalyst loading ratio (e.g. theoretical $M = 49300$ for 1 mol % Ni catalyst in entry 1). The above results suggest that linear polymers composed of monobrominated **3T** as a repeating unit are obtained in the polymerization reaction. Additionally, unless the organometallic monomer is completely consumed, a nickel species that is capable of incorporating additional monomer exists at the polymer end. Use of NiCl_2dppp also led to polymerization although a longer reaction period was found to be necessary (entry 7). However, prolonged reaction with NiCl_2dppe or the Ni NHC complex^{12,13} resulted in gelation. (entries 2 and 8) The reaction with Pd-PEPPSI as a catalyst also resulted in polymerization, albeit much more slowly (entry 9) and polymerization took place with slightly inferior efficiency when catalyzed by $\text{Pd}(t\text{Bu}_3\text{P})_2$ (entry 10). Although deprotonation with a lithium amide such as LDA followed by metal exchange with $\text{Mg}^{2a,14}$ or $\text{Zn}^{2a,15}$ ion might be an alternative choice to give a similar metalated species (monomer), it should be pointed out that the metalation protocol used here was achieved in a single step at room temperature.

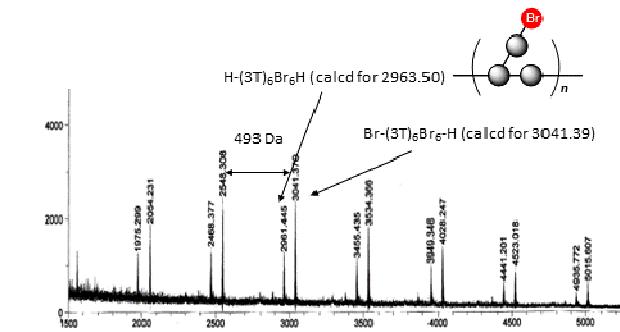


Fig. 1 MALDI-TOF mass spectrum of the polymerization product of **1a** (Table 1, entry 6)

Table 1 Polymerization of **1a** with $\text{TMPCMgCl}\cdot\text{LiCl}$ followed by nickel or palladium^a

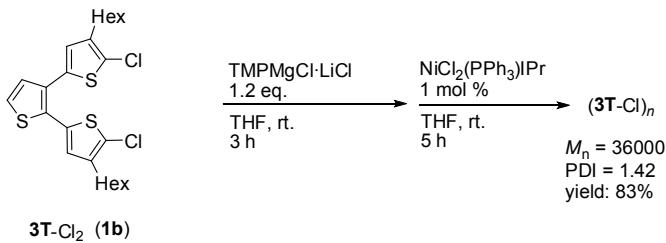
entry	catalyst (mol %)	time h	yield ^b %	M_n (M _{theor}) ^c	PDI
1	$\text{NiCl}_2(\text{PPh}_3)\text{IPr}$ (1.0)	2	98 (99)	44000 (49300)	1.30
2	(1.0)	24	gel ^d	--	--
3	(2.0)	2	88 (92)	21000 (24700)	1.20
4	(3.0)	2	93 (95)	15700 (16400)	1.23
5	(4.0)	2	80 (96)	13000 (12400)	1.23
6	(10.0)	2		4400 (4900)	1.12
7	NiCl_2dppp (1.0)	24	77 (89)	55000	1.56
8	NiCl_2dppe (1.0)	24	gel ^d	--	--
9	Pd-PEPPSI-SIPr (1.0)	70	83 (93)	28700	1.58
10	$\text{Pd}(t\text{Bu}_3\text{P})_2$ (1.0)	24	51 (86)	11000	1.93

^a Polymerization was carried out with 1.2 equiv $\text{TMPCMgCl}\cdot\text{LiCl}$ in 3 mL THF with **1a** (0.3 mmol) stirring at room temperature for 2 h followed by addition of $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$. ^b Conversion of monomer (%) is shown in parentheses. ^c The theoretical molecular weight based on the monomer/catalyst feed ratio given in parentheses. ^d Insoluble materials were formed in the polymerizing solution.

Measurement of viscosity also supports that the polymerization reaction proceeds in a linear-selective manner, while divergent

polymerization leading to hyperbranched polymer hardly occurs. The relationship between viscosity η and M_n can be expressed as, $\eta = K(M_n)^\alpha$ where K and α are constants based on the polymer properties; it has been suggested that an ideal linear polymer has an α value of ca. 0.5 while that of branched polymer is much smaller. Measurement of the viscosity of $(3T\text{-Br})_n$ revealed that it had an α of 0.88, which supports it being a linear polymer. However, Luscombe recently reported the synthesis of a hyperbranched polymer composed of branched oligothiophene, for which the α value is described as 0.19–0.31.^{9c} Furthermore, calculation of the α value of oligothiophene dendrimers 3T, 7T, and 15T showed ca. $\alpha = 0.20$. These results strongly suggest that the structure of $(3T\text{-Br})_n$ prepared by nickel-catalyzed polymerization is linear despite the presence of two possible reactive carbon-bromine bonds.

The deprotonative polymerization was found to take place also with the chloride analog $3T\text{-Cl}_2$ (**1b**) under similar conditions to afford $(3T\text{-Cl})_n$ smoothly as shown in Scheme 2.¹⁶ The average molecular weight of the obtained polymer again agreed with the catalyst loading/monomer feed ratio with $M_n = 36000$ and with a PDI of 1.42.



Scheme 2 Polymerization of $3T\text{-Cl}_2$ (**1b**) with $\text{NiCl}(\text{PPh}_3)\text{IPr}$

We next turned our attention to the molecular structure of the obtained polymer. Linear polymerization could proceed in two alternative manners either α - α conjugation leading to **A** of Figure 2 or α - β conjugation to afford **B**. According to the UV-vis spectrum of $(3T\text{-Br})_n$ exhibiting a λ_{max} of 432 nm, the structure of $(3T\text{-Br})_n$ is most likely to involve linear α - α conjugation **A**. We thus prepared the two monochlorinated **3Ts** **2** and **3**, and these chlorothiophenes were polymerized. The reaction of **2** proceeded similarly to that of $3T\text{-Cl}_2$ (**1b**) with deprotonation by the Knochel-Hauser base and following treatment with Ni-NHC catalyst (1 mol %)¹⁶ afforded α - α conjugated polymer **A'** (65% yield; $M_n = 22600$; PDI = 1.75). The regioisomer chloride **3** also reacted under similar conditions, although with a reduced polymerization efficiency (48% yield; $M_n = 11000$; PDI = 1.09) suggesting that catalyst transfer through unlikely bond alternation toward α - β conjugation took place less smoothly. The regioisomers **A'** and **B'** were then treated with NBS to afford the brominated polymers **A** and **B**, respectively, whose ¹H NMR spectra are shown in Fig. 3 (b) and (a). Comparing these NMR spectra with that of $(3T\text{-Br})_n$ reveals that the spectrum of brominated

polymer **A** from α - α conjugated polymer **A'** is almost identical to that of $(3T\text{-Br})_n$ and that signals assigned as α - β conjugation of **B** are observed at an intensity of less than 1:20. The M_n value of the linear polymer **A** from **A'** as estimated by SEC also showed reasonable correspondence with that based on viscosity measurement, which was interpolated from the calculated slope of $(3T\text{-Br})_n$ ($\alpha = 0.88$).^{8b} These results further support the hypothesis that polymerization of **1a** would be linear because of preferential selective α - α conjugation via nickel-catalyzed cross coupling.

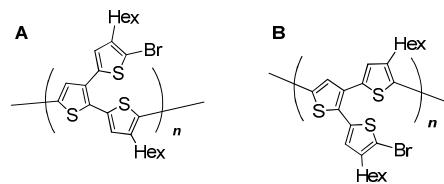
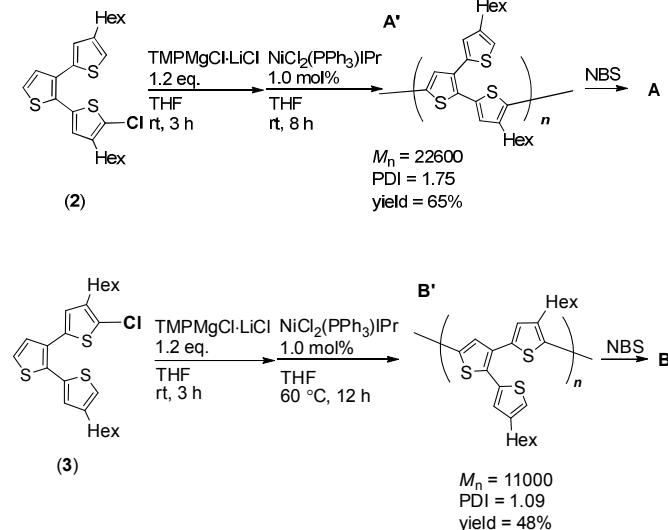


Fig. 2 α - α and α - β conjugated polymer



Scheme 3 Polymerization of monochlorinated **3T 2** and **3** with $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$

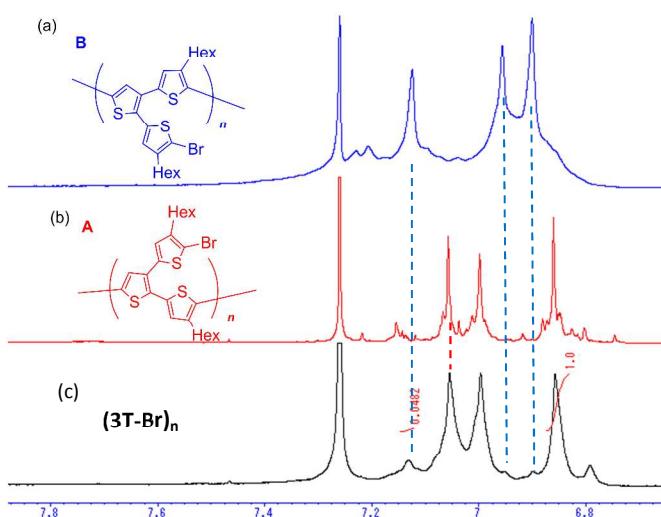
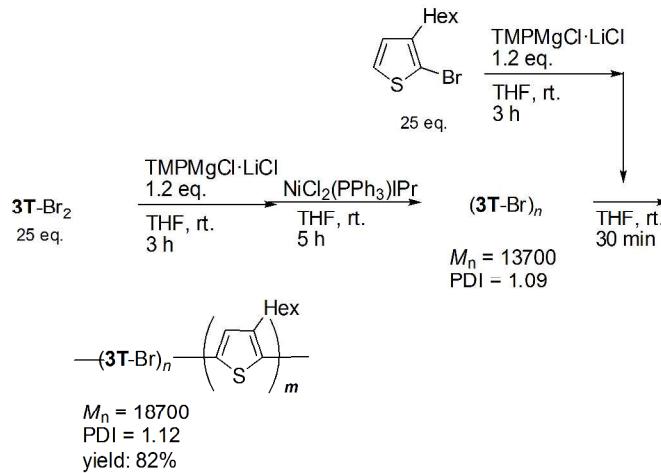


Fig. 3 ^1H NMR spectra of polymer **A** and **B** and the reduction product from $(3\text{T-Br})_n$

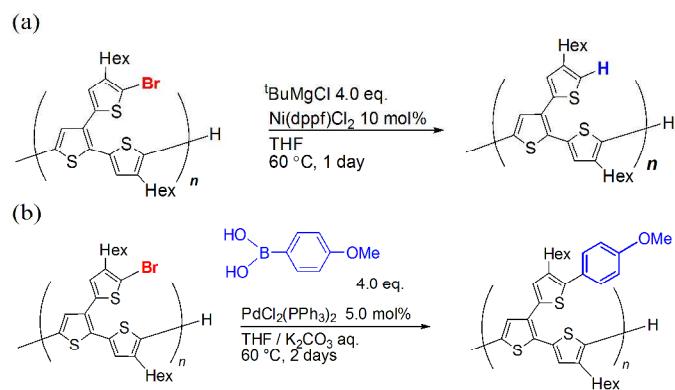
We next performed copolymerization of 3T-Br_2 with 2-bromo-3-hexylthiophene. After the polymerization of 3T-Br_2 (25 equiv relative to Ni catalyst) with $\text{TMPPMgCl}\cdot\text{LiCl}$ and $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$ at room temperature for 2 h ($M_n = 13700$; PDI = 1.09; $M_{\text{theor}} = 12300$), metallated thiophene (25 equiv), which was also formed in situ by the reaction of 2-bromo-3-hexylthiophene and $\text{TMPPMgCl}\cdot\text{LiCl}$, was added to the initial polymerization mixture. Further stirring of the reaction mixture afforded block copolymer. SEC profile clearly showed a shift of the peak of the initial polymer toward a higher molecular weight ($M_n = 18700$; PDI = 1.12; $M_{\text{theor}} = 16500$).



Scheme 4 Synthesis of block copolymer

Since the obtained linear polymer bears a bromo group at each side chain, functionalization of the carbon-bromine bonds was examined. Reductive transformation of $(3\text{T-Br})_n$ proceeded with $t\text{BuMgCl}$ as a reducing agent in the presence of NiCl_2dppf as a catalyst.¹⁷ Treatment of the polymer in THF under reflux

for 1 day formed the debrominated product as shown in Scheme 5(a). MALDI-TOF MS clearly identified the repeating unit of 3T-H (416.7 Da), as shown in Fig. 4(a). Transformation of the carbon-bromine bond of $(3\text{T-Br})_n$ was also carried out with arylboronic acid 4-MeOC₆H₄B(OH)₂ in the presence of palladium catalyst $\text{PdCl}_2(\text{PPh}_3)_2$ (Scheme 5b).¹⁸ Reaction at 60 °C for 2 days resulted in complete conversion to the arylated polymer and measurement by MALDI-TOF-MS showed reasonable agreement with the repeating arylterthiophene. (Fig. 4b)



Scheme 5 (a) Reductive transformation of $(3\text{T-Br})_n$ with $t\text{BuMgCl}$; (b) arylation by Suzuki-Miyaura coupling

(a)

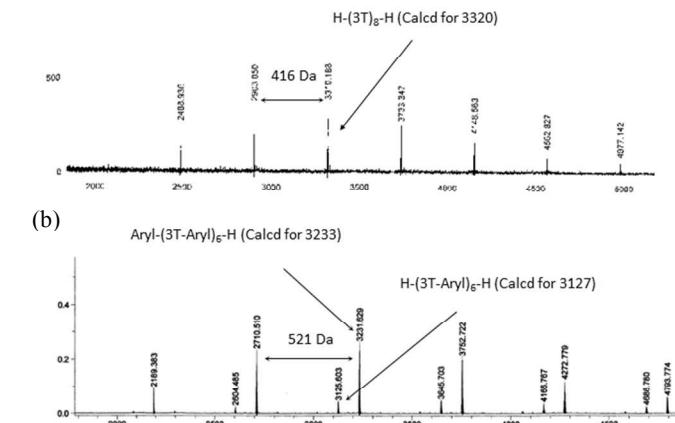
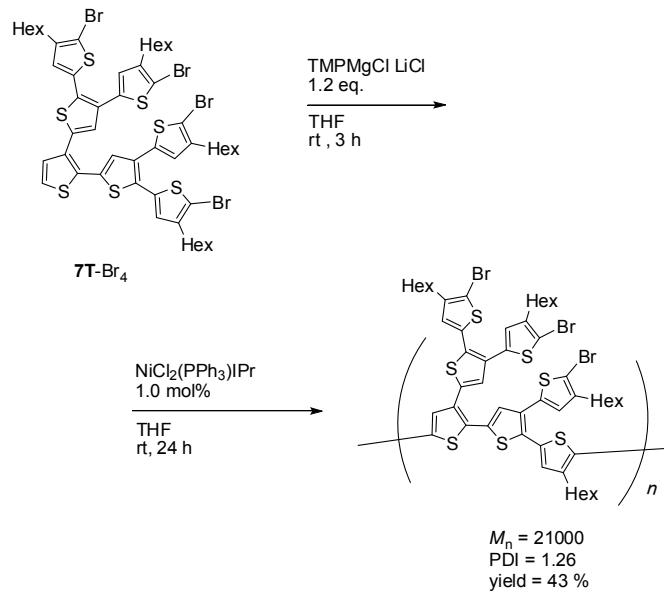


Figure 4 MALDI-TOF mass spectra of (a) debrominated; and (b) arylated polymers

Polymerization of an oligothiophene dendrimer composed of seven thiophene units with four bromo groups at the 2-position was also carried out under similar conditions.⁷ When the reaction was performed with 1 mol % nickel catalyst, $(7\text{T-Br}_3)_n$ was obtained in a slightly lower yield (43%) because of difficulties in effective deprotonation with TMPPMgCl. The

produced polymer had M_n and PDI of 21000 and 1.75 ($M_{\text{theor}} = 52000$), respectively, as shown in Scheme 6.



Scheme 6 Polymerization of **7T-Br₄**

Conclusions

We have shown that oligothiophene dendrimers bearing multiple carbon-bromine bonds suitable for use as monomers in cross-coupling polymerization. It was revealed that the monomer underwent selective linear polymerization, which was confirmed by MALDI-TOF MS analysis, while hyperbranched polythiophene was not obtained despite the presence of two polymerizable bromine functionalities. The molecular weight of the product polymer was controllable by adjusting the ratio of monomer feed/catalyst loading suggesting that catalyst-transfer-type cross-coupling polycondensation² took place. Because the produced polymer bears carbon-bromine bond in its side chains, further functionalizations through reduction and palladium-catalyzed arylation by transition metal catalysis were demonstrated. Poly(oligothiophene dendrimer) formed by linear polymerization is a novel class of structure with extended π -conjugation; thus, we anticipate its application towards new materials.

Acknowledgements

The authors thank Professor Takashi Nishino of Kobe University for discussion on the measurement of viscosity and its relationship with polymer structure. We thank KAKENHI (B) (Nos. 22350042 and 25288049) from the Japan Society for Promotion of Science (JSPS) for financial supports. S. T. thanks JSPS Fellowship for Young Scientists. This work was also partially supported by Special Coordination Funds for Promoting Science and Technology, Creation of Innovation

Centers for Advanced Interdisciplinary Research Areas (Innovative Bioproduction Kobe) by MEXT.

Notes and references

- (a) T. A. Chen and R. D. Rieke, *J. Am. Chem. Soc.*, 1992, **114**, 10087; (b) T. A. Chen, R. A. O'Brien and R. D. Rieke, *Macromolecules*, 1993, **26**, 3462; (c) T. A. Chen, X. Wu, and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233; (d) X. Wu, T. A. Chen and R. D. Rieke, *Macromolecules*, 1996, **29**, 7671; (e) R. S. Loewe, S. M. Khersonsky and R. D. McCullough, *Adv. Mater.*, 1999, **11**, 250; (f) J. Liu, D. W. Laird and R. D. McCullough, *Macromolecules*, 2004, **37**, 3526; (g) M. C. Iovu, E. E. Sheina, R. R. Gil and R. D. McCullough, *Macromolecules*, 2005, **38**, 8649; (h) M. Jeffries-El, G. Sauvé and R. D. McCullough, *Macromolecules*, 2005, **38**, 10346; (i) M. C. Stefan and A. E. Javier, I. Osaka and R. D. McCullough, *Macromolecules*, 2009, **42**, 30; (j) A. Yokoyama, R. Miyakoshi and T. Yokozawa, *Macromolecules*, 2004, **37**, 1169; (k) R. Miyakoshi, A. Yokoyama, and T. Yokozawa, *J. Am. Chem. Soc.*, 2005, **127**, 17542; (l) R. Miyakoshi, A. Yokoyama and T. Yokozawa, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 753; (m) T. Yokozawa and A. Yokoyama, *Chem. Rev.*, 2009, **109**, 5595; (n) R. Tkachov, V. Senkovsky, H. Komber, J.-U. Sommer and A. Kiriy, *J. Am. Chem. Soc.*, 2010, **132**, 7803; (o) Q. Wang, R. Takita, Y. Kikuzaki and F. Ozawa, *J. Am. Chem. Soc.*, 2010, **132**, 11420; (p) E. L. Lanni and A. J. McNeil, *J. Am. Chem. Soc.*, 2009, **131**, 16573; (q) H. A. Bronstein and C. K. Luscombe, *J. Am. Chem. Soc.*, 2009, **131**, 12894.
- For reviews: (a) T. Yokozawa and A. Yokoyama, *Chem. Rev.*, 2009, **109**, 5595; (b) R. D. McCullough, *Adv. Mater.*, 1998, **10**, 93.; (c) I. Osaka and R. D. McCullough, *Acc. Chem. Res.*, 2008, **41**, 1202; (d) K. Okamoto, J. Zhang, J. B. Housekeeper, S. R. Marder and C. K. Luscombe, *Macromolecules*, 2013, **46**, 8059; (e) K. Okamoto, C. K. Luscombe, *Polym. Chem.*, 2011, **2**, 2424.
- (a) J. Roncali, *Chem. Rev.* 1997, **97**, 173; (b) S. Günes, H. Neugebauer and N. S. Sarisiftci, *Chem. Rev.* 2007, **107**, 1324; (c) Y.-J. Cheng, S.-H. Yang, C.-S. Hsu, *Chem. Rev.* 2009, **109**, 5868.
- (a) H. Sirringhaus, N. Tessler and R. H. Friend, *Science* 1998, **280**, 1741; (b) H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, W. W. Meijer, P. Herwig and D. M. deLeeuw, *Nature* 1999, **401**, 685; (c) Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha and M. Ree, *Nat. Mater.* 2006, **5**, 197; (d) C. H. Woo, B. C. Thompson, B. J. Kim, M. F. Toney and J. M. J. Fréchet, *J. Am. Chem. Soc.* 2008, **130**, 16324.
- (a) F. Chen, P. G. Mehta, L. Takiff, and R.D. McCullough, *J. Mater. Chem.* 1996, **6**, 1763; (b) P. Gangopadhyay, G. Koeckelberghs and A. Persoons, *Chem. Mater.* 2011, **23**, 516. (c) D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* 2000, **100**, 2537; (d) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.* 2009, **109**, 897.
- (a) G. Ramakrishna, A. Bhaskar, P. Bäuerle and T. J. Goodson III, *Phys. Chem. A* 2008, **112**, 2018; (b) M. Mastalerz, V. Fischer, C.-Qi. Ma, R. A. J. Janssen, and P. Bäuerle, *Org. Lett.*, 2009, **11**, 4500; (c) C.-Qi. Ma, E. M. Osteritz, T. Debaerdemaeker, M. M. Wienk, R.-A.

J. Janssen and P. Bäuerle, *Angew. Chem., Int. Ed.* 2007, **46**, 1679; (d) M. R. Harpham, Ö. Süzer, C.-Qi. Ma, P. Bäuerle and T. J. Goodson III, *Am. Chem. Soc.* 2009, **131**, 973; (e) C. Xia, X. Fan, J. Locklin and R. C. Advincula, *Org. Lett.*, 2002, **4**, 2067; (f) S. Deng, G. Krueger, P. Taranekar, S. Sriwichai, R. Zong, R. P. Thummel and R. C. Advincula, *Chem. Mater.* 2011, **23**, 3302; (g) C. Xia, X. Fan, J. Locklin, R. C. Advincula, A. Gies and W. Nonidez, *J. Am. Chem. Soc.* 2004, **126**, 8735; (h) S. Deng, T. M. Fulghum, G. Krueger, D. Patton, J.-Y. Park and R. C. Advincula, *Chem. Eur. J.* 2011, **17**, 8929.

7 S. Tanaka, D. Tanaka, G. Tatsuta, K. Murakami, S. Tamba, A. Sugie and A. Mori, *Chem. Eur. J.* 2013, **19**, 1658.

8 T. V. Richter, C. H. Braun, S. Link, M. Scheuble, E. J. W. Crossland, F. Stelzl, U. Würfel and S. Ludwigs, *Macromolecules* 2012, **45**, 5782.

9 (a) T. V. Richter, S. Link, R. Hanselmann, S. Ludwigs, *Macromol. Rapid Commun.* 2009, **30**, 1323; (b) S. Link, T. Richter, O. Yurchenko, J. Heinze and S. Ludwigs, *J. Phys. Chem. B* 2010, **114**, 10703; (c) K. Okamoto, J. B. Housekeeper and F. E. Michael, *Polym. Chem.* 2013, **4**, 3499; (d) M. Scheuble, T. V. Richter, M. Goll, S. Link, J. T. L. Navarrete, A. Ruff, M. C. R. Delgadob and S. Ludwigs, *Polym. Chem.*, 2014, **5**, 6824.

10 (a) A. Krasovskiy, V. Krasovskaya and P. Knochel, *Angew. Chem., Int. Ed.* 2006, **45**, 2958; (b) W. Lin, O. Baron and P. Knochel, *Org. Lett.* 2006, **8**, 5673; (c) G. C. Clososki, C. J. Rohbogner and P. Knochel, *Angew. Chem., Int. Ed.* 2007, **46**, 7681; (d) C. J. Rohbogner, G. C. Clososki and P. Knochel, *Angew. Chem., Int. Ed.* 2008, **47**, 1503; (e) A. H. Stoll and P. Knochel, *Org. Lett.* 2008, **10**, 113; (g) M. Mosrin and P. Knochel, *Org. Lett.* 2008, **10**, 2497; (h) F. M. Piller and P. Knochel, *Org. Lett.* 2009, **11**, 445; (i) C. R. Hauser and H. G. Walker, *J. Am. Chem. Soc.* 1947, **69**, 295; (k) F. C. Frostick and C. R. Hauser, *J. Am. Chem. Soc.* 1949, **71**, 1350; (l) P. E. Eaton, C.-H. Lee and Y. Xiong, *J. Am. Chem. Soc.* 1989, **111**, 8016.

11 (a) S. Tamba, S. Tanaka, Y. Okubo, H. Meguro, S. Okamoto and A. Mori, *Chem. Lett.* 2011, **40**, 398; (b) S. Tamba, Y. Okubo, A. Sugie and A. Mori, *Polym. J.*, 2012, **44**, 1209; (c) S. Tamba, K. Fuji, H. Meguro, S. Okamoto, T. Tendo, R. Komobuchi, A. Sugie, T. Nishino and A. Mori, *Chem. Lett.* 2013, **42**, 281; (d) A. Mori, K. Ide, S. Tamba, S. Tsuji, Y. Toyomori and T. Yasuda, *Chem. Lett.* 2014, **43**, 640.

12 For reviews: (a) W. A. Herrmann, *Angew. Chem., Int. Ed.* 2002, **41**, 1290; (b) T. Weskamp, V. P. W. Böhm and W. A. Herrmann, *J. Organomet. Chem.* 2000, **600**, 12; (c) D. Bourissou, O. Guerret, F. P. Gabba and G. Bertrand, *Chem. Rev.* 2000, **100**, 39.

13 (a) D. S. McGuinness and K. J. Cavell, *Organometallics* 1999, **18**, 1596. (b) V. P. W. Böhm, T. Weskamp, C. W. K. Gstöttmayr and W. A. Herrmann, *Angew. Chem., Int. Ed.* 2000, **39**, 1602; (c) V. P. W. Böhm, C. W. K. Gstöttmayr, T. Weskamp and W. A. Herrmann, *Angew. Chem., Int. Ed.* 2001, **40**, 3387; (d) Y. Sato, R. Sawaki and M. Mori, *Organometallics* 2001, **20**, 5510; (e) G. M. Mahandru, G. Liu and J. Montgomery, *J. Am. Chem. Soc.* 2004, **126**, 3698; (f) S. Diez-Gonzalez, N. Marion and S. P. Nolan, *Chem. Rev.* 2009, **109**, 3612.

14 (a) R. D. McCullough, *Adv. Mater.* 1998, **10**, 93; (b) R. D. McCullough and S. P. Williams, *J. Am. Chem. Soc.* 1993, **115**, 11608; (c) R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem.* 1993, **58**, 904.

15 (a) R. D. McCullough and R. D. Lowe, *J. Chem. Soc., Chem. Commun.*, 1992, **1**, 70. (b) J. Liu and R. D. McCullough, *Macromolecules* 2002, **35**, 9882.

16 (a) S. Tamba, K. Shono, A. Sugie and A. Mori, *J. Am. Chem. Soc.* 2011, **133**, 9700; (b) K. Fuji, S. Tamba, K. Shono, A. Sugie and A. Mori, *J. Am. Chem. Soc.* 2013, **135**, 12208.

17 K. Shono, Y. Sumino, S. Tanaka, S. Tamba and A. Mori, *Org. Chem. Front.*, 2014, **1**, 678.

18 (a) N. Miyaura and A. Suzuki, *Chem. Rev.* 1995, **95**, 2457; (b) A. Suzuki, *J. Organomet. Chem.* 1999, **576**, 147; (c) S. Kotha, K. Lahiri and D. Kashinath, *Tetrahedron* 2002, **58**, 9633.

