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**.

Journal Name

COMMUNICATION

Synthesis of Poly(1,10-phenanthroline-5,6-diyl)s Having a π-Stacked, Helical Conformation

Weixi Yang[a] and Tamaki Nakano*[a]

**5,6-Diboromo-1,10-phenanthroline and 2,9-di-*n*-butyl-5,6-dibromo-1,10-phenanthroline were polymerized using a Ni catalyst to afford helical polymers in which the phenanthroline moieties are densely stacked on top of each other. Polymerization of the latter monomer using a chiral catalyst led to a preferred-handed helix. This is the first Ni-catalyzed helix-sense-selective polymerization of aromatic compound.**

Helical polymers are an important class of material that finds a wide range of applications such as chiral recognition, nonlinear optics, and chiral catalysis.[1] Such a conformation has been realized for various types of synthetic polymers including vinyl polymers, conjugated polymers and polymers containing hetero atoms in the main chain.[2] Among main-chain conjugated polymers, poly(*o*-phenylene) and its derivatives may be expected to form a helical conformation due to restricted rotation around single bonds connecting aromatic groups arising from steric hindrance and π-stacking between aromatic groups. However, examples of synthesis and structural analysis of poly(*o*-phenylene) and its derivatives are far more limited compared with poly(*para*-phenylene) and its derivatives. The first synthesis of poly(*o*-phenylene) was attempted by Wittig[3] through coupling of *o*-dilithiobenzene in the presence of transition metal salt resulting in products that seem to be cyclic compounds. Later, Ullmann reaction[4], Kumada coupling[5] and electrochemical polymerization[6] aiming at poly(*o*-phenylene) were also reported. Conventional step-by-step methods such as Suzuki coupling[7] and copper-mediated oxidative coupling[8] were also used. Recently, polymerizations of aryne and oxabicyclic alkene with copper and palladium catalysis, respectively, were developed.[9] As one of the most noticeable achievements, uniform poly(*o*-phenylene) derivatives up to 48-mer were synthesized through copper-mediated oxidative reaction of lithiated precursors starting from a 2,2'-biphenyl derivative and *n*-BuLi, and a tight helical

conformation was clarified through X-ray crystal analysis.[8] In this case, single-handed helix was obtained through resolution by triage of conglomerate crystals[8a] as well as chiral HPLC.[8b]

Herein, we report the synthesis, chemical structure and conformation of poly(1,10-phenanthroline-5,6-diyl) (**poly(Phen)**) and poly(poly(2,9-di-*n*-butyl-1,10-phenanthroline-5,6-diyl)) (**poly(DBPhen)**) as novel polymers whose main chain consists of 1,10-phenanthroline-5,6-diyl units through Ni-catalyzed polymerization (Scheme 1). The polymers were found to possess a helical conformation in which 1,10-phenanthroline-5,6-diyl units are densely stacked on top of each other. 1,10-Phenanthroline has been used as ligands for metallic species; the two polymers prepared in this work may be regarded as candidates of polymer ligand.
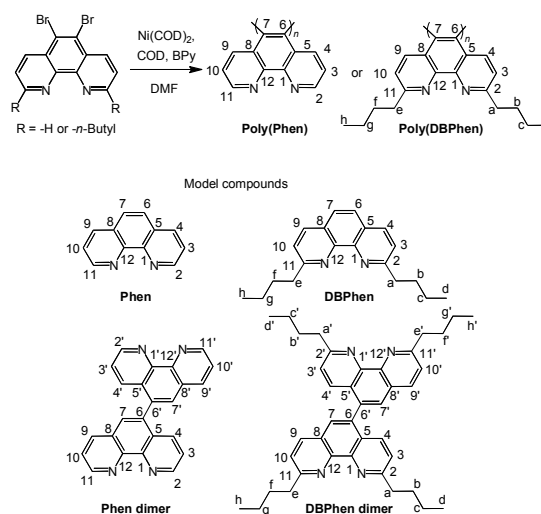
Scheme 1. Synthesis of poly(Phen) and poly(DBPhen) and structures of compounds studied in this work with atom numbering systems.

The conditions and results of polymerization are summarized in Table 1. 5,6-Dibromo-1,10-phenanthroline was prepared as monomer according to the literature[10] with modifications and was polymerized in *N,N*-dimethylformamide

a. Institute for Catalysis (ICAT) and Graduate School of Chemical Sciences and Engineering, Hokkaido University, N 21, W 10, Kita-ku, Sapporo 001-0021, Japan. Email:tamaki.nakano@cat.hokudai.ac.jp; Fax: +81-11-7069156; Tel: +81-11-7069155.

(DMF) at 85°C with a catalyst system consisting of 1,5-cyclooctadiene (COD), 2,2'-bipyridine and Ni(COD)$_2$ (Yamamoto coupling polymerization).[11] The obtained **poly(Phen)** was purified by washing with toluene, aq. ethylenediaminetetraacetic acid (EDTA), water, and benzene in this order. **Poly(Phen)** was almost insoluble in pure organic solvents such as DMF, methanol, and dimethyl sulfoxide (DMSO), and was soluble in DMF containing a small amount of aq. HCl or trifluoroacetic acid and in aq. HCl (DCl). Quaternary salt formation of the polymer may weaken inter-chain interactions. The DMF-insoluble **poly(Phen)** was mainly subjected to analyses hereafter.

Table 1. Synthesis of **poly(Phen)** and **poly(DBPhen)** using a Ni catalyst in DMF at 85 °C[a].

Entry	Polymer	Time (h)	Yield[b] (%)		DMF-insol. part		DMF-sol. part	
			DMF-insol.	DMF-sol.	$M_n^{c,d}$	$M_w/M_n^{c,d}$	$M_n^{c,e}$	$M_w/M_n^{c,e}$
1	**Poly(Phen)**	24	90	7[f]	18,100	1.05	ND[f]	ND[f]
2	**Poly(Phen)**	5	47	6[f]	9,100	4.03	ND[f]	ND[f]
3	**Poly(DBPhen)**	72	50	35	8,300	7.89	5,200	4.59
4	**Poly(DBPhen)**	24	18	65	4,300	6.88	2,700	5.32

[a][Monomer] 0.04 M, [Ni] 0.12 M, DMF 12 mL. [b]Washed with toluene, aq. EDTA (pH = 5) , aq. EDTA (pH = 9), aq. KOH (2 M), water and benzene in this order. [c]Determined by SEC (Column Shodex Asahapak GF-310HQ; Flow rate 0.5 mL/min) in DMF containing 30 mM LiCl (vs. standard poly(2-vinylpyridine)). [d]Samples for injection were dissolved in 1 mL of DMF containing 0.01 mL of conc. aq. HCl. [e]Samples for injection were dissolved in pure DMF. [f]The DMF-soluble materials did not show any clear signals in ^{1}H NMR spectra and SEC, suggesting that they are impurities.

In order to improve solubility of polymer, 2,9-di-*n*-butyl-5,6-dibromo-1,10-phenanthroline was synthesized as new monomer by bromination of 2,9-di-*n*-butyl-1,10-phenanthroline which was obtained through reaction of 1,10-phenanthroline with *n*-butyllithium. This compound was polymerized in the same manner as that for 5,6-dibromo-1,10-phenanthroline. The obtained polymer was washed with toluene, aq. EDTA, water, and benzene in this order. **Poly(DBPhen)** was found to be partially soluble in DMF; the DMF-soluble part was soluble in CHCl$_3$, methanol, DMSO, DMF containing a small amount of aq. HCl or trifluoroacetic acid and was insoluble in aq. HCl (DCl). The two *n*-butyl groups per unit seem to prevent aggregation of chains. The DMF-soluble **poly(DBPhen)** was mainly subjected to analyses hereafter.

Although a [Ni]/[monomer] ratio of 1.5 is often used in Yamamoto coupling polymerization,[11] in the polymerization of the two monomers, reaction was not effectively induced at this ratio and proceeded smoothly at a ratio of 3. Coordination of the 1,10-phenanthroline moiety of the monomers to Ni may reduce activity of the catalyst system. The monomers were almost completely consumed under the conditions indicated in Table 1. For both **poly(Phen)** and **poly(DBPhen)** syntheses, a higher molar mass was attained for a longer reaction time. Although the apparent molar masses of **poly(Phen)**s were higher than those of **poly(DBPhen)**s, fair comparison might be difficult because the two polymers have different chemical structures.

Structures of the two polymers were assessed by ^{13}C NMR spectra. As model dimers, 5,5'-bi-1,10-phenanthroline (**Phen dimer**) and 5,5'-bi-2,9-dibutyl-1,10-phenanthroline (**DBPhen dimer**) were synthesized. Fig. 1 indicates the ^{13}C NMR spectra of **poly(Phen)** (entry 1 in Table 1), **poly(DBPhen)** (entry 3 in Table 1), the model dimers, and 1,10-phenanthroline (**Phen**) and 2,9-dibutyl-1,10-phenanthroline (**DBPhen**) as unit models. The spectrum of **poly(Phen)** was taken in D$_2$O containing 35% DCl and those of the others in CDCl$_3$.

The ^{13}C NMR spectra of the polymers showed broader spectral patterns compared with the corresponding models, and signal broadening was also confirmed in ^{1}H NMR spectra (ESI, Fig. S40). The broad signals may arise from chain rigidity and also from non-uniformity of magnetic environment in a polymer chain.

The signal assignments of **Phen**,[12] **Phen dimer**, **DBPhen**, and **DBPhen dimer** were conducted using the HMQC, HMBC and DEPT45 methods starting from the H6(7) signals of **Phen** and **DBPhen** and the H7 signals of the dimers (ESI, Figs. S7-S11, S13-S17, S25-S31, and S33-S39). These signals were identified as they were the only singlet ones in the aromatic region of each compound in the ^{1}H NMR spectra (ESI, Figs. S7, S13, S25, and S33). The ^{13}C NMR spectra of the four model compounds indicate that formation of a single bond between monomeric units down-field shifts the signal of the carbon at which the new bond is formed (C6 and C6' of the dimer models). The signals of C6 and C6' of **Phen dimer** and **DBPhen dimer** appeared at around 135 ppm while the C6(7) signals of **Phen** and **DBPhen** at around 126 ppm and 125 ppm, respectively. **Poly(DBPhen)** indicated a spectral pattern similar to that of **DBPhen dimer** where the signals at around 135 ppm can be assigned to C6 and C7, supporting its chemical structure. On the other hand, the spectral comparison between **Phen dimer** and **poly(Phen)** was difficult due to the different solvents and also possibly due to partial quaternary salt formation of **poly(Phen)** with DCl. [13]C spectra of **Phen** and **Phen dimer** were also measured in D$_2$O-DCl; the spectrum of **Phen dimer** indicated rather complicated pattern probably due to partial quaternary salt formation (ESI, Fig. S41).
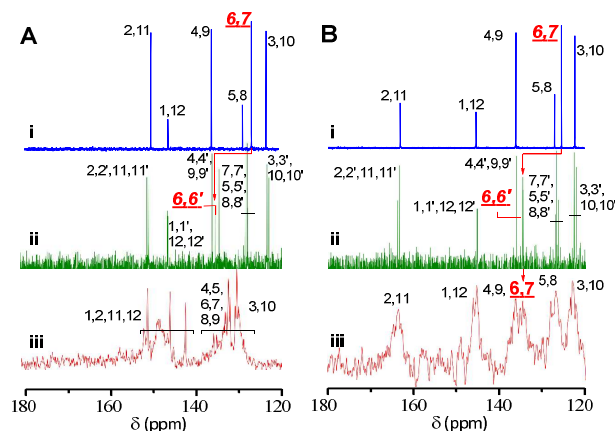

Fig. 1. 100 MHz ^{13}C NMR spectra of **Phen** (i), **Phen dimer** (ii) and **poly(Phen)** (entry 1 in Table 1) (iii) (panel A) and those of **DBPhen** (i), **DBPhen dimer** (ii) and **poly(DBPhen)** (entry 3 in Table 1) (iii) (panel B). The spectrum in A-iii was taken in D$_2$O containing 35% DCl with 4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt (DDS) standard and the others in CDCl$_3$ at room temperature.

COMMUNICATION

Information on conformation of **poly(Phen)** and **poly(DBPhen)** was obtained from UV-vis spectra (Fig. 2). Phen dimer and **DBPhen dimer** indicated slightly red-shifted and less structured bands compared with **Phen** and **DBPhen**, respectively. These features can be ascribed to the extended π-conjugation in the dimers. In the polymer spectra, much greater red shifts occurred, leading to broad signals in the range of 320-500 nm; this observation strongly supports that the polymers have rather long π-conjugation.
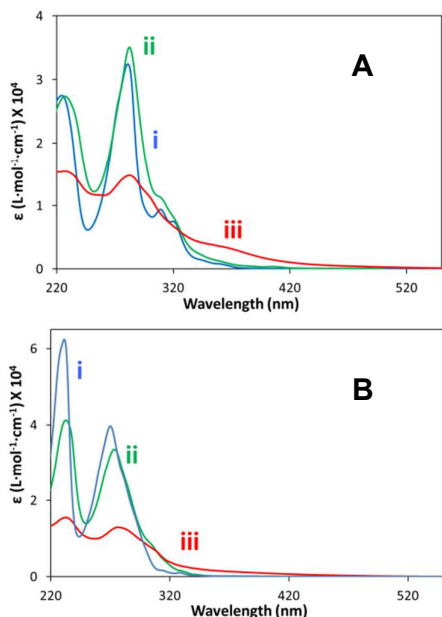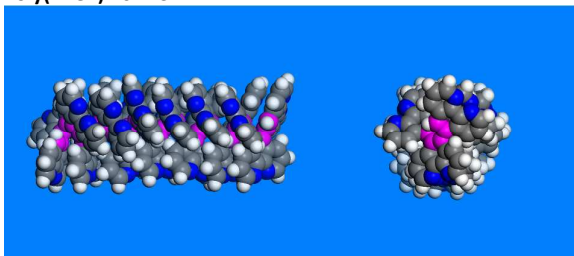

Fig. 2. UV spectra of **Phen** (i), **Phen dimer** (ii) and **poly(Phen)** (entry 1 in Table 1) (iii) (panel A) and those of **DBPhen** (i), **DBPhen dimer** (ii) and **poly(DBPhen)** (entry 3 in Table 1) (iii) (panel B). The spectra in A and B were taken in conc. aq. HCl and in MeOH, respectively. [conc. (residue) 0.06 mmol/L , room temperature, 2-mm cell].

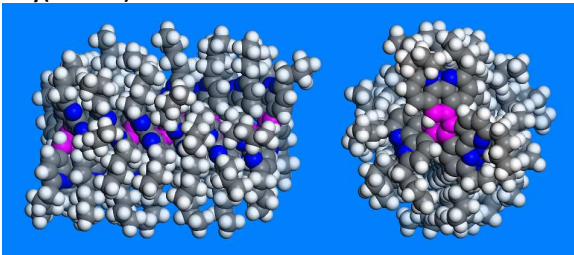**A. Poly(Phen)** 20-mer

B. Poly(DBPhen) 20-mer

Fig. 3. 3/1-Helical structures of **poly(Phen)** 20-mer (A) and **poly(DBPhen)** 20-mer (B) models obtained through molecular dynamics simulations at 298K for 15 nsec using the COMPASS force field.

Further, remarkable hypochromic effects were confirmed for both polymers, indicating that the 1,10-phenanthroline moieties in the main chain are densely stacked. Hypochromicity has been reported for π-stacked base pairs of DNAs[13] and π-stacked side-chain groups of vinyl polymer systems.[14] Considering the chemical structures, chain rigidity, long π-conjugation and π-stacking of the polymers discussed so far, we propose a 3/1-helical conformation as the most plausible structure (Fig. 3). Molecular dynamics simulations of 3/1-helices of poly(Phen) and poly(DBPhen) 20-mer models at 298K for 15 nsec using the COMPASS force field indicated that the conformations are stable enough as shown in Fig. 3.

The proposed conformation was supported by WAXD measurements of the two polymers (ESI, Fig. S47). **Poly(Phen)** and **poly(DBPhen)** indicated diffraction peaks at d = 3.93 Å and 4.16 Å, respectively. These d values were in fair agreement with average turn spacing distances of ca. 4.05 Å and 3.81 Å for **poly(Phen)** and **poly(DBPhen)** 20-mer models, respectively (ESI, Fig. S48).

The conformation was further confirmed by asymmetric polymerization (helix-sense selective polymerization, asymmetric helix-chirogenic polymerization) of 2,9-di-*n*-butyl-5,6-dibromo-1,10-phenanthroline leading to **poly(DBPhen)** using (*R*)- and (*S*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), (+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB), (+)-1-(2-pyrrolidinylmethyl)pyrrolidine (PMP) and (-)-sparteine (Sp) instead of achiral 2,2'-bipyridine (ESI, Table S1).
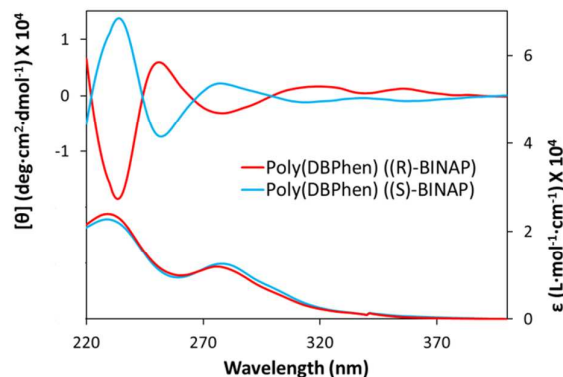

Fig. 4. UV (bottom) and CD (top) spectra of **poly(DBPhen)**s obtained by polymerization in DMF at 85°C using (*R*)- and (*S*)-BINAP at [2,9-dibutyl-5,6-dibromo-1,10-phenanthroline] = 0.2 M and at [Ni(COD)₂] = [COD] = [BINAP] = 0.6 M. [MeOH, conc. (residue) 0.4 mmol/L, room temperature , 1-mm cell]

The asymmetric polymerizations using the chiral ligands proceeded almost quantitatively as well as those using 2,2'-bipyridyl which were discussed earlier. The polymers obtained using (*R*)- and (*S*)-BINAP ((*R*)-BINAP; M_n 2100, M_w/M_n 3.04: (*S*)-BINAP; M_n 2700, M_w/M_n 3.26) indicated clear Cotton effects in circular dichroism (CD) spectra which were almost mirror images to each other (Figure 4). In a sharp contrast, the polymers obtained using DDB, PMP, and Sp did not show any detectable CD bands in spite of the fact that these ligands are efficient in asymmetric anionic polymerization of methacrylates and related monomers.[2a,b] In addition, the CD spectral patterns in Fig. 4 are completely different from those of BINAP (ESI, Fig. S50), indicating that the CD spectra do not arise from the ligand or its residues, if any, but from

the polymer chirality. This aspect was further examined by ^{31}P NMR analysis of optically active **poly(DBPhen)** which did not indicate the presence of the ligand or its residues in a significant amount (ESI, Fig. S52). Because **poly(DBPhen)** has no centers of chirality, the CD spectra are ascribed to preferred-handed helical chirality of the polymer chain. These results strongly support that **poly(Phen)** and **poly(DBPhen)** obtained using achiral 2,2′-bipyridyl ligand (Table 1) have a racemic helical conformation. In addition, stability of the preferred-handed poly(DBPhen) helix was examined in the temperature range of 0-60 °C in a $CHCl_3$ solution; no clear change in CD spectra were observed, indicating that the helix was stable enough under these conditions (ESI, Figure S51).

In summary, we synthesized novel helical polymers consisting of 1,10-phenanthroline-5,6-diyl units in the main chain. The polymerization of 2,9-di-*n*-butyl-5,6-dibromo-1,10-phenanthroline using the Ni-BINAP catalyst system may be the first example of asymmetric polymerization producing a preferred-handed helical poly(*o*-phenylene) derivative. In addition, asymmetric Yamamoto coupling polymerization of aromatic monomer is unprecedented to the best of our knowledge. Although we have proposed single-stranded helix as the simplest conformation, multi-stranded helix also might be possible.[15] The optically active poly(DBPhen) may be used as a chiral, macromolecular ligand for asymmetric synthesis and as a chiral polymer scaffold for polymer-metal complexes and supramolecular structures. Studies on these aspects are under way and results will be reported elsewhere.

Notes and references

1 (a) Y. Okamoto and T. Ikai, *Chem. Soc. Rev.*, 2008, **37**, 2593-2608; (b) C. Yamamoto and Y. Okamoto, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 227-257; (c) E. Yashima and C. Yamamoto, *Synlett*, 1998, 344-360; (d) T. Nakano, *J. Chromatogr. A*, 2001, **906**, 205-225; (e) S. Ito and K. Nozaki, In Catalytic Asymmetric Synthesis, 3rd ed.; I. Ojima, Ed.; Wiley: Hoboken, NJ, 2010; (f) T. Yamamoto, T. Yamada, Y. Nagata and M. Suginome, *J. Am. Chem. Soc.*, 2010, **132**, 7899-7901; (g) K. Watanabe, T. Sakamoto, M. Taguchi, M. Fujiki and T. Nakano, *Chem. Commun.*, 2011, **47**, 10996; (h) K. Shimomura, T. Ikai, S. Kanoh, E. Yashima and K. Maeda, *Nat. Chem.*, 2014, **6**, 429-434; T. Nakano, *Chem. Rec.*, 2014, **14**, 369-385.

2 (a) Y. Okamoto and T. Nakano, *Chem. Rev.*, 1994, **94**, 349-372; (b) T. Nakano and Y. Okamoto, *Chem. Rev.*, 2001, **101**, 4013-4038; (c) E. Yashima, K. Maeda, H. Iida, Y. Furusho and K. Nagai, *Chem. Rev.*, 2009, **109**, 6102-6211; (d) E. Yashima, K. Maeda and Y. Okamoto, *Nature*, 1999, **399**, 499-451; (e) M. M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger and J. V. Selinger, *Angew. Chem., Int. Ed.*, 1999, **39**, 3138-3154; (f) T. J. Deming and B. M. Novak, *J. Am. Chem. Soc.*, 1992, **114**, 7926-7927; (g) Z. Yu, X. Wan, H. Zhang, X. Chen and Q. Zhou, *Chem. Commun.*, 2003, **48**, 974-975; (h) Y. Wang, Y. Koyama, Y. Takanashi, J. Kumaki, J. Cui, X. Wan and T. Nakano, *Polym. Chem.*, 2014, **5**, 718-721.

3 (a) G. Wittig and G. Lehmann, *Chemische Berichte*, 1957, **90**, 875-892; (b) H. J. S. Winkler, G. Wittig, *J. Org. Chem.*, 1963, **28**, 1733-1740.

4 (a) E. Ibuki, S. Ozasa and K. Murai, *B. Chem. Soc. Jpn.*, 1975, **48**, 1868-1874; (b) S. Ozasa, Y. Fujioka, M. Fujiwara and E. Ibuki, *Chem. Pharm. Bull.*, 1980, **28**, 3210-3222.

5 E. Ibuki, S. Ozasa and Y. Fujioka, *Chem. Pharm. Bull.*, 1982, **30**, 2369-2379.

6 (a) B. Dong, L. Zheng, J. Xu, H. Liu and S. Pu, *Polymer*, **48**, 5548-5555; (b) J. Xu, H. Liu, S. Pu, F. Li and M. Luo, *Macromolecules*, 2006, **39**, 5611-5616.

7 (a) A. J. Blake, P. A. Cooke, K. J. Doyle, S. Gair and N. S. Simpkins, *Tetrahedron Lett.*, 1998, **39**, 9093-9096; (b) J. He, J. L. Crase, S. H. Wadumethrige, K. Thakur, L. Dai, S. Zou, R. Rathore and C. S. Hartley, *J. Am. Chem. Soc.*, 2010, **132**, 13848-13857; (c) S. M. Mathew and C. S. Hartley, *Macromolecules*, 2011, **44**, 8425-8432; (d) S. M. Mathew, J. T. Engle, C. J. Ziegler and C. S. Hartley, *J. Am. Chem. Soc.*, 2013, **135**, 6714-6722.

8 (a) E. Ohta, H. Sato, S. Ando, A. Kosaka, T. Fukushima, D. Hashizume, M. Yamasaki, K. Hasegawa, A. Muraoka, H. Ushiyama, K. Yamashita and T. Aida, *Nat. Chem.*, 2011, **3**, 68-73; (b) S. Ando, E. Ohta, A. Kosaka, D. Hashizume, H. Koshino, T. Fukushima and T. Aida, *J. Am. Chem. Soc.*, 2012, **134**, 11084-44087; (c) T. Kajitani, Y. Suna, A. Kosaka, T. Osawa, S. Fujikawa, M. Takata, T. Fukushima and T. Aida, *J. Am. Chem. Soc.*, 2013, **135**, 14564-14567.

9 (a) Y. Mizukoshi, K. Mikami and M. Uchiyama, *J. Am. Chem. Soc.*, 2015, **137**, 74-77; (b) S. Ito, K. Takahashi and K. Nozaki, *J. Am. Chem. Soc.*, 2014, **136**, 7547-7550.

10 M. Feng and K. S. Chan, *Organometallics*, 2002, **21**, 2743-2750.

11 (a) T. Yamamoto, T. Maruyama, Z.-H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda and S. Sasaki, *J. Am. Chem. Soc.*, 1994, **116**, 4832-4845; (b) T. Yamamoto, Y. Saitoh, K. Anzai, H. Fukumoto, T. Yasuda, Y. Fujiwara, B.-K. Choi, K. Kubota and T. Miyamae, *Macromolecules*, 2003, **36**, 6722-6729; (c) J. L. Ormsby, T. D. Black, C. L. Hilton, Bharat and B. T. King, *Tetrahedron*, 2008, **64**, 11370-11378.

12 P. Kircher, G. Huttner, K. Heinze, B. Schiemenz, L. Zsolnai, M. Buchner and A. Driess, *Eur. J. Inorg. Chem.*, 1998, **1998**, 663-887.

13 (a) I. Tinoco, *J. Am. Chem. Soc.*, 1960, **82**, 4785-4790; (b) W. Rohdes, *J. Am. Chem. Soc.*, 1961, **83**, 3609-3617; (c) J. D. Watson and F. H. C. Crick, *Nature*, 1953, **171**, 737-738.

14 (a) T. Nakano, K. Takewaki, T. Yade and Y. Okamoto, *J. Am. Chem. Soc.*, 2001, **123**, 9182-9183; (b) T. Nakano and T. Yade, *J. Am. Chem. Soc.*, 2003, **125**, 15474-15484; (c) T. Nakano, T. Yade, Y. Fukuda, T. Yamaguchi and S. Okumura, *Macromolecules*, 2005, **38**, 8140-8148; (d) T. Nakano, *Polym. J.*, 2010, **42**, 103-123; (e) T. Nakano, O. Nakagawa, M. Tsuji, M. Tanikawa, T. Yade and Y. Okamoto, *Chem. Commun.*, 2004, **126**, 144-145; (f) T. Nakano, M. Tanikawa, O. Nakagawa, T. Yade and T. Sakamoto, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 239-246.

15 (a) H. Goto, H. Katagiri, Y. Furusho and E. Yashima, *J. Am. Chem. Soc.*, 2006, **128**, 7176-7178; (b) M. Ikeda, Y. Tanaka , T. Hasegawa, Y. Furusho and E. Yashima, *J. Am. Chem. Soc.*, 2006, **128**, 6806-7; (c) E. Yashima, K. Maeda, Y. Furusho, *Acc. Chem. Res.*, 2008, **41**, 1166-80.