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Journal Name

COMMUNICATION

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

Weixi Yang and Tamaki Nakano

5,6-Dibromo-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. 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. 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 r-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 through coupling of o-dilithiobenzene in the presence of transition metal salt resulting in products that seem to be cyclic compounds. Later, Ullmann reaction, Kumada coupling and electrochemical polymerization aiming at poly(o-phenylene) were also reported. Conventional step-by-step methods such as Suzuki coupling and copper-mediated oxidative coupling were also used. Recently, polymerizations of arylene and oxabicyclic alkene with copper and palladium catalysis, respectively, were developed. 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. In this case, single-handed helix was obtained through resolution by triage of conglomerate crystals as well as chiral HPLC.

Herein, we report the synthesis, chemical structure and conformation of poly(1,10-phenanthroline-5,6-diy) (poly(Phen)) and poly(poly(2,9-di-n-butyl-1,10-phenanthroline-5,6-diy)) (poly(DBPhen)) as novel polymers whose main chain consists of 1,10-phenanthroline-5,6-diy units through Ni-catalyzed polymerization (Scheme 1). The polymers were found to possess a helical conformation in which 1,10-phenanthroline-5,6-diy 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.

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(DMF) at 85°C with a catalyst system consisting of 1,5-cyclooctadiene (COD), 2,2'-bipyridine and Ni(COD), (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.

| Entry | Polymer | Time (h) | Yield (%) | DMF-insol part | DMF-sol part | M\(_n\) / M\(_\infty\) | C HD/C N
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Poly(Phen)</td>
<td>24</td>
<td>90</td>
<td>138,100, 1.05</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>2</td>
<td>Poly(Phen)</td>
<td>5</td>
<td>47</td>
<td>8,300, 7.89</td>
<td>5,700, 4.59</td>
<td>2,700, 5.32</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Poly(DBPhen)</td>
<td>72</td>
<td>50</td>
<td>15,100, 1.05</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>4</td>
<td>Poly(DBPhen)</td>
<td>24</td>
<td>18</td>
<td>8,300, 6.88</td>
<td>5,700, 4.59</td>
<td>2,700, 5.32</td>
<td></td>
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* [Monomer] 0.04 M, [Ni] 0.12 M, DMF 12 mL. *Washed with toluene, aq. EDTA (pH = 5), aq. EDTA (pH = 9), aq. KOH (2 M), water, and benzene in this order. *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)). *Samples for injection were dissolved in pure DMF. *Samples for injection were dissolved in pure DMF. The DMF-soluble materials did not show any clear signals in \(^1H\) 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 a 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 \(D_2O\) 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 \(^1H\) 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, \(^{13}\)Phen dimer, DBPhen, and DBPhen dimer were conducted using the HMGC, 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 \(^1H\) 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 \(D_2O-DCl\); 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 \(D_2O\) containing 35% DCl with 4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt (SDS) standard and the others in CDCl\(_3\) at room temperature.

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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.

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 and π-stacked side-chains of vinyl polymer systems. 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, Table S1).

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 (M, 2100, Mw/Mn, 3.04: (S)-BINAP; M, 2700, Mw/Mn, 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.

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 CHCl₃ 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-$n$-octylphenyl-3,4-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. The optically active poly(DBPhen) may be used as a chiral, macromolecular ligand for asymmetric synthesis 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.

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Notes and references
