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Construction of Helically Stacked π-Electron Systems in Poly(quinolylene-2,3-methylene) Stabilized by Intramolecular Hydrogen Bonds

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Abstract: π -Stacked polymers, which consist of layered π -electron systems in a polymer, can be expected to molecular electronic devices. However, the construction of a stable π -stacked structure in a polymer is considerably challenging, because it requires sophisticated designs and precise synthetic methods. Herein, we present a novel π -stacked architecture based on poly(quinolylene-2,3-methylene), bearing alanine derivatives as the side chain, obtained through the living cyclocopolymerization of an *o*-allenylaryl isocyanide. In the resulting polymer, the neighboring quinoline rings of the main chain form a layered structure with π - π interactions, which is stabilized by intramolecular hydrogen bonds. The vicinal quinoline units form two independent helices and the whole molecule is a twisted tape structure. This structure is established on the basis of UV/CD spectra, theoretical calculations, and atomic force microscopy.

A DNA duplex is formed from a multilayered structure of an aromatic nucleobase pair via hydrogen bonds and π - π interactions. The layered *π*-electron systems exhibit unique optelectric properties, including electron transport,^[1] and DNA is regarded as an attractive model for molecular functional materials. To construct artificial layered π -electron systems, the construction of DNA-like polymer has advantages in that the π -conjugated molecules form a stable ordered structure along the polymer chain due to the covalent bonds, leading to very tight or close packing.^[2] Therefore, m-stacked polymers have received considerable attention, and several types of polymers^[3] and oligomers,^[4] have been synthesized. These studies are relevant to not only practical applications but also the investigation of the relationship between the physical properties and the polymer structures including the molecular length^[3b] or sequence. ^[4a, 4k, 4l] The general strategy for synthesizing π-stacked polymers is shown in Figure 1a, wherein the planar π -electron systems are connected at regular intervals with appropriate linkers. However, it is not easy to synthesize a sophisticated structure. Most π stacked polymers are based on the condensation or coupling reactions of π-electron systems with linkers, and it is difficult to control the molar mass, molar mass dispersity, and sequence, all of which are important factors that determine the properties of

polymer materials. Therefore, novel concepts to construct $\pi\text{-}$ stacked polymers are indispensable.

Recently, we achieved living cyclocopolymerization of *o*allenylphenyl isocyanide to afford a completely novel polymer architecture, poly(quinolylene-2,3-methylene) (poly-1), whose molar mass and the molar mass dispersity can be controlled (Figure 1b).^[5] The obtained poly-1 consists of π -electron system quinoline rings connected by methylene linkers, and a quinoline ring in poly-1 can be in the vicinity of another quinoline ring located two residues apart within the adjacent distance to allow for π - π stacking. This unique structure motivated us to explore new type of π -stacked polymers. However, a stable



Figure 1. The concept of this study: poly(quinolylene-2,3-methylene) bearing an amide group to form the stable π -stacked structure.

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stacked structure has not been observed for **poly-1** in solution because the π - π interactions between neighboring quinoline rings are not strong enough to stabilize the multilayered structure. Herein, we describe the construction of a novel π -stacked polymer using poly(quinolylene-2,3-methylene) as a scaffold by introducing an alanine residue into the side chain (Figure 1c). In the polymer, the quinoline rings form helically multilayered structures with π - π interactions stabilized by hydrogen bonds between the neighboring units.

In order to realize the stable π -stacked structure of the quinoline rings in **poly-1**, monomer **1a** bearing an amide group derived from L-alanine was designed and synthesized. The hydrogen bond chain between the neighboring amide residues allows the formation of the quinoline layered structure in poly-1a, and the helicity is determined by the chirality of alanine.^[6] According to the reported procedure, [5a] the polymerization of 1a initiated by [1.3-bis(diphenylphosphino)propane]PdMeCI (2) in dichloromethane at different initial feed ratios ([1a]/[2] = 10, 20,30, and 50) was conducted at 25 °C (Figure 2). In all cases, the polymerization proceeded with quantitative monomer conversion. After polymerization, the terminal palladium was removed via treatment with acetic acid to give quantitative yields of poly-1an. The molar mass (M_n) and molar mass dispersity were determined by SEC in THF using a polystyrene standard calibration. Since M_n exhibited a linear relationship with the [1a]/[2] feed ratio, the polymerization of **1a** also has a living nature (Figure 2). However, the molar mass dispersity became broader as $M_{\rm n}$ increased, probably due to the formation of a stable secondary structure, as will be described later. ¹H NMR spectroscopic measurement of poly-1a₅₀ was conducted in a mixture of CDCl₃ and DMSO-d₆ (1:1 v/v), wherein DMSO was added to inhibit the formation of hydrogen bonds between the amide side chains; the spectrum exhibited signals associated with the desired quinolylene-2,3methylene backbone (Figure S5).^[7] All the polymers showed good solubility in organic solvents, such as chloroform, tetrahydrofuran, dimethylformamide, toluene, and ethyl acetate.



Figure 2. Cyclocopolymerization of monomer 1a with palladium initiator 2, and the plots of M_n and M_w/M_n of **poly-1a**_n against the initial feed ratio of 1a and 2.

To investigate the polymer conformation of **poly-1a**, dimer (**3**: n = 2), trimer (**4**: n = 3), and hexamer (**5**: n = 6) were synthesized and analyzed by ¹H NMR spectroscopic measurement in CDCl₃

(Figure S7).^[8] The ¹H NMR spectra of **5** showed downfield shifts of hydrogen-bonded amide protons. Additionally, anisochronous signals of methylene linkers which show AB patterns and spreading of signals over a wide range of chemical shifts in the aromatic regions were observed, which were not seen in **3**. These results suggested that **5** forms a folding structure with π - π interactions.^[4i]

The conformation of poly-1a was investigated by UV-vis absorption and circular dichroism (CD) spectra (Figure 3a). The CD spectra of **poly-1a**₅₀ in chloroform showed the characteristic Cotton effects at 339 nm and 274 nm; these features were quite different from those of the corresponding monomeric unit 1' and poly-1b₅₀ containing a chiral ester group as the side chain instead of the amide group of poly-1a₅₀. The intensity of the Cotton effect depended on the molar mass of **poly-1a**_n (Figure 3b), and not on the concentration in the range from 3.8×10^{-1} to 3.8×10^{-3} mM (Figure S10a).^[9] These results suggested that **poly-1a** forms an optically active secondary structure without intermolecular aggregation at the concentration used in the CD measurements. The CD signals changed little when the initial feed ratio (n) exceeded 30, indicating that the secondary structure would be stable at n > 30. The IR spectra of **poly-1a**₅₀ in chloroform (5 mM) indicated intramolecular hydrogen bonds between the amide side chains, since the absorption of the amide N-H and C=O stretching bands was observed at 3258 cm⁻¹ and 1643 cm⁻¹ respectively, which was lower than the corresponding bands of 1' at 3433 cm⁻¹ and 1661 cm⁻¹ (Figure S9b). When DMSO was added to the solution of poly-1a50 in chloroform, a significant decrease in Cotton effect was observed in the CD spectrum (Figure 4a), and the intensity of the signals at 274 nm exhibited a non-linear relationship with the concentration of DMSO (Figure 4c). These results indicate that the intramolecular hydrogen bonds in **poly-1a**₅₀ cooperatively stabilize the secondary structure, which is supported by the fact that **poly-1b**₅₀ is CD silent (Figure 3a). The solution of poly-1a₅₀ in chloroform excited at 330 nm exhibited fluorescence emissions at 380 nm and 520 nm, which were probably caused by π - π interactions of the quinoline rings, since no emission was observed from the monomeric quinoline compound 1' (Figure S11). The original UV spectrum of poly-1a50 in chloroform showed a hypochromic effect, resulting in a broad signal, which was disappeared upon the addition of DMSO as a competitive reagent for hydrogen bond (Figure 4b). Such a hypochromic effect is observed when aromatic chromophores form a slip-stacked structure,[3b, 10] which suggests that the quinoline units in **poly-1a** adopt a stable π -stacked structure in chloroform.



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Figure 3. CD and UV spectra of (a) poly-1a₅₀, poly-1b₅₀ and 1', and (b) poly-1a_n in CHCl₃ at 25 °C. Concentration: [poly-1a₅₀] = 4.4×10^{-2} mM, [poly-1b₅₀] = 4.3×10^{-2} mM, [1'] = 4.0×10^{-2} mM, [poly-1a₃₀] = 4.3×10^{-2} mM, [poly-1a₂₀] = 4.3×10^{-2} mM, and [poly-1a₁₀] = 4.6×10^{-2} mM



Figure 4. (a) CD and UV spectra of **poly-1a**₅₀ in the mixture of CHCl₃ and DMSO at 25 °C, (b) an enlarged view of UV spectra in the range of 300–360 nm, and (c) the plots of the intensity of CD spectra at 274 nm (filled dot) and UV spectra at 337 nm (outlined square) against the ratio of DMSO in CHCl₃. Concentration: Concentration: [**poly-1a**₅₀] = 4.7×10^2 mM.

On the basis of these experimental results, we predicted the secondary structure of poly-1a in chloroform. An ideal poly(quinolylene-2,3-methylene) bearing an amide side chain derived from L-alanine methyl ester (poly-1a6') was constructed to form hydrogen bonds with the neighboring units (*i* and *i*+2), and a conformation search with energy minimization using MacroModel 11.9 with OPLS3e as the force field^[11] was conducted (Figure S12, and see Supporting Information for detailed calculations).^[12,13] To simulate the CD spectra, timedependent (TD) DFT calculations were performed. For a minimum unit forming π-stacked structure, a tetramer (poly-1a₄') was used. The initial structure of poly-1a4' was created from the optimized structure of **poly-1a**₆', as mentioned above, and reoptimized by DFT calculations at the B3LYP/6-31G** level. Subsequent TD-DFT calculations at the same level afforded reasonable UV and CD spectra. Although the calculated CD spectrum was not very accurate in the shorter-wavelength region, the calculated UV and CD spectra closely agreed with the observed spectra of poly-1a (Figure 5a). This result indicated that the structure of the calculated poly-1a4' is a reasonable local conformation of poly-1a. Based on the optimized structure of poly-1a₄', the molecular structures of poly-1a₁₀' and poly-1a₄₀' were constructed and optimized by molecular mechanics minimizations using MacroModel (Figure 5b, c). These optimized structures suggested that the amide side chains form hydrogen bonds between neighboring units, and that the polymer forms a right-handed (P) 21-like helix with a multilayered structure. During the molecular dynamics simulations under the condition at 300 K for 1 ns in chloroform, the layered structure and hydrogen bonds were maintained (Figure S15).[14] The calculated distance between the centers of the neighboring quinoline rings of poly-1a10' was 4.2 Å, and the distance between the faces of the

quinoline rings was 3.2 Å, which falls within the range of π - π interactions (Figure 5b).^[15] The vicinal quinoline units formed two independent helices and the whole molecule formed a twisted tape structure with a pitch of 40 Å (Figure 5c).

(a)

Δε (M⁻¹ cm⁻¹)

0

-50

-100

-150

50 269

337



Figure 5. (a) Simulated CD/UV spectra of the reasonable **poly-1a**' by TD-DFT calculation. (b) Proposal structure of **poly-1a**₁₀' obtained through molecular mechanics optimization. In the structure of side view, layered quinoline units and the amide side chain forming hydrogen bonds were emphasized. (c) Space filling structure of **poly-1a**₄₀'.

The helical structure of the poly(quinolylene-2,3-methylene) bearing amino acid residues was investigated by atomic force microscopy (AFM). Figure 6 and Figure S17 in Suporting Information show the AFM images of **poly-1a (C18)**₅₀, which was prepared from a monomer containing an alanine residue with octadecyl ester to promote crystallization by the long alkyl chain. A spin cast film was made from a diluted chloroform solution (0.01 mg/mL) on highly oriented pyrolytic graphite (HOPG), which was annealed at 50 °C for 8 h. The polymer chains were clearly resolved individually, in which the uniform helical morphology was found in each fiber with a pitch of 3.6 ± 0.4 nm. This result suggests that the proposed structure obtained by the above computational simulations is reasonable.

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Figure 6. AFM image of $poly-1a(C18)_{50}$ on HOPG. Schematic representation of the right-handed helical polymer is also shown

In conclusion, we have successfully synthesized a novel stacked π -electron system: poly(quinolylene-2,3-methylene). The quinoline backbones in the polymer forms a 21-like helically folding structure with π - π interactions stabilized by outer two N– H···O=C hydrogen bond chains and the whole molecule is a twisted tape structure. The spectroscopic data, computational calculations, and AFM images strongly suggest the proposed structure. The polymer is well-soluble in common organic solvents, and the stacked structure can be made to diordered by adding a hydrogen bond competitive reagent, DMSO. The presented novel π -stacked achitecture cannot be synthesized using conventional organic synthesis and polymerization, and such 21-helical conformation has been known only for limited types of polymers^[3j,3k] and some polydienes in the solid state.^[16] Additionally, this polymer is prepared by living polymerization of 1, and further modification of the molecular design, such as the monomer sequence and end-structure, is possible. Additionally, the resulting polymer has an optically active helical structure, suggesting potential use in chiral opto-electronic devices. Further research on the synthetic methods and the optical and electrochemical properties of the polymer is in progress.

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A novel type of π -stacked polymer was synthesized via cyclocopolymerization of an o-allenylaryl isocyanide. In the poly(quinolylene-2,3-methylene) bearing alanine derivatives as the side chain, the quinoline backbone forms a layered structure with π - π interactions stabilized by intramolecular hydrogen bonds. The structure was established on the basis of spectroscopic analysis and theoretical calculations and confirmed by AFM measurement.