Synthesis of a series of soluble main-chain chiral nonracemic poly(alkyl-aryl ketone)

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Abstract. A series of main-chain chiral polyketones have been synthesized through condensation polymerization of a dihalide and a diketone with optically pure binaphthyl moiety as linkage in the polymer backbone. The solubility of the polymers can be easily enhanced by substituents at the alpha position next to the carbonyl groups. Reducing the steric hindrance of the substituents in the monomers increases the reactivity of the polymerization. The chiral polymers exhibit large optical rotations. Circular Dichroism (CD) spectra of the polymers are similar to those of the corresponding monomers. The novel synthetic strategy may have great impact on future development of palladium catalyzed condensation polymerizations. The highly soluble chiral polymers synthesized allow for preparation of materials in the form of thin films and have potentials applications in various areas such as chiral separation and recognition.

Keywords: polymer synthesis, molecular engineering, main-chain chiral polyketone, polycondensation

1. Introduction

Main-chain chiral polymers are of great interest because of their important applications in chiral separation and recognition [1–4]. In order to achieve such goals materials must be stable and possess functional groups. Considerable attention has been focused on the synthesis of optically active polymers with chirality in the main-chain because the polymers typically exist or have the tendency to form helical and rigid-rod configuration, which offers enhanced capability in chiral applications [5–8]. Although it has constantly been great synthetic challenges in constructing main-chain chiral polymers, there are a number of strategies developed to build chirality into the polymer backbones. These include the polymerization of chiral monomers and asymmetric polymerization of achiral monomers using chiral catalysts [3, 9–16]. The asymmetric polymerization requires a

careful design of catalysts and laborious screening for the right chiral ligands. Direct polymerization of chiral monomers usually results in polymers of decreased processibility, which has been overcome by attaching long alkyl substituents [5, 6]. The drawback is the alteration of rheological behavior of the polymers.

Polyketones are a class of high performance materials that have attracted a great deal of attention due to their high thermal stability, which is a result of the incorporation of thermally stable carbonyl and/or aromatic groups in the polymer backbones [17–19]. These polymers typically exhibit high glass transition temperatures and high melting points [17], which makes them ideal candidates for use as stationary phase in chromatography applications. Aromatic polyketones are synthesized by Friedel-Crafts or nucleophilic aromatic substitution reactions [20–25]. The materials are usually insolu-

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ble and intractable. Aliphatic polyketones have been prepared through the copolymerization of carbon monoxide with ethylene or α -olefins [9, 26–29]. Previously we have developed a new polymerization route for the construction of aromatic alkyl polyketones using palladium phosphine complexes [30]. To further extend our research in new polymer synthesis, we have developed the strategy of synthesizing main-chain chiral polyketones using palladium catalyzed condensation polymerization. The chirality of the polyketone main chain is achieved by utilizing chiral binaphthyl moiety, which has been previously reported as chiral monomer for other polymer synthesis [31–37]. The synthesized chiral polyketones have been extensively characterized by ^1H and ^{13}C NMR, gel permeation chromatography (GPC), polarimeter, UV-Vis spectrometry and circular dichroism (CD). To the best of our knowledge, this is the first time that soluble main-chain chiral aliphatic aromatic polyketones are reported.

2. Experimental section

2.1. Materials and methods

Solvents (hexane, benzene, diethyl ether) were pre-dried using 3 Å molecular sieves, degassed and stirred over benzophenone ketyl. The dried and degassed solvents were vacuum-transferred into a flame-dried flask equipped with a Teflon valve and stored under N_2 . Other solvents were distilled from either CaH_2 or P_2O_5 before use. All the chemicals used were purchased from either the Aldrich Chemical Company or ACROS Organics. Optically pure binaphthol was resolved according to literature procedures [38]. Optical rotation was measured on a Rudolph Autopol III polarimeter and a JASCO-J-720 circular dichroism spectroscopy. ^1H NMR spectra were measured with a Bruker AM 250 (250 MHz) spectrometer. ^{13}C NMR spectra were recorded at 62.9 MHz on a Bruker AM 250 spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) equipped with a Waters 410-differential refractometer. A flow rate of 1.0 ml/min was used and samples were prepared in THF. Polystyrene standards were used for calibration.

2.2. Synthesis

Synthesis of (R)-(+)-6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl (1)

This compound was synthesized in 97.5% yield (mp 208–209°C) from optically pure (R)-(+)-2,2'-dihydroxy-1,1'-binaphthyl following a reported procedure [39]. Characterizations by ^1H NMR are consistent with reported data.

Synthesis of (R)-(+)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl (2)

(R)-(+)-6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl (3.99 g, 8.49 mmol) and anhydrous K_2CO_3 (3.5 g, 27.3 mmol) were added in dry CH_3CN (50 ml) followed by a slow addition of CH_3I (1.56 ml, 25 mmol). The mixture was refluxed for two days and cooled to room temperature before poured into 200 ml of water. The mixture was filtered and recrystallized from methylene chloride-benzene (1:1 mixture) to give the desired product (3.8 g, yield 89.5%). ^1H NMR (CDCl_3): δ 4.12 (s, OCH_3 , 6 H), 7.30 (d, 2 H), 7.64 (d, 2 H), 7.83 (d, 2 H), 8.26 (d, 2 H), 8.36 (s, 2 H). ^{13}C NMR (CDCl_3): δ 56.62, 114.8, 117.3, 118.9, 126.8, 128.7, 129.7, 129.8, 130.1, 132.3, 155.1.

Synthesis of (R)-(+)-6,6'-diiodo-2,2'-dimethoxybinaphthyl (3)

A solution of (R)-(+)-6,6'-dibromo-2,2'-dimethoxybinaphthol (4.72 g, 0.01 mol) and KI (16.6 g, 0.1 mol) in DMF (80 ml) was prepared and brought to reflux. While the solution was still warm, NiBr_2 (1.4 g, 6.48 mmol) and tri-*n*-butyl phosphine (1.0 ml, 4.0 mmol) was added. Refluxing was continued overnight. Upon cooling, the solution was diluted with 200 ml of benzene, and washed with several portions of water and dried over MgSO_4 . The solvent was evaporated and the solid was recrystallized thrice from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solvent mixture (1:1) to give a yellowish powder (yield 78%). ^1H NMR (CDCl_3): δ 4.11 (s, OCH_3 , 6 H), 7.30 (d, 2 H), 7.63 (d, 2 H), 7.83 (d, 2 H), 8.25 (d, 2 H), 8.36 (s, 2 H). ^{13}C NMR (CDCl_3): δ 56.9, 88.8, 114.9, 119.1, 127.1, 128.9, 131.0, 132.9, 135.1, 136.8, 155.5. Element analysis: Calculated: C 46.67%, H 2.85%. Found: C 46.23%, H 2.82%.

Synthesis of (R)-(-)-6,6'-dipropionoyl-2,2'-dimethoxy-1,1'-binaphthyl (4)

To a Schlenk flask was charged with (R)-(+)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl (1.89 g, 4.0 mmol) and dry THF (50 ml). The solution was cooled to -78°C in a dry ice-acetone bath and a hexane solution of BuLi (1.6 M, 5.52 ml, 8.8 mmol) was added slowly. After the mixture was stirred for 2 hours, N,N'-dimethylpropionamide (1.1 ml, 10 mmol) was added dropwise via a syringe. The solution was allowed to warm to room temperature overnight and was quenched by adding 10% HCl (50 ml) solution. The organic layer was separated, dried over MgSO_4 and evaporated. The residue was purified by flash chromatography on silica gel using benzene-ethyl acetate (15:1) as eluent to give pure product 0.935 g (yield 54.9%). ^1H NMR (CDCl_3): δ 1.27 (t, CH_3 , 6 H), 3.09 (q, CH_2 , 4 H), 3.81 (s, OCH_3 , 6 H), 7.13 (d, 2 H), 7.55 (d, 2 H), 7.81 (d, 2 H), 8.16 (d, 2 H), 8.55 (s, 2 H). ^{13}C NMR (CDCl_3): δ 8.6, 31.9, 56.7, 114.5, 118.9, 124.7, 125.5, 128.2, 130.2, 131.8, 132.3, 136.3, 157.1, 200.8. Element analysis: Calculated: C 78.85%, H 6.14% Found: C 78.43%, H 6.05%.

Synthesis of (S)-(-)-2,2'-dimethoxy-1,1'-binaphthyl (5)

The optically pure (S)-(-)-2,2'-dimethoxy-1,1'-binaphthyl was prepared by the reaction of (S)-(-)-2,2'-dihydroxy-1,1'-binaphthyl with CH_3I using the similar procedure as described in the preparation of (R)-(+)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl.

Synthesis of (S)-(-)-3,3'-dipropionoyl-2,2'-dimethoxy-1,1'-binaphthyl (7)

To a Schlenk flask was charged with (S)-(-)-2,2'-dimethoxy-1,1'-binaphthyl (1.57 g, 5 mmol), TMEDA (1.6 ml, 10.5 mmol) and dry ether (75 ml). A hexane solution of *n*-butyl lithium (1.6 M, 7.1 ml, 11.3 mmol) was added dropwise. The mixture was stirred for 3 hours at room temperature, and cooled to -78°C . Propionaldehyde (1.04 ml, 15 mmol) was added over a period of 10 minutes. The solution was stirred for 2 hr at -78°C and then warmed to room temperature and stirred for another 3 hours. The reaction was quenched by addition of an aqueous solution of HCl (10%). After evaporating the

solvent, the residue was redissolved in acetone (50 ml), and Jones reagent was added dropwise into the solution. The color changed from red to green and then to red again. The reaction was stopped when the red color persisted. Evaporating the solvent gave an oil-like substance. The material was purified using flash chromatography on silica gel using dichloromethane-hexane (3:1, with 1% ethyl acetate) as eluent to give a white crystal 0.965 g (yield 45%). ^1H NMR (CDCl_3): δ 1.27 (t, CH_3 , 6 H), 3.14 (q, CH_2 , 4 H), 3.39 (s, OCH_3 , 6 H), 7.14 (d, 2 H), 7.33 (t, 2 H), 7.45 (t, 2 H), 7.98 (d, 2 H), 8.19 (d, 2 H). ^{13}C NMR (CDCl_3): δ 8.9, 36.7, 62.2, 125.4, 125.8, 125.9, 128.5, 129.5, 130.2, 130.9, 134.4, 135.6, 153.9, 205.3. Element analysis: Calculated: C 78.85%, H 6.14% Found: C 78.68%, H 6.15%.

Synthesis of (S)-(+)-6,6'-dipropionoyl-2,2'-dimethoxy-1,1'-binaphthyl (8)

This compound was prepared from commercial (S)-(+)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl (stereoisomer of **2**) following the same procedures as described in compound **4**. The ^1H NMR and ^{13}C NMR characterization resembles that for **4**.

General procedure for the polymerization

To an oven-dried flask equipped with a Teflon valve containing a spin-bar was charged with $\text{Pd}(\text{OAc})_2$ (6.7 mg, 0.0299 mmol), $\text{P}(t\text{-Bu})_3$ (3.3 mg, 0.0163 mmol) and *t*-BuONa (100 mg, 1.04 mmol). The Schlenk tube was degassed and refilled with nitrogen. Arene dihalide (0.5 mmol), diketone (0.5 mmol) and THF (2 ml) were added. The resulting mixture was heated under nitrogen to 70°C for 24 hr. The mixture was cooled to room temperature and precipitated into methanol. The polymer obtained was redissolved in THF and reprecipitated several times to yield an off-white powder. The yields range from 60–92%. **Poly-(R)-(+)-9** and **poly-(R)-(-)-10** were synthesized by the reaction of **4** with 1,4-phenylene and 4,4'-biphenylene, respectively. **Poly-(S)-(+)-11** and **poly-(S)-(-)-12** were synthesized by the reaction of **7** with 1,4-phenylene and 4,4'-biphenylene, respectively. **Poly-(R)-(+)-9**. ^1H NMR (CDCl_3): δ 1.47 (CH_3 , 6 H), 3.70 (OCH_3 , 6 H), 4.75 (CH , 2 H), 6.99–8.49 (H–Ar, 14 H). ^{13}C NMR (CDCl_3): δ 19.8, 47.2, 56.7, 114.3, 118.7,

125.4, 128.1, 128.6, 131.3, 131.8, 132.0, 136.2, 140.3, 157.2, 200.2. **Poly-(R)-(-)-10**. ^1H NMR (CDCl_3): δ 1.57 (CH_3 , 6 H), 3.71 (OCH_3 , 6 H), 4.82 (CH , 2 H), 7.03–8.55 (H–Ar, 18 H). ^{13}C NMR (CDCl_3): δ 19.6, 47.2, 56.4, 114.1, 118.5, 125.2, 127.5, 127.8, 128.1, 131.0, 131.5, 131.7, 135.9, 139.1, 140.6, 156.9, 199.8. **Poly-(S)-(+)-11**. ^1H NMR (CDCl_3): δ 1.54 (CH_3 , 6 H), 3.25 (OCH_3 , m, 6 H), 4.69 (CH , 2 H), 6.90–8.19 (H–Ar, 14 H). **Poly-(S)-(-)-12**. ^1H NMR (CDCl_3): δ 1.62 (CH_3 , 6 H), 3.25 (OCH_3 , m, 6 H), 4.81 (CH , 2 H), 6.98–8.19 (H–Ar, 18 H). ^{13}C NMR (CDCl_3): δ 18.6, 51.8, 62.4, 124.8, 125.2, 125.7, 127.3, 128.3, 128.9, 129.4, 130.0, 131.1, 134.3, 135.3, 139.4, 140.0, 153.4, 205.2. **Poly-(S)-(+)-10** was synthesized by reaction of **8** with 4,4'-biphenylene with the ^1H NMR characterization the same as for **poly-(R)-(-)-10**.

3. Results and discussion

Previously a facile synthesis of polyketones by cross-coupling condensation polymerization has been reported by our research group [30]. To further synthesize optically-active chiral polyketones, the initial attempt involved the reaction of (*R*)-(+)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl (**2**) with 1,4-diacetylbenzene under the reported cross-coupling conditions. The reaction took place read-

ily to yield a solid which was insoluble in any organic solvents. Therefore, it has been difficult to process and characterize the resulted polymer using solution techniques. We reasoned that the infusibility might be attributed to the rigid polymer backbone structures. In order to prepare soluble chiral polyketones, a model reaction of compound **2** with 1,4-dipentanoylbenzene (Figure 2) was conducted and surprisingly the resulting polymer product was completely soluble in common organic solvents including methylene chloride, chloroform, THF and DMF. We believed that the solubility was enhanced by the asymmetric center introduced in the polymer backbone. The structures of the polymers were studied by ^1H NMR spectroscopy. The peaks at δ 4.75 ppm in ^1H NMR and at δ 200 ppm in ^{13}C NMR corresponded to methine and carbonyl resonances in the polymer, respectively. The molecular weight of the polymers was however low as revealed by GPC ($M_w = 7900$). It was speculated that the low molecular weight might associate with the relative low oxidative addition activity of carbon-bromide bond with palladium complexes. To test this thought, a further experiment was carried out by polymerization of 1,4-dipentanoylbenzene with 6,6'-diiodo-2,2'-dimethoxy-1,1'-binaphthyl (**3**), which was synthesized with 83% yield by nickel-catalyzed exchange reaction of **2** with KI following a reported procedure [40] (Figure 1). The

Figure 1. Synthesis of optically active monomers

Figure 2. Palladium catalyzed polymerization of **2** with 1,4-dipentanoylbenzene

product can be easily isolated and purified by recrystallization. The substitution of both bromides by iodides was confirmed by the disappearance of quaternary aromatic carbon resonance next to the bromide at δ 117.3 ppm and the appearance of a peak at 88.8 ppm corresponding to the quaternary aromatic carbon resonance adjacent to iodide in ^{13}C NMR spectra. The driving force for such a reaction is the formation of thermodynamically more stable KBr. Indeed, the condensation polymerization of **3** and 1,4-dipentanoylbenzene yielded polymers with slightly higher molecular weights ($M_w = 8900$).

By studying the structures of the monomers, it was noticed that compounds **2** and **3** possessed sterically bulky binaphthyl rings, which might hamper the subsequent displacement of the bromides or iodides in the intermediates formed from the oxida-

tive addition of palladium complexes. To reduce the steric hindrance, we looked into the polymerization of (*R*)-(+)-6,6'-dialkanoyl-2,2'-dimethoxy-1,1'-binaphthyl (**4**) with 1,4-dihalobenzene or 4,4'-dihalobiphenyl, where the alkanoyl groups were directly connected onto the binaphthyl rings and the halides were attached to the less hindered phenyl groups. Compound **4** was synthesized in good yield by first treating **2** with BuLi to generate 6,6'-dilithio-2,2'-dimethoxy-1,1'-binaphthyl, which further reacted with *N,N*-dimethylpropionamide. The products were characterized by both ^1H and ^{13}C NMR spectroscopy. The polymerization was carried out by condensation reaction of **4** and 1,4-dibromobenzene to yield main-chain chiral polymers (Figure 3). A significant increase in the molecular weight was observed (Table 1). This supports our rationale that steric hindrance has

Figure 3. Construction of optically active main-chain polymers

Table 1. Polymerization results, optical rotation, and solubility

Entry ^a	M _w	PDI	[α] _D	Soluble in
poly-(R)-(+)-9 ^b	16 800	2.44	1.65	CHCl ₃ , CH ₂ Cl ₂ , THF, DMF, partially in Bz
poly-(R)-(-)-10 ^c	19 400	2.77	-108.30	CHCl ₃ , CH ₂ Cl ₂ , THF, DMF, partially in Bz
poly-(S)-(+)-10 ^c	21 200	2.61	78.10	CHCl ₃ , CH ₂ Cl ₂ , THF, DMF, partially in Bz
poly-(S)-(+)-11 ^b	8 260	2.36	5.78	CHCl ₃ , CH ₂ Cl ₂ , THF, DMF, Bz
poly-(S)-(-)-12 ^c	10 800	2.24	-60.10	CHCl ₃ , CH ₂ Cl ₂ , THF, DMF, Bz

^aR and S denote the stereoconfigurations of the optically active monomers^bthe linker between the chiral binaphthyls is 1,4-phenylene^cthe linker between the chiral binaphthyls is 4,4'-biphenylene

played a significant role in effecting the outcome of this type of polymerization. Similarly, reaction of 4,4'-dihalobiphenyl with **4** under the same conditions also yielded polymers with enhanced molecular weights.

To prepare other type of chiral polymers, the reactions of (S)-(-)-3,3'-dihalo-2,2'-dimethoxy-binaphthyl with 1,4-dipropionylbenzene was also investigated. However, only oligomers were obtained and the products could not be clearly identified. This might be a combination effect of deactivation of the palladium intermediate and the steric hindrance of binaphthyl rings. Similarly, the polymerization of (S)-(-)-3,3'-dipropionyl-2,2'-dimethoxybinaphthyl (**7**) was also studied, where halides are not directly bound to the bulky binaphthyl ring. In contrast to the synthesis of **4**, the reaction of (S)-(-)-3,3'-dihalo-2,2'-dimethoxy-binaphthyl with BuLi and subsequent treatment of the resulting product with N,N-dimethylpropionylamide was sluggish and yielded no desired products, which was attributed to the stabilization of the lithium ion imposed from the adjacent methoxy and less electrophilic nature of the amide. This has been confirmed by the readily reaction of 3,3'-dilithio-2,2'-dimethoxybinaphthyl with propionaldehyde to produce an alcohol intermediate **6** in high yield. Compound **6** was easily oxidized by Jones agent to give **7** in good yield (Figure 1). The condensation polymerization of **7** with 1,4-dihalobenzene and 4,4'-dihalobiphenylene proceeded smoothly yielding main-chain chiral polymers with molecular weights up to 11 000 (Figure 3). The experimental result supports our analysis on the reactivity of this type of polymerization reactions.

The structures of the resulting polymers were characterized by both ¹H and ¹³C NMR spectroscopy. Chiral optical properties were studied by polarimeter and circular dichroism (CD) spectroscopy. Fig-

Figure 4. UV-Vis and CD spectra of **poly-(R)-(-)-10** and monomer **4**

ure 4 shows the UV-Vis and CD spectrum of **poly-(R)-(-)-10** and its corresponding monomer (**4**). The UV absorptions of the chiral polymer and monomer are nearly identical. The CD spectrum of **poly-(R)-(-)-10** exhibits slightly hypsochromic shift as compared to that of **4**. Large optical rotations were observed for chiral polymer **poly-(R)-(-)-10** ($[\alpha]_D = -108.3$) comparable to those of the pure monomer **4** ($[\alpha]_D = -112.7$). As a comparison, **poly-(S)-(+)-10** exhibited a large optical rotation of $[\alpha]_D = 78.1$. The different optical activity for **poly-(R)-(-)-10** and **poly-(S)-(+)-10** was further evidenced by circular dichroism (Figure 5). It is interesting to note that the substituents can alter the direction of the polarized light. For polymers with R stereoconfiguration, more rigid linker such as biphenylene between the two chirality generating binaphthyl groups give polymers with large negative optical rotations ($[\alpha]_D = -108.3$, Table 1) indicating that the binaphthyl chiral environment is not disturbed. When shorter bridge such as 1,4-phenylene is used, the sign of the optical rotation has reversed to slightly positive ($[\alpha]_D = 1.65$, Table 1), an indication of the change of configuration of the polymer chain. CD spectra of the poly-

Figure 5. CD spectra of **poly-(R)-(-)-10** and **poly-(S)-(+)-10**

mers are similar to those of the monomers, suggesting little formation of secondary chiral conformations, and polymers maintain their original rigidity. It is important to note that the configuration of the newly created chiral centers in the chiral polymers might be important to the properties of the resulting main-chain chiral polymers. Further investigations on the stereochemistry of the chiral polymers and its effect on properties of chiral polymers will be conducted to delineate the structure-property relationship. Solubility tests indicate that the synthesized polymers are readily soluble in organic solvents such as chloroform, methylene chloride, benzene, DMF and THF (Table 1). Thermal properties of the synthesized polymers such as measurements of glass transition temperatures (T_g), thermal decomposition experiments (T_d) and other measurements on physical properties are currently in progress and will be reported in due time.

4. Conclusions

A simple route for the synthesis of the first soluble optically active main-chain chiral polyketones has been demonstrated using palladium catalyzed condensation reactions of dihalide and diketones. The reactivity of the monomers can be tuned by exchanging the positions of halide and alkanoyl substituents on the aryl rings. Higher molecular weight polymers can be obtained by reacting binaphthyl alkyl ketones with 1,4-dihalobenzene or 4,4'-dihalobiphenyl. Optical rotation and CD data indicate that the polymers adopt little helical configuration. The high solubility of the synthesized main-chain chiral aliphatic aromatic polyketones

allows for materials to be made in the form of thin films and will expand potential applications of polyketones in various areas including chiral separation and recognition. Further measurements on thermal properties of the synthesized materials and synthetic strategy development of higher molecular weight poly(alkyl-aryl ketone) are currently under investigation.

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