Supramolecular Template-Directed Synthesis of Stable and High-Efficiency Photoluminescence 9,10-Diphenylanthryl-Bridged Ladder Polysiloxane

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ABSTRACT: A soluble well-defined 9,10-diphenylanthryl-bridged ladder polysiloxane (**DPAnLP**) was prepared via supramolecular assembly-directed condensation polymerization of silanols. The ladder superstructure (**LS**) was obtained via a synergistic interaction of H-bonding and π - π stacking between polymerizable precursor 2-*tert*-butyl-9,10-bis(methyldihydroxylsilyl)anthracene in organic solvent. The resultant **LS** was then used as template to direct the condensation of silanol groups to obtain **DPAnLP** with high regularity. It was found that **DPAnLP** can emit blue light (430 nm) with great stability and high efficiency

in both solution and solid film, which indicated a well organizing of fluorophore within confined environment (ladder structure). TGA and DSC measurements showed that **DPAnLP** had good thermal stability, and cyclic voltammetry detection gave a low-lying highest occupied molecular orbital level. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2491–2497, 2010

KEYWORDS: ladder polymer; luminescence; polysiloxanes; selfassembly; supramolecular structures

INTRODUCTION Conjugated compounds have been attracting considerable attention arising from their electrooptical properties and thereof multiple applications in display technique and other fields.^{1,2}Among them, anthracene and its derivatives have been widely studied because of their interesting photo- and electroluminescent properties as well as good electrochemical properties.³⁻⁵ To improve their poor filmforming and processing properties,⁶ polymeric materials containing anthracene moieties were developed.⁷⁻¹² However, random chain aggregation of aromatic subunit easily undermines the stability of luminescent properties and thus deteriorates materials' long-term stability and emission efficiency, which is the biggest problem affecting the performance of light-emitting diodes (LEDs).^{13–15} To solve this problem, several methods, such as copolymerization or blending of conjugated polymers with other materials and grafting of large sterically hindered groups or oligomer on polymer backbone, have been developed to tune resultant polymer microstructure.¹⁶⁻¹⁸ Toward this goal, we adopt a different strategy to incorporate light-emitting unit into polymer backbone while forming well-defined ladder structure to afford good stability and solubility in common solvents.

Because of the unique double-stranded molecular structure, ladder polysiloxanes are found to have much greater resistance to irradiation, thermal and chemical degradation than a single-chained polysiloxane. In addition, they possess great adhesion to various substrates and good solubility in common organic solvents, which can be readily used to prepare thin film devices. Consequently, their unique structure promises great opportunities of application in numerous areas.¹⁹⁻²² In the early 1980s, our group proposed a novel "supramolecular architecture-directed stepwise coupling/ polymerization" (SCP) synthesis strategy, in which the supramolecular assemblies from reactive monomer precursors gave well-defined ladder superstructure (LS) and were used as templates to direct polymerization.²³ Within the LS, the double-stranded polymer backbones were bridged with bulky flat molecules, which offer noncovalent interactions to direct oriented self-assembly. Using this strategy, a series of regular organo-bridged ladder polysiloxanes have been successfully synthesized by using different supramolecular interactions, such as H-bonding, π - π stacking, and donoracceptor effect.²⁴⁻²⁶ We thus consider using a light-emitting unit as the bridge within ladder polysiloxane to optimize their properties. Herein, we report the synthesis of blue light photoluminescence (PL) 9,10-diphenylanthryl-bridged ladder polysiloxane (DPAnLP) via SCP method (Scheme 1). Aiming to improve materials stability, emission efficiency, and solubility, we consider following aspects in polymer design: (1) selecting the well-known luminophore 9,10-

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diphenylanthracene as ladder bridge to prevent undesired aggregation, (2) incorporating a *tert*-butyl group to minimize random aggregation of planar anthracene units and improve the material solubility,²⁷ and (3) expecting that the ladder polysiloxane backbone will provide materials good thermal stability and film-forming capability as well as adhesive ability to various substrates, which are advantageous for the fabrication of optoelectronic devices with high performance.

EXPERIMENTAL

Materials

Dibromobenzene, 2-*tert*-butylanthraquinone, potassium iodide, sodium hypophosphite monohydrate, methyltrichlorosilane, and *n*-butyllithium (1.6 M in hexane) were purchased from Alfa Aesar and used as received. Tetrahydrofuran (THF) and dioxane were distilled over sodium benzophenone complex.

Synthesis of 2-*tert*-Butyl-9,10-bis(4bromophenyl)anthracene (1)

1,4-Dibromobenzene (7.08 g, 30 mmol) was dissolved in anhydrous THF (300 mL) followed by slow addition of *n*-butyllithium (18.75 mL, 1.6 M in hexane) under stirring at -78 °C. To the suspension, 2-*tert*-butylanthraquinone (3.84 g, 15 mmol) dissolved in THF (60 mL) was added dropwise at -78 °C. The mixture was then stirred for 3 h and then slowly warmed up to room temperature. THF was removed by rotary evaporation, and the product was dissolved in ether (300 mL). The ether solution was washed using cold DI water (800 mL), and the aqueous solution was further washed twice with ether (50 mL). The combined organic fractions were dried over magnesium sulfate, and the volatiles were removed in vacuum to give a foamy residue. To this residue were added potassium iodide (9.0 g, 54 mmol), sodium hypophosphite monohydrate (9.0 g, 102 mmol), and acetic acid (90 mL). Then, the mixture was refluxed for 2 h. After cooling the solution to room temperature, a white precipitate was collected, washed with DI water, and dried. A total of 7.88 g of pure product was obtained by recrystallization from THF. Yield, 95%.

¹H NMR (CDCl₃, 400 MHz, δ , ppm): 1.28 (s, 9H, --CH₃), 7.33-7.37 (m, 6H, C₆H₄, *H*-6 and *H*-7 of anthracene), 7.47 (dd, 1H, $J_1 = 9.0$ Hz, $J_2 = 2.0$ Hz, *H*-3 of anthracene), 7.57 (d, 1H, J = 1.4 Hz, *H*-1 of anthracene), 7.63 (m, 3H, *H*-4, *H*-5, and *H*-8 of anthracene), 7.73-7.76 (m, 4H, C₆H₄); MALDI-TOF MS (*m*/*z*) calcd. for C₃₀H₂₄Br₂, 544.02; found, 544.1 [M + H]⁺.

Synthesis of Methyldiethoxylsilyl Chloride

Methyltrichlorosilane (150 mL, 127 mmol) and alcohol (146 mL, 254 mmol) (molar ratio 1:2) were slowly mixed in petroleum ether 30–60 (120 mL) at its boiling point. The mixture was then distilled to give a colorless liquid product (127–128 °C) with 63% yield (135 g).

¹H NMR (CDCl₃, 400 MHz, δ , ppm) 0.45 (s, 3H, Si–CH₃), 1.25 (t, 6H, J = 7.3 Hz, –CH₂CH₃), 3.87 (q, 4H, J = 7.2 Hz, –OCH₂CH₃); ²⁹Si NMR (59.6 MHz, δ , ppm) –29.32.

Synthesis of 2-*tert*-Butyl-9,10bis(methyldiethoxylsilyl)anthracene (M1)

Compound **1** (2.72 g, 5 mmol) was dissolved in THF (150 mL) followed by dropwise addition of *n*-butyllithium (6.9 mL, 1.6 M in hexane) at -78 °C. The reaction was stirred for about 8 h before methyldiethoxylsilyl chloride (3 mL, 12 mmol) was added. The mixture was then slowly warmed up to room temperature. After about 5 h, THF and unreacted methyldiethoxylsilyl chloride were removed by vacuum distillation. The obtained solid was treated with dichloromethane (300 mL)/water (50 mL) system, and the organic phase was dried over sodium sulfate. The concentrated solution (5 mL) was isolated by chromatography on silica gel columns (CH₂Cl₂/petroleum ether = 1/1 and ethyl acetate/petroleum ether = 1/40). After removing eluents, 1.46 g of light yellow powder was obtained. Yield, 45%; $R_{\rm f} = 0.5$ (ethyl acetate/petroleum ether = 1/9).

¹H NMR (CDCl₃, 400 MHz, δ , ppm): 0.51 (s, 6H, Si—*CH*₃), 1.25 (s, 9H, –(*CH*₃)₃), 1.30–1.36 (t, 12H, *J* = 7.3 Hz, -OCH₂*CH*₃), 3.95 (q, 8H, *J* = 7.2 Hz, –O*CH*₂ *CH*₃), 7.29–7.31 (m, 2H, *H*-6 and *H*-7 of anthracene), 7.42 (dd, 1H, *J*₁ = 8.2 Hz, *J*₂ = 1.8 Hz, *H*-3 of anthracene), 7.49–7.52 (m, 4H, *C*₆*H*₄), 7.54 (d, 1H, *J* = 1.2 Hz, *H*-1 of anthracene), 7.62 (m, 3H, *H*-4, *H*-5, and *H*-8 of anthracene), 7.85–7.89 (m, 4H, *C*₆*H*₄); ²⁹Si NMR (59.6 MHz, δ , ppm) –17.40; MALDI-TOF MS (*m*/*z*) calcd. for C₄₀H₅₀O₄Si₂, 650.32; found, 650.2 M⁺.

Synthesis of 2-*tert*-Butyl-9,10bis(methyldihydroxylsilyl)anthracene (M2)

To a solution of **M1** (2.6 g, 4 mmol) in THF (300 mL), water (4 mL) and two drops of 0.5 M HCl were added with stirring at 0 °C. After 12 h, ether (80 mL) and water (80 mL) were added. The ether layer was separated and washed with water (25 mL) three times. The solution was then dried over sodium sulfate and filtered. The filtrate was condensed to \sim 20 mL and precipitated using hexane (50 mL) followed by filtration to give a cake-like product. The product was dried under vacuum at room temperature, and 1.92 g of white powder was obtained. Yield, 89.2%.

¹H NMR (acetone- d_6 , 400 MHz, δ , ppm) 0.41 (s, 6H, Si— CH_3), 1.26 (s, 9H, —(CH_3)₃), 5.64 (s, 4H, —OH), 7.09 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.0 Hz, H-3 of anthracene), 7.25–7.50 (m, 5H, C_6H_4 , H-1 of anthracene), 7.60–7.66 (m, 5H, H-4, H-5, H-6, H-7, and H-8 of anthracene), 7.95–7.98 (m, 4H, C_6H_4); ²⁹Si NMR (59.6 MHz, δ , ppm) –19.55; MALDI-TOF MS (m/z) calcd. for $C_{32}H_{34}O_4Si_2$, 538.2; found, 538.3 [M + H]⁺.

Preparation of DPAnLP

M2 (1.08 g, 2 mmol) was dissolved in THF/dioxane (50 mL, v/v = 1:1). Then, two drops of concentrated H₂SO₄ were added to the mixture to catalyze the condensation reaction. The reaction medium was stirred at 40 °C for 96 h. To end cap the terminal silanol group of the polymer, pyridine (0.64 g, 8 mmol) and trimethylchlorosilane (0.88 g, 8 mmol) dissolved in THF/dioxane (10 mL, v/v = 1/1) were added dropwise into the flask under stirring. The mixture was stirred at room temperature for another 24 h. Filtration was applied to remove the small amount of gel generated during the condensation process. Adding water (10 mL) to the filtrate caused instantaneous precipitation of a white solid, which was dried in a vacuum oven at 40 °C for 24 h to obtain the desired polymer (**DPAnLP**) with 86% yield (0.87 g).

FTIR (KBr, thin film, cm⁻¹): 1600 (phenyl), 1259 (Si—*CH*₃), 1010–1100 (Si—O—Si). ¹H NMR (CDCl₃, 400 MHz, δ , ppm): 0.85–0.96 (br s, 3H, Si—*CH*₃), 1.27 (br s, 9H, —(*CH*₃)₃), 6.47–6.58, 7.06–7.10, and 7.28–7.91 (br m, 15H, phenyl-*H*); ²⁹Si NMR (59.6 MHz, δ , ppm): –22.31.

Characterization

Gel permeation chromatography (GPC) was performed on a Waters 150-C GPC equipped with Ultrastyragel columns (HT2, HT3, and HT4) at 35 °C. THF was used as eluent, and polystyrene standards were used as calibrations. The FTIR measurement was performed with a Perkin-Elmer80 spectrometer, and the samples were prepared using solvent casting on KBr flake. UV-vis spectra were obtained on a Shimadzu UV-vis spectrometer model UV-1601PC. Fluorescence spectra were recorded on a Hitachi F-4500. NMR spectra were obtained on a Bruker Avance DPS-400 (400 MHz) spectrometer. MALDI-TOF mass spectrometric measurements were performed on a Bruker Biflex MALDI-TOF mass spectrometer. X-ray diffraction (XRD) analysis was recorded on a Rigaku D/MAX 2400 diffractometer. Differential scanning calorimetry (DSC) was measured by using a Mettler Toledo Star-822 differential scanning calorimeter at a scanning rate of ± 10 °C/min under nitrogen atmosphere. Thermogravimetric analyses (TGA) was performed using a 7 Series thermal analysis system (Perkin-Elmer). The sample was heated from 40 to 600 °C at a rate of 10 °C/min under nitrogen purge (70 mL/min). Cyclic voltammetry was recorded on CHI660B voltammetric analyzer (CH Instruments) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in CH₂Cl₂ at room temperature under nitrogen with a scanning rate of 0.1 V/s. A glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode were used. The experiments were calibrated with the internal standard ferrocene/ferrocenium (Fc) redox system assuming that the energy level of Fc is 4.8 eV under vacuum.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and DPAnLP

Compound 1 was synthesized referring to literature procedure.²⁷ M1 was prepared through lithium-halogen exchange followed by treatment with methyldiethoxylsilyl chloride from 1. To minimize possible side reactions, we used anhydrous THF and kept reaction temperature at -78 °C. The reaction was monitored using thin layer chromatography. Purified target product was obtained after column chromatography with yield of 45%. M2 was synthesized through hydrolysis of M1. In this reaction, dilute M1 solution (\sim 0.013 M in THF), diluted acid (0.5 M HCl) as catalyst, and low temperature (0 °C) were used to suppress the undesired condensation between the formed silanols. HCl was removed via water wash from ether solution, and white product was precipitated from hexane. Note that M2 needed to be stored in an environment free of base or acid for following use because of highly reactive silanols (Scheme 1).

M2 was found to be able to spontaneously assemble into LS via presumably synergistic interactions of silanols' squareplanar H-bonding²⁸ and 9,10-diphenylanthryl bridges' π - π stacking (Scheme 1). The noncovalent LS was then used to direct condensation polymerization of reactive silanol groups to form target **DPAnLP**. As the weak noncovalent interactions are extremely susceptible to external conditions, for example, temperature, the electrodonating ability of medium, and the polarity of medium, extreme precautions were taken to avoid breaking LS during the polymerization and thus ensure the formation of high-ordered **DPAnLP** instead of branched or crosslinking products. After trying several selective solvent systems and reaction conditions, we found that the polymerization performed in THF/dioxane (v/v = 1/1) mixture below 50 °C gave the best results. We supposed that the reasons were possibly due to the characteristics of THF/dioxane mixture, which has low polarity and low electrodonating ability. In particular, Williams used to point out that the acidic environment is favorable to the formation of H-bonding between the silanols.²⁹ In addition, acidic catalyst usually has stronger condensing ability than basic ones for silanols with electrodonating groups.²⁹ Therefore, concentrated



FIGURE 1 FTIR spectra of M1, M2, and DPAnLP.

sulfuric acid was chosen as the condensation catalyst. Completion of polymerization was determined by FTIR. To stabilize **DPAnLP**, Me₃SiCl was used to end cap Si—OH end groups at the end of polymerization. The separated yield was about 86%. Solubility test found that **DPAnLP** was readily soluble in CH₂Cl₂, THF, acetone, and so forth. The weight-average molecular weight (M_w) of **DPAnLP** was determined to be 57.9 kDa with PDI = 1.46 by GPC in THF with polystyrene as standards.

The progress of hydrolysis and condensation process could be well monitored by FTIR, ¹H NMR, and ²⁹Si NMR. For FTIR spectra (Fig. 1), the peak around 1600 cm⁻¹ is attributed to phenyl group, whereas the peaks around 2960 and 1260 cm^{-1} are ascribed to Si-CH₃ group. Moreover, M1 shows strong peaks at 1165, 1078, and 1022 cm⁻¹, which is attributed to asymmetric Si-O-C stretch for the ethoxy group, and symmetric Si-0-C stretch falls at 796 cm⁻¹. For M2, these peaks from ethoxy group disappear, and characteristic peaks of hydroxyl group emerge, indicating the complete hydrolysis of **M1**. The large absorption band at 3293 cm^{-1} corresponds to hydrogen-bonded silanols, and the peak around 853 cm⁻¹ is originated from the Si–O stretching vibration of Si-OHs group. For the FTIR spectrum of DPAnLP, the characterizing absorptions of Si-OH group disappear, and two strong peaks in the region of 1000-1100 cm⁻¹ show up, which corresponds to asymmetric Si-O-Si stretching vibration. For ¹H NMR characterization (Fig. 2), when **M1** is hydrolyzed to M2, resonances of hydrogens in Si $-OCH_2CH_3$ [δ 3.95 (m, 8H) and 1.30–1.36 (t, 12H) ppm] disappear, and protons of Si–OH [δ 5.64 (s, 4H) ppm] show up. Completion of polymerization is confirmed from the disappearance of Si—OH protons, suggesting formation of DPAnLP. Also, chemical shift variation in ²⁹Si NMR spectra among M1 (δ = -17.40 ppm), M2 ($\delta = -19.55$ ppm), and DPAnLP ($\delta =$ -22.31 ppm) shown in Figure 3 also supports the functional



FIGURE 2 ¹H NMR spectra of M1, M2, and DPAnLP.

group change during the process of hydrolysis and condensation.

Confirmation of the Ladder Structure of LS and DPAnLP As the **LS** is not only the precursor but also the template of polymerization to form ladder polymers in **SCP** strategy, formation of defect-free and stable **LS** would be a key point of preparing ladder polymers with high regularity. Freeze-drying was used to prepare solid samples provided that fast cool could presumably maintain the nanostructure of **LS**. XRD was then applied to characterize ordering of **LS**.²¹ As shown in Figure 4, the XRD profile of freeze-dried **LS** sample from THF/dioxane solution (v/v = 1/1, 10 mg/mL) shows two characteristic peaks with 2 θ around 7.68° (1.15 nm) and 11.50° (0.77 nm) corresponding to ladder width and ladder thickness, respectively. Moreover, ²⁹Si NMR spectrum of **LS** in Figure 3 shows a distinct resonance ($\delta = -19.55$



FIGURE 3 ²⁹Si NMR spectra of M1, M2 (in the form of ladder superstructure), and DPAnLP.



FIGURE 4 (a) XRD profiles of **LS** (namely the assembly of **M2**) and **DPAnLP**; (b) molecular-simulated **DPAnLP** with five repeat units (by Materials Studio).

ppm) with a half-height width (Δ) of less than 1 ppm, indicating that all *Si*-atoms in **LS** are in the almost identical chemical environment. It is known that the narrower the resonance peak of the silicon atoms, the higher the regularity.²³ These results support our assumption that **LS** primarily consists of regular ladder structure, instead of randomly interlaced or branched structures.

The ladder structure of **DPAnLP** was also verified from XRD characterization. The XRD profile of **DPAnLP** film (ca. 15 μ m) on glass slide cast from its THF solution (10 mg/mL) shows two peaks at 20 around 6.06° (1.46 nm) and 11.70° (0.76 nm), respectively, (Fig. 4). According to previous report,¹⁶ the former represents the intramolecular chain-to-chain distance (i.e., the width of the ladder) of the polymer, and the latter is the thickness of the macromolecular chain. This result is consistent with the predicted values (1.48 and 0.75 nm) on the basis of molecular simulation calculation (by Materials Studio). Note that the ladder width of **DPAnLP** (1.46 nm) is larger than that of **LS** (1.15 nm). It is known that **LS** is noncovalent supramolecular aggregates, and its dimension is subject to variation of numerous environmental factors, for example, solvents, sample preparation procedure,

and molecular weight. As a result, the ladder width of LS may vary slightly depending on sample's histories. Such effects were observed before.³⁰ Here, a less electron-donating solvent and freeze-drying method were combined to prepare XRD samples, which might lead to relative smaller ladder width of LS compared with corresponding DPAnLP. However, the exact mechanism was not clear given available data. As for ladder thickness, molecular simulation image of **DPAnLP** gives about 0.75 nm of an alternating structure, which is supposed to result from the steric repulsion between *t*-butyl groups. In addition, the diffusing peak in the region of $2\theta \approx 20^{\circ}$ -25° ($d \approx 0.44$ -0.35 nm) is assigned to the π - π interaction distance between adjacent 9,10-diphenylanthryl. The intensity of this peak is increased for DPAnLP when compared with LS, which may be ascribed to the stronger π - π interactions within covalent-linked **DPAnLP** than those within supramolecular LS. Similarly, the XRD result, as well as the signal peak at $\delta = -22.31$ ppm with Δ < 1 ppm, fully verifies the high regular ladder structure of DPAnLP. Apparently, the regular ladder structure maintained after silanol condensation. We suppose that the DPAnLP would have much better stability compared to its LS precursor as the double covalent linkage between 9,10-diphenylanthryl will increase its stability and intramolecular ordering.

Optical Properties of DPAnLP

Because of good solubility in organic solvents, **DPAnLP** can be easily fabricated to films by casting, spin-coating, and dipping techniques. Based on this, the UV-vis absorption and PL properties of **DPAnLP** were investigated both in THF solution and thin film (Fig. 5). Transparent and uniform polymer films were prepared on quartz by spin-casting from THF solution at room temperature. The λ_{max} values are in the range of 260-460 nm. Absorption band between 350 and 400 nm with characteristic vibronic pattern can be attributed to the $\pi \rightarrow \pi^*$ transition of anthracene.³¹ **DPAnLP** exhibits an emission band around 430 nm with $\lambda_{ex} = 374$ nm. Note that there is only less than 2 nm red shift for UV-vis and PL spectra when the sample was varied from solution to film, suggesting no aggregation of chromophore during film preparation. We suppose that the negligible variation of spectra between solution and film was due to confinement of 9,10diphenylanthryl moieties within individual double-stranded ladder structure. Postsolution processing did not induce substantial change of local rearrangement of 9,10-diphenylanthryl units, which as return offered good film-forming property. The fluorescence quantum efficient yield ($\Phi_{\rm F}$) of **DPAnLP** in THF is found to be 0.89 using 9,10-diphenylanthracene as a reference standard (cyclohexane solution, $\Phi_{\rm F} =$ 0.9).³² This value is notably higher than the reported values for some anthracene-containing compounds, such as 0.47 of 2-tert-butyl-9,10-bis[4-(iminostilbenyl)phenyl]anthracene²⁷ and 0.44 of 9-phenyl-10-(4-triphenylamine)anthracene.³³ As expected, **DPAnLP** has good emission stability at high temperature because intramolecular aggregation of chromophores is effectively prevented by the rigid ladder structure, and intermolecular aggregation of chromophores is disfavored by the



FIGURE 5 (a) Absorption and photoluminescence emission spectra of **DPAnLP** in THF solution and thin film; (b) emission intensity of the spin-coated **DPAnLP** film before and after annealing at 200 °C for 2 h ($\lambda_{ex} = 374$ nm).

repulsion of bulky *tert*-butyl groups. PL spectra of **DPAnLP** show little variation after heating the film at 200 °C in air for 2 h (Fig. 5). This result demonstrates that **DPAnLP** is free of low energy defects (e.g., caused by crystallization) and has great thermal and color stability.

Electrochemistry of DPAnLP

Electrochemical behaviors of **DPAnLP** were investigated using cyclic voltammetry (Fig. 6). Onset of oxidation wave determined with ferrocene as internal reference is 0.85 V. Ionization potential (I_P) is thus estimated to be 5.65 eV according to the Halmiton Equation: I_P (eV) = E_{ox}^{onset} + 4.8.³⁴ In addition, band gap (E_{gap}) estimated from UV absorption spectra is about 2.92 eV, and then electron affinity (E_A) is calculated to be 2.73 eV according to $E_A = I_P - E_{gap}$. It is known that the oxidation process and I_P value are closely correlated with the removal of electrons (hole-injection) from the highest occupied molecular orbital (HOMO). There-



FIGURE 6 The cyclic voltammograms of **DPAnLP** at a scan rate of 0.1 V/s.

fore, compared to 5.70 eV of 9-phenyl-10-(4-triphenylamine)anthracene,³³ the lower I_P value, namely the lower HOMO level, means higher hole-injection ability.

Thermal Property of DPAnLP

We also investigated thermal stabilities of **DPAnLP** using TGA and DSC (Fig. 7). **DPAnLP** begins to decompose at 318.6 °C and losses about 50% of its weight at 407.4 °C. DSC measurement shows only a glass transition temperature



FIGURE 7 (a) TGA curve and (b) DSC trace of DPAnLP.

($T_{\rm g}$) around 152.0 °C, however, without any melting peaks. The $T_{\rm g}$ is surprisingly higher than those of anthracene-containing small molecules, for example, 104 °C of 9-phenyl-10-(4-triphenylamine)-anthracene.³³ We suppose the increase of $T_{\rm g}$ was due to the introduction of regular ladder polysiloxane chain. For **DPAnLP**, its high $T_{\rm g}$ is probably an underlying reason for its great thermal and color stability, which opens a promising synthetic strategy in polymer chemistry to make stable and efficient luminescence polymer materials.

CONCLUSIONS

In summary, a blue light PL **DPAnLP** was synthesized using the **SCP** method. Its high regularity was well characterized using XRD and ²⁹Si NMR. Compared with common anthracene-containing compounds, the ladder structure and the *tert*-butyl group effectively prevent the undesired aggregation of chromophores and offer a higher Φ_F of 0.89. The unique ladder polysiloxane structure offers **DPAnLP** better film-forming ability, thermal stability, and emission stability. Electrochemistry measurement shows a low-lying HOMO level. Moreover, our versatile synthetic strategy offers an opportunity to prepare various PL polymeric materials and may lead to preparation of electroluminescence polymeric materials after slight modification.

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