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Thermodynamically stable, highly emissive poly(diphenylacetylene) derivative containing long alkyl side chain without silylene linkage

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ABSTRACT

A PDPA derivative with a long alkyl side chain connected directly onto the backbone (**1**) was synthesized and compared to a corresponding polymer with a silylene linkage between the side chain and the backbone (**2**). Polymers **1** and **2** showed similar solubilities: both polymers dissolved well in organic solvents such as toluene, THF, and chloroform but not in polar solvents such as DMF and alcohols. When cast from toluene solutions, smooth and transparent films were readily obtained. Thermogravimetric analysis showed that **1** was more thermally stable than **2** owing to the absence of the relatively weak silylene linkage. Differential scanning calorimetry showed that **1** exhibited a local thermodynamic relaxation due to the long alkyl side chains at a higher temperature than **2**. In photoluminescence spectroscopy, **1** was found to be more emissive, with quantum yields being as high as 63.1 and 27.4% in solution and films, respectively, while those of **2** were 49.4 and 20.6%. Consequently, **1** was more thermally stable, stiffer, and more emissive than **2**.

1. Introduction

Conjugated polymers (CPs) are key materials for optoelectronic device applications. Among them, poly(diphenylacetylene)s (PDPAs) and related nano-sized and hybrid materials have recently attracted great interest as optical sensors, imaging probes, and actuators in addition to their applications as gas-permeable membranes [1]. In general, conventional CPs show remarkably attenuated photoluminescence (PL) due to the intense intermolecular π-π interactions and dense chain packing structures caused by their intrinsically planar geometries. On the other hand, PDPAs show considerable emission even in the solid state because of their non-planar geometries and highly twisted backbones [1]. The PL of PDPAs is known to originate from an intramolecular excimer formed in the intramolecular stack structure (IaSS) of the pendant phenyl rings [2]. As is common with CPs, alkyl side chains have been attached to these pendant phenyl rings to disrupt molecular symmetry, leading to improved solubility in common organic solvents. On the other hand, very unique PL emission behavior not usually expected in CPs is seen in PDPAs. As the chain conformation differs considerably depending on the length and/or the substitution position of the alkyl side chains, changing these factors can have a significant effect on the resulting PL emission. For example, long alkyl chains serve as an internal plasticizer to loosen the IaSS, leading to significantly enhanced PL emission [2–4]. In particular, when alkyl chains are attached to the *para* positions of the side phenyl rings, PDPAs become more emissive through a highly efficient radiative emission decay channel [5]. Therefore, the alkyl side chains play a crucial role in maximizing the PL emission when designing novel PDPA derivatives for advanced applications. However, there is one factor that has been overlooked in previous synthetic strategies: the use of silylene linkages between the alkyl side chains and the backbone. Early on, Masuda et al. synthesized PDPA derivatives containing silylene linkages by attaching the alkyl chains to one of the two phenyl rings through a substitution reaction between lithiated phenyl groups and trialkylchlorosilanes

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during the synthesis of the corresponding monomers [6]. Since then, silylene linkages have become a staple for the synthesis of PDPA derivatives. Despite the fact that silicon has a larger atomic radius and adopts higher coordination numbers than carbon, the influences of the silylene linkage on the thermal stability, thermodynamic, and PL properties of PDPAs have never been examined in detail. Although a new category of PDPA derivatives has recently been synthesized with polymethylated ring moieties fused to the pendant phenyl rings, their physical properties other than their gas permeabilities were not examined [7]. In this study, we synthesized a new PDPA derivative having a long alkyl side chain without a silylene linkage (**1** in Fig. 1) and compared its properties with those of an analogous polymer containing a silylene linkage (**2** in Fig. 1). Herein, we describe the details of the resulting thermogravimetric, thermodynamic, and spectroscopic analyses.

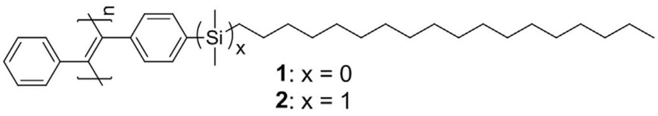

Fig. 1. Chemical structures of PDPAs without (**1**) and with (**2**) a silylene linkage.

2. Experimental section

2.1. Materials

Polymer **2** was synthesized according to a method reported in the literature [8]. The monomer of **1** (**5** in Scheme 1) was synthesized with reference to literature methods [9,10]. $Pd(PPh_3)_2Cl_2$ was prepared by mixing stoichiometric amounts of $PdCl_2$ and triphenylphosphine in hot DMF. $Pd(dppf)Cl_2$ and other reagents were purchased from TCI Co. and used without further purification. Dehydrated solvents (THF and diethyl ether) were obtained from Kanto Chemical Co. Other chemicals including solvents were purchased from Aldrich and TCI and used as received.

2.2. Synthesis of 1 (Scheme 1)

2.2.1. 1-Bromo-4-octadecylbenzene (**3**)

A three-necked flask was equipped with a Dimroth condenser, dropping funnel, magnetic stirrer bar, and a three-way stopcock then flushed with dry nitrogen. Magnesium turnings (0.63 g, 25.9 mmol), a catalytic amount of iodine, and dry THF (2 mL) were placed in the flask. The mixture was then stirred until the brown color of the iodine disappeared. 1-Bromooctadecane (8.63 g, 25.9 mmol) in dry THF (15 mL) was added dropwise at a rate sufficient to cause gentle self-refluxing. When the addition was finished, the reaction mixture was stirred for an additional 30 min at 40 °C. Another three-necked flask was equipped with a Dimroth condenser, magnetic stirrer bar, rubber septum, and three-way stopcock and flushed with dry nitrogen. 1,4-Dibromobenzene (6.11 g, 25.9 mmol), $Pd(dppf)Cl_2$ (212 mg, 0.259 mmol), and dry diethyl ether (15 mL) were placed in the flask and the solution was warmed to 40 °C. The above-synthesized 1-octadecylmagnesium bromide was then slowly added through a Teflon® cannula at 40 °C with stirring. The resulting mixture was refluxed for 2 days and then poured into water. After removal of the catalyst residue by filtration, the filtrate was extracted with diethyl ether. The organic layer was washed with brine and dried over anhydrous $MgSO_4$, and the solvent was evaporated. The resulting crude product was purified by flash silica gel column chromatography (eluent: hexane) to give **3** (5.27 g, 50%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.36 Hz, 2H), 7.05 (d, J = 8.36, Hz, 2H), 2.55 (t, J = 7.53 Hz, 2H), 1.57 (m, 2H), 1.34–1.19 (m, 31H), 0.88 (t, J = 6.65 Hz, 3H).

2.2.2. 2-Methyl-4-(4-octadecylphenyl)-3-butyn-2-ol (**4**)

3 (2.00 g, 4.88 mmol), triphenylphosphine (257 mg, 0.98 mmol), copper(I) iodide (278 mg, 1.46 mmol), $Pd(PPh_3)_2Cl_2$ (175 mg, 0.25 mmol), and triethylamine (20 mL) were placed into a three-necked flask equipped with a Dimroth condenser, three-way stopcock, magnetic stirrer bar, and rubber septum. 2-Methyl-3-butyn-2-ol (431 mg, 5.12 mmol) was then added to the solution. The resulting mixture was refluxed and stirred for 24 h. After removal of the solvent by evaporation, the crude residue was extracted with diethyl ether, and the ether solution was washed with 2 N HCl aq., sat. $NaHCO_3$ aq., and brine and dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained crude product was purified by flash silica gel column chromatography (eluent: hexane:ethyl acetate 4:1 v/v) to give **4** (704 mg, 35%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.32 Hz, 2H), 7.11 (d, J = 8.32 Hz, 2H), 2.58 (t, J = 7.53 Hz, 2H), 2.00 (s, 1H, –OH), 1.61 (s, 6H), 1.60–1.56 (m, 2H), 1.34–1.19 (m, 31H), 0.88 (t, 3H, J = 6.64 Hz).

2.2.3. 1-(4-Octadecylphenyl)-2-phenylacetylene (**5**)

A heterogeneous solution of **4** (660 mg, 1.60 mmol), bromobenzene (251 mg, 1.60 mmol), $Pd(PPh_3)_2Cl_2$ (112 mg, 0.16 mmol), copper(I) iodide (30 mg, 0.16 mmol), and tetrabutylammonium iodide (59 mg, 0.16 mmol) in a mixture of toluene (1 mL) and 5 M NaOH aq. (2.5 mL) was degassed by sonication under reduced pressure for a short time. The mixture was heated at 80 °C for 24 h, and then cooled to ambient temperature. The reaction solution was filtered through a silica gel pad, and the filtrate was concentrated using a rotary evaporator. The crude product was purified by flash silica gel column chromatography (eluent: hexane) to give the desired product (290 mg, 42%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 2H), 7.44 (d, J = 8.24 Hz, 2H), 7.38–7.28 (m, 3H), 7.16 (d, J = 8.24 Hz, 2H), 2.61 (t, J = 7.53 Hz, 2H), 1.61 (m, 2H), 1.35–1.20 (m, 31H), 0.88 (t, J = 6.70 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.44, 131.53, 131.49, 128.45, 128.29, 128.04, 123.49, 120.34, 89.58, 88.69, 35.91, 31.92, 31.25, 29.70 (× 4C), 29.66 (× 5C), 29.57, 29.48, 29.36, 29.25, 22.69, 14.12. IR (KBr) 2918, 2848, 2359, 1463, 751, 723, 688 cm^{-1}. Anal. Calcd. for $C_{32}H_{46}$: C, 89.24; H, 10.76. Found: C, 89.09; H, 10.97.

2.2.4. Poly[1-(4-Octadecylphenyl)-2-phenylacetylene] (**1**)

Polymerization of **5** was carried out under dry nitrogen using the following conditions: $[M]_0 = 0.16$ M, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM, in toluene at 80 °C for 48 h. The polymerization procedure was as follows. A monomer solution was prepared in a two-necked flask by mixing **5** (210 mg, 0.49 mmol) and toluene (1.29 mL). Another two-necked flask was charged with $TaCl_5$ (21.5 mg, 0.06 mmol), n-Bu_4Sn (39 μL, 0.12 mmol), and toluene (1.5 mL), and the catalyst solution was aged at 80 °C for 15 min. The monomer solution was then added to the catalyst solution and stirred at 80 °C for 48 h. The polymerization was quenched by adding a small amount of methanol. The polymerization mixture was diluted with toluene and poured into methanol while stirring to precipitate the resulting polymer, **1**, as yellow solid. The polymer was isolated by filtration and dried. The polymer yield was determined to be 78% by gravimetry.

2.3. Instruments

^1H and ^{13}C NMR were recorded on a Varian 400-MR spectrometer, while infrared spectra were recorded on a JASCO FT/IR-4200 spectrometer. Number-average molecular weight (M_n) and