Synthesis of Cyano-substituted Through-space Poly(p-arylenevinylene)

Yasuhiro Morisaki,* Lin Lin, and Yoshiki Chujo*
Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Katsura, Nishikyo-ku, Kyoto 615-8510

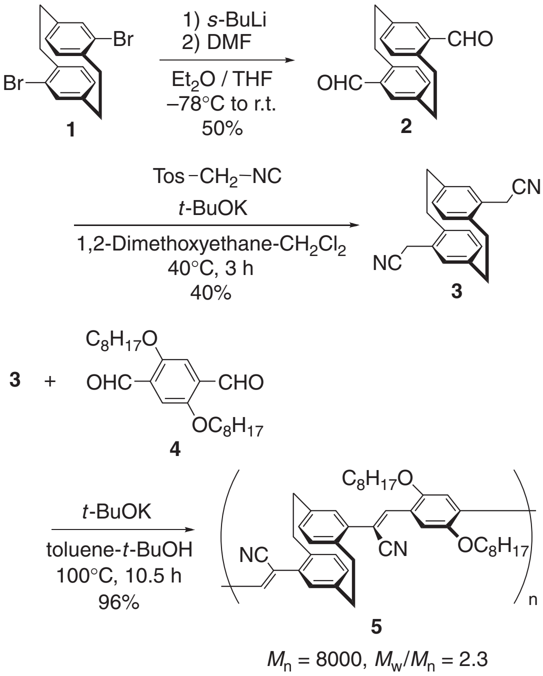
(Received April 27, 2009; CL-090421; E-mail: ymo@chujo.synchem.kyoto-u.ac.jp)

The Knoevenagel reaction of pseudo-p-bis(cyanomethyl)-[2.2]paracyclophane with 2,5-dialkoxy-1,4-diformylbenzene was carried out to yield the cyano-substituted through-space poly(arylenevinylene). Thermal, optical, and electrochemical properties are described.

Over the past two decades, conjugated poly(p-arylenevinylene)s (PAVs) have been intensively investigated for their unique electrical and optical properties.[1] The first report of the application of a PAV in light-emitting diodes (LEDs)[2] triggered extensive research on the development of high performance conjugated polymers such as poly(p-aryleneethynylene)s and poly(p-arylene)s in addition to PAVs. The introduction of cyano groups into vinylene units in the PAV backbone lowers its HOMO–LUMO band gap energy, leading to bathochromic shifts of absorption and emission spectra. Thus, cyano-substituted poly(p-phenylenevinylene)s (PPVs) are observed to emit red light.[3]

Recently, we reported the synthesis of through-space conjugated polymers containing cyclophane moieties as the key repeating unit.[4,5] Most of the through-space conjugated polymers were prepared by palladium-catalyzed coupling reactions.[5] We found that the conjugation length of the polymers increased as a result of π–π stacking, and that they emitted intense fluorescence despite the presence of the π-stacked structures in the polymer chain. The expansion of the substrate scope of the newly developed through-space conjugated polymers is an important subject, and investigating their properties is necessary for making advances in the field of the conjugated polymers. Thus, in this study, we synthesized a new type of cyano-substituted through-space PAV by the Knoevenagel reaction of pseudo-p-bis(cyanomethyl)[2.2]paracyclophane with 2,5-dialkoxy-1,4-diformylbenzene and elucidated its properties.

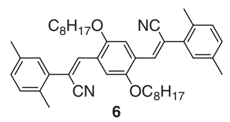
Pseudo-p-diformyl[2.2]paracyclophane (**2**) has been synthesized;[6] however, its synthetic procedure and analytical data are unknown. Thus, we synthesized **2** by our own method, as shown in Scheme 1. The synthesis of monomer **3** was carried out by the reaction of **2** with 4-toluenesulfonylmethyl isocyanide (Scheme 1). Then, cyano-substituted through-space PAV was synthesized by carrying out the typical Knoevenagel reaction of **3** with 2,5-dioctyloxy-1,4-diformylbenzene (**4**) in the presence of t-BuOK in toluene-t-BuOH at 100 °C for 10.5 h. The reaction was quenched with AcOH, and toluene was added to obtain the crude polymer in the form of an orange powder, which included an insoluble component in common organic solvents. The insoluble component was washed with water and THF, and the soluble component was purified by reprecipitation from MeOH to obtain the corresponding polymer **5** in total 96% isolated yield. FTIR spectra of both the insoluble and soluble polymers confirmed that they had the same structure (Figure S7).[7] Absorption intensities of stretching vibrations of CH and CN indicated that insoluble polymer formation was due to high molecular weight rather than crosslinking. Polymer **5** was found to be thermally stable (Figure S10),[7] and the soluble component of **5** could be processed into an amorphous thin film by casting or spin-coating from its toluene solution. The number-average molecular weight (M_n) of the soluble component of **5** was estimated to be 8000 with M_w/M_n of 2.3 by gel permeation chromatography (GPC) in eluent $CHCl_3$ (polystyrene standards).



Scheme 1. Synthesis of monomer **3** and polymer **5**.

The absorption spectra of polymer **5** and model compound **6** were measured in $CHCl_3$ solution, as shown in Figure 1. Polymer **5** exhibited absorption peaks at 436 and 360 nm in $CHCl_3$ at room temperature, which can be attributed to the π–π^* transition bands of the conjugated PAV backbone.[8a] The absorption maximum ($\lambda_{max} = 436$ nm) and the absorption edge (onset $\lambda = 525$ nm) of **5** exhibited clear bathochromic shifts relative to those of **6** ($\lambda_{max} = 413$ nm, onset $\lambda = 500$ nm), as shown in Figure 1. This result indicates the extension of the conjugation length of **5** as a result of π–π stacking. The band gap energy (E_g) of **5** was estimated to be approximately 2.4 eV on the basis of the absorption edge. On the other hand, it is reported that through-bond conjugated PPV exhibits λ_{max} of around 465 nm[8] and $E_g = 2.2$ eV,[8c] indicating through-bond conjugated PPV is more effective for the extension of the conjugation length than the through-space conjugation.

Fluorescence emission spectrum of polymer **5** was obtained from sufficiently diluted $CHCl_3$ solution (2.6×10^{-6} M)[9] at



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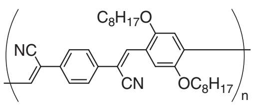

Through-bond conjugated PPV
λ_{max} = 467 nm,[8a] E_g = 2.2 eV

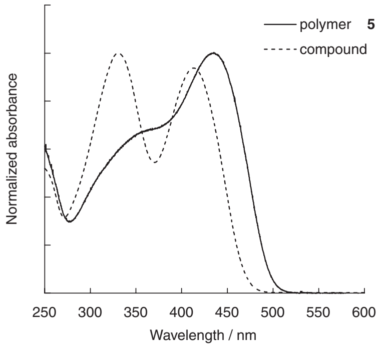

Figure 1. Absorption spectra of **5** and **6** in $CHCl_3$ (2×10^{-4} M).

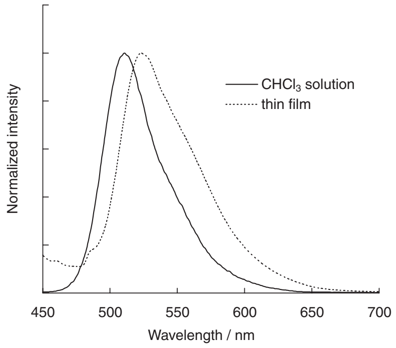

Figure 2. Fluorescence emission spectra of **5** in $CHCl_3$ (2.6×10^{-6} M) and in the film state.

room temperature with an excitation wavelength of 430 nm, and an emission peak was observed at 510 nm in the visible green region (Figure 2). The fluorescence emission spectrum of **5** red-shifted 13 nm in comparison with that of **6** (Figure S12),[7] and the quantum efficiencies of **5** and **6** were 32 and 30%, respectively. Despite the π-stacked structure, excimer emission was not observed in the case of **5**; this is because emission of [2.2]paracyclophane-containing through-space conjugated polymers occurs from the monomer state rather than the phane state (excimer state).[4b,10] The emission wavelength (510 nm) of **5** was shorter than that of the through-bond conjugated polymer (557 nm).[8b] The spin-coated thin film of **5** emitted green light with $\lambda_{max} = 524$ nm, which was red-shifted from that of its solution (Figure 2).

In order to estimate the HOMO and LUMO energy levels of polymer **5**, cyclic voltammetry (CV) was carried out using a thin film coated on an ITO glass electrode. Cyclic voltammograms were obtained in CH_3CN solution of 0.1 M Et_4NBF_4 using a three-electrode cell with a Pt counter electrode and a Ag/AgCl reference electrode. Figure 3 shows cyclic voltammograms obtained after the first and second scan at a scan rate of 100 mV s^{-1}. The oxidation process gave an onset peak at approximately 1.0 V, and in the cathodic scan, the onset reduction potential was observed at about -1.1 V (vs. Ag/Ag$^+$). The HOMO and LUMO energy levels of **5** were roughly estimated to be -5.2 and -2.8 eV, respectively. The band gap energy was approximately 2.4 eV, which was in good agreement with the calculated value of the band gap energy estimated from its absorption spectrum.

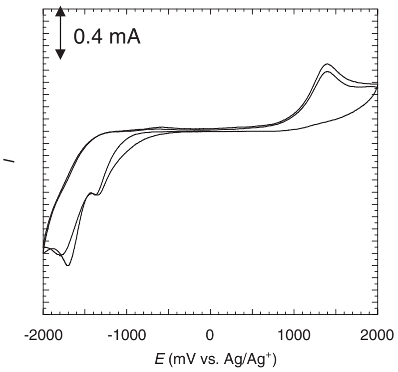

Figure 3. Cyclic voltammograms of **5** on an ITO electrode in CH_3CN containing 0.1 M Et_4NBF_4 (vs. Ag/Ag$^+$) at a scan rate of 100 mV s^{-1}.

In conclusion, we synthesized novel cyano-substituted through-space conjugated PAV containing the [2.2]paracyclophane unit in the main chain by the Knoevenagel reaction. Thermal, optical, and electrochemical properties were investigated, indicating that the polymer can be potentially applied in optoelectronic devices. The presence of the π-stacked structure in the polymer chain would be merit for the occurrence of the effective charge transfer in materials. Studies on the effect of the substituted position of the cyano group on the optical behavior as well as further investigations on using the polymer for device fabrication are currently underway.

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