

# Metathesis polymerization of diphenylacetylenes possessing electron-donating and electron-withdrawing groups and emission properties of polymers



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## ARTICLE INFO

### Article history:

Received 20 October 2015

Received in revised form 10 December 2015

Accepted 11 December 2015

Available online 31 December 2015

### Keywords:

Poly(diphenylacetylene)  
Metathesis polymerization  
Photoluminescence

## ABSTRACT

Diphenylacetylenes containing electron-donating groups ( $-O-n-C_8H_{17}$ : **1A**,  $-OCH_3$ : **1B**,  $-SCH_3$ : **1C**) and electron-withdrawing groups ( $-COOCH_3$ : **1a**,  $-COCH_3$ : **1b**,  $-CF_3$ : **1c**,  $-CN$ : **1d**) were polymerized using  $TaCl_5/n-Bu_4Sn$ . The polymerization of diphenylacetylenes possessing both an *n*-octyloxy group and an electron-withdrawing group (**1Aa**, **1Ab**, **1Ac**) was also examined in the same conditions. Electron-donating group-containing monomers (**1A–C**) polymerized to afford relatively high-molecular-weight polymers ( $M_n = 240,000$ – $622,000$ ). Ester-containing monomers (**1a** and **1Aa**) also polymerized to give polymers with high molecular weights, while the polymerization of acetyl- and trifluoromethyl-containing monomers (**1b**, **1c**, **1Ab**, **1Ac**) gave low-molecular-weight polymers. Cyano-containing monomer (**1d**) did not polymerize because cyano groups deactivated tantalum catalysts. Polymers having electron-donating groups (**2A–C**) emitted green-colored lights, and the emission maxima were around 505 nm. Ester-containing polymers **2a** and **2Aa** showed yellow-colored emissions, and the emission maxima were 520 nm. These polymers showed emission red-shifts between the solution and cast film.

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## 1. Introduction

Poly(thiophene)s, poly(fluorine)s, poly(*p*-phenylenevinylene)s, and other  $\pi$ -conjugated polymers have been studied due to their interesting electronic and optical properties [1–3].  $\pi$ -Conjugated polymers possessing electron-donating and electron-withdrawing groups exhibit low-lying charge-transfer excited states and large second-order optical nonlinearities [4–7], and then they are promising candidates for photo-luminescence, photoconductivity, and optical storage devices. Polyacetylenes are also  $\pi$ -conjugated polymers and have interesting features based on conjugated main chain. It is well known that unsubstituted polyacetylene exhibits metallic conductivity when it is doped, but unsubstituted polyacetylene is no-emissive probably because the cofacial strong packing structure results in self-quenching. Mono-substituted polyacetylenes exhibit very weak luminescence similar to unsubstituted polyacetylenes. On the other hand, disubstituted acetylene polymers exhibit strong luminescence because the substituents prevent the polymer chain packing [8–11]. However,

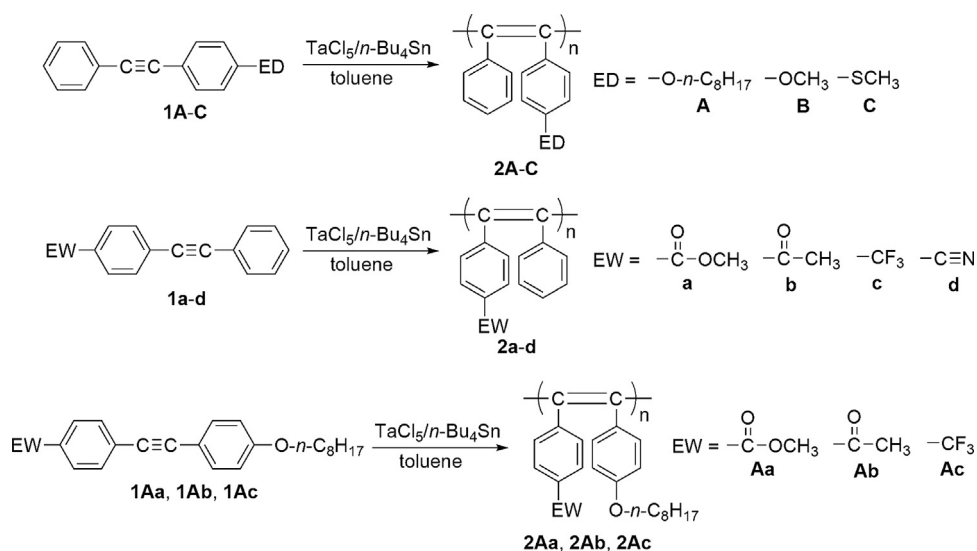
it has not been clarified that what substituents are suitable to high emission and how the substituents affect the luminescence. Especially, there are few reports on the luminescence of polyacetylenes containing electron-donating and electron-withdrawing groups.

Disubstituted acetylenes polymerize with transition metal catalysts such as  $NbCl_5$ ,  $TaCl_5$ , and  $WCl_6$  to provide the corresponding polymers, but it is difficult to obtain polar group-containing polymers because the transition metal catalysts are intolerant to polar groups [12,13]. Recently, Tang and coworkers reported the synthesis of disubstituted acetylene polymers containing polar groups [14–19]. For example, poly(diphenylacetylene)s possessing ester groups were successfully synthesized by the metathesis polymerization with  $WCl_6/Ph_4Sn$  catalyst [16]. From the results, disubstituted acetylenes with relatively low polarity can polymerize using transition metal catalysts.

In the present study, the metathesis polymerizations of novel disubstituted acetylenes having alkoxy and thioalkoxy groups as an electron-donating group were investigated using  $TaCl_5/n-Bu_4Sn$  (Scheme 1). We also examined the polymerization of monomers having ester, acetyl, trifluoromethyl, and cyano groups as an electron-withdrawing group. Moreover, the monomers possessing both an electron-donating group (*n*-octyloxy) and an electron-

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**Scheme 1.** Metathesis polymerization of diphenylacetylenes having electron-donating (ED) and electron-withdrawing (EW) groups.

withdrawing group (ester, acetyl, and trifluoromethyl) were polymerized. The absorption and emission spectra of the obtained polymers were studied in  $\text{CHCl}_3$  and cast film.

## 2. Experimental

### 2.1. Measurements

The molecular weight distribution (MWD) of polymers were measured by gel permeation chromatography (GPC) in  $\text{CHCl}_3$  (at a 1.0 mL/min flow rate) at 40 °C on a Shimadzu LC-10AD chromatograph equipped with three polystyrene gel columns (Shodex K-804L, K-805L, and K-807L) and a Shimadzu RID-6A refractive index detector. The weight-average molecular weight ( $M_w$ ) and polydispersity ratio [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ )] were calculated from chromatograms based on a polystyrene calibration.  $^1\text{H}$  (500 MHz) and  $^{13}\text{C}$  (125 MHz) NMR spectra were recorded on Jeol LA-500 instrument in  $\text{CDCl}_3$  at room temperature. IR spectra of polymers were recorded on a Nicolet iS5 spectrometer. UV-vis absorption was measured with HITACH U-3900H spectrophotometer and optical emission was measured with PerkinElmer LS-55 fluorescence spectrometer.

### 2.2. Materials

*p*-Bromophenol, *p*-bromoanisole, *p*-bromomethylthiobenzene, methyl *p*-bromobenzoate, *p*-acetylbromobenzene, *p*-bromo(trifluoromethyl)benzene, *p*-bromocyanobenzene, 2-methyl-3-

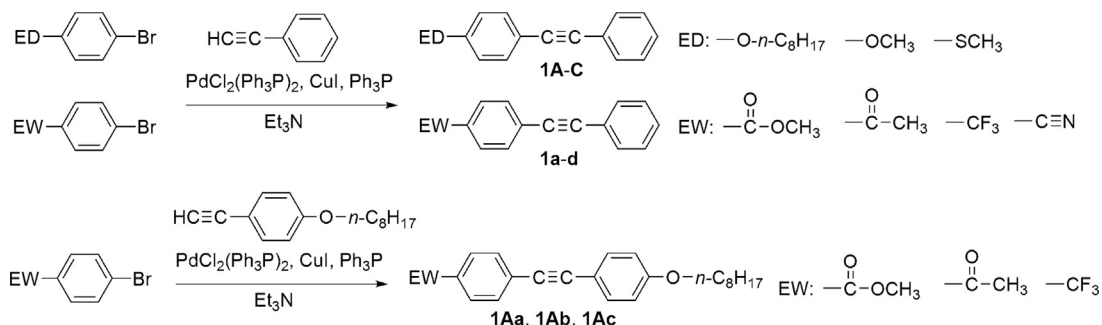
butyne-2-ol, 1-bromooctane, and common organic solvents were commercially obtained from Wako Pure Chemicals, Ind., Ltd., and used without further purification. Phenylacetylene, and tantalum (V) chloride (99.999%) were commercially obtained from Aldrich Chemistry, Ind., Ltd., and used without further purification. Toluene which is polymerization solvent was purified by two times of distillation in the presence of  $\text{CaH}_2$ . Tetra-*n*-butyltin which is cocatalyst for polymerization was purchased from Wako Pure Chemicals, Ind., Ltd., and used after distillation under reduced pressure.

*p*-Bromo-*n*-octyloxybenzene and *p*-ethynyl-*n*-octyloxybenzene were synthesized according to the literature [20]. Monomers (**1A-C**, **1a-d**, **1Aa**, **1Ab**, and **1Ac**) were synthesized as shown in Scheme 2 and the detailed procedures and analytical data are described below.

### 2.3. Monomer synthesis

#### 2.3.1. 1-(*p*-*n*-Octyloxyphenyl)-2-phenylacetylene (**1A**)

A 500 mL three-necked flask was equipped with a three-way stopcock, a reflux condenser, and a magnetic stirring bar. Dichlorobis(triphenylphosphine)palladium(II) (0.10 g, 0.14 mmol), cuprous iodide (0.10 g, 0.53 mmol), and triphenylphosphine (0.10 g, 0.38 mmol) were put in the flask. After the flask was flushed with nitrogen, *p*-bromo-*n*-octyloxybenzene (7.0 g, 0.024 mol) and phenylacetylene (3.1 g, 0.030 mol) in triethylamine (250 mL) were added to it. The mixture was stirred for 24 h at reflux temperature (ca. 90 °C). After the triethylamine was evaporated, ether (200 mL) was added, and the insoluble salt was filtered off. The solution was



**Scheme 2.** Synthetic schemes of monomers.

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