Synthesis and Characterization of a Novel Linear Conjugated Polymer, Poly(2,5-didodecyloxy-1,4-phenyleneoctatetraynylene)

Masashi Kijima,* Ikuo Kinoshita, and Hideki Shirakawa
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573

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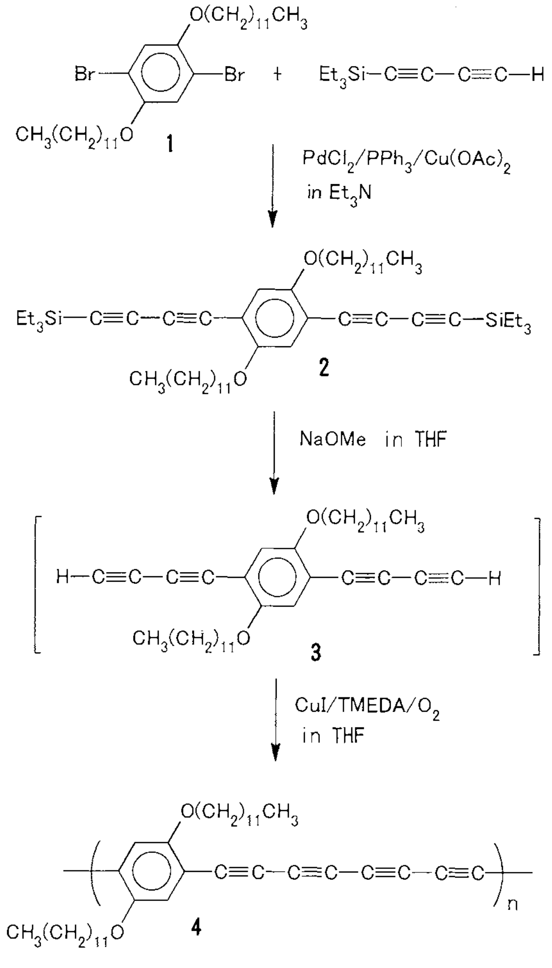
A novel linear conjugated polymer, poly(2,5-didodecyloxyphenyleneoctatetraynylene), was synthesized by an oxidative coupling of 2,5-didodecyloxy-1,4-dibutadiynylbenzene in presence of a CuCl-TMEDA catalyst under O_2. The polymer was stable under air and soluble in organic solvents. The structural analyses and the characterizations were carried out by Raman, NMR, and UV-Vis.

Synthesis of polyethynylene, $-(C\equiv C)_n-$, is significant for chemical proof of a new carbon allotrope consisted of only sp hybrid carbons with respect to carbyne and for development of a new polymer with a conjugated system of alternating carbon-carbon triple and single bonds. However, little is known about polyethynylene. Some attempts for synthesis of polyethynylene by chemical and electrochemical manners have resulted in ill-characterized insoluble black materials,[1] which is probably due to instability of linear carbon chain. Stabilization of the linear carbon chain by end-capping has been known to be an effective manner for synthesis of stable polyethynyl compounds.[2] Recently, we have succeeded to synthesize and characterize poly(2,5-dialkoxyphenylenebutadiynylene)s[3] in which the *p*-phenylene moiety is interposed between the butadiynylene segments in order to stabilize them. Such poly(arylene-*alt*-oligoethynylene)s are not only meaningful as a model for polyethynylene but also have received much attention as optoelectronic materials.[4] However little is investigated about conjugated polymers having a longer ethynylene segment.[5]

Therefore, we considered it worthwhile to synthesize and characterize a novel conjugated polymer having the longer linear carbon segments than butadiynylene. Here we report the synthesis of poly(2,5-didodecyloxy-1,4-phenyleneoctatetraynylene) **4** through copper-catalyzed oxidative coupling of 1,4-butadiynyl-2,5-didodecyloxybenzene **3** under Hay conditions.[6]

The synthetic route of **4** is summarized in Scheme 1. To obtain monomer **3**, 1,4-dibromo-2,5-didodecyloxybenzene **1** (3 mmol) prepared from 1,4-didodecyloxybenzene according to the reported method[7] was reacted with 4-fold excess of triethylsilylbutadiyne in the presence of $PdCl_2$ (0.6 mmol), $Cu(OAc)_2$ (0.6 mmol), PPh_3 (1.98 mmol) in 100 mL of Et_3N at 85 ℃ for 15 h under Ar. After the reaction, the product was purified through general extraction using CH_2Cl_2-H_2O, silica gel chromatography using hexane as an eluent, and recrystallization, affording a yellow powder of silyl protected 1,4-dibutadiynylbenzene **2** in 34% yield. Since isolation of the monomer **3** results in black insoluble residue, the polymerization was carried out without isolation of **3** as following. Desilylation of **2** (0.5 mmol) in 10 mL of THF was carried out by addition of NaOMe (54 mg) dissolved in 1mL of MeOH for 3 h at room temperature. After a general extraction work up using CH_2Cl_2-aq. HCl, the solvent was replaced with THF for several evaporations. Into the THF solution (10 mL) containing **3**, was added a THF solution (10 mL) of Hay catalyst prepared from CuCl (0.13 mmol) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (0.13 mmol) under O_2. The polymerization was carried out for 48 h at room temperature under O_2. The polymer dissolved in $CHCl_3$ was purified by reprecipitation for several times from aq. HCl-MeOH and MeOH, yielding red-brown solid in 60%.



Scheme 1.

The polymer **4** was unexpectedly well soluble in $CHCl_3$, THF, and benzonitrile at room temperature, and can be made a thin cast film from the solution exhibiting a lustrous red-orange color. GPC analysis shows M_n = 15600 and M_w/M_n = 3.5. The degree of polymerization is estimated to be about 28 from the M_n value.

The chemical structure of polymer **4** was identified by Raman, IR, NMR, UV-Vis, and elemental analysis.[8] A characteristic Raman peak was observed at 2119 cm^{-1} (excited with 785 nm laser) due to symmetric stretching vibration of conjugated C≡C linkage of the octatetrayne segment (Figure 1A). The value shifted lower in wavenumber than that of poly(2,5-dialkoxy-1,4-phenylenebutadiynylene)[3] and was comparable with that of 1,8-diphenyloctatetrayne.[9] The lower shift attributes to a weakened bond strength by an extended π-conjugation. IR spectrum showed a strong absorption at 2195 cm^{-1} due to an asymmetric stretching mode of triple bonds in the octatetrayne segment (Figure 1B). IR absorptions at 2922 and 2852 cm^{-1} and at 1216 cm^{-1} suggest the presence of the alkoxy side substituent.

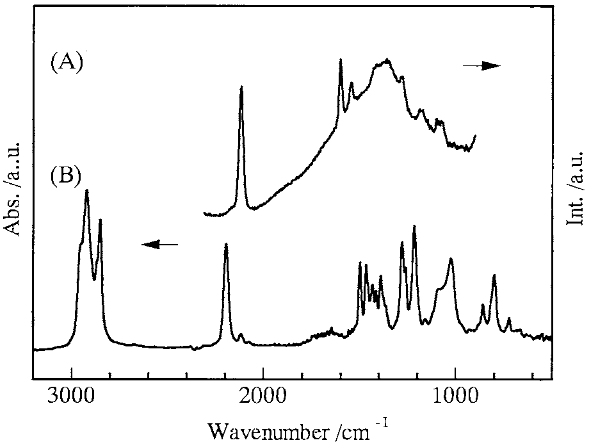


Figure 1. Raman (ex. 785 nm) (A) and IR (B) spectra of **4**.

^{1}H and ^{13}C NMR spectra also suggest the structure of polymer **4**.[10] However octatetrayne carbon signals that should be observable in the region of 60-80 ppm[11] are too weak to be assigned in the ^{13}C NMR spectrum.

UV-Vis spectrum of **4** showed a vibronic pattern with an absorption maximum at 488 nm (Figue 2). The E_g is estimated from an edge of the absorption to be 2.25 eV being smaller than that of the corresponding poly(phenylenebutadiynylene) (λ_{max}= 424 nm, E_g = 2.5 eV).[3] The large red shift of the λ_{max} value compared with that of diphenyloctatetrayne (λ_{max}= 398 nm) suggests an extended π-conjugation through the polymer main chain. The polymer showed an fluorescence (λ_{max}= 510 nm) somewhat weaker intensity than that of the polyphenylene-butadiynylene.[3]

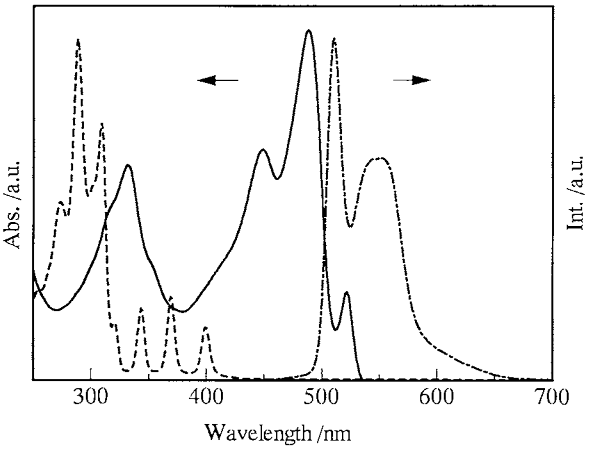


Figure 2. UV-Vis spectra of polymer **4** (——), diphenyloctatetrayne (·········), and fluorescence (ex. 420 nm) spectrum of **4** (– · –) in $CHCl_3$.

In conclusion, a novel conjugated polymer having an octatetraynyl carbon-chain segment in the main chain was successfully synthesized. The octatetrayne segment in the polymer was found to be not only stabilized by the phenylene segment but also contributed to an extended π-conjugation through the main chain.

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8 Elemental analysis: Found C, 83.25; H, 9.5%. Calcd for $(C_{38}H_{52}O_2)_{27}(C_{30}H_{52}O_2Br)Br$: C, 83.4; H, 9.65%. The polymerization terminates with the reaction of 2,5-dialkoxy-1-bromo-4-butadiynylbenzene contaminated in the monomer **3**. The composition is estimated by taking into account a degree of polymerization (about 28).

9 Data for poly(2,5-didodecyloxy-1,4-phenylenebutadiynylene, Raman: 2200 cm^{-1}. Data for 1,8-diphenyloctatetrayne, Raman: 2130 cm^{-1}.

10 ^{1}H NMR data in $CDCl_3$: δ (ppm) 0.87(6H, t, CH_3), 1.23-1.46 (36H, m, CH_2), 1.78 (4H, CH_3CH_2), 3.94 (4H, t, OCH_2), 6.91 (4H, s, Ph), ^{13}C NMR data in $CDCl_3$: 14.0, 22.7, 26.0, 29.1, 29.3, 29.6, 32.0, 70.0, 112.5, 118.1, 156.0 ppm.

11 ^{13}C NMR signals of diphenyloctatetrayne appear at 63.7, 67.2, 74.4, 77.7, 120.5, 128.8, 130.0, and 133.2 ppm.