Synthesis of PPV-Based Conjugated Oligomer Containing Tropone in Main Chain

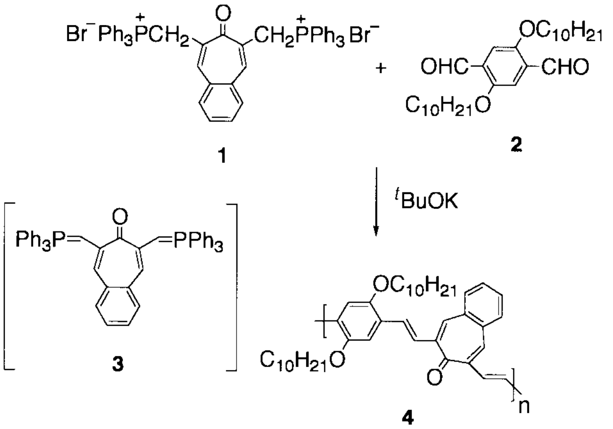
Koji Takagi,* Yukimi Nishikawa, Hideo Kunisada, and Yasuo Yuki
Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555

(Received August 13, 2001; CL-010787)

The synthesis of a tropone-containing PPV-based conjugated oligomer by the Wittig polycondensation was investigated, where the tropone unit was introduced as the conjugated segment. Although the NMR and IR studies revealed the low molecular weight of the resulting product, no side reaction toward the carbonyl group in the tropone ring occurred to maintain the tropone structure as evidenced by the MALDI(Matrix-Assisted Laser Desorption Ionization)-TOFMS spectrum. The UV–vis and PL spectra gave preliminary information on the optical property of the tropone-containing conjugated oligomer.

Conjugated polymers and oligomers have been attracted increasing attention for the application to light-emitting diodes, plastic lasers, sensors, and so on. A number of conjugated polymers such as poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenylene) (PPP), polythiophene (PT), and polyfluorene (PF) have been synthesized in a controlled manner to give many functional materials. Since PPV and its derivatives are among the most promising candidate in organic electroluminescent (EL) devices and nonlinear optical (NLO) materials, many research groups are challenging to produce novel polymers with improved opto-electronic properties. Synthetic chemistry has allowed the manipulation of the HOMO–LUMO band gap energy, the solubility and processability, and the solid-state morphology of polymers. The introduction of various electron-withdrawing substituents onto the vinylene[1] or the phenylene[2] moiety in PPV derivatives was investigated to enhance the electron affinity from the motivation to utilize as the electron transport layer in EL device. The tuning of the optical property was also achieved by the insertion of the non-conjugated segment into the fully conjugated PPV backbone, decreasing the efficient conjugation length.[3]

Tropone, seven-membered fully conjugated ketone, is predicted to be aromatic and energetically very stable compound. Troponoid compounds are useful mesogen in liquid crystalline materials due to their large dipole moment and rigid planar structure.[4] However, to the best of our knowledge, neither the π-conjugated polymer nor oligomer containing tropone derivatives has been studied so far. In this communication, we describe the synthesis of a PPV-based conjugated oligomer including benzotropone unit in the main chain to disclose the Wittig polycondensation behavior and the fundamental optical properties.



Scheme 1.

Table 1. Synthesis of **4** by Wittig polycondensation under various conditions[a]

Solvents[b]	Temp./°C	Yield[c]/%	M_n[d]	M_w/M_n[d]
$CHCl_3$/EtOH	r.t.	78	3,300	1.47
	50	85	3,400	1.64
$CHCl_3$/THF	50	N.P.[e]	-	-
THF/DMF	50	81	3,000	1.93

[a]Conditions: ^{t}BuOK (base) = 4.5 equiv, polymerization time = 3 days. [b]Volume ratio v/v = 1/1. [c]Isolated yield after precipitation into MeOH followed by Soxhlet extraction with MeOH. [d]Estimated by GPC (THF system) using standard polystyrene samples. [e]No polymerization.

The conjugated oligomer (**4**) was synthesized by the Wittig polycondensation between bis(phosphonium) salt (**1**) and dialdehyde (**2**) having long alkoxy chains as the solubilizing group (Scheme 1). **1** was synthesized by the condensation of diethyl ketone and phthalaldehyde, followed by the bromination with *N*-bromosuccinimide, and finally the reaction with triphenylphosphine in 23% total yield.[5] The reaction in $CHCl_3$/EtOH mixed solvent using ^{t}BuOK at room temperature gave **4** in 78% yield as a reddish powder (Table 1).[6] The polymerization in THF/DMF mixed solvent or at an elevated temperature (50 °C) similarly afforded corresponding products in high yields. The isolated **4** readily dissolved into $CHCl_3$ and THF as well as toluene for the sake of long alkoxy chains to obtain a cast film on the glass plate that was too brittle to get a free-standing film. The number-averaged molecular weight and the polydispersity of **4** were estimated by gel permeation chromatography (GPC) in THF using calibration curves made from standard polystyrene samples to be 3,300 and 1.47, respectively, from which the degree of polymerization was found to range from five to six.

The peaks assignable to the terminal aldehyde proton were observed at 10.4 ppm and 1675 cm^{-1} in the ^{1}H NMR and IR spectra, respectively, because the molecular weight of **4** was confined by the low solubility in the polymerization solvents. The peak of the terminal ylide proton also appeared at 2.38 ppm, which was further confirmed by the isolation of bis(ylide) (2.33 ppm) as the crude product from **1** (**3** in Scheme 1). In the

^{13}C NMR spectrum, the peak due to the carbonyl carbon originated from the tropone unit was unambiguously observed at 186.3 ppm. The oligomer was predominantly consisted of the *trans*-vinylene conformation because the methylene proton signal adjacent to the oxygen ($-OCH_2-$) was detected solely at 4.08 ppm in the ^{1}H NMR spectrum and the signal of the C–H out-of-plane bending mode in the *trans*-vinylene structure was found at 968 cm^{-1} in the IR spectrum.[7] The MALDI-TOFMS spectrum of **4** exhibited three signals per degree of the polymerization, which can be clearly assigned to **4** with aldehyde and ylide termini (Figure 1). These results indicate that the oligomerization proceeds through the conventional Wittig polycondensation and unwanted side reaction between the carbonyl group in the tropone skeleton and the ylide is not a serious problem in the present system.

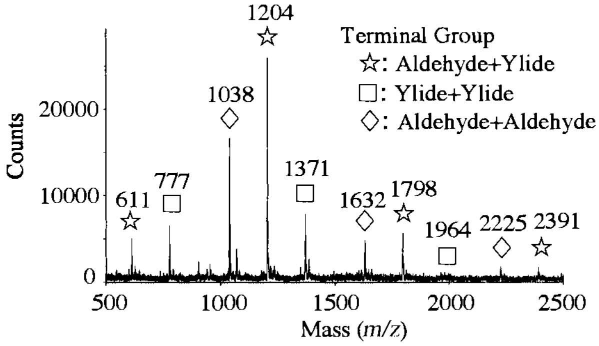


Figure 1. MALDI-TOFMS spectrum of **4** (matrix: α-CHCA (α-cyano-4-hydroxycinnamic acid)).

The thermal stability of **4** was evaluated by the TGA measurement under an air stream. The onset temperature of the decomposition was 230 °C and the 10% weight loss from the original mass was observed at 385 °C. The oligomeric PPV obtained under the same condition (M_n = 3,600) showed the 10% weight loss at 352 °C. Therefore the introduction of the benzotropone unit into the PPV backbone improved the heat-resistance. The absorption and fluorescence spectra of **4** measured in $CHCl_3$ at room temperature are shown in Figure 2. Since the absorption maximum due to the π–π* transition in **4** (432 nm) is blue-shifted compared with that of PPV (485 nm, not shown here), benzotropone may be an insufficient aromatic unit for the complete π-electron delocalization of the main chain, yielding the diminished effective conjugation length. The absorption edge of the spectrum was measured to be 575 nm, from which the HOMO–LUMO band gap energy was calculated to be 2.16 eV. When **4** was excited at 432 nm light in $CHCl_3$, the luminescence having a peak maximum at 564 nm was obtained, which corresponds to orange-yellow light. Since the absorption spectrum of benzotropone can be changed by the protonation of the carbonyl group,[8] the optical character of **4** is expected to be controlled by the acid strength (pK_a) that will be reported in near future.

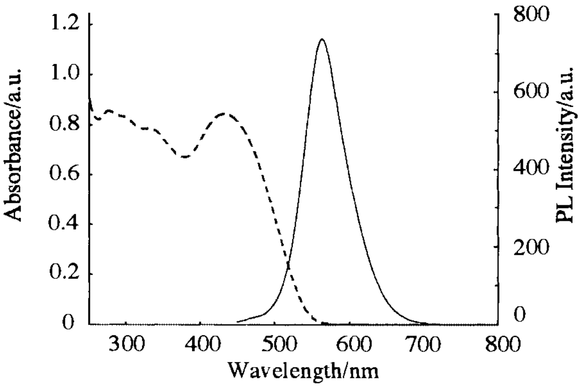


Figure 2. UV–vis absorption (dotted line) and fluorescence (solid line, excited at 432 nm) spectra of **4** measured in $CHCl_3$ (1×10^{-5} M) at room temperature.

We wish to thank Professor T. Kinoshita for the measurement of absorption and fluorescence spectra. This research was financially supported by Yazaki Memorial Foundation for Science and Technology and Tatematsu Foundation.

References and Notes

1 a) N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, *Nature*, **365**, 628 (1993). b) V. Boucard, T. Venazzi, D. Ades, G. Sauvet, and A. Siove, *Polymer*, **38**, 3697 (1997).

2 a) F. H. Boardman, A. W. Grice, M. G. Rüther, T. J. Sheldon, D. D. C. Bradley, and P. L. Burn, *Macromolecules*, **32**, 111 (1999). b) R. Riehn, J. Morgado, R. Iqbal, S. C. Moratti, A. B. Holmes, S. Volta, and F. Cacialli, *Macromolecules*, **33**, 3337 (2000). c) M. R. Pinto, B. Hu, F. E. Karasz, and L. Akcelrud, *Polymer*, **41**, 8095 (2000).

3 a) S.-H. Jung, H. K. Kim, S.-H. Kim, Y. H. Kim, S. C. Jeoung, and D. Kim, *Macromolecules*, **33**, 9277 (2000). b) M. Zheng, A. M. Sarker, E. E. Gürel, P. M. Lahti, and F. E. Karasz, *Macromolecules*, **33**, 7426 (2000). c) M. Belletête, J.-F. Morin, S. Beaupré, M. Ranger, M. Leclerc, and G. Durocher, *Macromolecules*, **34**, 2288 (2001).

4 a) M. Takemoto, A. Mori, and S. Ujiie, *Chem. Lett.*, **1999**, 1177. b) M. Hashimoto, S. Ujiie, and A. Mori, *Chem. Lett.*, **2000**, 758.

5 Spectrum data of **1**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.58 (d, J = 3.96 Hz, 2H, tropone ring), 7.81–7.52 (34H, benzene ring), 5.11 (d, J = 14.56 Hz, 4H, $-CH_2P$). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 183.6, 147.5, 135.4, 134.7, 134.5, 132.1, 131.2, 130.9, 130.7, 130.4, 119.4, 117.6, 29.5, 28.5. IR (KBr) ν (cm^{-1}) 1614, 1567, 1548, 1484, 1438, 1380, 1342, 1108, 738, 690.

6 Spectrum data of **4**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 10.5 (s, 0.2H, terminal aldehyde), 8.01–6.85 (12H, aromatic and vinylene protons), 4.08 (bs, 4H, $-OCH_2-$), 2.38 (s, 0.2H, terminal ylide), 1.89–0.81 (38H, $-OCH_2C_9H_{19}$). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 188.9, 186.3, 156.0, 151.1, 141.1, 140.3, 136.2, 134.6, 133.7, 130.7, 129.2, 127.2, 126.1, 125.4, 124.4, 110.4, 69.4, 31.7, 29.4, 26.2, 22.5, 14.0. IR (KBr) ν (cm^{-1}) 2923, 2852, 1675, 1602, 1585, 1492, 1467, 1423, 1386, 1203, 1027, 968, 750.

7 Y. Pang, J. Li., B. Hu, and F. E. Karasz, *Macromolecules*, **32**, 3946 (1999).

8. E. K.-Jensen, N. Tarköy, A. Eschenmoser, and E. Heilbronner, *Helv. Chim. Acta*, **39**, 786 (1956).