Preparation and Properties of Conjugated Polymers Containing 1,2-Diaryl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene Units

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Conjugated polymers containing sterically protected 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene units were prepared and their properties were investigated. Red shifts of the polymers were observed, compared to the corresponding monomeric species, which indicates extension of the π system on polymerization.

Heteroatom-containing conjugated polymers are of current interest, because of their various functionalities.[1] Conjugated polymers containing π-bonded heavier main group elements are also attractive. Some polymers containing multiply bonded phosphorus atoms[2] have recently been prepared and their properties were investigated: Gates[3] and Protasiewicz[4] prepared π-conjugated polymers containing P=C bond in the main chain. However the polymers are either sensitive to oxygen or moisture,[3] and the extension of the conjugation is supposed to be limited,[4] because the P=C π-plane and the aromatic π-plane of the sterically protecting group are nearly perpendicular in energetically favored conformation.[5] Thus, properties of other types of conjugated system containing multiply bonded phosphorus atoms are of interest.

We have reported preparation of the first polymer containing 3,4-diphosphinidenecyclobutene (abbreviated to DPCB) moieties and its polymer complex,[6,7] as well as catalytic activity of the related DPCB-polymer.[8] However the DPCB units are electronically isolated each other by methylene chains. We now report here preparations and properties of π-conjugated polymers containing the DPCB units. In these polymers, the phosphorus-carbon π-bonds are incorporated in the π-system of the polymer.

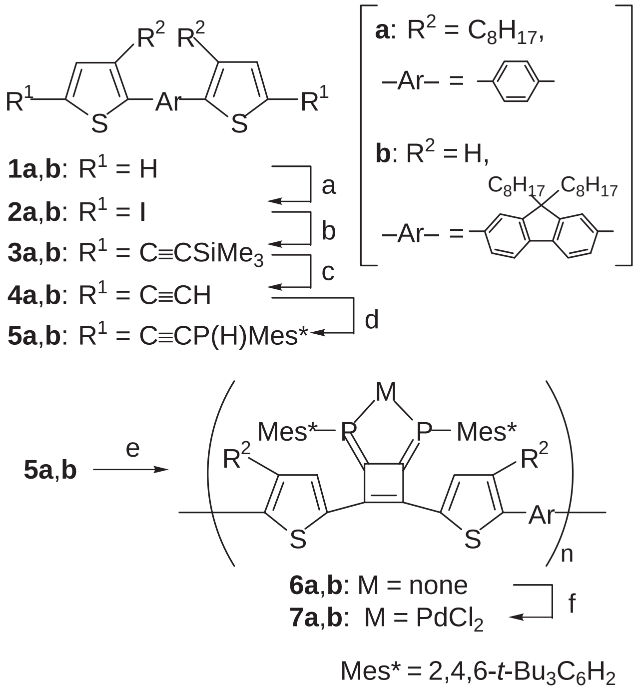
The synthetic route for the polymer is shown in Scheme 1. The DPCB derivatives are normally prepared from ethynylphosphines via bis(phosphaallene) intermediates.[8,9] Thus, we prepared compounds **5a** and **5b**, as monomeric precursors. Compound **1a**,[10] bearing an octyl group to increase polymer solubility, was prepared as follows. A Kumada coupling of 1,4-dibromobenzene with 3-octyl-2-thienylmagnesium bromide in the presence of $Pd_2(dba)_3$ and *N*-heterocyclic carbene ligand [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene chloride][11] afforded **1a** in 89% yield,[12] while **1b**[13] was prepared by the Suzuki coupling of 2,7-diiodo-9,9-dioctylfluorene and 2-thiopheneboronic acid in 91% yield. Reaction of **1a** and **1b** with NIS, followed by the Sonogashira coupling and desilylation, afforded **4a** and **4b** in 63 and 77% yield, respectively (in 3 steps). Compounds **4a** and **4b** were then converted to **5a** (87%) and **5b** (70%) by metallation of **4a** and **4b** with ethylmagnesium bromide in THF followed by reaction with chloro(2,4,6-tri-*t*-butylphenyl)phosphine.[14] Compounds **5c** and **5d** (Chart 1) were also prepared from **4c** and **4d**[15] in a similar manner (**5c**: 40% yield; **5d**: 48% yield).

As the precursors **5a**–**5d** were obtained, preparation of the polymers by a similar method reported previously[8] were studied. Polymers **6a** and **6b** were successfully obtained from **5a** and **5b** in 32 and 38% yield, respectively, after reprecipitation from Et_2O-MeOH. These polymers turned out to be stable in air. The yields for **6a** and **6b** were better than that for alkylene-linked DPCB polymer **8**.[8] On the other hand, attempted preparation of polymers from **5c** and **5d** resulted in the formation of comlplex mixtures of products including oligomeric products ($M_n <$ 3000), probably because propagation was prevented by steric repulsion between the DPCB units.

6a: Red solid; ^{31}P NMR (162 MHz, $CDCl_3$) δ 198.6 [br, (*E*,*Z*)-DPCB moiety], 177.1 [br, (*E*,*Z*)-DPCB moiety], 171.3 [br, (*E*,*E*)-DPCB moiety], and −71.8 (s, terminal moiety); IR (KBr) 1591, 1460 (br), 1392, 1362, 1238, 1203 (br), 1120, and 833 cm^{-1}; M_n 59600, M_w/M_n 72.4.[16]

6b: Red resin; ^{31}P NMR ($CDCl_3$) δ 171.1 [br, (*E*,*E*)-DPCB moiety] and −71.6 (s, terminal moiety); IR (KBr) 1593 (br), 1460 (br), and 800 cm^{-1}; M_n 4500, M_w/M_n 4.4.

It should be mentioned that several problems for the alkylene-linked DPCB polymer **8** have been overcome in the case of **6**: (i) The solubility of **6** for common organic solvents was improved; (ii) in the preparation of **6**, intramolecular cyclization



Scheme 1. (a) NIS, $CHCl_3$, AcOH; (b) $Me_3SiC{\equiv}CH$, NEt_3, CuI, $Pd(OAc)_2$, PPh_3, DMF; (c) NaOH–MeOH, THF; (d) (i) EtMgBr, THF; (ii) Mes*P(H)Cl; (e) (i) *n*-BuLi, DME; (ii) $BrCH_2CH_2Br$, then reflux in toluene; (f) $PdCl_2(MeCN)_2$, THF.

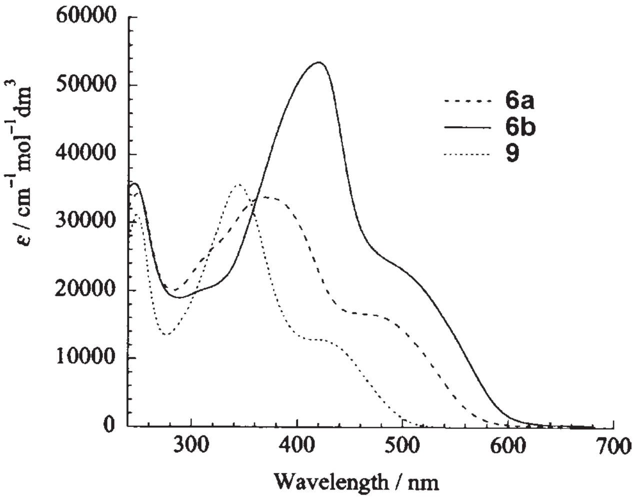


Figure 1. UV–vis spectra of **6a**, **6b** and **9** in CH_2Cl_2. Molar absorption coefficients for **6a** and **6b** are calculated based on the formal repeating unit.

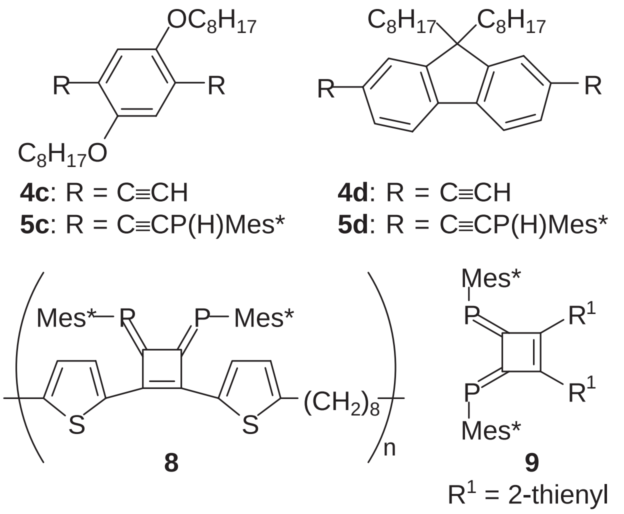


Chart 1.

was suppressed to lead to better yield due to the rigidity of linkers; (iii) polymer **6** is expected to show better electronic interaction between the DPCB moieties, due to π-conjugation: Figure 1 shows UV–vis spectra of **6a** and **6b** and the related compound **9**.[9c] Apparent red shifts were observed in the π–π^* absorption bands of **6a** and **6b**, compared with that of **9**.[17] These facts indicate relatively good π conjugation in **6a** and **6b**. The degree of the red shift is **6a** $<$ **6b**, probably because the octyl group on the thienyl ring of **6a** hinders coplanarity between the thienyl and phenylene moieties.

Next, transition metal complex formation of the polymers was investigated. When 1 molar amount of $PdCl_2(MeCN)_2$ was allowed to react with the polymers in THF at room temperature for 3 h, dark brown polymer complexes **7a** and **7b** were obtained in ca. 65% and 70% yield, respectively. **7a**: ^{31}P NMR (THF-C_6D_6) δ 152 (br.); IR (KBr) 1718, 1591, 1462, 1437, and 1122 cm^{-1}; **7b**: ^{31}P NMR (THF-C_6D_6) δ 150 (br.); IR (KBr) 1724, 1595, 1460, 1265, 1122, 1072, and 802 cm^{-1}.[18]

This is the first example of the complex formation of conjugated polymer containing double bonded phosphorus. These polymer metal complexes can be regarded as an example of ‘assembled complexes,’ which are of current interest.[19]

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