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Synthesis of Novel π-Conjugated Polymer Having an Enyne Unit by Palladium-Catalyzed Three-Component Coupling Polymerization and Subsequent Retro-Diels−Alder Reaction

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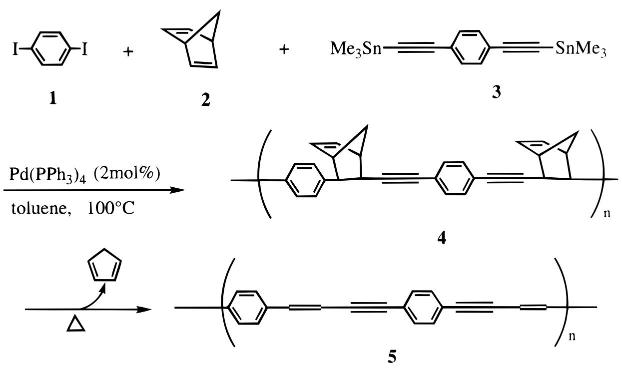
Development of new π-conjugated polymers is of importance because of their potential application in advanced materials with electroconductive, liquid crystalline, optical nonlinear properties, etc.[1,2] The palladium-catalyzed polymerization system represents a useful strategy for the preparation of these polymers. For instance, the application of the Suzuki coupling,[3] the Stille coupling,[4] the Sonogashira coupling,[5] and the Heck reaction[6] enables to supply a wide variety of conjugated polymers, including polyarylenes, poly(arylene−ethynylene)s, and poly(arylene−vinylene)s.

On the basis of the palladium-catalyzed ternary coupling reactions, we reported recently the three-component polycondensations using bis(allene)s[7] or bis(acetylene)s[8] to obtain highly functionalized polymers such as poly(arylene−vinylene)s consisting of the building blocks originating from the three kinds of monomers. That is, the application of appropriate three-component coupling reactions to the polycondensation systems might provide a new synthetic method for sequentially controlled functional polymers such as π-conjugated polymers with additional features. To explore other possibilities and to prepare novel π-conjugated polymers having enyne moieties as repeating units with ordered sequence, we report herein the three-component coupling polymerization of diiodobenzene (**1**), norbornadiene (**2**), and bis(organostannane) (**3**) and the subsequent retro-Diels−Alder reaction (Scheme 1).

Scheme 1



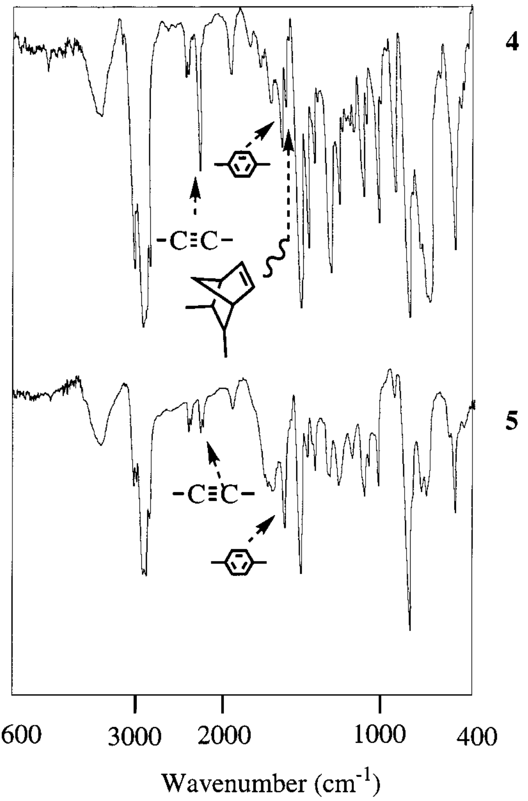


Figure 1. IR spectra of the polymers (**4** and **5**).

On the basis of the coupling reaction reported by Kosugi et al.,[9] the three-component coupling polymerization of *p*-diiodobenzene (**1**), norbornadiene (**2**), and 1,4-bis[(trimethylstannyl)ethynyl]benzene (**3**) was carried out at 100 °C for 2 days in toluene by using Pd(PPh$_3$)$_4$ as a catalyst (2 mol %).[10] A polymer with a number-average molecular weight (M_n) of 13 500 and a polydispersity of 1.48 (GPC, relative to polystyrene) possessing sequentially three regular building blocks (**4**) was obtained in 82% yield. The pale yellowish powdery polymer (**4**) thus obtained is soluble in common organic solvents and has a good film-forming character when cast from CHCl$_3$. The structure of **4** was confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectra and elemental analysis.[11] By thermogravimetric analysis (TGA), the onset of the retro-Diels−Alder reaction was observed at ca. 116 °C (lower than that of a model compound by ca. 62 °C),[12,13] and the 10% weight loss (T_{d10}) was observed at 203 °C. The polymer (**4**) is stable at room temperature. However, when heated at 165 °C under vacuum either in solution or after being processed into thin film, **4** was converted into a polymer having enyne units (**5**) via the retro-Diels−Alder reaction with release of cyclopentadiene (Scheme 1). Although the resulting polymer (**5**) is insoluble in organic solvents, the progress of the reaction could be monitored by the IR spectra of the polymer. As shown in Figure 1, the C=C stretching of the norbornene moieties in **4** at 1570 cm^{-1} completely disappeared, and the characteristic peaks for *p*-phenylene units at 837, 1013, 1404, 1506, and 1601 cm^{-1} could be observed prominently after the reaction. The *trans*- and *cis*-alkene C−H bendings were also observed at 1672 and 720 cm^{-1}, respectively.

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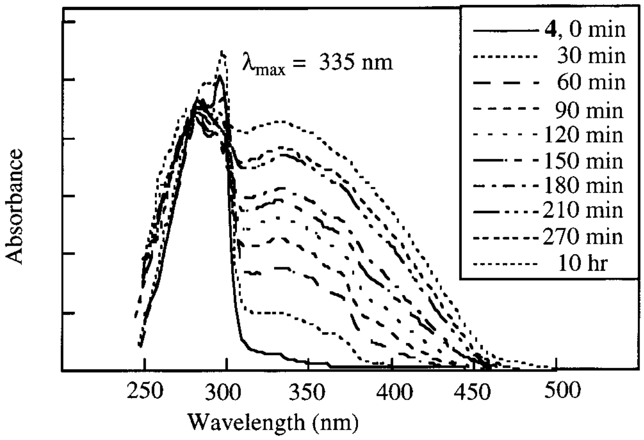

Figure 2. Change in UV/vis spectra by retro-Diels−Alder reaction under vacuum at 165 °C (traces taken every 30 min).

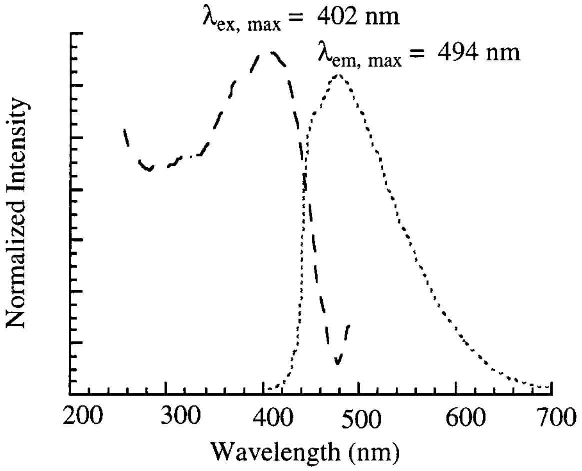

Figure 3. Emission (···) and excitation (- - -) spectra of **5**.

During the thermal transformation process, we could observe a gradual color change from colorless to yellow which might be due to an increase in the average degree of conjugation along the polymer backbone. This color change can be monitored by UV/vis spectroscopy: as the reaction progressed, the absorption spectrum of the polymer displayed a clear red shift and its λ_{max} and shoulder reached 335 and ca. 500 nm, respectively (Figure 2). Emission and excitation spectra of the resulting polymer (**5**) were acquired on thin film with optical absorption maxima of 0.5 (Figure 3), from which their maxima were observed at 494 and 402 nm, respectively.

The three-component polymerization might be suitable for preparation of a variety of functional polymers including π-conjugated polymers, since three building blocks are expected to be incorporated into the polymer structures with ordered sequence. Synthesis of soluble π-conjugated polymers having enyne moieties as repeating units and the detailed study of their properties are currently ongoing.

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(10) To a test tube equipped with a magnetic stirrer chip were added $Pd(PPh_3)_4$ (0.0231 g, 0.01 mmol), **1** (0.165 g, 0.50 mmol), **2** (0.9214 g, 10 mmol), **3** (0.226 g, 0.5 mmol), and toluene (2 mL), and the mixture was kept stirring at ambient temperature for 15 min under nitrogen. The tube was then sealed under reduced pressure. After the reaction at 100 °C for 2 days, the reaction mixture was precipitated with methanol and then with *n*-hexane. The precipitate was freeze-dried from benzene. **4**: yield 82% (0.156 g, 0.41 mmol).

(11) **4**: ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.64 (>CH_2 (7), 2H), 2.11 (>CH_2 (7), 2H), 2.89−3.09 (HC (1), HC (2), HC (3), HC (4), 8H), 6.20−6.38 (−HC═CH− (5, 6), 4H), 6.61−7.15 (−C_6H_4−, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 37.3, 46.0, 46.7, 48.1, 49.7 (C (1), C (2), C (3), C (4), C (7)), 84.3, 93.9 (−C≡C−), 122.6, 128.0, 130.7, 136.5 (−C═C− (5, 6), 140.0. IR (KBr): 3142, 3057, 2970, 2872, 2222 (−C≡C−), 1905, 1786, 1720, 1664, 1603, 1572 (C═C in norbornene), 1543, 1508, 1452, 1404, 1377, 1313, 1253, 985, 904, 837, 761 cm^{-1}. Anal. Calcd for $C_{30}H_{24}$: C, 93.71%; H, 6.29%. Found: C, 91.58%; H, 6.42%; Cl, 0.55%. The observed lower carbon content is most probably due to contamination of the palladium catalyst.

(12) To estimate the thermal stability of the model compound (*cis, exo*-1,4-bis[2-{2-(4-dodecyloxyphenyl)bicyclo[2,2,1]heptenyl}ethynyl]benzene), TGA analysis was carried out under nitrogen (at a heating rate of 10 °C/min), from which the weight loss started at 178 °C and the 10% weight loss was observed at 231 °C.

(13) TGA data of the polymer **4** (taken at a heating rate of 10 °C/min) indicate that the retro-Diels−Alder reaction proceeded at lower temperature compared with that of the model compound. This difference might be explained by the difference in the thermodynamic energy between the starting norbornene and enyne derivatives.

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