



Polymer communication

Synthesis of sequential poly(1,3-phenyleneethynylene)-based polyradicals and through-space antiferromagnetic interaction of their solid state



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ABSTRACT

Some 1,3-PPE-based polyradicals with pendent phenoxy radicals whose repeating unit consisted of four 1,3-phenyleneethynylene units were synthesized via polymerization between monomers and trimeric monomers in the presence of the Pd(PPh₃)₄ complex catalysts. The ESR spectra of the polyradicals in dichloromethane showed unimodal broad signals. For the solid samples which were prepared from the dichloromethane solution by evaporating the solvent and by drying in vacuo, the signal intensity decreased with broadening of peak-to-peak line-width (ΔH_{pp}). However, the ESR spectra almost recover to the initial intensity and shapes due to redissolving in dichloromethane. In particular, the decrease of doubly integrating the ESR signal (I_{ESR}) was more remarkable for the polyradical bearing galvinoxyl and phenoxy residues than others. This behavior suggests that strong antiferromagnetic interaction partially arose for the polyradical.

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1. Introduction

The magnetic properties of π -conjugated polyradicals are one of the most attractive research fields about the new functional polymer materials [1–4]. Numerous π -conjugated polymers substituted with pendent radicals have been synthesized and characterized [5,6]. Ferromagnetic through-bond interaction between the pendent spins was theoretically predicted for regioregular head-to-tail π -conjugated macromolecules possessing conjugated pendent radicals by using simple polyene models and other π -conjugated polymers [7–9], and some of them actually exhibited the expected ferromagnetic behavior through their π -conjugated backbone [10–27]. However, the through-space magnetic interaction between the polyradical chains has not been investigated well. Most of polyradicals consisted of one or two monomer species, and variety of close packing between monomers was limited. Actually, their magnetic properties between polyradical chains only exhibited weak antiferromagnetic interaction. Sequential polymers have repeating unit consisting of some kind of monomers, which would

lead to regulated close packing between monomers, and some sequential polymers exhibited regulated higher order structure [28–31]. Poly(phenyleneethynylene) (PPE) is one of the most possible backbone structure for magnetic π -conjugated polyradicals and various PPE-based polyradicals have been investigated [15,16,32–39]. PPE would be effective backbone structure for alignment of polymer chain because the linear ethynylene nature restricts flexibility of the conformation. Actually, some poly(1,3-phenyleneethynylene) (1,3-PPE) derivatives formed helical structure [40–42] and extended-chain structure [42]. In this study, we synthesized some 1,3-PPE-based polyradicals (**1b–3b**) with pendent phenoxy radicals whose repeating unit consisted of four 1,3-phenyleneethynylene units, and discussed their magnetic interaction using ESR.

2. Experimental section

2.1. Materials

(3,5-Diiodophenyl)hydrogalvinoxyl (**4**) was synthesized according to the literature procedures [39]. Tetrakis(triphenylphosphine)palladium (0) (Pd(PPh₃)₄) (Aldrich Co.) was

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used without further purification. Other conventional reagents were used as-received or purified by conventional methods.

2.2. Synthesis of monomers and trimeric monomers

The monomers and trimeric monomers were synthesized as shown in Schemes 1 and 2 based on the previously described procedures [19,39,43,44].

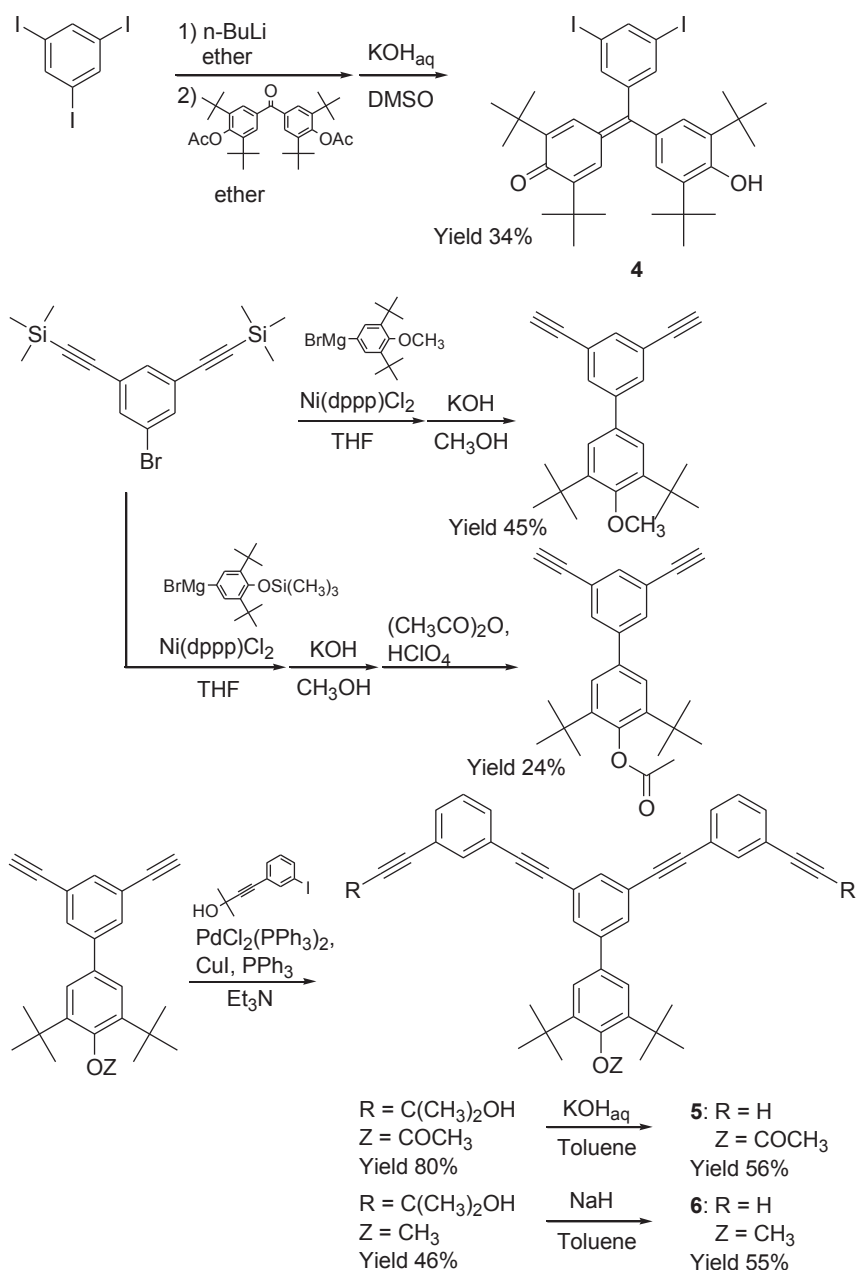
2.2.1. Trimeric monomer 5

The crude product was purified by silica gel column separation with chloroform/hexane (3/2 v/v) as an eluant to give the trimeric monomer **5**. $^1\text{H NMR}$ (CDCl_3 , 400 MHz; ppm): δ 7.70 (dd, 2H, $J = 1.4$, 1.3 Hz, ArH), 7.67 (t, 1H, $J = 1.4$ Hz, ArH), 7.66 (d, 2H, $J = 1.4$ Hz, ArH), 7.54 (ddd, 2H, $J = 7.8$, 1.4, 1.4 Hz, ArH), 7.52 (s, 2H, PhH), 7.47 (ddd, 2H, $J = 7.8$, 1.4, 1.4 Hz, ArH), 7.33 (dd, 2H, $J = 7.8$, 7.8 Hz, ArH), 3.11 (s,

2H, $\text{C}\equiv\text{CH}$), 2.38 (s, 3H, COCH_3), 1.42 (s, 18H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C NMR}$ (CDCl_3 ; ppm): δ 171.55, 143.03, 142.22, 136.52, 135.19, 133.16, 132.03, 131.93, 130.40, 128.49, 125.34, 123.67, 123.32, 122.55, 89.23, 88.99, 83.11, 77.88, 35.63, 31.51, 22.69. IR (KBr pellet; cm^{-1}): 3295 ($\nu_{\text{C-H}}$), 2968 ($\nu_{\text{C-H}}$, t-Bu), 1761 ($\nu_{\text{C=O}}$).

2.2.2. Trimeric monomer 6

The crude product was purified by silica gel column separation with ethyl acetate/hexane (1/5 v/v) as an eluant to give the trimeric monomer **6**. $^1\text{H NMR}$ (CDCl_3 , 400 MHz; ppm): δ 7.74 (dd, 2H, $J = 1.4$, 1.3 Hz, ArH), 7.65 (m, 3H, ArH), 7.54 (ddd, 2H, $J = 7.8$, 1.4, 1.4 Hz, ArH), 7.47 (ddd, 2H, $J = 7.8$, 1.4, 1.4 Hz, ArH), 7.46 (s, 2H, PhH), 7.34 (dd, 2H, $J = 7.8$, 7.8 Hz, ArH), 3.74 (s, 3H, OCH_3), 3.11 (s, 2H, $\text{C}\equiv\text{CH}$), 1.50 (s, 18H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C NMR}$ (CDCl_3 ; ppm): δ 159.74, 144.20, 142.47, 135.18, 135.17, 133.67, 132.01, 131.92, 130.39, 130.22, 128.49,



Scheme 1. Synthesis of monomer **4**, trimeric monomers **5** and **6**.

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