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Poly(*p*-ethynylphenyl)galvinoxyl: Formation of a New Conjugated Polyradical with an Extraordinarily High Spin Concentration

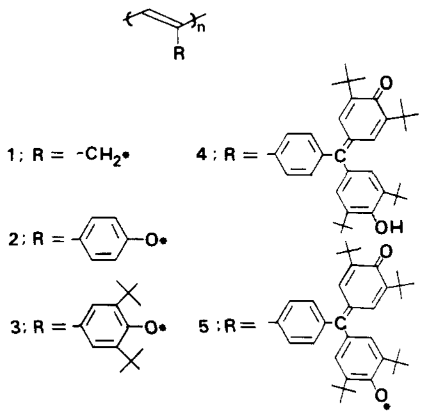
Recently, synthesis of organic polyradical macromolecules with a π-conjugated system has been of interest because magnetically cooperative phenomena are expected between the unpaired spins even in purely molecular-based materials.[1a–c] Each radical center could interact directly and/or indirectly through the π-electron system, and these macromolecules show, in principle, superparamagnetic properties if there is a ferromagnetic interaction among the radical centers. While theoretical calculations[2–5] have been proposed for various model compounds such as 1 and 2 (Chart I), only a few polymers with elucidated chemical structures have been synthesized[6,7] due both to difficulties in synthesis and to a lack of chemical stability. For example, in a previous paper[6] we reported the synthesis of poly[(3,5-di-*tert*-butyl-4-oxyphenyl)acetylene] (**3**) as a model compound of poly[(4-oxyphenyl)acetylene] (**2**)[5] having a directly interacted spin system and also the formation of a conjugated stable polyradical macromolecule with chemical stability and a high spin concentration.

Tyutyulkov showed, on the other hand, the possibility of an indirect magnetic interaction for polyradical macromolecules with localized radical centers in each monomer unit.[3] This paper describes the synthesis of poly[4-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]phenylacetylene] (abbreviated as poly[(*p*-ethynylphenyl)hydrogalvinoxyl]) (**4**) and also the formation of its polyradical macromolecule, **5**, through chemical oxidation. **5** is one of the model polymers with an indirect magnetic interaction; the unpaired electron is mainly localized at the phenylgalvinoxyl side chain, whose spin density is distributed mainly over the galvinoxyl substituent, but also over the phenyl ring to some extent by a spin polarization mechanism.[8]

The corresponding monomer, (*p*-ethynylphenyl)hydrogalvinoxyl (**6**), was synthesized by modifying an organometallic synthetic pathway reported by Kurreck.[9] Methyl 4-[(trimethylsilyl)ethynyl]benzoate[10] was treated with (2,6-di-*tert*-butyl-4-lithiophenoxy)trimethylsilane, followed by elimination of three protecting trimethylsilyl groups with aqueous KOH in THF (Scheme I).[11] **6** was polymerized with W-, Mo-, or Rh-based catalysts according to the polymerization procedure for substituted acetylenes.[12,13] **4** was obtained as a dark red powder and was soluble in $CHCl_3$, benzene, tetrahydrofuran, alcohols, and acetone.[14] The $\bar{M}_n$ of **4** was (1–2) × 10^4 (GPC, polystyrene standard) depending on the polymerization conditions.

The UV–vis spectrum of **4** showed a strong absorption at 419 nm (in CH_2Cl_2, $\epsilon = 2.4 \times 10^4$ L/(cm·mol) monomer unit) attributed to the quinoid chromophore of the hydrogalvinoxyl residue. Treatment of the polymer solution with excess alkali yielded the dark blue phenolate anion of **4** (λ_{max} = 600 nm). Strong absorption at 450 nm was observed with an increase in the ESR signal intensity, when the **4** solution was carefully oxidized with fresh PbO_2 or alkaline $K_3Fe(CN)_6$ under an oxygen-free atmosphere.

Chart I



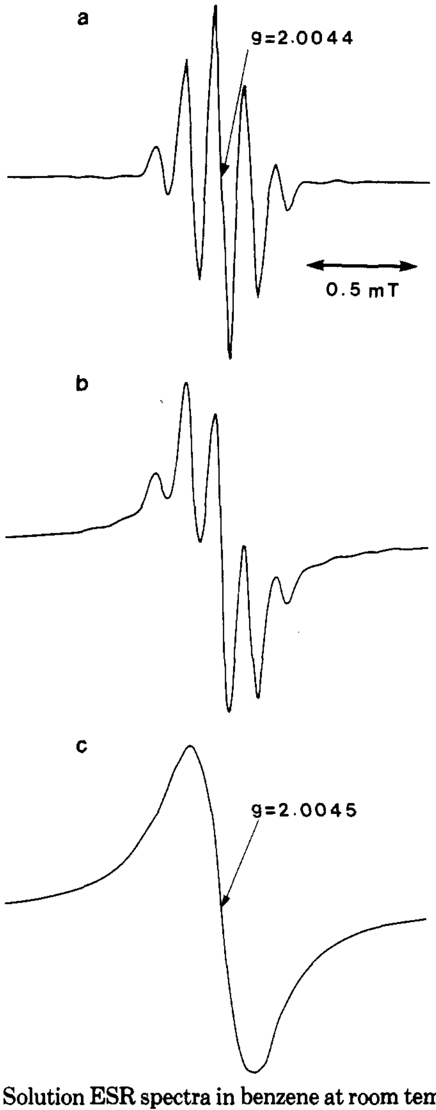


Figure 1. Solution ESR spectra in benzene at room temperature: (a) oxidized monomer **6**; (b) polyradical macromolecule **5** immediately after oxidation; (c) **5** with high spin concentration (70 mol %, 3.6 × 10^{-4} mol/L).

The solution ESR spectrum of the oxidized monomer **6** gives a hyperfine structure at a *g*-value of 2.0044 with a relative signal intensity of 1:4:6:4:1 attributed to the magnetic interaction of an unpaired electron with four equivalent protons (Figure 1a). Polyradical macromolecule **5** with a low spin concentration (<10 mol %) also gives a broadened but similar spectrum (b) to that of (a), which indicates that the unpaired electron is localized mainly over the galvinoxyl substituent in **5**. The spectrum becomes broader and coalesces to a single broad line (c) with the increase in spin concentration, suggesting that local spin concentration within the macromolecular domain is relatively high even in the dilute solution. This broadening can be explained by an intrachain dipole–dipole interaction due to the reduced distance among the polymer-bound radical sites accompanying the increase in spin concentration. The spin concentration in the solution reached 4.9 × 10^{23} spins/monomer mol. GPC curves of **5** were almost the same as those of **4**, which supports the notion

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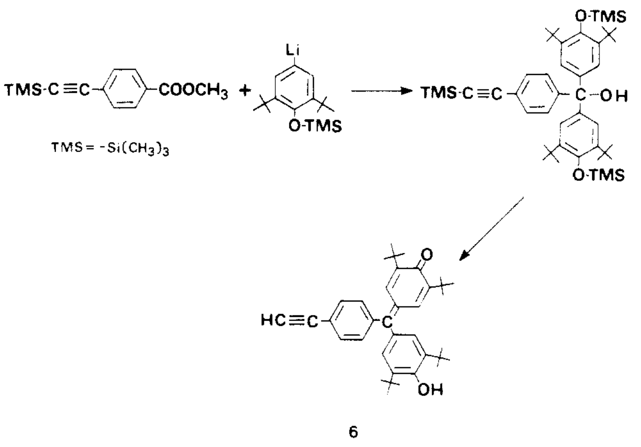
Scheme I



that oxidation does not bring about oxidative degradation or cross-linking of the main chain.

5 was chemically stable in the solid state and had a spin concentration of 4.8×10^{23} spins/mol, which is the highest value for the polyradical macromolecule already reported. The ESR signal intensity in the solid state was proportional to the reciprocal of the absolute temperature in the temperature range 120–320 K, which indicates that the formed unpaired spins obey Curie's law. The line width of the ESR signal in the solid state is 0.25 mT at room temperature, but it rapidly increased below 170 K and reached 1.70 mT at 120 K, which suggests a short-range ordering among the unpaired spins.

Magnetic properties of the polyradical at low temperature will be reported in the following paper.

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(11) 4-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]phenylacetylene. Yield: 42%, bright orange crystals. Mp: 244 °C. MS: m/z 522 (M^+). ^1H NMR ($CDCl_3$, Me_4Si standard): δ 7.70–7.02 (m, 8 H, phenyl and quinoid), 5.50 (s, 1 H, hydroxy), 3.21 (s, 1 H, ≡CH), 1.40 (s, 18 H, *tert*-butyl), 1.30 (s, 9 H, *tert*-butyl), 1.22 (s, 9 H, *tert*-butyl). ^{13}C NMR ($CDCl_3$, Me_4Si standard): δ 83.5 (*C*≡CH), 78.2 (C≡CH). IR (KBr pellet, cm^{-1}): 3635 (ν_{-OH}), 3300 ($\nu_{\equiv CH}$), 2100 ($\nu_{C\equiv C}$). Anal. Calcd for $C_{37}H_{46}O_2$: C, 85.0; H, 8.9. Found: C, 84.8; H, 9.2.

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(14) Yield: ca. 3%, orange powder. IR (KBr pellet, cm^{-1}): 3635 (ν_{OH}), 730 ($\delta_{C=CH}$). ^1H NMR (THF-d_8, Me_4Si standard): δ around 1.0–1.4 (*tert*-butyl), 6.0–7.5 (phenyl, quinoid, methine). $\nu_{\equiv CH}$ and $\nu_{C\equiv C}$ in the IR spectrum and peaks assignable to the ethynyl group in ^1H and ^{13}C NMR spectra given in ref 11 had completely disappeared. Anal. Calcd for $(C_{37}H_{46}O_2)_n$: C, 85.0; H, 8.9. Found: C, 84.6; H, 9.0.

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