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(5) The inherent viscosity of the copolymer used in the present experiments was 0.37 dL/g (0.2% in 50 mM phosphate, pH 7.54, 28 °C).

(6) Samples were irradiated at room temperature in borosilicate glass vials in a Rayonet RMR 400 minireactor equipped with four 350 nmHg vapor lamps and a merry-go-round apparatus. Polymer concentration was 0.5 mg/mL.

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(9) Calorimetric samples were prepared by adding 1.5 mg of DPPC to 1.5 mL of a 1.0 mg/mL solution of the copolymer in 50 mM potassium phosphate buffer, pH 7.55. This suspension was heated to ca. 45 °C for 1 min and agitated on a vortex mixer for 1 min. The heating and agitation were repeated 3 times, and the sample was degassed under vacuum. Calorimetric scans were recorded on a Microcal MC-1 scanning microcalorimeter at a heating rate of 15 °C/h.

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(12) Samples for determination of dye release rates were prepared by adding 15–20 mg of EYPC to 2.0 mL of a 200 mM calcein solution in 50 mM potassium phosphate buffer, pH 7.14. The sample was agitated on a vortex mixer at room temperature for 3 min and sonicated (Branson Sonifier) at 0 °C for 30 min at 30 W. The sample was then centrifuged in a Beckman JA-20 rotor at 15 000 rpm and 10 °C for 30 min. The top 1.5 mL of the sample was placed on a Sepharose CL-4B column (1.6 × 20 cm) and eluted at 5 °C with 50 mM phosphate buffer; 1.5-mL fractions were collected. Unilamellar vesicles with entrapped calcein eluted in fractions 15–27 as determined by following the optical density of the fractions at 250 nm. Vesicle fractions were adjusted to pH 7.55 with 0.1 N NaOH. Unilamellar vesicles (0.75 mL) were added to 0.75 mL of a 1.0 mg/mL polymer solution in 50 mM phosphate buffer, pH 7.55. The fluoresence of the samples at 530 nm was monitored as a function of time on a Perkin-Elmer MPF-66 spectrometer, with excitation at 495 nm.

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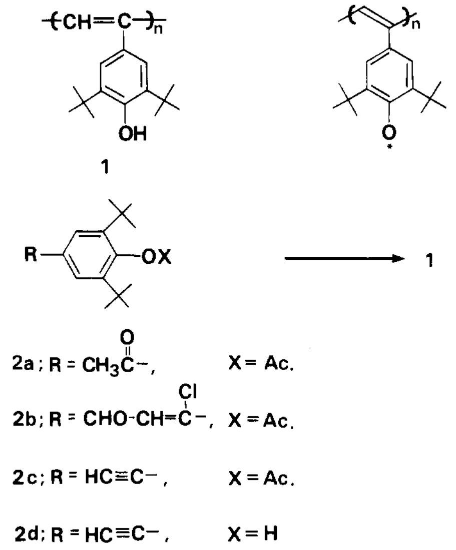
Poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene]: Formation of a Conjugated Stable Polyradical

There is currently a great interest in preparing organic polymers containing a stable radical.[1-3] Poly[(4-hydroxyphenyl)acetylene] is theoretically expected[4,5] through its oxidation to yield a π-conjugated organic polyradical or a macromolecule having its full spin proportional to its molecular weight. However, poly[(4-hydroxyphenyl)acetylene] and its derivatives have not been synthesized. This paper describes the synthesis of poly[(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene] (1) and the formation of its polyradical as shown in the idealized Scheme I.

4-Acetyl-2,6-di-*tert*-butylphenyl acetate (**2a**) prepared as in the literature[6] was converted by a Vilsmeier reaction[7] to β-chloro-3,5-di-*tert*-butyl-4-acetoxycinnamaldehyde (**2b**).[8] The aldehyde was hydrolyzed to yield (3,5-di-*tert*-butyl-4-acetoxyphenyl)acetylene (**2c**).[9] **2c** was deacetylated with $LiAlH_4$ in THF to give (3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene (**2d**).[10]

Scheme I



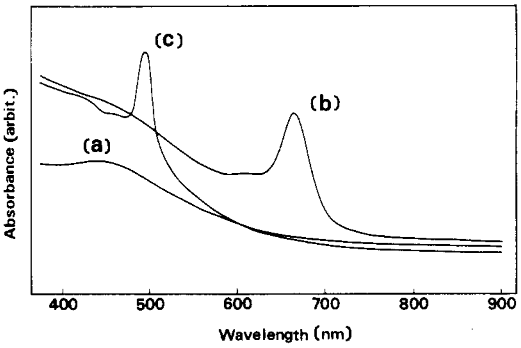


Figure 1. UV–vis spectra of 1: (a) 1 in benzene; (b) 1 in the methanol containing excess KOH; (c) 1 after the oxidation with fresh PbO_2 in benzene.

2d was polymerized with WCl_6 in CCl_4, according to the polymerization procedure for substituted acetylenes.[11] 1 was obtained as a dark red powder and was soluble in $CHCl_3$, benzene, tetrahydrofuran, alcohol, and acetone. The structure represented in 1 was confirmed by elemental analysis and IR.[12] The molecular weight of 1 was 1–3 × 10^4 (GPC, polystyrene standard) with $\bar{M}_n/\bar{M}_w$ = 1.6–2.0.

UV–vis spectrum of 1 (Figure 1) showed a broad absorption with a maximum at 450 nm that extended to 600 nm, which indicates a fairly long π-conjugated system in the main chain. Treatment of the polymer solution with excess alkali yields the dark green phenolate anion of 1 (λ_{max} = 655 nm). Careful oxidation of 1 with fresh PbO_2 under an oxygen-free atmosphere gives a deep brownish solution. A strong absorption band appeared at 495 nm, corresponds to the 2,6-di-*tert*-butyl-4-phenylphenoxy radical (λ_{max} = 496 nm[13]), and occurs at wavelengths longer than that of 2,6-di-*tert*-butyl-4-alkylphenoxy radicals (λ_{max} = ca. 400 nm[14]). This indicates that the phenoxy substituent is conjugated with the polyacetylene main chain to some extent. The absorption intensity of the oxidized 1 solution suggested formation of the phenoxy radical of 1 in high concentration and stayed constant upon standing at room temperature over a day. This radical formation of 1 is in contrast to the radical formation of the corresponding low molecular phenols, e.g. 3,5-di-*tert*-butyl-4-hydroxycinnamate; the latter had been reported to give bisquinone methides irreversibly.[15] The sterically crowded structure of 1 probably suppresses bond formation between unpaired electrons.

ESR spectra of the oxidized 1 solutions show strong broad absorptions with hyperfine splitting, which give a

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high spin concentration of 5.4–7.1 × 10^{22} spins per molar (hydroxyphenyl)acetylene residue (2.3–3.0 × 10^{20} spins/g). Surprisingly, these oxidized polymers are found to be paramagnetic even in the solid state (3.8–6.2 × 10^{22} spins/mol), indicating that the formed radical species are very stable, probably due to a resonance stabilization of unpaired electrons through the conjugated main chain and to a steric effect of the polymer chain. IR spectra showed the strong peaks at 1660 and 1610 cm^{-1} attributed to phenoxy radical, and the O–H stretching vibration at 3630 cm^{-1} had completely disappeared. GPC curves of 1 after oxidation were the same as that of 1: This is consistent with the assumption that the oxidation does not bring about oxidative degradation or cross-linking of the main chain.

Magnetic properties of the polyradical will be reported in a future paper.

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Registry No. 1, 116233-36-4.

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(8) Yield 51% (based on 2,6-di-*tert*-butylphenol); pale yellow powder; mp 127–128 °C; ^1H NMR ($CDCl_3$, Me_4Si standard, ppm) δ 10.2 (1 H, d, aldehyde), 7.7 (2 H, s, phenyl), 6.6 (1 H, d, methine), 2.3 (3 H, s, acetoxy), 1.4 (18 H, s, *t*-Bu); IR (KBr pellet, cm^{-1}) 1760 ($\nu_{C=O}$ acetoxy), 1670 ($\nu_{C=O}$ aldehyde), 1600 ($\nu_{C=C}$). Anal. Found: C, 67.5; H, 7.4; Cl, 10.6. Calcd ($C_{19}H_{25}O_3Cl$): C, 67.7; H, 7.5; Cl, 10.5.
(9) Yield 70%; white crystal; mp 59 °C; ^1H NMR ($CDCl_3$, Me_4Si standard, ppm) δ 7.4 (2 H, s, phenyl), 3.0 (1 H, s, $\equiv CH$), 2.3 (3 H, s, acetoxy), 1.3 (18 H, s, *t*-Bu); IR (KBr pellet, cm^{-1}) 3300 ($\nu_{\equiv CH}$), 2100 ($\nu_{C\equiv C}$), 1760 ($\nu_{C=O}$ acetoxy). Anal. Found: C, 79.3; H, 8.7. Calcd ($C_{18}H_{24}O_2$): C, 79.4; H, 8.9.
(10) Yield 92%; white crystal; mp 107 °C; ^1H NMR ($CDCl_3$, Me_4Si standard, ppm) δ 7.2 (2 H, s, phenyl), 5.2 (1 H, s, hydroxy), 2.7 (1 H, s, CH), 1.40 (18 H, s, *t*-Bu); IR (KBr pellet, cm^{-1}) 3620 (ν_{O-H}), 3270 ($\nu_{\equiv C-H}$), 2100 ($\nu_{C\equiv C}$). Anal. Found: C, 83.3; H, 9.6. Calcd ($C_{16}H_{22}O$): C, 83.5; H, 9.6. Preparation of **2d** has been reported previously (Hauff, S.; Krauss, P.; Rieker, A. *Chem. Ber.* **1972**, *105*, 1446) by condensation of 2,6-di-*tert*-butyl-*p*-benzoquinone and lithium acetylide and by the following reduction of the quinol, but the reported yield was less than 1%.
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(12) Anal. Found: C, 83.2; H, 9.4; O, 6.7. Calcd ($(C_{16}H_{22}O)_n$): C, 83.5; H, 9.6; O, 6.9. IR (KBr pellet, cm^{-1}) 3630 (ν_{O-H}), 1600 ($\nu_{C=C}$), 900, 865 ($\delta_{C=C}H$), $\nu_{\equiv C-H}$ and $\nu_{C\equiv C}$ given in the ref 10 had completely disappeared; ^1H NMR ($CDCl_3$, Me_4Si standard, ppm) δ 1.4 (*t*-Bu), 5.0 (hydroxy), 6.8 (phenyl or methine). But the ^1H and ^{13}C NMR spectra were broadened probably due to the cis- and trans-mixed polyacetylene structure as reported for poly(phenylacetylene) (Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975**, *8*, 717).
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Alkoxy-Substituted Poly(diarylsilanes): Thermochromism and Solvatochromism

Soluble, high molecular weight polysilane polymers are attracting attention as an interesting new class of radiation-sensitive materials for which a number of applications have been described.[1] The electronic structure of these materials is particularly interesting since the chromophore is the σ-bonded polymer backbone.[2,3,5d] The absorption spectra depend not only on the nature of the substituents but also on molecular weight[4] and the conformation of the backbone.[5]

Recently, we have reported that poly(bis(*p*-alkylphenyl)silanes) are the most red shifted of all polysilane derivatives and have tentatively ascribed this observation to the presence of long, all-trans backbone segments even in solution.[5c,6] Some further support for this hypothesis based on light-scattering studies has recently been reported.[7]

For some time, we have been interested in the chemistry and spectroscopy of substituted poly(diarylsilanes), particularly those which incorporate substituents which would be expected to influence the polymer spectral properties and polarizability. We describe here the synthesis and spectroscopic characterization of a variety of alkoxy-substituted poly(diarylsilanes) and report on their unusual thermo- and solvatochromism.

The desired substituted dichlorosilane monomers were prepared by the condensation of the corresponding alkoxyphenyl Grignard or lithium reagents with silicon tetrachloride as previously described for the preparation of the *p*-alkylphenyl derivatives.[6] The unsymmetrically substituted derivatives were prepared in a stepwise fashion via the corresponding substituted trichlorosilanes. The structures of the monomeric dichlorosilanes were supported by their analytical and spectral data. In this regard, ^{13}C NMR was particularly useful for the characterization of the unsymmetrical derivatives, since all of the carbon resonances were separated and easily identifiable.

The polymerization of the highly purified dichlorodiarylsilanes was performed using commercial sodium dispersion as previously described,[6] and the results are shown in Table I. The yields reported for the isolated and purified polymers are low (<10%), which is typical for the preparation of sterically hindered polysilanes, but the procedure is unoptimized.

The polymer structures were consistent with their analytical and spectral data. For the diaryl derivatives, the ^1H NMR signals for the aromatic hydrogens and the aliphatic methylene protons α to oxygen were extremely broad and structureless at room temperature. In a typical polymer such as **2**, these absorptions appeared as broad, featureless resonances around 5.0–6.8 and 3.2–4.0 ppm, respectively. The situation improves somewhat at elevated temperatures (60 °C) where these signals narrow to 1.45 and 0.47 ppm and some fine structure appears. In general, the ^{13}C spectra were much more diagnostic, particularly at elevated temperatures. For example, the ^{13}C spectrum of **2** at 60 °C showed four separated aromatic carbon resonances at 159.1, 138.9, 120.6, and 113.7 ppm, and the methylene carbon adjacent to oxygen appeared at 67.9 ppm. The remaining carbons of the aliphatic chain were also separated and easily identified. The IR spectra of the poly((alkoxyphenyl)silanes) are all quite similar, with a number of characteristic strong bands in the region from 1000 to 1600 cm^{-1}, particularly around 1250 cm^{-1}. In fact, the infrared spectra of films of the model monoaryl polymer **1** and the bis(*p*-alkoxyphenyl) polymer **2** overlay almost exactly, except in the region from ~750 to 850 cm^{-1}

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