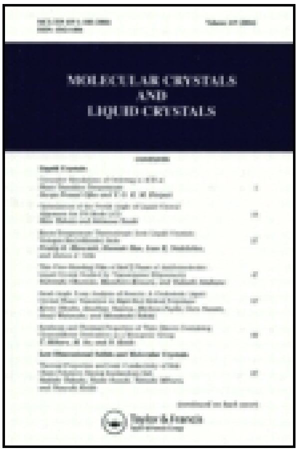

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Polyacetylene Derivatives with Chain-Sided Phenoxy and Galvinoxyl Radicals

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POLYACETYLENE DERIVATIVES WITH CHAIN-SIDED PHENOXY AND GALVINOXYL RADICALS

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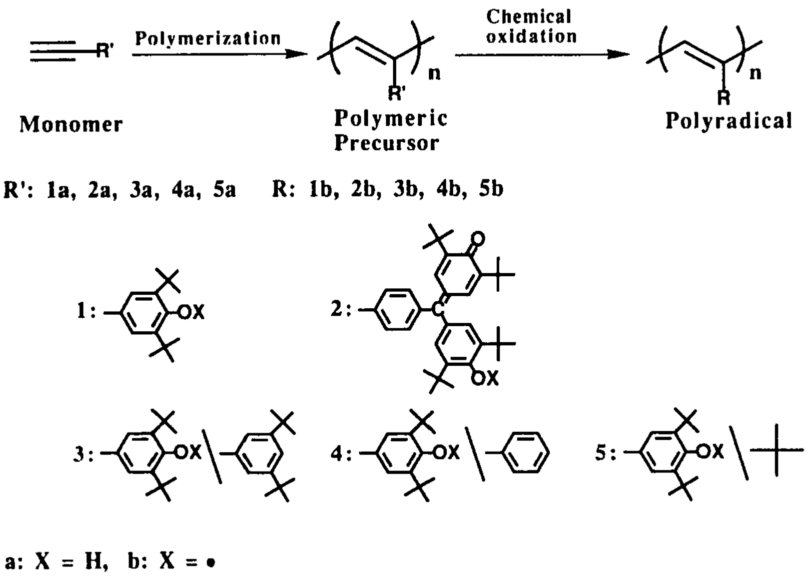
Abstract Polyacetylene derivatives bearing chain-sided, π-conjugated and bult-in phenoxy radicals were synthesized. They were soluble in common solvents and gave a transparent thin-film. ESR indicated partial delocalization of the unpaired electron generated in the chain-sided group into the main chain. But any ferromagnetic interaction between the spins could not be observed.

INTRODUCTION

π-Conjugated polyradical macromolecules consisting of both a π-conjugated main chain and chain-sided and π-conjugated stable radical moieties are expected as one of the potential candidates to realize ferromagnetic molecules, because they accumulate radical moieties along one conjugated polymer chain. The π-conjugated linear polyradical chains are desirable for magnetic materials in the next generation, because they may have magnetic characteristics associated with molecular-leveled density besides molding and thin-film forming ability, flexibility, light weight, solvent solubility, and optical transparency. π-Conjugation polyradicals have been often prepared by using a polyacetylenic main-chain structure, and spin correlation through their π-conjugated electronic structures has been discussed.[1-7] Among them the spin state of **1b** is interesting because the unpaired electron generated in the side-chain delocalizes into the conjugated polyene structure of the main-chain. It is effective for precise discussion on the spin state extended into the π-conjugated electronic structure to study with ESR the **1b** derivatives to suppress intrachain dipole-dipole interaction between the radical moieties. This paper describes preparation, characterization and electronic state of the copolymers, **3b**, **4b** and **5b**, consisted of 3,5-di-*tert*-butyl-4-hydroxyphenylacetylene **1a** with diamagnetic comonomers, 3,5-di-*tert*-butylphenylacetylene **6**, phenylacetylene **7** and *tert*-butylacetylene **8** , respectively.



SCHEME 1

PREPARATION AND PROPERTY

The polymers,**1** and **2**, were prepared by polymerizing the acetylenic precursors of radical species with W, Mo, or Rh catalyst, according to the previously reported our papers.[1,2] The copolymers, **3**, **4** and **5**, were also prepared by copolymerization in the presence of WCl_6 catalyst (TABLE I). Comparing the conversion rate of these acetylenic monomers, feed ratio of the monomers was decided. The copolymers, **3**, **4** and **5**, were obtained as a dark red, orange and a pale orange powder, respectively. The molecular weight of the copolymers was determined by GPC (polystyrene standard);The molecular weight of the copolymers was beyond 10^4, and unimodal molecular weight distribution indicated the formation of copolymers. Composition of the copolymers was determined by the relative absorbance ratio, $3650cm^{-1}(\nu_{OH})/2800cm^{-1}(\nu_{t\text{-}Bu})$ of the infrared spectra.

X-Ray diffractometry of the copolymers indicated that they are amorphous. Differential scanning calorimetry gave endothermic peaks at ca. room temperature for the copolymers (TABLE I), which are ascribed to a local motion of the *tert*-butyl groups. The copolymers were not decomposed at least below 200°C.

The copolymers were soluble in common solvents, such as benzene, chloroform, and acetone. Intrinsic viscosity of the copolymer solutions was above 0.1 dl/g (TABLE I), which suggests that the molecular weight of the copolymers is high enough, e.g. to form a thin film. Casting the $CHCl_3$ solution of the *tert*-butylacetylene copolymer **5** gave a transparent and pale orange colored film. This result indicates that π-conjugated acetylenic copolymers of the monomer bearing radical moiety and diamagnetic monomers are available also to provide compounds with molding and film-forming capability.

TABLE I Polyacetylenes bearing Conjugated Hydroxyphenyl Group

Polymer	Content of 1a (%)	$\overline{Mw}$ 10^{-4}	$\overline{Mw}/\overline{Mn}$	Colour	Solubility	[η] (dl/g)	T_{conf} (°C)	$T_{d10\%}{}^{a}$ (°C)
1a	-	3.7	2.8	dark brown	bz, chl, ace, al	0.13	34	270
6	-	4.1	2.0	red	bz, chl, ace	0.17	38	240
7	-	5.1	2.8	orange	bz, chl, ace			
8	-	19	2.1	white	bz, chl, ace	0.69	10	270
3a	24	3.4	2.6	dark red	bz, chl, ace, al	0.12	36	240
3a	32	3.8	2.5	dark red	bz, chl, ace, al			
4a	30	4.5	2.2	orange	bz, chl, ace	0.21	10	250
5a	35	8.8	2.2	pale orange	bz, chl, ace	0.23	11	270

Polymerization 35°C, $[Monomer]_0$=0.2M, $[Cat]/[Monomer]_0$=1/50,
Solvent CCl_4, Catalyst WCl_6.
a:Temperature for 10% weight loss with a heating rate of 20°C/min

The copolymers were easily converted to the polyradical **1-5b**, through the chemical oxidation with active PbO_2 or $K_3Fe(CN)_6$.

ELECTRONIC STATE

ESR spectrum of the polyradical **1b** as oxidized in solution gave a complexed hyperfine structure(FIGURE 1b), which is explained as the mixed spectrum of those of **3b** and **5b**. Solution ESR spectrum of the polyradical **3b** showed a 3-lined hyperfine structure with the intensity ratio 1:2:1, attributed to the interaction with two protons in the phenyl ring (FIGURE 1a). Dihedral angle between the polyene main chain and the chain-sided phenoxy group is so twisted in **3b** that spin is considered to delocalize within the range of the chain-sided group. On the other hand, in the spectrum of the polyradical **5b** g-value shifted to higher field, a-value decreased and the signal was broadened in comparison with those of **3b** (FIGURE 1c). It is suggested that unpaired electron in **5b** is much more delocalized than in **3b** involving the main chain neighbored with the chain-sided radical unit. This explanation was supported by simulation that the spectrum of the polyradical **1b** is the mixture of those of **3b** and **5b**.

The polymers, **1a**, **3a** and **5a**, showed broad visible absorption with the maxima at 450, 480 and 400nm, respectively(FIGURE 2). This suggests that they contain a developed π-conjugated system in the main chain, compared to poly(phenylacetylene)

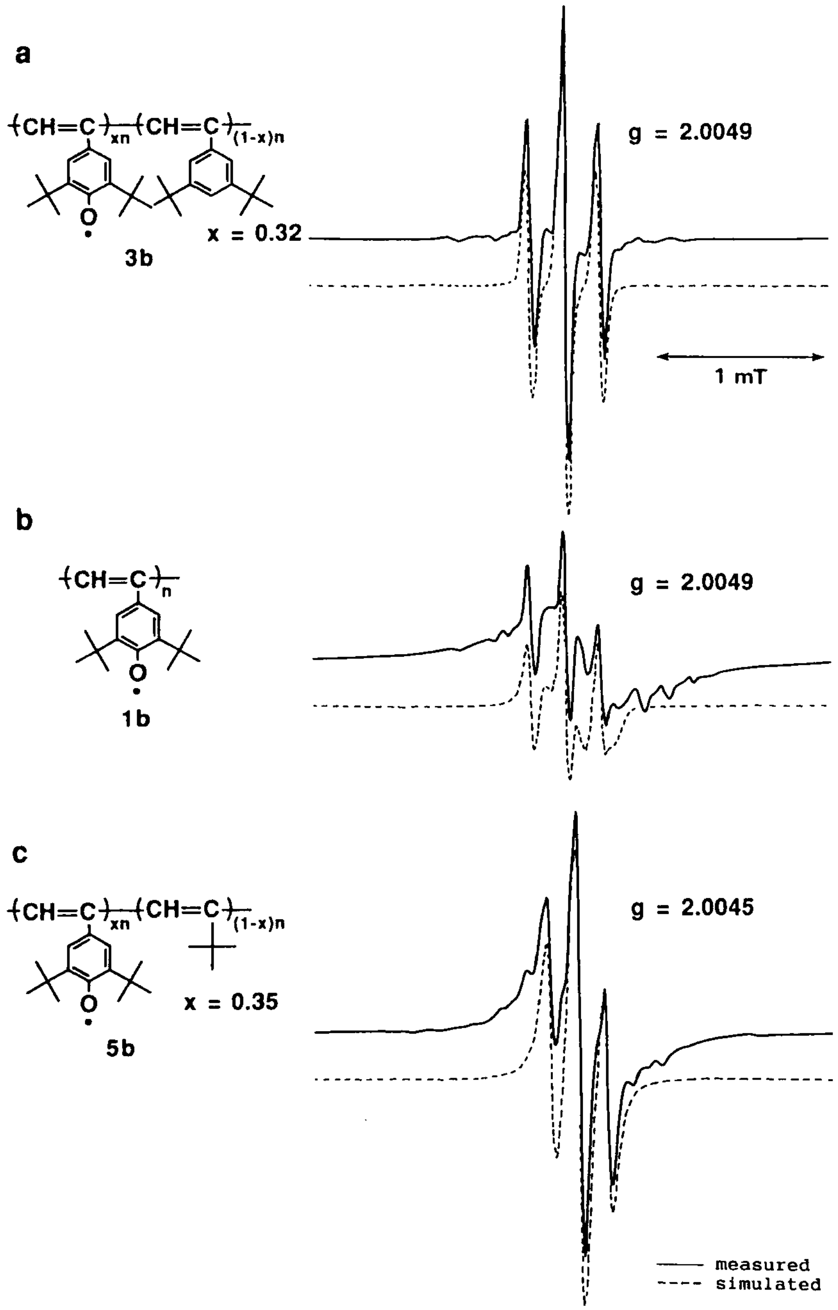


FIGURE 1 ESR Spectra of the Polyradicals in Benzene at 293 K.

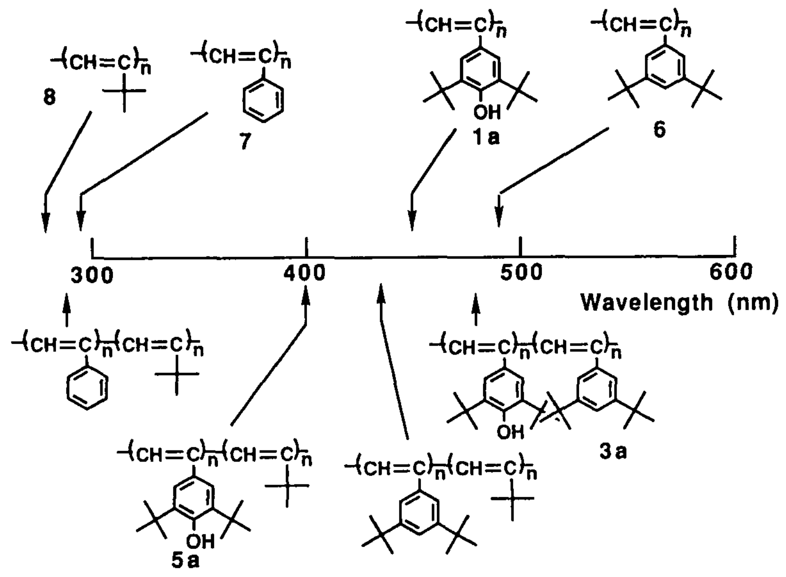


FIGURE 2 UV/visible Absorption Peaks of the Copolymers.

and poly(*tert*-butylacetylene), which show no maxima in the visible range. These visible absorptions would be explained as follows. **1a** possesses more bulky chain-sided group than that of poly(phenylacetylene), which suppresses motions of both the pendant group and the main chain. Rotational motion of *tert*-butyl groups in **6** is not affected by the hydoroxyl group, as in **1a**, which would cause an increase in steric restriction between the chain-sided groups and a developed π-conjugation for the main chain. Poly(*tert*-butylacetylene) had no absorption in visible region, and thus it is suggested that π-conjugative action in **5a** is restricted only at short range of the main chain connected with the phenyl group.

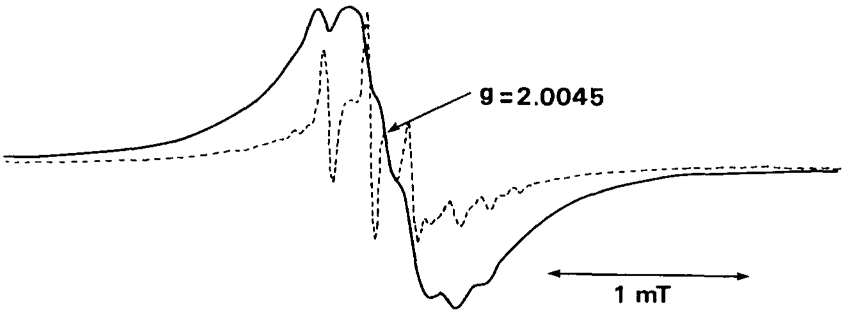
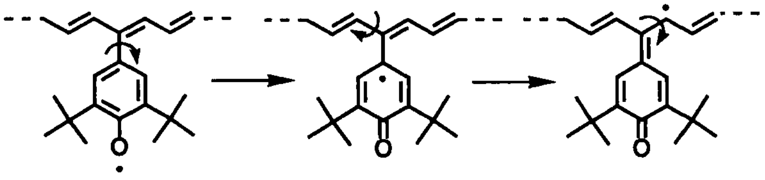


FIGURE 3 ESR Spectra of the Polyradical **1b** in Benzene at Room Temperature; solid line: redissolved polyradical, dashed line: polyradical as oxidized.

ESR signal of the polyradical **1b** changed to a broad one with a slight hyperfine structure by standing the sample solution at room temperature or by freeze-drying and redissolving (FIGURE 3). The bonding structural change in the macromolecule is presumed to be promoted by the molecular perturbation through the above treatments, and finally, it is suggested that the unpaired electron totally delocalizes into the main chain as one of tautomeric structures and the chain-sided phenoxy group is converted to a quinoid structure (SCHEME 2).



SCHEME 2

MAGNETIC PROPERTY

Saturation magnetization of the polyradicals, **1b** and **2b**, was estimated to be 2.3 and 5.3 emu/g, respectively, by using a SQUID magnetometer. By assuming one radical monomer unit $S=1/2$, spin concentration of the polyradicals was 0.1 and 0.5 /unit mol, respectively. The spin concentrations agreed with those estimated by integrating the ESR signal at $\Delta M_s = +1$. The magnetization curve of **1b** almost coincided with the Brillouin curve of $S=1/2$, and one of **2b** deviated slightly from that of $S=1/2$, indicating a weak antiferromagnetic interaction in the polyradical **2b**. Unfortunately, any ferromagnetic interaction could not be observed between intrachain spins through bond in the polyacetylene derivatives, which was expected from the theoretical calculation. Torsion in the polyacetylenic main chain and/or twisted phenoxy radical moieties would inhibit extended conjugative exchange throughout the polymer.

Acknowledgment

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