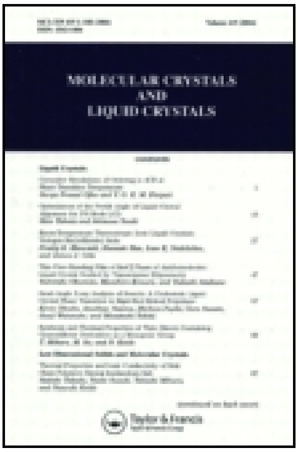

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Poly(Phenylvinylene) and Poly(Phenylene-Vinylene) with Nitroxide Radicals

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POLY(PHENYLVINYLENE) AND POLY(PHENYLENE-VINYLENE) WITH NITROXIDE RADICALS

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Abstract Poly(phenylvinylene) and poly(phenylenevinylene) with *tert*-butylnitroxide as a built-in radical group were synthesized. Precursor polymers were obtained by the polymerization of the corresponding acetylene and styrene derivatives by Rh and Pd catalysts. They were soluble in common solvents and their chemical oxidation under moderate condition gave the corresponding polyradicals.

INTRODUCTION

A macromolecule consisting of π-electron network is expected as material to provide a transmission of spin up and down, because HOMO, LUMO and NOMO of the π orbital extend on the whole of molecule.[1-4] For an alternate π-conjugated molecule, one can star in such a way that no two starred or unstarred spin positions are adjacent. Ground-state spin quantum number (S) can be derived from the number of starred π centers (n^*) and unstarred ones (n^o) according to eq (1).[1]

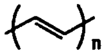
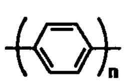
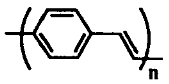
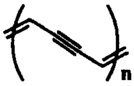
$$S = (n^* - n^o)/2 \qquad (1)$$

At $n^* = n^o$ the total spin is zero, and the ground state is a singlet. For alternate π-conjugated macromolecules, if there is a difference between n^* and n^o, an increase or decrease of S will be observed depending on bond connectivity of the polymer. When the theorem is applied to conjugated polyenes, polymers of acetylene with a radical substituent at every carbon atom, can be a candidate for the high-spin polymer whose spin multiplicity increases in proportion to its molecular size.

Poly(acetylene), poly(phenylene), poly(phenylenevinylene), poly(diacetylene) and so on are available as π-conjugated main-chains for the conjugated polyradicals (TABLE I). Unsubstituted polyacetylene involves a greatly developed π-conjugation system with high coplanarity, while the polyene -C=C- main-chains of substituted polyacetylenes easily result in decrease of coplanarity and conjugation length.[5]

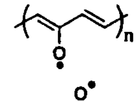
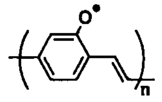
Although poly(phenylene) causes little steric hindrance among substituents, steric hindrances between bulky substituents and/or between hydrogens of neighboring phenyl ring decreases its coplanarity and conjugation length. It is difficult to regulate head-to-tail (H-T) polymerization, though chemical and electrochemical synthesis are available for the polymerization. For poly(phenylenevinylene) (PPV), its coplanarity and conjugation length are maintained even after a radical substituent is introduced in *o*-position of the phenylene. The H-T structure would be brought about under a specific polymerization condition. Substituted PPVs are soluble in common organic solvents, which guarantees their chemical structures.

TABLE I Characteristics of Conjugated Polymer Chains

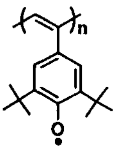
Polymer		Method of polymerization	Solvent solubility	Mol. wt	Planarity of π -system	Conjugation length
	Unsubstituted	Chemical	Insol	High	Coplanar	Very long
Poly(acetylene)	Substituted	Chemical	sol	Very high	Distorted	Short or middle
	Unsubstituted	Chemical Electrochemical	Insol	Low	Coplanar	Long
Poly(phenylene)	Substituted	Chemical Electrochemical	sol	High	Distorted (Coplanar)	Short
	Unsubstituted	Chemical	Insol	Very high	Coplanar	Long
Poly(phenylene-vinylene)	Substituted	Chemical	sol	Very high	Coplanar	Long
 Poly(diacetylene)	Unsubstituted	UV-Irrad, Thermal	Insol	Very high	Coplanar	Very Long

Correlation between the chemical structure and the stabilization of high spin state has been discussed using model oligomers of organic polyradicals corresponding to their series of polymers.[4] It was in agreement with predictions from Ovchinnikov's simple rule for alternate systems. Ferromagnetic coupling was maintained for the poly(phenylene) and PPV system up to five monomer units with relatively large magnitudes of the high-spin to low-spin gap. The polyacetylene system was also expected by the Ovchinnikov's rule to show high-spin ground state. However, the higher oligomer possessed nearly a degenerated HS-LS gap. In contrast to the polyacetylene compounds, **1** and **2**, PPV derivatives, **3** and **4**, have a potential as a high spin polymer (TABLE II).

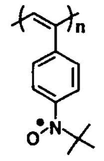
TABLE II Energy Gaps between Ground and Excitated States of Oligomers[a)]

Structure		Oligomer length			
		2	3	4	5
	$S_{GS}^{b)}$	1	3/2	2	5/2
	$DE_{GS\text{-}ES}^{c)}$	3.3	0.5	0.3	0.3
	$S_{GS}^{b)}$	1	3/2	2	5/2
	$DE_{GS\text{-}ES}^{c)}$	3.5	2.7	2.7	2.2

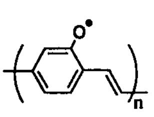
a) Cited from the refarence: Lahti and Ichimura.[4]
b) Ground spin(GS) quantum number.
c) Energy gap in kcal/mol between GS and next higher excited state(ES) of spin SEX=SGS-1. For DE>0,the GS is high spin.



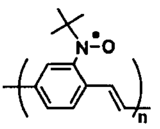
1



2



3



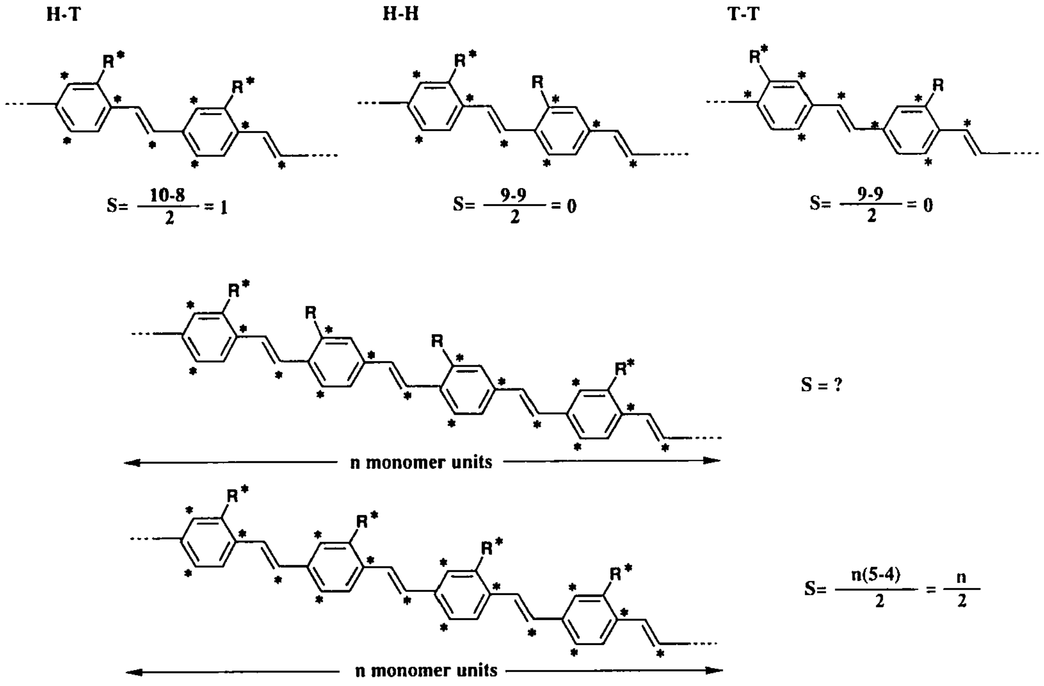
4

POLYMERIZATION

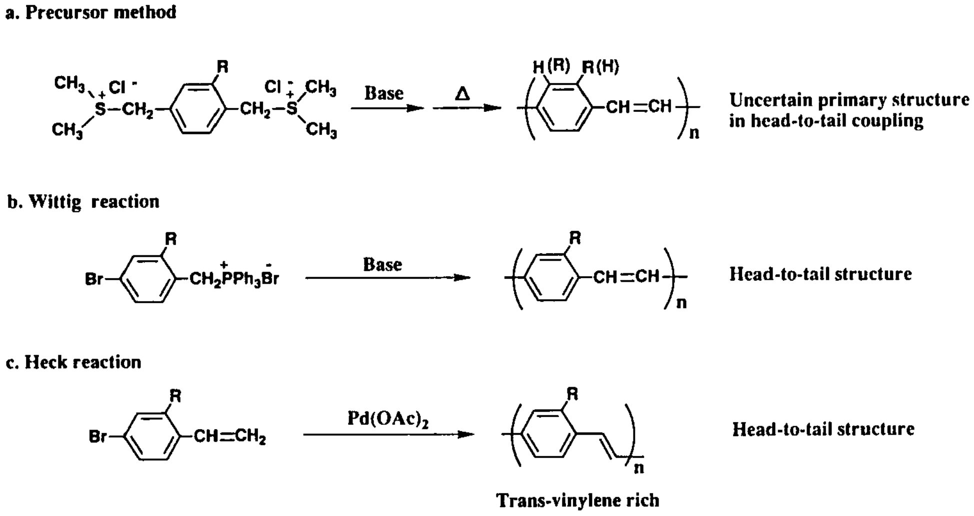
A mono-substituted PPV involves three coupling structures, head-to-tail (H-T), head-to-head (H-H), and tail-to-tail (T-T), to form the PPV chain. Ground-state spin quantum number is estimated to be S=1 for H-T and S=0 for H-H and T-T. The polyradical consisting of the restricted primary structure of H-T is to show the spin multiplicity in proportion to the degree of polymerization (SCHEME 1).

PPVs had been synthesized by precursor methods to produce electronic conducting polymers.[6] Although their molecular weights are sufficiently high, they are lack in the restricted primary structure of H-T, because the polymerization proceeds through coupling of the same terminal functional groups (SCHEME 2a). We succeeded in preparing the H-T PPV polymers through Wittig reaction or Heck reaction (SCHEME 2b,c). From the standpoints of the steric hindrance effect in the reaction and of the development in π-conjugation, the Heck reaction was more favorable than Wittig reaction because *trans*-vinylene structure was predominant in the obtained polymer.

We synthesized PPVs bearing radical precursor unit, hexyloxy group or N-*tert*-butylhydroxyamino group (SCHEME 3). The Corresponding *o*-substituted-*p*-bromostyrene monomers, 4-bromo-2-hexyloxystyrene (**5**) and 4-bromo-N-*tert*-butyl-

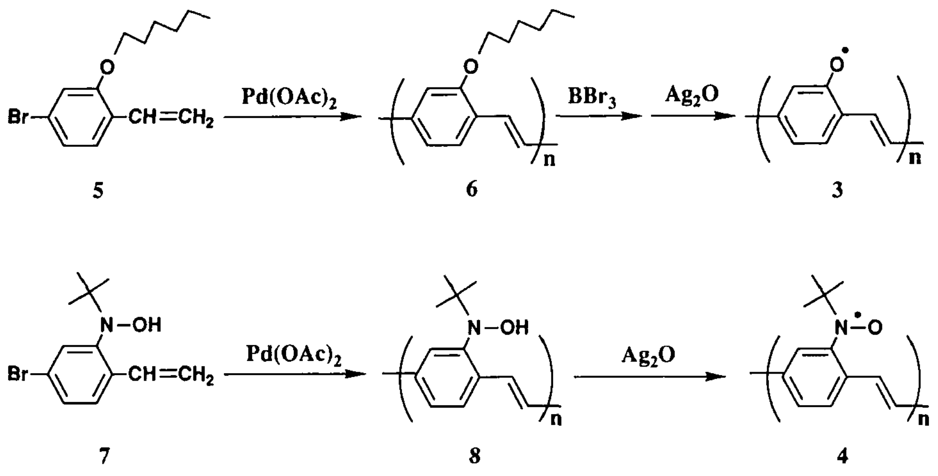


SCHEME 1



SCHEME 2

2-hydroxyaminostyrene (7), were polymerized by palladium acetate catalyst in DMF. Hexyloxy-substituted PPV 6 was obtained as an orange powder with molecular weight ca. 1 x 10^4, and N-*tert*-butylhydroxyamino-substituted PPV 8 was as a yellow powder with one of 2 x 10^3 (TABLE III). 6 was soluble in chloroform, THF, benzene, DMF, and insoluble in methanol and hexane. It is suggested that the solubility of 6 was enhanced by the substitution with the hexyloxy group, in comparison with unsubstituted PPV[7]. The polymer 6 in solution fluoresced a yellow green color, which supported the *trans*-vinylene structures. IR spectra of 6, 8 indicated out-of-plane bending mode of the *trans*-vinylene bond hydrogen at 970 cm^{-1} and disappearance of stretching vibration of the C=C bond of vinyl group at 1630 cm^{-1}. ^{13}C-NMR spectra of 6 gave 8 lines ascribed to carbons of the vinylene and phenyl ring, which supports that the H-T coupling in the PPV chain of 6.



SCHEME 3

TABLE III Polymerization of 5 and 7

Monomer	Time (hr)	Yield (%)	$\overline{Mw}$ x 10^3	$\overline{Mw}/\overline{Mn}$	Color	Solubility
5	24	20	9.8	1.8	Orange	bz, chl, THF, DMF
7	16	3	1.7	1.5	Yellow	bz, chl, THF, DMF

Polyacetylene derivatives, 1 and 2, corresponding to the PPV, 3 and 4, were obtained via the polymerization of the corresponding hydroxyl monomers by using the transition metal catalyst, e.g. W, Mo, Rh, and the following chemical oxidation.[8-10]

ELECTRONIC STATE AND MAGNETIC PROPERTY

The polyacetylene, **1** and **2**, showed the absorption maxima in visible region[8], which suggested their more developed π-conjugation than that of unsubstituted poly(phenylacetylene) without absorption maximum in visible region. But it is presumed that the substituting in **1** and **2** cause a torsion of the polyacetylenic main-chain and π-conjugated system. As the chemical oxidation proceeding, the visible absorption at 490nm attributed to the phenylnitroxide appeared for the polyradical **2**, and the solution ESR spectrum was broaden because of a high local concentration of the radical site along the main-chain (FIGURE 1). The low molecular model compound, N-*tert*-butyl 4-vinylphenylnitroxide, showed the spectrum with the hyperfine structure assigned to the protons not only in the phenyl ring but also in the vinyl group. Therefore the spin distribution of the unpaired electrons into the main-chain and the interaction between unpaired electrons are expected also for the polyradical **2**. However, the ESR spectrum gave only the signal (g=2.006) in $\Delta M_s=\pm 1$ attributed to the nitroxide radical species. Forbidden transition of $\Delta M_s=\pm 2$ ascribed to a triplet state was not observed even at 77K. It is considered that the torsional or twisted structure in the substituted polyacetylenic main-chain of **2** inhibits a spin exchange through the π-conjugated system.

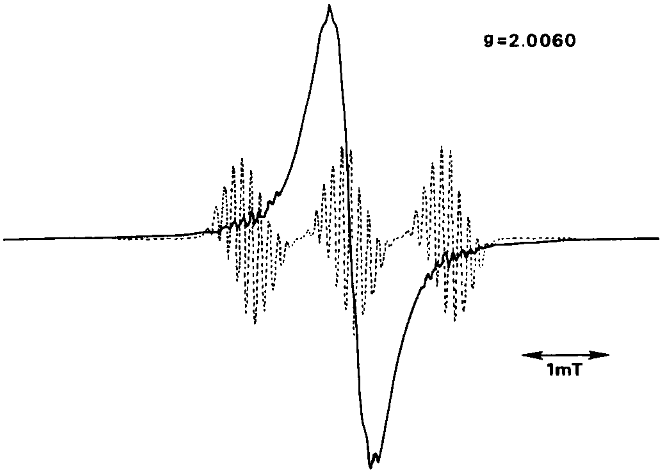
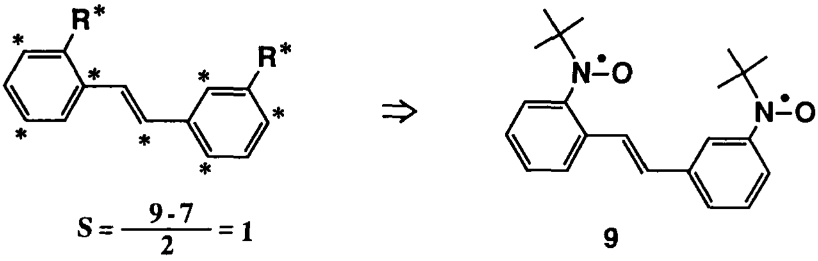


FIGURE 1 ESR Spectra of the Polyradical **2** in Benzene at room temperature; solid line : **2** (spin concentrasion 61 mol%), dashed line : N-*tert*-butyl 4-vinylphenylnitroxide.

Solution ESR spectrum of the PPV **4** showed hyperfine structure with g=2.006, a_N=1.36, supporting the nitroxide radical at low spin concentration, whose spin distributed on the phenyl ring. Solution ESR spectrum of the dimer model, *o,m'*-stilbenebis(N-*tert*-butylnitroxide) (**9**) showed 5 lined hyperfine structure caused by two nitrogen nuclear, in which unpaired electrons exhibit entirely the spin exchange interaction. The spectrum in toluene glass at 77K showed the fine structure in $\Delta M_s = \pm 1$ with D=64.45, E=8.15, and triplet signal in $\Delta M_s = \pm 2$.



9

SCHEME 4

The magnetization curve of **2** deviated downward from the theoretical one of S=1/2 at low temperature, which suggested an antiferromagnetic interaction among the unpaired electrons. This deviation from the theoretical value was suppressed by dilution with diamagnetic polystyrene: the antiferromagnetic deviation was ascribed to an interchain interaction. The polyradical **4** diluted with polystyrene gave the magnetic susceptibility with a maximum at ca.70K.

Torsion in the polyene main-chain and/or twisted phenyl radical moieties would inhibit any intramolecular spin exchange for the polyacetylene derivatives. The PPV derivatives, of which dimer showed sufficient spin exchange, maintained their planarity in the main-chain even after the introduction of the radical substituents.

Acknowledgment

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