

SHORT COMMUNICATIONS

New Method for the Preparation of Poly(2,5-thienylene), Poly(*p*-phenylene), and Related Polymers

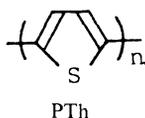
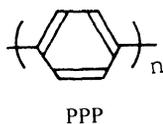
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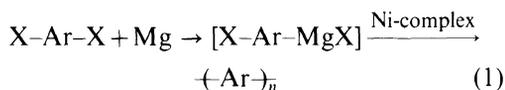
Poly(*p*-phenylene) (PPP) and poly(2,5-thienylene) (PTh) having a π -conjugation system along the polymer chain show electrically conducting properties when doped with electron acceptor or electron donor.¹⁻³ Their electrically conducting properties and applications to devices such as polymer battery, electrochromic devices, and field effect transistor have been reported.



PPP and PTh have been prepared by a number of methods including:

a) reaction of benzene with CuCl_2 in the presence of AlCl_3 under non-catalytic⁴ and catalytic⁵ conditions.

b) Ni-catalyzed dehalogenation polycondensation of dihaloaromatic compounds,^{2,6}

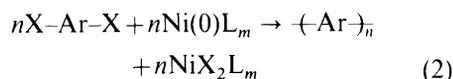


c) decarboxylic acid reaction from a precursor polymer,⁷ and

d) electrochemical oxidation of benzene and

thiophene.^{3,8}

Among these methods, method b) affords polymers with relatively well-defined linkage between the monomer units. As an extension of dehalogenation polycondensation using magnesium (eq. 1), we developed a new polycondensation using the zero-valent nickel complex itself as the dehalogenating reagent in order to expand such a type of dehalogenation polycondensation (*e.g.*, polycondensation under different reaction conditions using different solvents, etc.) and found that the new polycondensation affords PPP and PTh in high yields,



This polymerization is based on coupling reactions of halogenated aromatic compounds with zero-valent nickel complex.⁹

As zero-valent nickel complexes, mixtures of bis(1,5-cyclooctadiene)nickel, $\text{Ni}(\text{cod})_2$, and neutral ligand L have been employed,



To a DMF (*N,N*-dimethylformamide) solution of $\text{Ni}(\text{cod})_2$ (1.0—1.2 mol/mol of X-Ar-X),

Table I. Preparation of poly(2,5-thienylene) and poly(*p*-phenylene) by the dehalogenation polycondensation of corresponding dihalogenated aromatic compounds with mixtures of Ni(cod)₂ and neutral ligand L

Run	Monomer	Ligand ^a	Temp.	Time	Yield ^b
			°C	h	%
1	2,5-Dibromothiophene	PPh ₃	100	16	92
2	2,5-Dibromothiophene	PPh ₃	80	16	100
3	2,5-Dibromothiophene	PPh ₃	60	16	86
4	2,5-Dibromothiophene	PPh ₃	40	16	80
5	2,5-Dibromothiophene	bpy	60	16	91
6	2,5-Dichlorothiophene	PPh ₃	60	16	55
7	3-Cyano-2,5-dibromothiophene	PPh ₃	60	16	91
8	3-Methyl-2,5-dibromothiophene	PPh ₃	60	16	76
9	1,4-Dibromobenzene	PPh ₃	60	16	26
10	1,4-Dibromobenzene	bpy	60	16	99

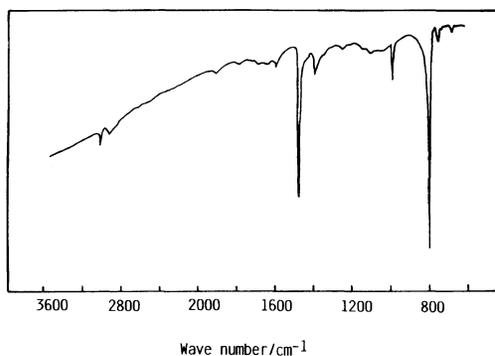
^a PPh₃ = triphenylphosphine; bpy = 2,2'-bipyridine.

^b Based on carbon recovered.

1,5-cyclooctadiene, and neutral ligand (1.0–1.2 mol/mol of X–Ar–X), the monomer X–Ar–X was added and the mixture was allowed to react under nitrogen. The polymer formed was collected by filtration, washed with aqueous solutions of EDTA (with pH = 3 and 9 in this order) to remove nickel compounds, and dried under vacuum.

Table I summarizes the results of the polycondensation. As shown in Table I, the polycondensation affords the polymer in high yields. Use of 2,2'-bipyridine(bpy) as the ligand L usually gave higher yields than those of PPh₃. This is especially remarkable in the preparation of PPP (Runs 9 and 10). The higher yields attained by using bpy may be due to the formation of intermediate *cis*-type Ni(R)(R')(bpy) in which coupling between R and R' proceeds smoothly.¹⁰

The IR spectra of PPP, PTh, and poly(3-methyl-2,5-thienylene) (Run 8) are essentially the same as those of previously prepared polymers obtained by using magnesium as the dehalogenation reagent (method b).^{2,6} However, they show much weaker ν(C–X) bands (ν(C–Br) for PPP and PTh: 967 and 1065 cm⁻¹, respectively) than those of the polymers prepared by method b).

**Figure 1.** IR spectrum of PPP (Run 10).

PPP prepared by the present method seems to have a higher degree of polymerization than PPP prepared by the other methods as judged from its IR spectrum and relatively low bromine content. The IR spectrum of the present PPP shows out-of-plane vibration at $805 \pm 2 \text{ cm}^{-1}$ ($\delta(\text{para})$) and those of the terminal phenyl unit at 760 cm^{-1} ($\delta(\text{mono}_1)$) and 690 cm^{-1} ($\delta(\text{mono}_2)$). It is generally recognized that the *R* value, $R = A(\delta(\text{para})) / (A(\delta(\text{mono}_1)) + A(\delta(\text{mono}_2)))$ (*A* = absorbance of the peak), increases with the degree of the polymerization of PPP.^{4,6}

The IR spectrum of the present PPP (Figure 1) shows very weak $\delta(\text{mono}_1)$ and $\delta(\text{mono}_2)$,

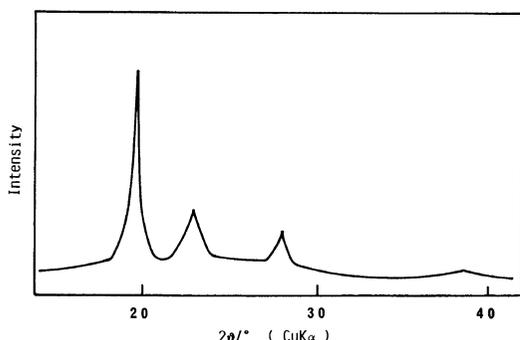


Figure 2. X-Ray diffraction pattern of powder PTH (Run 5).

and the *R* value for the present PPP (*R* value = 12.7) is much larger than those for PPPs reported by Kovacic and his coworkers (*R* value = 4.6) and prepared using magnesium (method b)) (*R* value = 1.9–3.9). This fact, together with the relatively low content of bromine, indicate that the present PPP has a relatively high degree of polymerization. The present PPP contains 2.7% of bromine (*Anal. Found.* C, 93.1%; H, 5.7%; Br, 2.7%. *Calcd for:* C, 94.7%; H, 5.3%). This bromine content corresponds to a molecular weight of 2960 (DP of 38) and 5930 (DP of 76) if the polymer had bromine at one terminal unit and at both terminal units, respectively. PTH also contained relatively low bromine ($1.0 \pm 0.3\%$), which corresponds to DP of about 100 and 200 if the polymer has bromine at one terminal unit and at both terminal units, respectively.

The X-ray diffraction pattern of the present PTH indicates considerably sharp peaks (Figure 2), revealing that it has high crystallinity. The X-ray diffraction pattern of PTH prepared by method b) shows broader peaks. This also indicates that the present polycondensation using the zero-valent nickel complex proceeds with high selectivity. The X-ray diffraction pattern of PPP shows sharp peaks at 19.7° , 22.9° , 28.1° , 38.5° , and 43.2° ($\text{CuK}\alpha$).

The PTH showed electrical conductivity of $6 \pm 2 \text{ Scm}^{-1}$ when the polymer powder was doped with iodine (about 1 g/1 g of polymer)

and the iodine-polymer adduct powder was pressed into a pellet. The electrical conductivity remained almost constant after allowing the iodine adduct to stand at room temperature for 150 days under air.

Use of $\text{BrCH}=\text{CHBr}$ as the monomer in the reaction with a mixture of $\text{Ni}(\text{cod})_2$ and L (PPh_3 or bpy) gave a black solid, whose IR spectrum was similar to that of *trans*-poly(acetylene)¹¹ showing a characteristic sharp absorption peak at 1010 cm^{-1} . Iodine doping of the black solid (powder), however, gave only low electrical conductivity (10^{-3} Scm^{-1}). When magnesium was used as the dehalogenation reagent, the reaction brought about the evolution of acetylene and gave no polymer.

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