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Mini review

Cross-coupling reactions for preparation of π-conjugated polymers

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Abstract

Various π-conjugated aromatic polymers have been prepared by utilizing organometallic C–C coupling reactions. The π-conjugated polymers include poly(thiophene), poly(3-alkylthiophene), poly(pyridine), and poly(2,2′-bipyridyl). Some of the polymers form metal complexes, which show catalytic activity for redox reactions. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

π-Conjugated polymers are the subject of many recent papers. Cross coupling dehalogenative polycondensation for preparation of π-conjugated polymers was reported for the first time in 1977 by us [1a,2]. Now the polycondensation has been developed by many research groups and is contributing to the understanding of the chemistry and physics of π-conjugated polymers, e.g.

$$n\text{X–Ar–X} + n\text{Mg} \rightarrow n[\text{X–Ar–MgX}] \overset{\text{Ni complex}}{\rightarrow} (\text{Ar})_n \tag{1}$$

[1]

$$n\text{X–Ar–X} + n\text{Zn} \overset{\text{Ni complex}}{\rightarrow} (\text{Ar})_n \tag{2}$$

[3]

$$n\text{X–Ar–X} + n\text{Ni(0)Lm} \rightarrow (\text{Ar})_n \tag{3}$$

[4]

$$n\text{X–Ar–X} + n\text{HC}\equiv\text{C–Ar}'\text{–C}\equiv\text{CH} \overset{\text{Pd complex}}{\rightarrow} (\text{Ar–C}\equiv\text{C–Ar}'\text{–C}\equiv\text{C})_n \tag{4}$$

[5]

$$n\text{X–Ar–X} + n\text{R}_3\text{Sn–Ar}'\text{–SnR}_3 \overset{\text{Pd complex}}{\rightarrow} (\text{Ar–Ar}')_n \tag{5}$$

[6]

$$n\text{X–Ar–X} + n(\text{HO})_2\text{B–Ar}'\text{–B(OH)}_2 \times \overset{\text{Pd complex}}{\rightarrow} (\text{Ar–Ar}')_n \tag{6}$$

[7]

These polycondensations are considered to proceed through basic organometallic reactions such as oxidative addition [8], disproportionation [9], and reductive elimination [10]. We have long been concerned with these basic organometallic reactions, by isolating transition metal complexes such as MR_2Ln (R = organic group) [10,11] and Pd(Ar)(C≡CAr′)Ln [12] and by revealing their basic reactivity (e.g. reductive elimination [10–12].

2. Syntheses of π-conjugated polymers

Fig. 1 shows π-conjugated ploy(arylene)s prepared by our groups [2]. Many of the polymers were for the first time prepared by us. For example, poly(thiophene-2,5-diyl) PTh and poly(3-alkylthiophene-2,5-diyl) were reported in 1980 [13] and 1982 [14], respectively, and material patents were allowed under the name of our university.

p-Type, electron-donating π-conjugatred poly(arylene) such as polythiophenes and polypyrroles can also be prepared by chemical and electrochemical oxidation of the corresponding aromatic compounds [15]. However, the organometallic polycondensations afford the polymers with well-controlled bonding between the

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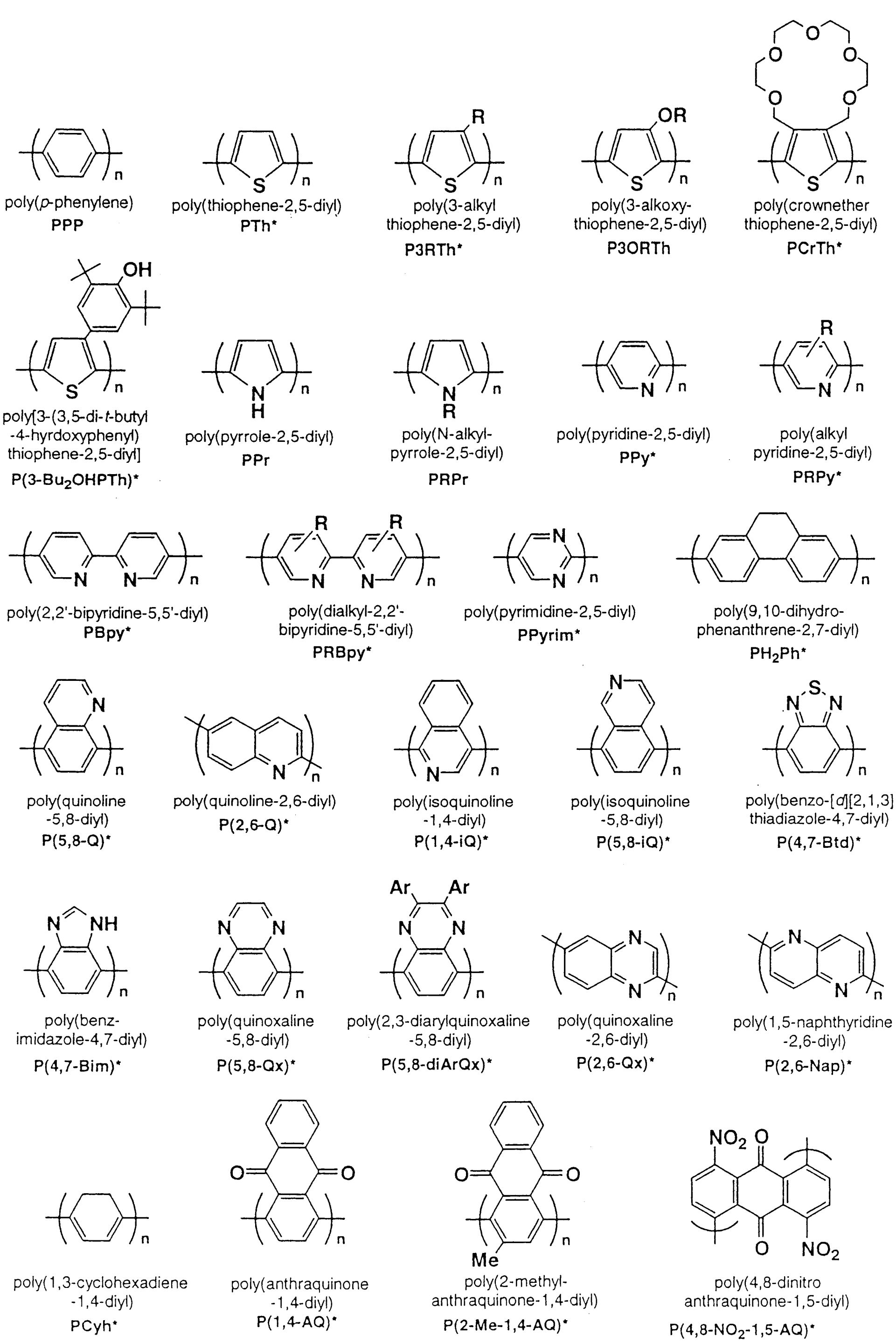


Fig. 1. π-Conjugated polymers prepared by the organometallic processes in our group. Polymers with * mark were for the first time prepared in the author's group.

monomeric units. Recently, regioregular head-to-tail type poly(3-alkylthiophene) has been successfully prepared according to the organometallic polycondensation [16]. For n-type, electron-accepting poly(arylene)s such as polypyridines and polyphenanthrolines, preparation *via* the chemical or electrochemical oxidation of the corresponding aromatic compounds is impossible, and they are prepared according to the organometallic polycondensation.

Among the Ni-promoted polycondensations (Eqs. (1)–(3)), the methods 1 and 2 can produce the π-conjugated poly(arylene)s at relatively low cost. The method 3 uses rather expensive Ni(0)Lm complex in a stoichromatric amount. However, the polycondensation

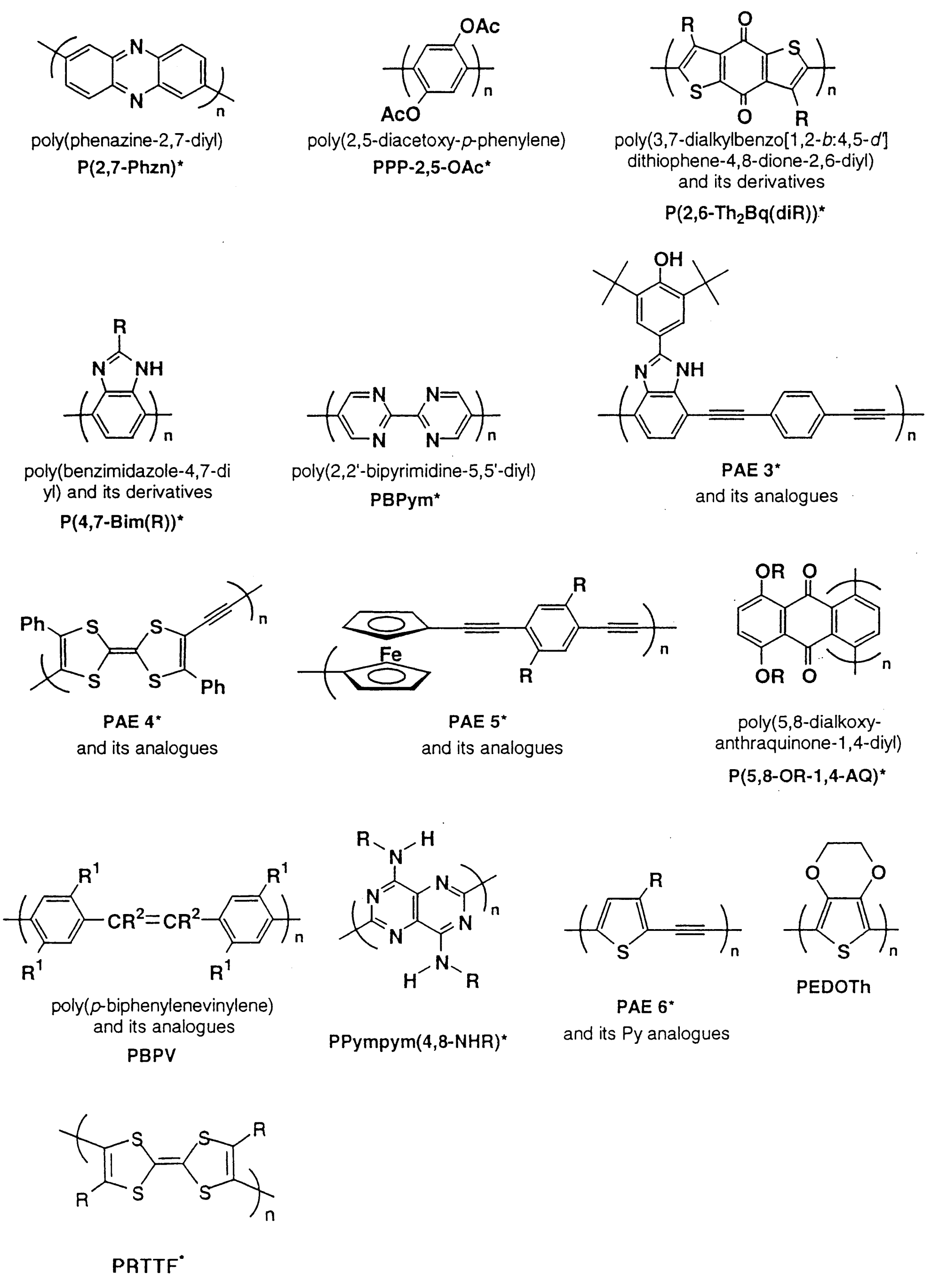


Fig. 1 (*Continued*)

using Ni(0)Lm is versatile for various kinds of aromatic dihalides, and even polyquinones can be obtained according to the polycondensation (cf. Fig. 1).

3. Functionalities of the π-conjugated polymers

The π-conjugated polymers consisting of electron-donating aromatic units (thiophene, pyrrole, furan, etc.) receive chemical and electrochemical oxidation to give p-type conducting materials. On the other hand, the polymers constituted of electron-accepting aromatic units (pyridine, quinoline, quinoxaline, etc.) undergo chemical and electrochemical reduction to give n-type conducting materials. Some of the polymers are now used as conducting materials in industry.

The polymers show electrochromism, electroluminescence, large third order non-linear optical susceptibility, photovoltaic behavior, and recently superconductivity. The construction of diodes and field effect transistors (FET) with the polymers is also possible. The construction of electroluminescence devices is the subject of

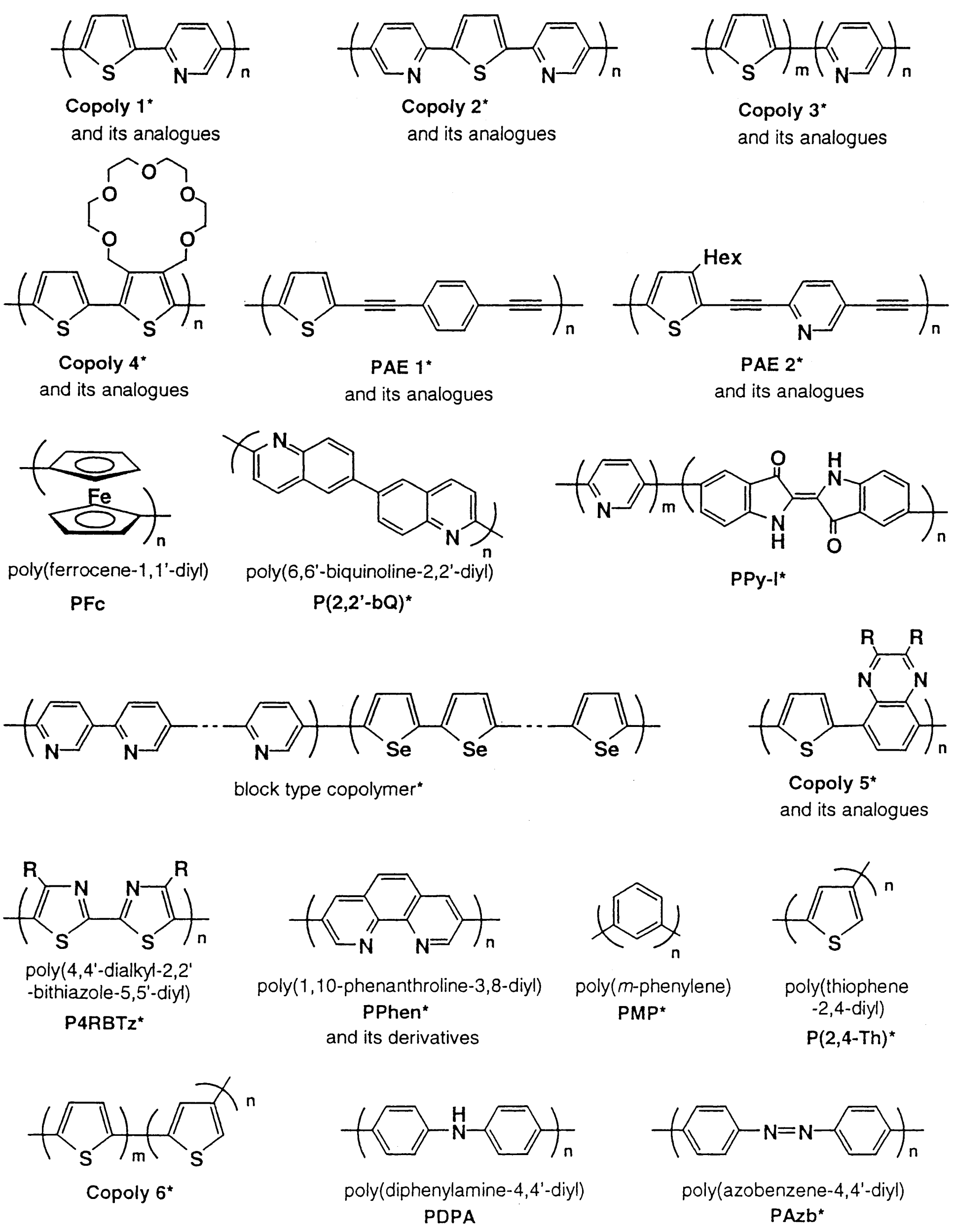
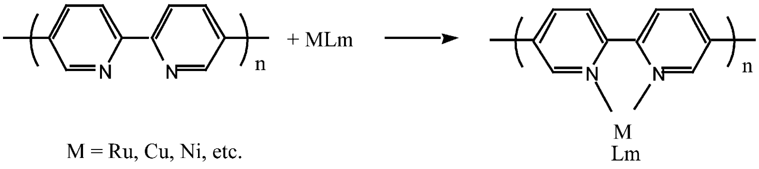


Fig. 1 (*Continued*)

recent interest, and many efforts have been made by using various π-conjugated poly(arylene)s.

Some of the polymers such as poly(2,2′-bipyridyl), PBpy, and poly(2,2′-bipyrimidine, PBPym, form transition metal complexes, e.g.



(7)

The metal complexes of PBpy show high catalytic activity for redox reactions such as photoevolution of H_2 from aqueous solution [17a] and oxycarbonylation of methanol to give dimethylcarbonate ($2MeOH + CO + 1/2O_2 \rightarrow MeOCOOMe + H_2O$; catalyst = $CuCl_2$ complex of PBpy) [17b]. The high catalytic activity is related to the presence of mobile electrons along the polymer chain, which makes the redox reaction at the metal center easier. Cyclic voltammograms of the metal complexes of the π-conjugated polymers usually exhibit broader peaks compared with those of the corresponding low molecular weight metal complexes [17a], which is considered to be due to electron exchanges between metal centers bonded to the π-conjugated polymers. The PBpy complex of $[Ru(bpy_2)]^{2+}$ shows certain electrical conductivity [17a], although PBpy itself is an insulator; generation of a carrier species due to an MLCT electronic state of the metal complex of PBpy is suggested.

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