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Synthesis of π-Conjugated Soluble Poly(aryleneethynylene) Type Polymers and Their Properties

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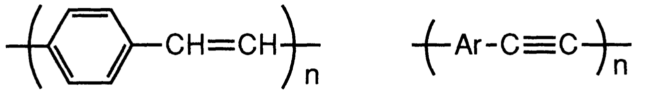
Pd-catalyzed coupling reactions with dihaloaromatic compounds X-Ar-X and diethynylaromatic compounds HC≡C-Ar'-C≡CH give new soluble π-conjugated polymers $\left(Ar-C\equiv C-Ar'-C\equiv C \right)_n$ when Ar and/or Ar' group is pyridine-2,5-diyl or has a long chain alkyl substituent.

Preparation and properties of poly(phenylenevinylene) PPV and its derivatives have been extensively studied.[1)] However, those of poly(aryleneethynylene) PAE having a structure similar to that of PPV have received much less attention presumably due to low solubility of most of PAE's so far prepared.[2a,c)] We now report the preparation of new soluble PAE type polymers and properties of the polymers. Obtaining a series of the processable PAE type polymers are expected to give bases for comprehension of chemical and physical properties of π-conjugated polymers and their application.



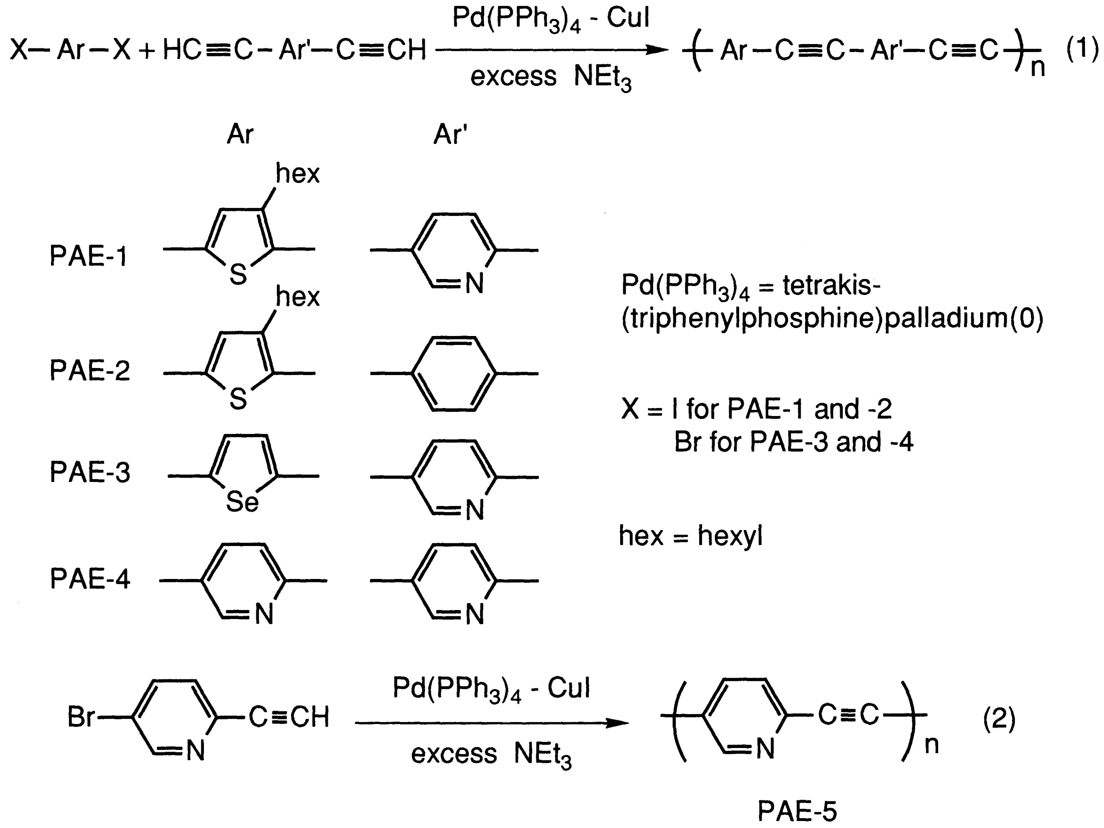
PPV PAE

The soluble PAE type polymers have been prepared by Pd-catalyzed polycondensation expressed by Eq.1 and 2 (Scheme 1) at 50-110 ° C in toluene, in a manner similar to that previously reported.[2a, b)] , [3)] The polymers thus prepared were reprecipitated, washed repeatedly with methanol, dried under vacuum and obtained in 93-100% yields.

The PAE type polymers having alkyl-substituted thiophene-2,5-diyl and/or pyridine-2,5-diyl unit are soluble in organic solvents; PAE-1 and -2 are soluble in chloroform and tetrahydrofuran (e.g., solubility of PAE-1 in $CHCl_3$ = ca. 10 mg cm^{-3}), PAE-4 and -5 in formic acid, and PAE-3 in formic acid, chloroform and N-methyl-2-pyrrolidone. Such effects of alkyl substituent[4a-d)] and pyridine-2,5-diyl group[4e,f)] on the enhancement of solubility of poly(arylene)s have been reported.

^1H NMR spectrum (Fig. 1) of PAE-1 is reasonable for the structure shown above, showing peaks at δ 0.89 (3H, t, J=5 Hz, $(CH_2)_5C\underline{H}_3$), 1.25—1.68 (8H,$CH_2(C\underline{H}_2)_4CH_3$), 2.78 (2H, $C\underline{H}_2C_5H_{11}$), 7.13 (ca. 0.4H, $C_4\underline{H}S$), 7.20 (ca. 0.6H, $C_4\underline{H}S$), 7.48 (1H, d, J=8 Hz, C_5H_3N), 7.78 (1H, d, J=8 Hz, C_5H_3N), 8.76

(1H, s, C_5H_3N) ppm. The appearance of the two peaks for $C_4\underline{H}S$ may be attributed to the presence of both head-to-tail and head-to -head units with regard to the direction of the hexyl group in the 3-hexylthiophene-2,5-diyl unit. PAE - 2 also shows a reasonable ^1H NMR spectrum.



$Pd(PPh_3)_4$ = tetrakis-(triphenylphosphine)palladium(0)

X = I for PAE-1 and -2
Br for PAE-3 and -4

hex = hexyl

Scheme 1.

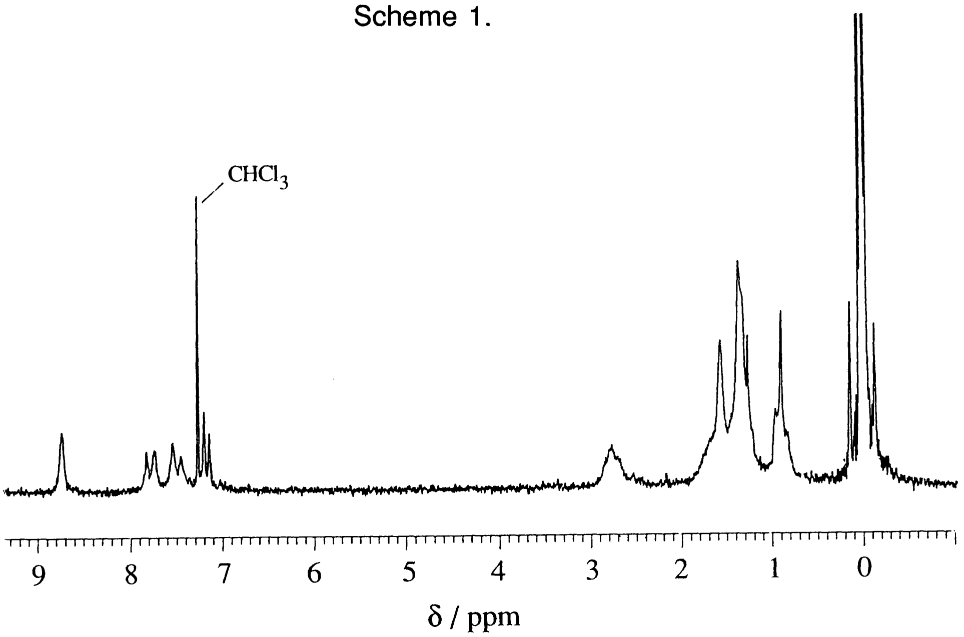


Fig. 1. ^1H NMR Spectrum of PAE-1 (in $CDCl_3$).

IR spectra of PAE-1 through PAE-5 support the structures shown above, giving rise to a medium absorption peak of ν(C≡C) at about 2200 cm^{-1} and strong δ(C-H) absorption peaks of aromatic rings in a range of 720 — 1020 cm^{-1}. PAE-4 and PAE-5 give essentially the same CP-MAS solid ^{13}C-NMR spectrum to each other,[5)] suggesting PAE-4 is mainly constituted of head-to-tail units, which are to be formed exclusively by the reaction expressed by Eq. 2.

PAE-1, PAE-2, and PAE-5 have molecular weight of 48 x 10^4, 9.6 x 10^4, 21 x 10^4, respectively, as determined by light scattering method.[6)] PAE-1 is amorphous as judged from its powder X-ray diffraction pattern, and the polymer has the density of 1.05 g cm^{-3}.

Films of the PAE type polymers shown above can be easily obtained by casting the solutions of the polymers on substrates, and the film of PAE-1 on Pt plate is electrochemically active to give rise to a cyclic voltammogram (CV) shown in Fig. 2.

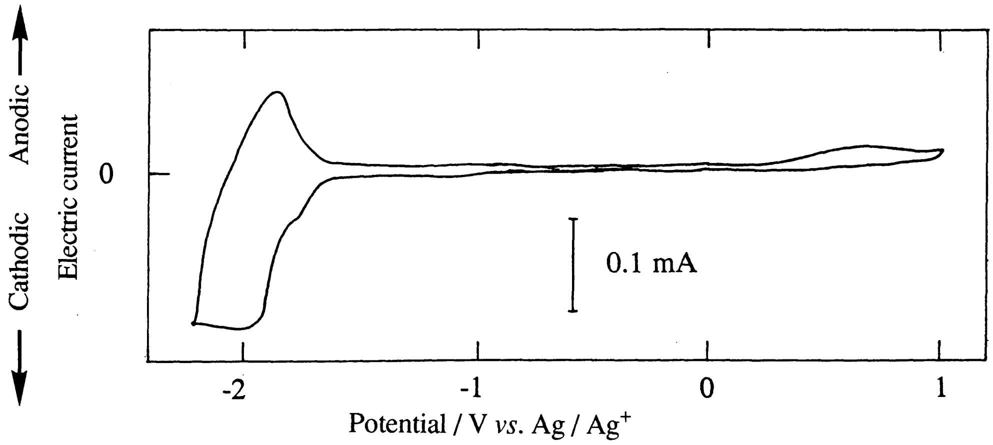


Fig. 2. CV curve of PAE-1 laid on Pt plate in an CH_3CN solution of $[NEt_4][ClO_4]$ (0.1 M) at 50 mV s^{-1} at room temperature.

It is known that thiophene ring has a rather electron-donating property in π-conjugated polymers whereas pyridine ring has electron-accepting property.[7)] The observation of the electrochemically active cycle only in the reducing region for PAE-1 (Fig. 2) indicates that PAE-1 has essentially an electron-accepting property presumably due to the presence of both the electron-withdrawing pyridine-2,5-diyl and -C≡C- groups. PAE-2 also exhibits an active redox cycle at about -2.2 V *vs*. Ag / Ag^+.

The PAE type polymers shown above have high thermal stability. No thermal decomposition was observed below 300 °C as determined by TGA, and PAE-1 showed 75% residual weight at 600 °C.

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5) PAE-4: CP-MAS solid ^{13}C-NMR : δ : 86.4 (C≡C), 94.2 (C≡C), 123.4 (C_5H_3N), 132.5 (C_5H_3N), 145.2 (C_5H_3N), 156.9 (C_5H_3N) ppm. PAE-5: CP-MAS solid ^{13}C-NMR : δ : 87.7 (C≡C), 94.7 (C≡C), 118.8 (C_5H_3N), 129.0 (C_5H_3N), 140.3 (C_5H_3N), 151.1 (C_5H_3N) ppm. Although the peak positions obtained in the ^{13}C-NMR spectra of PAE-4 and PAE-5 show some difference, the absorption patterns of the two spectra are considered to be essentially same.

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