Preparation and Optical Properties of Soluble π-Conjugated Poly(aryleneethynylene) Type Polymers

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π-Conjugated poly(aryleneethynylene) type polymers $\{C{\equiv}C{-}Ar{-}C{\equiv}C{-}Ar'\}_n$ (Ar and/or Ar' = pyridine-2,5-diyl or alkyl-substituted arylene) synthesized by a palladium-catalysed coupling reaction are soluble in organic solvents and processable to make good thin films by casting, have large refractive index increment ($\Delta n/\Delta c$ = 0.29–0.38), and exhibit photoluminescence as well as fairly strong third harmonic generation, $\chi^{(3)}$ value of about 10^{-10} esu.

Optical properties of π-conjugated polymers have been the subject of a number of recent papers on nonlinear optics, photoluminescence, electroluminescence, electrochromism and dichroism.[1] Among such polymers poly(*para*-phenylenevinylene) PPV and its derivatives have attracted special attention because of their large $\chi^{(3)}$ values,[2] strong electroluminescence,[3] and ease in the preparation of their films from cast films of their precursor polymers.

In contrast to PPV, optical properties of poly(aryleneethynylene) $\{Ar{-}C{\equiv}C\}_n$ having a structure analogous to that of PPV, have received much less attention, although it was previously reported that π-conjugated poly(arylene-ethynylene-arylene-ethynylene) PAE type polymers were readily obtained *via* Pd-catalysed polycondensation,[4] [see eqns. (1) and (2)].

$$n\,X{-}Ar{-}X + n\,HC{\equiv}C{-}Ar'{-}C{\equiv}CH \xrightarrow[NEt_3]{\text{Catalyst}} \underset{PAE}{\{Ar{-}C{\equiv}C{-}Ar'{-}C{\equiv}C\}_n} \quad (1)$$

$$n\,X{-}Ar{-}X + n\,BrMgC{\equiv}C{-}Ar'{-}C{\equiv}CMgBr \xrightarrow{\text{Catalyst}} \underset{PAE}{\{Ar{-}C{\equiv}C{-}Ar'{-}C{\equiv}C\}_n} \quad (2)$$

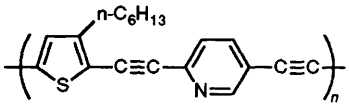
X: halogen. Catalyst: Pd complex + CuI [eqn. (1)] or Pd complex [eqn. (2)]

Most of the π-conjugated PAE type polymers so far reported, however, have only low solubility, and were not

Table 1 Poly(aryleneethynylene) type polymer

Polymer	Ar[a]	Ar'[a]	M_w[b]	ρ_v[c]	$\Delta n/\Delta c$[d] /cm^3 g^{-1}	Absorption λ_{max}/nm	Fluorescence[e] λ_{max}/nm
PAE-1	Hex-C_4HS	C_5H_3N	48×10^4	0.034	0.38	426[h]	465, 495
PAE-2	Hex-C_4HS	C_6H_4	9.6×10^4	0.011	0.34	403[h]	455, 485
PAE-3[f]	C_5H_3N	C_5H_3N	21×10^4	<0.01	0.29	340[i]	430[i]
PAE-4	C_2H_2Se	C_5H_3N	[g]	[g]	[g]	460[i]	525[i]

[a] C_5H_3N: pyridine-2,5-diyl. Hex-C_4HS: 3-hexylthiophene-2,5-diyl. C_6H_4: 1,4-phenylene. C_4H_2Se: selenophene-2,5-diyl. [b] Molecular weight determined by light scattering method.[6] [c] Degree of depolarization. [d] Refractive index increment. [e] Irradiation light = 430 nm (PAE-1), 405 nm (PAE-2), 340 nm (PAE-3), or 440 nm (PAE-4). [f] This polymer was prepared by using 2-ethynyl-5-bromopyridine instead of a mixture of 2,5-diethnylpyridine and 2,5-dibromopyridine. [g] Not measured. [h] In chloroform. [i] In formic acid.



PAE-1

suited to the investigation of their optical properties. On the other hand, it is now recognized that the use of alkyl-substituted arylene[5a–e] and/or pyridine-2,5-diyl unit[5f,5g] in poly(arylene) type polymers enhances solubility of the polymers in organic solvents.

On this basis, we have prepared the PAE type π-conjugated polymers consisting of the alkyl-substituted arylene unit and/or pyridine-2,5-diyl unit, investigated optical properties [specifically $\chi^{(3)}$] of the polymers, and now report the results.

Carrying out the polycondensation according to eqn. (1) affords the PAE type polymers with arylene units of 3-hexylthiophene-2,5-diyl, pyridine-2,5-diyl, 1,4-phenylene and selenophene-2,5-diyl (see Table 1); a 1 : 1 mixture of X–Ar–X (X = I for PAE-1 and -2, and Br for PAE-4) and HC≡C–Ar'–C≡CH was stirred at 50–110 °C in toluene in the presence of $Pd(PPh_3)_4$ (1 mol% per the monomer), CuI (2 mol%) and an excess of NEt_3 under N_2 in a manner similar to that previously reported[4a] and the obtained polymer was washed with methanol: yields for PAE-1, 2, 3, and 4 were 100, 93, 60 and 100%, respectively.

The polymers have high molecular weights (see Table 1) as determined by light scattering method,[6,†] which also reveals that they have a considerably large refractive index increment ($\Delta n/\Delta c$ = 0.29–0.34 cm^3 g^{-1}) presumably owing to the presence of delocalized electron along the polymer chain.[5g] Usual non-π-conjugated polymers have the $\Delta n/\Delta c$ value of 0.1–0.2 cm^3 g^{-1}. The non-zero ρ_v values of PAE-1 and -2 (ρ_v = 0.011–0.034) are comparable with that of {*p*-C_6H_4CONH}$_n$ (ρ_v = 0.0268) with high molecular weight (M_w = 38400) and a relatively rigid structure, indicating that PAE-1 and PAE-2 also have a rigid structure. However, the ρ_v values are considerably lower than that of rigidly linear poly(pyridine-2,5-diyl) PPy (ρ_v = 0.33)[5f,5g] presumably owing to the much higher molecular weight of PAE-1 and -2 than that of PPy (M_w = 3800) and/or the presence of the bulky hexyl substituent.

PAE-1 and -2 are soluble in organic solvents such as chloroform and toluene, and PAE-3 and -4 are in formic acid. Good quality films of PAE-1 and -2 were obtained by casting from chloroform solution, and the film of PAE-1 thus prepared (thickness = 12.5 nm) on a glass substrate exhibited a fairly strong THG with the $\chi^{(3)}$ value of about 10^{-10} esu as measured at 1.9 μm fundamental wavelength, which was obtained using a different-frequency generation of a Q-switched Nd: YAG laser and a tunable dye laser. The PAE-1 and -2 show absorption peaks at 426 and 403 nm, respectively, in chloroform and PAE-1, -2, -3 and -4 emit visible light when irradiated with UV or visible (340–440 nm) light (Table 1). The strong fluorescence of the PAE type polymers indicates that they are potentially useful electroluminescent materials.

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† Solvents of PAE-1 and -2 are chloroform, whereas formic acid is used for PAE-3. The results of molecular weight determination are still preliminary, because rigid π-conjugated polymer molecules may easily coagulate. A light scattering study indicated that there exist coagulations for PAE-1 and -3. GPC analysis (eluent = chloroform) indicated that PAE-1 and PAE-2 had M_w of 19000 and 96000 (*vs.* polystyrene), respectively. PAE-1 prepared at 50 °C contained 4.2% iodine.

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