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Poly(aryleneethynylene) Type Polymers Composed of *p*-Phenylene and 2,5-Thienylene Units. Analysis of Polymerization Conditions and Terminal Group in Relation to the Mechanism of the Polymerization and Chemical and Optical Properties of the Polymer

Takakazu Yamamoto* and Keisuke Honda

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

Naoki Ooba and Satoru Tomaru

NTT Opto-electronics Laboratories, Nippon Telegraph and Telophone Corporation, Naka-gun, Ibaraki 319-11, Japan

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ABSTRACT: Palladium-catalyzed polycondensation between *p*-diethynylbenzene (HC≡C−Ph−C≡CH) and 2,5-diiodo-3-hexylthiophene (I−Th(Hex)−I) has been carried out under various conditions by changing the polymerization temperature, medium, and added amines. The polycondensation gives the polymer (PAE-1) with a M_n of about 3×10^4 (by GPC, polystyrene standards) and an $[\eta]$ value of 0.8 dL g^{-1}. By using neat NEt_3 as the medium, the polymerization proceeds fast. ^1H-NMR spectroscopic analysis indicates that oligomeric PAE-1 obtained at short polymerization time has a C−I bond (−Th(Hex)−I bond) as the major terminal group, which is consistent with results of the basic Pd-catalyzed C−C coupling reaction. The C−I terminal bond of oligomeric PAE-1 reacts with 1,3,5-triethynylbenzene and 1,2,4,5-tetraethynylbenzene to give polymers with M_n values of 8.7×10^5 and 2.3×10^6 (by GPC), respectively, and the polymers are considered to have star-type structures. All the polymers show two (main and sub) photoluminescence PL peaks at 456 ± 3 and 486 ± 2 nm. The C≡C bond of PAE-1 is susceptible to trans-type hydrogenation with SMEAH (sodium bis(2-methoxyethoxy)aluminum hydride) and DIBAL (diisobutylaluminum hydride) as well as to chlorofluorination by a mixture of *N*-chlorosuccinic imide and a pyridinium salt of $(HF)_xF^-$.

Introduction

The following palladium-catalyzed C−C coupling reaction[1−3] (eq 1) has been utilized to the preparation of various π-conjugated poly(aryleneethynylene) PAE-type polymers (eq 2).[4−6]

$$\mathrm{Ar{-}C{\equiv}CH + Ar'X \xrightarrow[NR_3]{Pd-Cu} Ar{-}C{\equiv}C{-}Ar'} \qquad (1)$$

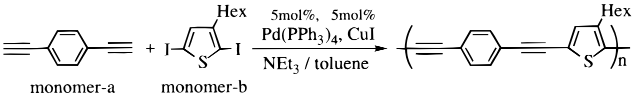
$$n\mathrm{HC{\equiv}C{-}Ar{-}C{\equiv}CH} + n\mathrm{X{-}Ar'{-}X} \xrightarrow[NR_3]{Pd-Cu} \underset{\mathrm{PAE}}{(\mathrm{C{\equiv}C{-}Ar{-}C{\equiv}C{-}Ar'})_n} \qquad (2)$$

The PAE-type polymers have interesting optical (e.g., large third-order nonlinear optical susceptibility $\chi^{(3)}$), electrochemical, and electrical properties,[4−6] and their potential usefulness in electronic and optical devices[7] has also been reported. However, there remain some unclarified points about the polymerization as well as about the structure and chemical reactivity of the polymer. For example, the terminal group of the polymer has not been clarified well and chemical reactivity of the −C≡C− group has not been revealed well. In this paper we report (i) the effect of the polymerization conditions on the molecular weight of the polymer and determination of the terminal unit (e.g., C−I or −C≡CH) in the propagating species, (ii) utilization of the terminal group for the next-step polymerizations, (iii) chemical conversion of the −C≡C− bond to a C=C double bond, and (iv) analysis of the photoluminescent and nonlinear optical behavior of the polymer.

The present study is focused on the polycondensation using p-$C_6H_4(C{\equiv}CH)_2$ and 2,5-diiodo-3-hexylthiophene as the monomers in eq 2, since these monomers are easily obtained and the obtained polymer has good solubility in organic solvents. In addition, good solubility of the monomers in various solvents makes it possible to carry out the polymerization under various conditions. Results[3,8] from recent investigations on each of elementary steps (*vide infra*) of the basic coupling reaction (eq 1) contribute to a better understanding of the polymerization process.

Results and Discussion

Polymerization. Table 1 summarizes results of the polycondensation between p-$C_6H_4(C{\equiv}CH)_2$ (monomer a) and 2,5-diiodo-3-hexylthiophene (monomer b) catalyzed by a mixture of $Pd(PPh_3)_4$ and CuI.



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As shown in Table 1, when a 1:1 mixture of toluene and NEt_3 is used as the reaction medium, the polymerization at room temperature requires a long polymerization time. On the other hand, the polymerization at 60 °C is almost completed in 12 h. The polymerization at both temperatures gives PAE-1 in high yield (>80%), except for the polymerizations at short times

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Table 1. Polycondensation between p-$C_6H_4(C{\equiv}CH)_2$ and 2,5-Diiodo-3-hexylthiophene[a]

run	solvent	temp, °C	time, h	yield, %	$10^{-4}M_n$[b]	$10^{-4}M_w$[b]	λ_{max}, nm[c]	$10^{11}\chi^{(3)}$,[d] esu
1	Tol + NEt_3[e]	rt[g]	24	51	0.84	0.95	411	
2	Tol + NEt_3	rt	96	94	2.8	3.0	418	3.0 (650 Å)
3	Tol + NEt_3	rt	120	100	1.3	2.6	415	
4	Tol + NEt_3	60	3	66	0.66	2.0	412	
5	Tol + NEt_3	60	6	81	0.52	0.88	409	
6	Tol + NEt_3	60	12	86	2.9	7.5	418	
7	Tol + NEt_3	60	24	88	2.8	7.9	418	
8	Tol + NEt_3	60	34	83	3.2	5.1	418	3.8 (440 Å) 3.0 (780 Å) 4.2 (210 Å),[h] 3.4 (440 Å)[h]
9	NEt_3	rt	1	89	2.5	9.2	421	
10	NEt_3	rt	7	99	3.4	11	421	
11	NEt_3	rt	24	100	3.0	13	419	
12	Tol + DCHA[f]	rt	24	84			419	

[a] Catalyst = $Pd(PPh_3)_4$ (5 mol % per the monomer) + CuI (5 mol %). [b] Determined by GPC ($CHCl_3$, polystyrene standard). [c] In $CHCl_3$ unless otherwise noted. [d] Third-order nonlinear optical susceptibility. Thickness of the film used is given in parentheses. [e] A 1:1 mixture of toluene and NEt_3. [f] Dicyclohexylamine. [g] Room temperature (about 25 °C). [h] Data of PAE-1 prepared at 110 °C.[4d,17]

(run 1 (51%) and run 4 (66%)). The M_w value ($(6.5 \pm 1.4) \times 10^4$; determined by GPC) of the PAE-1 obtained at 60 °C (runs 6−8) is comparable to that (9.6×10^4; determining by the light scattering method)[4d] of PAE-1 obtained at 110 °C. The polymer obtained in no. 8 shows an $[\eta]$ value of 0.82 dL g^{-1} at 30 °C in $CHCl_3$, and the relation[9] between the M_n and $[\eta]$ values of this polymer suggests that the PAE-1 has comparable or somewhat higher stiffness compared with poly(3-hexylthiophene-2,5-diyl). The polymer may contain a diacetylenic unit, $-C{\equiv}C-C{\equiv}C-$, formed by coupling between two molecules of monomer a, as suggested previously by Trumbo and Marvel[5a] for an analogous polymerization. However, the content of such a unit, if any, in PAE-1 is considered to be small, since the ^{1}H-NMR spectrum of PAE-1 with a sufficient molecular weight (Figure 1a) shows a simple peak pattern and the peak area ratios agree with a 1:1 ratio between the units from monomer a and monomer b, respectively.

When the solvent is changed to neat NEt_3 (runs 9−11), the polymerization proceeds more easily and the obtained polymer has a higher molecular weight.

The basic reaction (eq 1) of the polycondensation most probably proceeds through the following elementary reactions,

$$ArC{\equiv}CH + Cu(X)L_a + NR_3 \rightarrow Cu(C{\equiv}CAr)L_a + [R_3NH]X \quad (4)$$

$$Ar'X + Pd^0L_b \xrightarrow{\text{oxidative addition}} Pd(Ar')(X)L_b \quad (5)$$

$$Cu(C{\equiv}CAr)L_a + Pd(Ar')(X)L_b \xrightarrow{\text{transmetalation}} Cu(X)L_a + Pd(C{\equiv}CAr)(Ar')L_b \quad (6)$$

$$Pd(C{\equiv}CAr)(Ar')L_b \xrightarrow[\text{(orC−C coupling)}]{\text{reductive elimination}} Pd^0L_b + ArC{\equiv}CAr' \quad (7)$$

$$\text{total: } ArC{\equiv}CH + Ar'X + NR_3 \rightarrow ArC{\equiv}CAr' + [R_3NH]X \quad (8)$$

$$L = \text{ligand } (PPh_3, \text{solvent, etc.}),\ Pd^0L_b = \text{zerovalent Pd complex},\ X = \text{halogen}$$

and the oxidative addition of Ar′X (eq 5) is considered to be the rate determining step based on synthetic results.[1,2]

Recent basic organometallic research also indicates that reactions 4,[3,8] 6,[3] and 7[3] are fast processes and suggests that the oxidative addition of ArX (eq 4)[10] is the slowest step among the above elementary reactions. Use of neat NEt_3 will cause partial replacement of the PPh_3 ligand of added $Pd(PPh_3)_4$ with highly basic NEt_3, and this may be the reason for the higher rate of polymerization in neat NEt_3. The increase in the basicity of zerovalent transition metal complexes usually enhances the reactivity of the transition metal complex against the oxidative addition (eq 5).[10,11] Coordination of NEt_3 to propagating $\cdots-C{\equiv}C-Cu$ acetylide terminal may also partly contribute to the higher rate of polymerization.

Although neat NEt_3 gives the polymer with the higher molecular weight at room temperature, most part of the research described below (e.g., the next-step polymerization) is carried out with a mixture of NEt_3 and toluene due to the ease of handling the polymerization system and better solubility of PAE-1 in toluene. However, use of neat NEt_3 may be suited for the practical purpose of preparing the PAE-type polymers.

As shown in Table 1, PAE-1 with the M_n value of $(5-8) \times 10^3$ (runs 1, 4, and 5) gives a $\pi-\pi^*$ absorption band at about 410 nm, and the absorption band shifts to a longer wavelength with an increase in the molecular weight to reach about 420 nm. A 1:1 mixture of dicyclohexylamine and toluene also gives PAE-1 with a long λ_{max} of 419 nm in 84% yield (run 12). However, use of other amines (1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,4-diazabicyclo[2.2.0]octane (DMCO)) in toluene or use of NEt_3 in other solvents (THF and $CHCl_3$) affords the PAE-1 with shorter λ_{max} (401−414 nm) in lower yields (22−52%; after 24 h at room temperature).

IR spectra of the polymers listed in Table 1 are almost identical to that of the previously reported PAE-1.[4f] They exhibit a $\nu(C{\equiv}C)$ band of disubstituted acetylene at 2194 cm^{-1}; however, $\nu(C{\equiv}C)$ (about 2100 cm^{-1}) and $\nu(C-H)$ (about 3300 cm^{-1}) bands of terminal acetylene are not observed.

Terminal Group of the Polymer. Figure 1 compares ^{1}H-NMR spectra of two samples of the PAE-1 with a high molecular weight (M_n = 32 000, run 8 in Table 1) and a low molecular weight (M_n = 5200, run 5). As shown in the part a in Figure 1, the polymer with the M_n value of 32 000 gives a simple ^{1}H-NMR pattern with only one peak for Th-H (thiophene ring-attached hydrogen; δ 7.07 ppm). On the other hand, the polymer with the M_n value of 5200 gives rise to an additional peak at δ 6.91 ppm, which is assigned to the terminal group. Comparison of the chemical shift with those of various thiophene derivatives such as those[12] shown

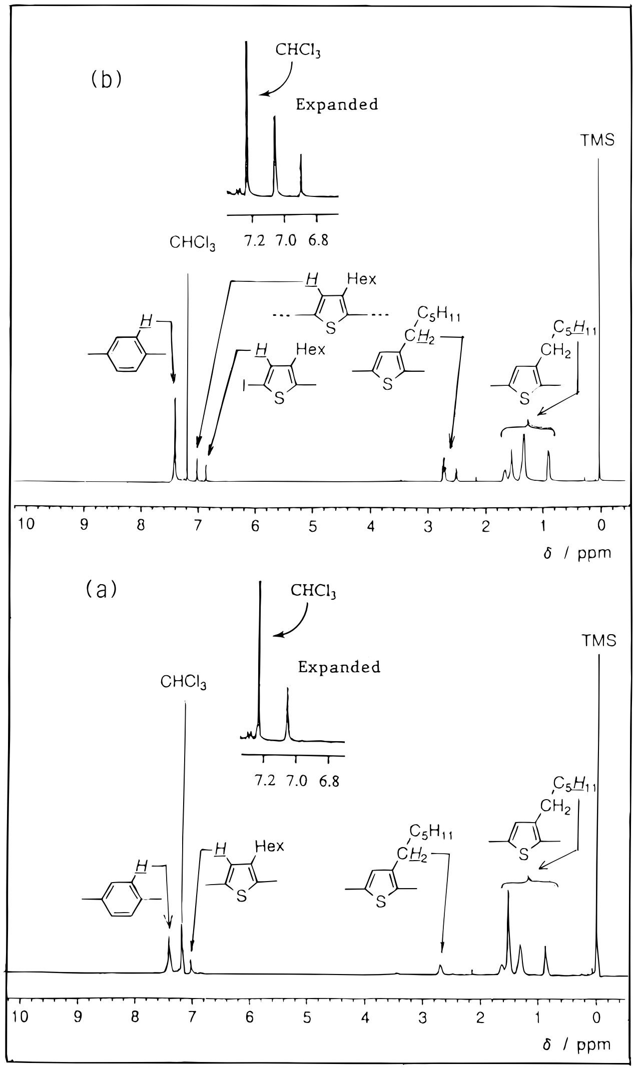
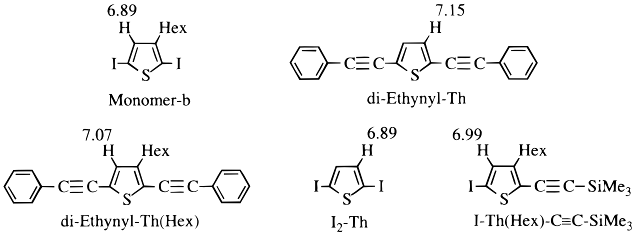
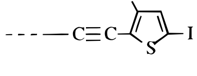


Figure 1. ^{1}H-NMR spectra of PAE-1 in CDCl$_3$: (a) run 8; (b) run 5.

Chart 1. Thiophene Derivatives and Their δ Values

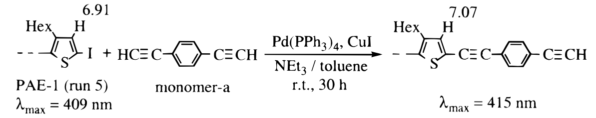


below in Chart 1 (cf. Experimental Section) suggests that the polymer has the following iodide terminal group.



Müllen[6c] and Moigne[6i] and their co-workers also suggested the presence of the C—X terminal group in the PAE-type polymer. In addition to the terminal group shown above, the polymer may have a terminal −C≡C—Th(Hex)—I group with the Hex group at the opposite position. The Th-H signal of this unit is considered to be included in the signal at δ 7.07 ppm.[13]

Treatment of the polymer with monomer a under the polymerization conditions actually causes complete disappearance of the Th-H at δ 6.91 ppm. The product



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gives rise to an absorption band at a longer wevelength (eq 9) due to expansion of the π-conjugation system[14] and becomes less soluble in organic solvents owing to its higher content of the nonsubstituted phenylene group. Peak areas of the ^{1}H-NMR signals of PAE-1 with the low molecular weight roughly agree with its M_n value. All the data support that the oligomeric PAE-1 has the C—I bonds at both polymer ends. PAE-1 with a higher molecular weight may have both the C—I and −C≡CH terminal groups. However, even in this case, the polymer seems to have the C—I bond as the major terminal group when it is recovered from the polymerization system containing monomer b.

If one assumes the following propagation reactions,

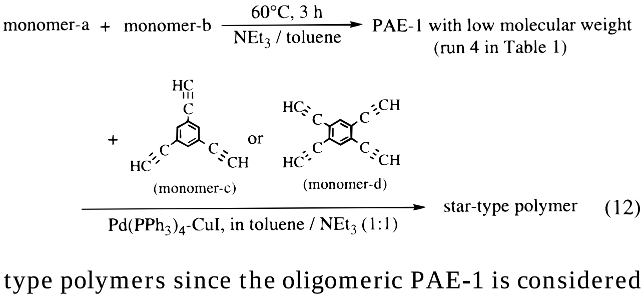
$$\underset{\text{(oligomer with C—I terminal)}}{\text{olimonomer—I}} + \underset{\text{monomer a}}{\text{HC}\equiv\text{C—Ph—C}\equiv\text{CH}} \xrightarrow[\text{NEt}_3]{\text{Pd–Cu}} \text{oligomer—C}\equiv\text{C—Ph—C}\equiv\text{CH} \quad (10)$$

$$\text{oligomer—C}\equiv\text{CH} + \underset{\text{monomer b}}{\text{I—Th(Hex)—I}} \xrightarrow[\text{NEt}_3]{\text{Pd–Cu}} \text{oligomer—C}\equiv\text{C—Th(Hex)—I} \quad (11)$$

$$\text{rate of reaction: eq 11} > \text{eq 10}$$

the results shown above indicate that reaction 11 proceeds more easily than reaction 10. Since the oxidative addition of Ar′X to the Pd(0) complex (eq 5) is regarded as the rate-determining step in the basic C—C coupling reaction (eq 1), these data suggest that the Pd(0) complex reacts more easily with the C—I bond in monomer b (eq 11) than with the C—I bond in oligomer I (eq 10). The C—halogen bond in polymeric organic halides (e.g., poly(vinyl chloride)) usually has a lower reactivity (e.g., against Mg) than the usual organic halides,[15] and enhancement of the reactivity of the C—I bond in monomer b by another electron-withdrawing I is also conceivable since such an enhancement of the reactivity against the Pd(0) complex by an electron-withdrawing substituent is known.[10]

Utilization of the Terminal Group. Addition of triethynyl- and tetraethynylbenzene (monomer c and monomer d) to the polymerization system after the formation of oligomeric PAE-1 is expected to give star-



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type polymers since the oligomeric PAE-1 is considered to have the C—I group at the both ends. Application of the basic coupling reaction (eq 1) to the preparation of

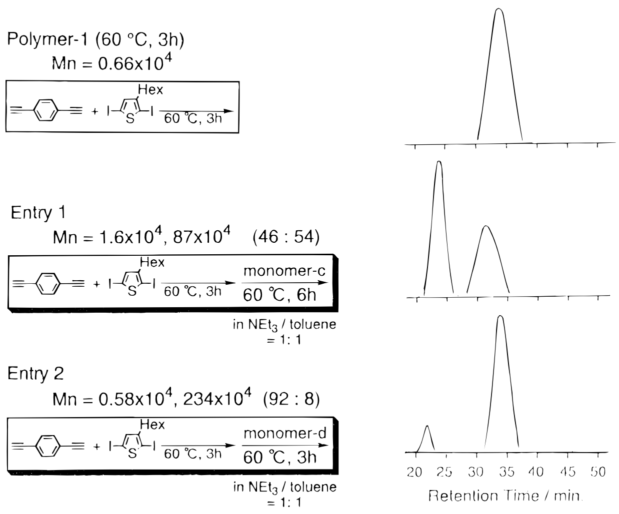


Figure 2. GPC traces of polymers. PAE-1 (run 4 in Table 1); entry 1, after the reaction with monomer c (60 °C, 6 h); entry 2, after the reaction with monomer d (60 °C, 3 h). Eluent = $CHCl_3$.

dendric polymers by using multifunctional monomers like monomer c has been reported.[5a,16]

Figure 2 shows GPC traces of the products obtained in the reaction expressed by eq 12. As shown in Figure 2, the treatment of the oligomeric PAE-1 with an excess amount of monomer c or monomer d affords polymers with very high molecular weights.[14] The reaction with monomer c for 6 h at 60 °C (entry 1 in Figure 2) gives a fraction with a very high molecular weight. The bimodal GPC trace of the polymer suggests that the $-C{\equiv}CH$ group in monomer c acquires a higher reactivity after coupling of other $-C{\equiv}CH$ group(s) in monomer c with the oligomeric PAE-1. Use of monomer d in eq 12 also gives a polymer with a high molecular weight. These results are also consistent with the presence of the C—I group at both ends of the oligomeric PAE-1.

IR spectrum (Figure 3) of the polymer obtained by the reaction with monomer c (Entry 1) shows an out-of-plane δ(CH) vibration peak of the 1,3,5-trisubstituted benzene unit at 884 cm^{-1}. The polymer gives rise to a ν(C—H) peak of the terminal $-C{\equiv}CH$ group; however, its relative intensity against the δ(CH) absorption peak at 884 cm^{-1} is decreased compared with that observed with the monomer c. This polymer gives rise to a small peak of the $-C{\equiv}CH$ group at δ 3.2 ppm in its ^{1}H-NMR spectrum. The polymer obtained in entry 1 shows the $\pi-\pi^*$ absorption band at the same position as original PAE-1, suggesting that effective expansion of the π-conjugation system does not take place through the 1,3,5-triethynylbenzene unit.

The IR spectrum of the polymer obtained by the reaction with monomer d (entry 2) shows a δ(CH) vibration peak of 1,2,4,5-tetrasubstituted benzene at 908 cm^{-1}. Addition of cuprous acetylide obtained by an in situ 1:3 reaction of monomer c and CuI (instead of monomers-c in Figure 2)

$$\text{oligomeric PAE-1} \xrightarrow{\substack{\text{Cu(I) acetylide of}\\ \text{monomer c (CuI +}\\ \text{NEt}_3\text{ + monomer c)}}} \text{next-step polymerization} \quad (13)$$

gives insoluble products presumably due to a high-order expansion (or cross-linking) of the polymer system.

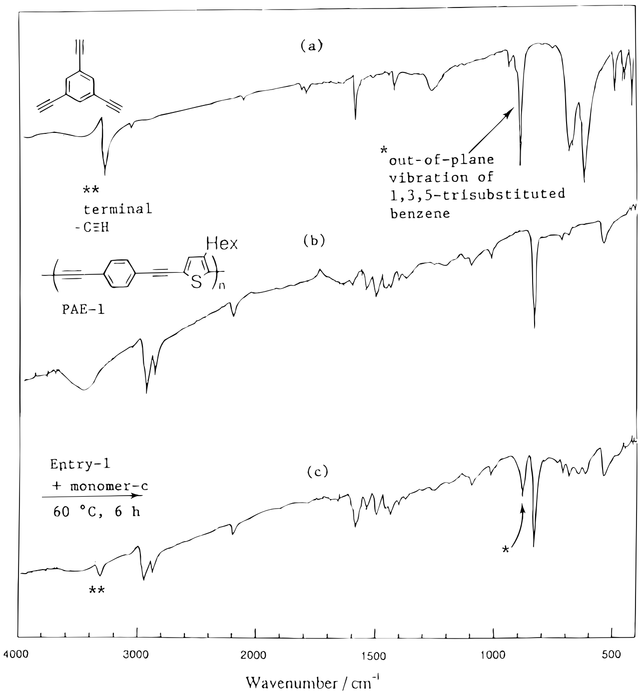


Figure 3. IR spectra of (a) monomer c, (b) PAE-1, and (c) the polymer obtained in entry 1 (Figure 2).

Optical Properties. Films of all PAE-1's prepared under the various conditions (including previously applied conditions (110 °C, 2 h))[4f] give a peak $\chi^{(3)}$ (third-order nonlinear optical susceptibility)[4d] value, $\chi^{(3)}_{max}$, of $(3.6 \pm 0.6) \times 10^{-11}$ esu at $\lambda_f = 1350$ nm (or $\lambda_f/3 = 450$ nm; λ_f = fundamental wavelength irradiated against the polymer film). The dependence of the $\chi^{(3)}$ value on λ_f and the $\chi^{(3)}_{max}$ value are essentially the same as those of PAE-1 prepared at 110 °C and reported previously,[4d] and the $\chi^{(3)}_{max}$ value is given in the last column of Table 1. A channel wavequide by using the third-order nonlinear optical properties has been reported.[7] As shown in Table 1, there is a trend that a thinner film gives a larger $\chi^{(3)}_{max}$ value.

Figure 4 depicts photoluminescence PL spectra and excitation spectra of the polymers, and Table 2 lists the photoluminescence data. All of the polymers exhibit a main photoluminescence at 456 ± 3 nm, which agrees with the onset position of the UV—visible spectrum of PAE-1, as usually observed with π-conjugated polymers. The photoluminescence has a quantum yield (Φ) of about 30%.

The photoluminescence spectra show a clear shoulder peak at 486 ± 2 nm and additional vague shoulder peaks with an energy difference of 1350 cm^{-1} in the region of longer wavelengths. Similar structures in the photoluminescence spectra have been observed with other poly(aryleneethynylene)-type polymers[4d] and poly(arylenevinylene) (PAV)-type polymers.[18]

Both the excitation spectra monitored at the main peak (453 nm) and the shoulder peak (486 nm) of the photoluminescence give a peak at the same position (423 ± 3 nm, the last column in Table 2), which agrees with the λ_{max} position of the absorption band. These results indicate that both the main and shoulder photoluminescence peaks originate from the same electronic excitation.

As shown in Figure 4 and Table 2 (cf. footnote *b*), the relative intensity of the shoulder peak is increased for the copolymers with monomer c and monomer d (eq 12),

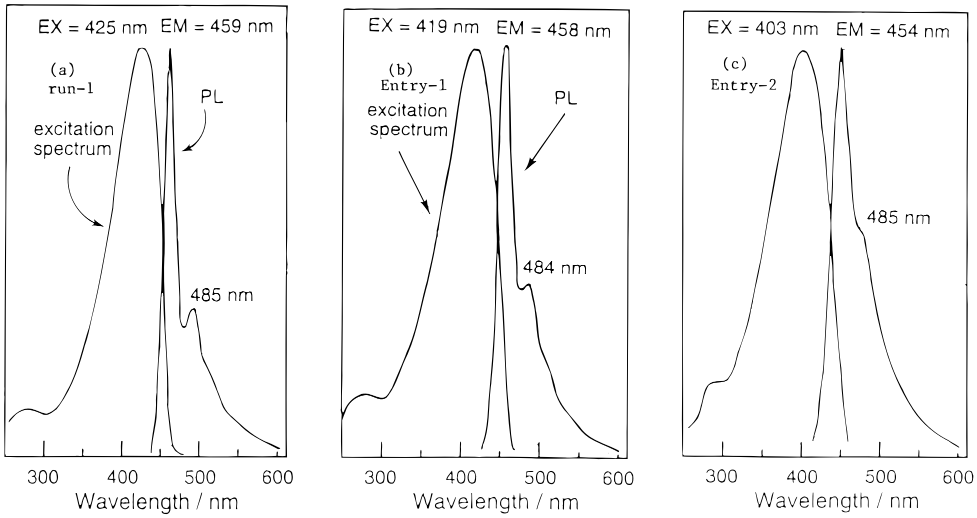


Figure 4. Photoluminescence PL and excitation spectra of (a) PAE-1 (run-8), (b) the polymer obtained in entry-1 (Figure 2), and (c) the polymer obtained in entry-2. Measured in $CHCl_3$. Excitation spectra are monitored at the main photoluminescence peak. Monitoring at the shoulder peak gives essentially the same excitation spectrum.

Table 2. Photoluminescence PL Data of Polymers[a]

polymer	absorption λ_{max}, nm	photoluminescence[b] λ_{max}, nm (relative intensity)	Φ, %[c]	excitation spectrum λ_{max}, nm
run-1[d]	411	459, 488* (0.37)	26	420
run-8[d]	418	459, 485* (0.37)	35	425
entry 1[e]	409	458, 484* (0.42)	38	419
entry 2[e]	409	454, 485* (0.51)	29	403

[a] In $CHCl_3$. [b] The * mark indicates a shoulder peak. Relative intensity = relative intensity of the PL peak with * against that of the PL peak without *. [c] Quantum yield. [d] Cf. Table 1. [e] Cf. Figure 2.

suggesting that a possible vibronic coupling[18] is affected by mutual interaction of the chain of PAE-1 and such interaction takes place more effectively between the branched PAE-1 units in the star-type copolymer.

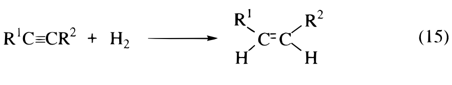
As for the photoluminescence of the film, the quantum yield Φ becomes lower (<3%), presumably due to the presence of thermal quenching route(s) in the excimer-type adduct formed between a photoexcited PAE-1 and original PAE-1 in the solid state.

Chemical Transfer of the C≡C Bond to the C=C Bond. Hydrogenation. The acetylenic −C≡C− bond generally has a high reactivity against addition reactions to the −C≡C− bond,

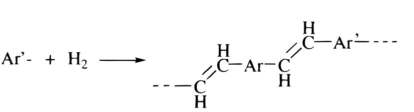
$$R^1C{\equiv}CR^2 + A{-}B \rightarrow R^1AC{=}CR^2B \qquad (14)$$

although disubstituted acetylenes usually possess a lower reactivity compared with terminal acetylenes. Our previous investigation reveals[4d] that the PAE-type polymer has an even lower reactivity than the disubstituted acetylenes in transition metal (e.g., Lindler catalyst)-assisted hydrogenation of the −C≡C− bond.

Since the transition metal-assisted hydrogenation causes cis-addition of H_2, occurrence of such hydrogenation in the PAE-type polymer will require severe movement of the polymer chain (R^1 and/or R^2 in eq 15), and this may be the reason for the difficulty of the transition-metal-assisted hydrogenation of the PAE-type polymers. On the other hand, trans-hydrogenation of the PAE-type polymer will be accompanied with minor motion of the polymer chain.



$$R^1C{\equiv}CR^2 + H_2 \longrightarrow (R^1)(H)C{=}C(R^2)(H) \qquad (15)$$

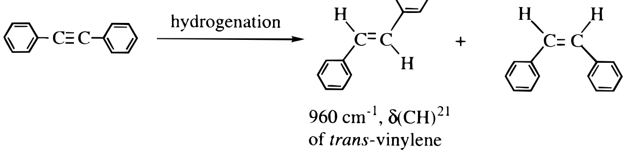


$$-C{\equiv}C{-}Ar{-}C{\equiv}C{-}Ar'{-} + H_2 \longrightarrow {-}{-}{-}CH{=}CH{-}Ar{-}CH{=}CH{-}Ar'{-}{-}{-} \qquad (16)$$

On the basis of this consideration, we have investigated the hydrogenation of PAE-1 and its model compound (Ph−C≡C−Th−C≡C−Ph; cf. Chart 1) with SMEAH (sodium bis(2-methoxyethoxy)aluminum hydride $Na[(CH_3OCH_2CH_2O)_2AlH_2]$) and DIBAL (diisobutylaluminum hydride $Al(i\text{-}C_4H_9)_2H$). SMEAH usually gives trans-hydrogenated products of acetylenes,[19] and DIBAL affords trans- or cis-hydrogenated product depending on the reaction conditions.[20]

Table 3 summarizes results of the hydrogenation of PAE-1 and related compounds with (i) SMEAH, (ii) DIBAL, (iii) H_2−Pd/C system, (iv) H_2−$PdCl_2$ system, and (v) H_2−$RhCl(PPh_3)_3$ (Wilkinson catalyst) system.

All of the these hydrogenating reagents and systems can hydrogenate diphenylacetylene to give *trans*- and/or *cis*-stilbene.



(17)

However, as described above, application of the same reaction conditions for the hydrogenation of PAE-1 by using the systems (iii)−(v) does not lead to the hydrogenation and only the original PAEs are recovered, as judged from IR spectroscopy.

On the other hand, use of SMEAH or DIBAL causes a change in the IR spectrum of PAE-1. The IR spectra of the recovered polymers after the treatment with SMEAH and DIBAL (charts d and e in Figure 5) clearly indicate a new peak at 940 cm^{-1} (last column in Table 3), which can be assigned to the out-of-plane δ(CH) vibration[21] of the *trans*-CH=CH− group. These results

Table 3. Hydrogenation of PAE-1 and Related Compounds[a]

no.	acetylenic compound	reactant[b] (mol/1 mol of unit)	temp, °C[c]	time, h	results[d]
H-1	Ph−C≡C−Th−C≡C−Ph	SMEAH (2.0)	rt	30	δ(CH) at 951 cm^{-1}, str
H-2	Ph−C≡C−Th−C≡C−Ph	DIBAL (2.0)	60	6	δ(CH) at 951 cm^{-1} (Figure 5b), str
H-3	PAE-1	SMEAH (2.0)	rt	48	δ(CH) at 940 cm^{-1} (Figure 5d), med
H-4	PAE-1	SMEAH (10.0)	rt	144	δ(CH) at 939 cm^{-1}, med
H-5	PAE-1	DIBAL (2.0)	60	6	δ(CH) at 939 cm^{-1} (Figure 5e), wk
H-6	PAE-1	H_2, Pd/c (0.1)[e]	rt	14	no reaction
H-7	PAE-1	H_2, $PdCl_2$ (0.1)[e]	rt	14	no reaction
H-8	PAE-1	H_2, $RhCl(PPh_3)_3$ (0.01)[e]	rt	110	no reaction
H-9	PAE-2	SMEAH (2.0)	r.t.	48	δ(CH) at 952 cm^{-1}, med
H-10	PAE-2	DIBAL (2.0)	rt	8	δ(CH) at 950 cm^{-1} (Figure 5g), med

[a] Carried out in toluene. [b] SMEAH = $Na[CH_3OCH_2CH_2O)_2AlH_2]$. DIBAL = $AlH(i\text{-}C_4H_9)_2$. [c] rt = room temperature. [d] Position of the peak assigned to δ(CH) of *trans*-vinylene group is given. str = strong, med = medium, and wk = weak. [e] At 1 atm, excess H_2.

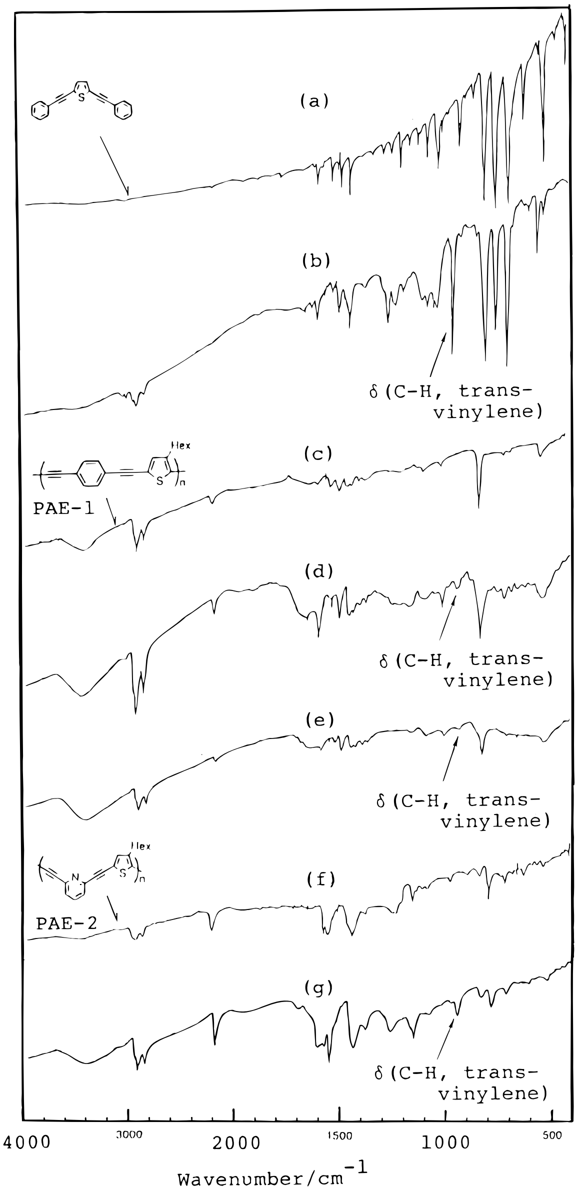
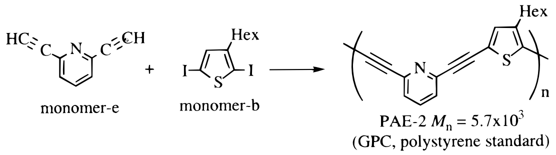


Figure 5. IR spectra of the hydrogenated products of (a) Ph−C≡C−Th−C≡CPh, (c) PAE-1, and (f) PAE-2: (b) Ph−C≡C−Th−C≡C−Ph with DIBAL (no. H-2 in Table 3), (d) PAE-1 with SMEAH (no. H-3), (e) PAE-1 with DIBAL (no. H-5), and (g) PAE-2 with DIBAL (no. H-10).

indicate that the −C≡C− bond in PAE-1 can be hydrogenated by the reagents. However, the degree of the hydrogenation does not seem high, since there remains the ν(C≡C) absorption bands in the IR spectra. Determination of the degree of hydrogenation was not possible due to low solubility of the hydrogenated polymer. The treatment of the polymer with SMEAH and DIBAL may cause a bridging reaction.

Ph−C≡C−Th−C≡C−Ph (Chart 1) is also hydrogenated by these reagents, and the IR spectrum of the product (chart b in Figure 5) exhibits a sharp δ(CH) absorption peak of the *trans*-CH=CH− group at 951 cm^{-1}.

The following newly prepared PAE-2 can be also hydrogenated to give the δ(CH) absorption peak of the *trans*-CH=CH− group at about 950 cm^{-1} (no. H-9 and H-10 in Table 3 and chart g in Figure 5).

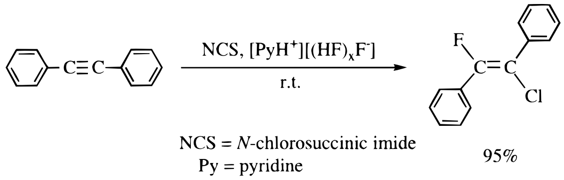


(18)

$$\xrightarrow[\text{or DIBAL}]{\text{SMEAH}} \text{hydrogenated} \qquad (19)$$

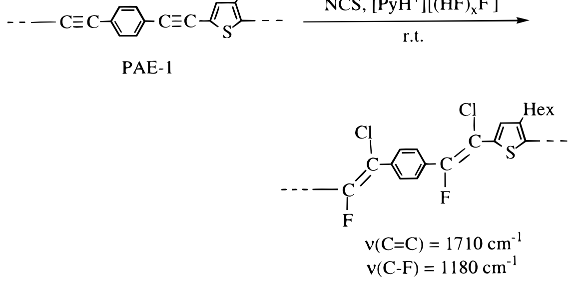
The degree of the hydrogenation of PAE-2 seems comparable to that of PAE-1, revealing that the structure (linear or zigzag structure) of the main chain does not have much effect on the ease of the hydrogenation.

Chlorofluorination. Diphenylacetylene is easily chlorofluorinated to give a trans addition product.[22] Use



(20)

of the same reagent in the reaction with PAE-1 also gives the chlorofluorinated product, whose IR spectrum exhibits sharp vinylic ν(C=C)[23] and ν(C−F)[22] absorption peaks at 1710 and 1180 cm^{-1}, respectively. As shown



(21)

in Figure 6, the ν(C≡C) absorption peak of PAE-1 at 2194 cm^{-1} disappears after the reaction, supporting that almost all the C≡C bonds in PAE-1 undergo the chlorofluorination.

Conclusion

The palladium-catalyzed polycondensation to give poly(aryleneethynylene)-type polymer PAE-1 proceeds well under various conditions (from room temperature to 110 °C, in a 1:1 mixture of toluene and NEt_3 or neat NEt_3 etc.) and polymers with a M_n value of about 3×10^4 are formed. Oligomeric PAE-1 obtained at short polymerization time has the C—I unit as the main terminal group, which is consistent with the results of basic organometallic chemistry. The C—I terminal bond of oligomeric PAE-1 can be utilized to the next-step polymerization, and the star-type polymers with very high molecular weights can be prepared by the reaction with 1,3,5-triethynylbenzene and 1,2,4,5-tetraethynylbenzene. PAE-1 prepared under various conditions gives essentially the same $\chi^{(3)}_{max}$ value and gives rise to main and shoulder photoluminescence peaks. The C≡C bond of PAE-1 is inert against transition metal-catalyzed hydrogenation; however, it is susceptible to the trans-type hydrogen promoted by SMEAH and DIBAL as well as to the trans-type chlorofluorination by a mixture of NCS and $[PyH^+][(HF)_xF^-]$.

Experimental Section

Materials. 3-Hexyl-2,5-diiodothiophene,[4d] $Pd(PPh_3)_4$,[24] monomer c,[5a,25] monomer d,[26] monomer e,[27] $RhCl(PPh_3)_4$,[28] and 3-hexyl-5-iodo-2-[2-(trimethylsilyl)ethynyl]thiophene[29] were prepared according to the literature. *p*-Diethynylbenzene, SMEAH, DIBAL, and NCS, $[PyH^+][(HF)_xF^-]$ were used as purchased. Acetylides of monomer a and monomer c were prepared in situ by mixing the monomer and CuI (1 mol/1 mol of −C≡CH) in the presence of excess NEt_3 at room temperature for 3 h. Solvents were dried and stored under N_2.

Polymerization. The Pd-catalyzed polycondensation between monomer a and monomer b was carried out under N_2 in a manner analogous to that previously reported.[4d] PAE-1 (run 8 in Table 1): Anal. Calcd: C, 82.7; H, 6.3. Found: C, 81.0; H, 5.9. Preparation of PAE-2 was carried out analogously. The Pd-catalyzed polycondensation between oligomeric PAE-1 and monomer c was carried out as follows. The oligomeric PAE-1 was prepared in situ from monomer a (81.4 mg, 0.646 mmol), monomer b (242 mg, 0.646 mmol), $Pd(PPh_3)_4$ (37.4 mg, 0.03 mmol), and CuI (6.2 mg, 0.03 mmol) in a mixture of toluene (10 mL) and NEt_3 (10 mL) at 60 °C (reaction time = 3 h; reaction conditions for run 4 in Table 1). To this polymerization system was added a toluene (10 mL) solution of monomer c (97.0 mg, 0.646 mmol). After stirring at 60 °C for the time shown in Figure 2, the reaction mixture was poured into 400 mL of methanol. The precipitate was collected by filtration and dissolved in $CHCl_3$. The $CHCl_3$ solution was poured into excess methanol, and the yellow precipitate was collected by filtration and dried under vacuum to yield 209 mg of yellow polymer. The polycondensation between oligomeric PAE-1 and monomer d was carried out analogously.

In the case of the reaction of oligomeric PAE-1 with monomer a, isolated oligomeric PAE-1 was used instead of oligomeric PAE-1 prepared in situ. The same molar amount of monomer a as that used to prepare the isolated PAE-1 was added to isolated PAE-1 in a 1:1 mixture of toluene and NEt_3 containing $Pd(PPh_3)_4$ (5 mol % per monomer a) and CuI (5 mol % per monomer a).

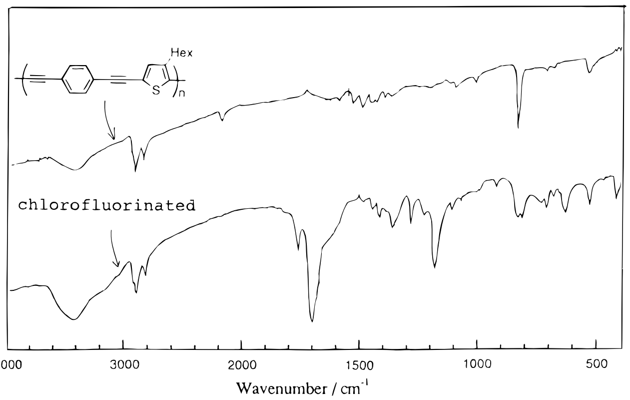


Figure 6. IR spectrum of chlorofluorinated product of PAE-1 according to eq 21 (lower chart).

Model Compounds Listed in Chart 1. 2,5-Dibromothiophene (1.47 g, 6.06 mmol), $Pd(PPh_3)_4$ (350 mg, 0.30 mmol), and CuI (58 mg, 0.30 mmol) were added to 40 mL of toluene. After the mixture was stirred at room temperature for a while, phenylacetylene (1.36 g, 13.3 mmol) was added, and the temperature was raised gradually to 60 °C. After 10 h, the product was purified by column chromatography (SiO_2; eluent = hexane) to yield 1.28 g (74%) of (diethynyl)Th (creamy yellow solid). Anal. Calcd for $C_{20}H_{12}S$: C, 84.5; H, 4.3. Found: C, 84.9; H, 4.2. ^{1}H-NMR ($CDCl_3$): δ 7.15 (s, 2H), 7.21−7.21 (m, 10H). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 82.29, 94.06, 122.57, 124.64, 128.41, 128.66, 131.48, 131.83. $\lambda_{max}(CHCl_3)$ = 350 nm.

A mixture of monomer b (1.80 g, 4.29 mmol), phenylacetylene (1.75 g, 17.2 mmol), $Pd(PPh_3)_4$ (253 mg, 0.2 mmol), and CuI (42 mg, 0.2 mmol) in a mixture of toluene (40 mL) and NEt_3 (40 mL) was stirred for 6 h at room temperatrure. Purification by column chromatography (SiO_2: eluent = hexane) gave a deep yellow oil of (diethynyl)Th(Hex) in 80% yield. ^{1}H-NMR ($CDCl_3$): δ 0.86 (s, 3H, CH_3), 1.34 (6H, CH_2), 1.63 (2H, β-CH_2), 2.13 (2H, α-CH_2), 7.07 (s, Th-H), 7.19 (6H, *m,p*-H), 7.52 (4H, *o*-H). All the syntheses were carried out under N_2 by using standard Schlenk techniques.

Hydrogenation and Chlorofluorination. PAE-1 (30 mg, 0.105 mmol monomer unit) and toluene (10 mL) were added to a Schlenk tube. After stirring for 2 h at room temperature, a toluene solution (60 L, 0.21 mmol) of SMEAH (3.59 M) was added to the mixture dropwise to carry out the hydrogenation (no. H-3 in Table 3). The color of the solution immediately changed from orange to deep blue. After stirring for 48 h at room temperature, the reaction mixture was slowly added to 70 mL of 1 M hydrochloric acid to obtain a reddish brown precipitate. After the mixture was stirred overnight, the reddish brown precipitate was recovered by filtration and dried under vacuum to yield a reddish brown powder (28 mg), whose IR spectrum is shown in Figure 5 (chart d). Other hydrogenations listed in Table 3 were carried out analogously.

Hydrogenation of PAE-1 with H_2 in the presence of transition metal catalysts was carried out under 1 atm of H_2 at room temperature.

NCS (31 mg, 0.23 mmol) and 3 mL of CH_2Cl_2 were added to a 60 mL polyethylene bottle under N_2. To this bottle were added $[PyH^+][(HF)_xF^-]$ (1 mL) and PAE-1 (28 mg, 0.095 monomer mmol) dissolved in 7 mL of CH_2Cl_2 in this order at room temperature. After stirring for 30 min at room temperature, a saturated aqueous solution of $NaHCO_3$ was added dropwise to stop the reaction. The product was extracted with chloroform. The chloroform solution was washed with water repeatly and dried under vacuum to yield 20 mg of an orange powder, whose IR spectrum is shown in Figure 6. Decreasing the amount of $[PyH^+][(HF)_xF^-]$ to 1/5 or less did not cuase the chlorofluorination.

Measurements. IR spectra were recorded on a JASCO IR-810 spectrometer. NMR spectra were taken using a JEOL X-400 or FX-100 spectrometer. UV−visible and photoluminescence spectra were measured with Shimadzu UV-3100PC and Hitachi F4010 spectrometers, respectively. GPC curves were measured with a Shimadzu liquid chromatography system with a Shodex 80M column and a 6A refractive index detector (solvent = $CHCl_3$).

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(14) Coupling between molecules of PAE-1 (e.g., by oxidative coupling between the $-C{\equiv}CH$ groups) does not proceed under the conditions. Stirring isolated PAE-1 (λ_{max} = 409 nm, run 5 in Table 1) in a 1:1 mixture of toluene and NEt_3 in the presence of $Pd(PPh_3)_4$ and CuI at 60 °C for 24 h (the same conditions applied in run 7 in Table 1) causes no change in the λ_{max} position.

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