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Synthesis and properties of poly(phenylacetylene)s with pendant imino groups

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Summary

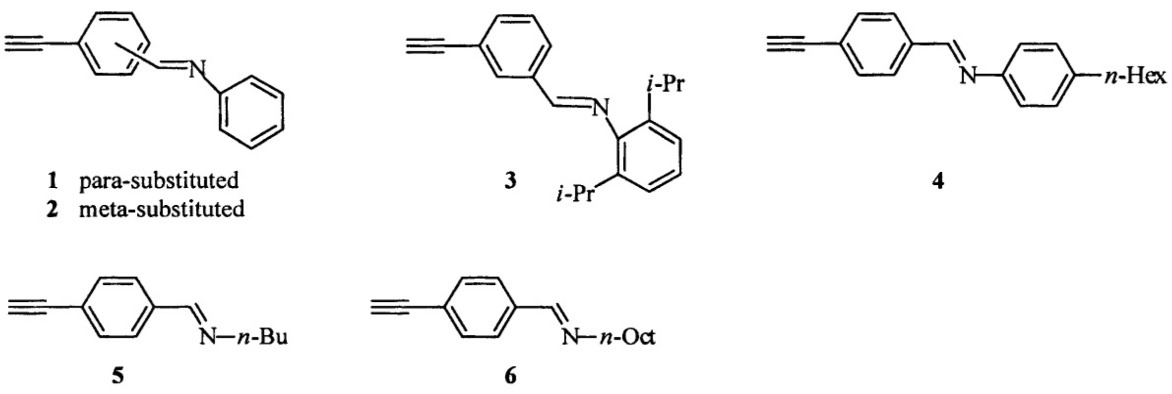
Polymerization of phenylacetylenes containing imino groups with a variety of transition metal catalysts was investigated. The monomers employed were *N*-(4-ethynylbenzylidene)aniline (**1**), *N*-(3-ethynylbenzylidene)aniline (**2**), *N*-(4-ethynylbenzylidene)-2,6-diisopropylaniline (**3**), *N*-(4-ethynylbenzylidene)-4-hexylaniline (**4**), *N*-(4-ethynylbenzylidene)butylamine (**5**), and *N*-(4-ethynylbenzylidene)octylamine (**6**). All of the monomers smoothly polymerized with $[(nbd)RhCl]_2$-Et_3N to give polymers in excellent yields, whereas no polymerization took place with W, Mo, and Fe catalysts. The produced polymers were orange to red solids and soluble in common organic solvents except for poly(**1**). UV-vis spectra of the polymers indicated that the main chains possess a similar degree of conjugation to that of poly(phenylacetylene). However, the stability of polymer backbone toward oxidative cleavage in solution remarkably improved, which is contributed by the electron-withdrawing character of imino groups.

Introduction

It is well known that polyacetylene exhibits characteristic optical, electrical and magnetic properties based on the arrangement of alternating double and single bonds along the backbone [1,2]. Introduction of appropriate substituents onto polyacetylene makes it possible to improve its stability, processability and solubility [3,4]. Simultaneously, however, the conjugation of the main chain is drastically reduced because the repulsion between pendant groups causes a twist of the main chain. Thus, most of high molecular weight polymers of substituted acetylenes, especially those from aliphatic acetylenes, are colorless or only slightly colored, and show quite low unpaired-electron densities. Among them, polymers from monosubstituted arylacetylenes possess relatively wide conjugation, which means that pendant aromatic groups allow the main chain to exist in relatively planar structures [5]. In particular, the main-chain conjugation is remarkably enhanced by the introduction of bulky ortho substituents [4] or condensed aromatic rings [6-12].

However, polymers from monosubstituted arylacetylenes are still unstable, and oxidative cleavage of main chains is unavoidable in solution [13,14]. Especially, a very rapid decrease in molecular weight is observed in chloroform, where high molecular weight poly(phenylacetylene) degrades to oligomers within few hours. Therefore, the decrease in the electron density of main chains would be effective for improving the stability of polymers from monosubstituted arylacetylenes. In the present study, we investigated the polymerization behavior of a new series of substituted phenylacetylenes containing

Chart



1 para-substituted
2 meta-substituted
3
4
5
6

Table 1. Polymerization of Azomethine-Containing Phenylacetylenes with $[(nbd)RhCl]_2$–Et_3N

Run	Monomer	Conv. (%)[a]	Yield (%)[b]	$M_w/10^3$ [c]	M_w/M_n [c]
1	**1**	85	85	insol.	–
2	**2**	100	100	1,280	7.35
3	**3**	100	95	1,000	1.70
4	**4**	100	100	840	6.68
5	**5**	80[d]	80	6.4[e]	2.30
6	**6**	90	90	nd[f]	nd[f]

[a] By GC. [b] MeOH-insoluble product. [c] Estimated by GPC ($CHCl_3$, PSt standard). [d] By gravimetric method. [e] A fraction that passed a membrane filter [f] Not determined.

azomethines, typical electron-withdrawing groups, with the purpose to produce high molecular weight poly(phenylacetylene)s with improved stability in solution.

Results and discussion

The monomers employed are illustrated in Chart. All of the monomers were readily accessible by the condensation of 3- or 4-(2-trimethylsilylethynyl)benzaldehydes with the corresponding amines, followed by the desilylation under alkaline conditions. Pd-catalyzed coupling of trimethylsilylacetylene with *N*-(4-bromobenzylidene)aniline failed due to the decomposition of Pd catalyst. The use of tetraalkylammonium fluoride is unnecessary because the traditional alkaline desilylation smoothly took place without anionic oligomerization of the monomers.

We first examined the polymerization by using a variety of transition metal catalysts that are effective for the polymerization of phenylacetylene [3,4]. Attempts to use metathesis catalysts based on W and Mo led to the deactivation of the catalysts by the imino functional groups. For example, WCl_6-Ph_4Sn, $MoCl_5$-Ph_4Sn, and $MoOCl_4$-*n*-Bu_4Sn resulted in no conversion of **1**. An Fe-based catalyst, $Fe(acac)_2$-Et_3Al, was also inactive for **1**. In a similar way, a metal carbonyl catalyst, $WCl_2(CO)_3(AsPh_3)_2$, which shows high activity in the production of high molecular weight polymers from arylacetylenes [15], provided no polymer. Even monomer **3** with an imino group protected by the bulky 2,6-diisopropyl group gave a similar result when WCl_6-Ph_4Sn was employed.

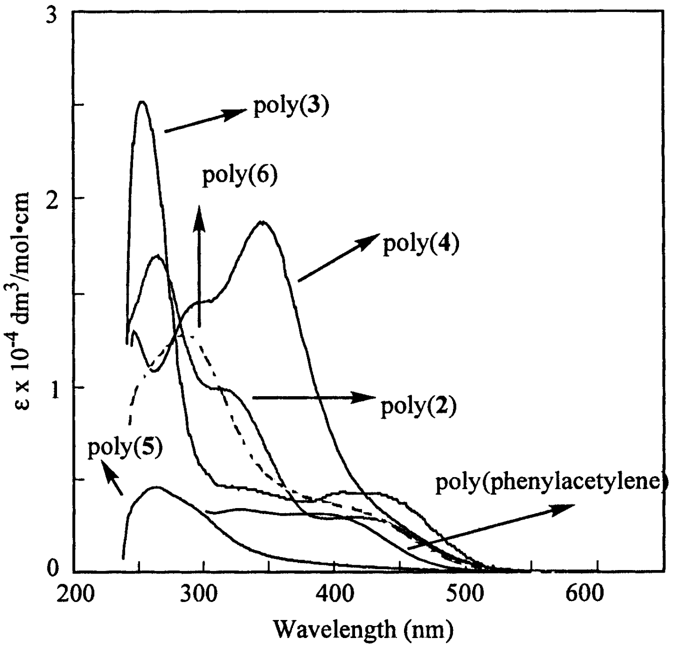


Figure 1. UV-vis spectra of poly(**2**)–poly(**6**) and poly(phenylacetylene) in $CHCl_3$.

On the other hand, the excellent ability of Rh catalysts to tolerate a wide range of functional groups allowed the formation of polymers (Table 1). For instance, the polymerization of **1** started instantaneously by adding the catalyst solution in toluene, and the viscosity of the system rapidly increased accompanying the color change of the solution into dark red. The polymers were obtained in excellent yields as methanol-insoluble fractions from all of **1**-**6**. In contrast to the poor solubility of the polymer from **1**, its meta isomer, **2**, gave quantitative yield of a polymer with good solubility in toluene, chloroform, THF, etc (run 2). A similar tendency regarding the solubility is recognized in the poly(phenylacetylene)s with azobenzene moieties [16]. GPC measurement of the polymer exhibited very high molecular weight of poly(**2**) (>10^6). A soluble polymer was also attainable by incorporating a flexible long alkyl chain onto the aromatic ring (monomer, **4**) even if the azomethine group was attached to the para position of the aromatic ring (run 4). Although substitution of a phenyl ring on nitrogen to aliphatic groups permits the production of apparently soluble polymer in high yields (runs 5 and 6), it was impossible to estimate their molecular weights by GPC because their solutions could not pass membrane filters. This is partly because the stronger basicity of nitrogen atoms of **5** and **6** than that of **2** allows the formation of microgel through the coordination of the pendant azomethines to Rh ions. This hypothesis can be supported by the fact that the polymer solution became completely homogeneous after the treatment with an excess of sodium salt of ethylenediaminetetraacetic acid.

Similarly to the general feature of the polymerization of arylacetylenes with Rh catalysts, the main chain of the present polymers consists of almost cis-transoidal structure. For example, poly(**4**) exhibits a sharp singlet signal at δ 5.87 that can be assigned as the olefinic protons in the cis-transoidal main chain. From the integrated intensities of the olefinic and azomethine protons around 8 ppm, the cis contents were estimated to be almost quantitative (90-100%). The polymers were bright orange to red solids, which depends on the structure of the side chain. Namely, the color of the polymers from meta-substituted monomers (**2** and **3**) is bright orange, and para-substituted ones gave deep-red polymers. UV-vis spectra of the polymers (Figure 1) clearly indicated no significant difference in the cutoff wavelengths (500-540 nm) with one another, and they are almost the same as that of poly(phenylacetylene) (530 nm). These results mean that the order of main chain conjugation is not significantly increased

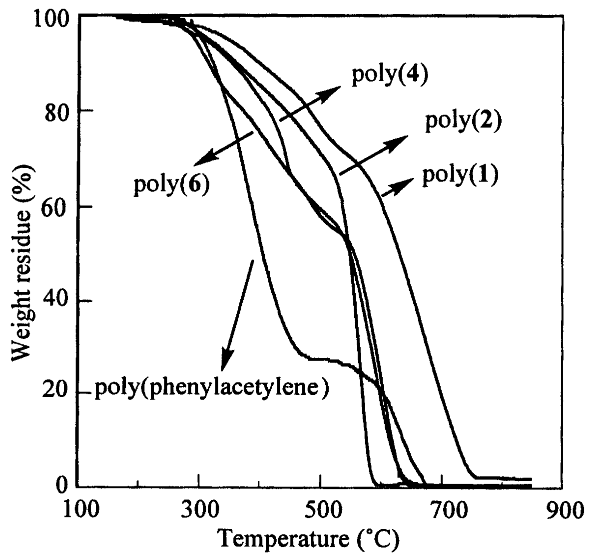


Figure 2. TGA curves of poly(**1**), poly(**2**), poly(**4**), poly(**6**) and poly(phenylacetylene) (in air, heating rate 10°C/min)

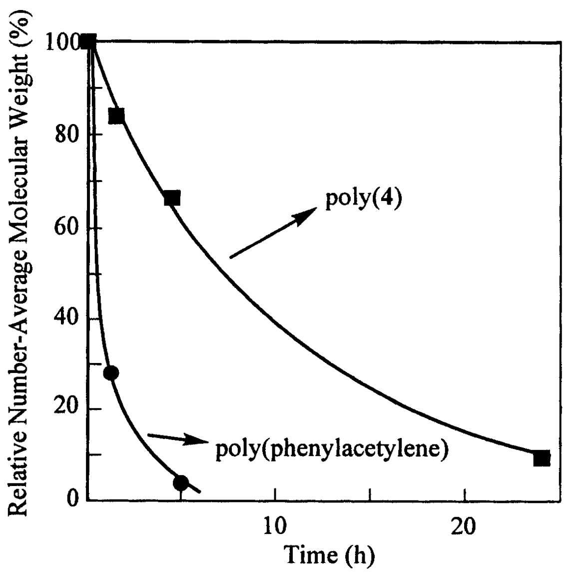


Figure 3. Time dependence of relative number average molecular weight (%) of poly(**4**) and poly(phenylacetylene) in $CHCl_3$.

by the introduction of azomethine groups. TGA analyses in air showed good thermal stability of the polymers, which was superior to that of poly(phenylacetylene) (Figure 2). For example, the weight residue at 500°C for poly(**1**), poly(**2**), poly(**4**), and poly(**6**) were 78, 72, 59, and 60%, respectively, whereas that of poly(phenylacetylene) was approximately 25%.

Although the introduction of imino groups did not result in the enhancement of the main chain conjugation, the stability in solution was remarkably improved. Figure 3 shows the time dependence of relative molecular weight of poly(**4**) and poly(phenylacetylene) in chloroform estimated by GPC. A very rapid degradation of poly (phenylacetylene) was observed within 4 h, whereas that of poly(**4**) was rather slow. In other words, introduction of electron-withdrawing groups is effective to stabilize the polymer main chain against oxidative decomposition.

Experimental

General. All the polymerization runs were carried out in standard laboratory glassware, and the solvents used in the experiments were purified by the usual methods. All the reagents in monomer synthesis were used as purchased without further purification.

Polymerization. Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock under a nitrogen atmosphere. Unless otherwise specified, the polymerization conditions were as follows: In toluene, 30 °C, 24 h, $[M]_0$ = 200 mM, [Cat] = 1.0 mM, [Cocat] = 2 mM. Monomer conversions were determined by gas chromatography. Polymers were isolated by precipitation in a large excess of methanol for poly(**1**)-poly(**4**), or hexane for poly(**5**) and poly(**6**), and the yields of the polymers were determined by gravimetry.

Polymer Characterization. The molecular weights of the polymers were estimated by gel permeation chromatography ($CHCl_3$ as an eluent, polystyrene standards). IR spectra, UV-visible spectra, and NMR spectra were recorded on a Shimadzu. FTIR-8100 spectrophotometer, a Shimadzu UV-2200 spectrophotometer, and a JEOL GSX-270 or EX-400 spectrometer, respectively. Thermogravimetric analyses (TGA) were conducted in air on a Perkin-Elmer TGA7 thermal analyzer.

Monomer Synthesis. Preparation of **1** is described below as a typical procedure. Into a solution of 4-bromoiodobenzene (10.0 g, 35 mmol) in triethylamine (50 mL) was added bis(triphenylphosphine)palladium dichloride (74 mg, 0.10 mmol), CuI (76 mg, 0.4 mmol) and a solution of trimethylsilylacetylene (3.47 g, 35 mmol), and the mixture was stirred for 2 h at rt. Triethylamine was removed under reduced pressure, and Et_2O was added to the residue. After filtration of the mixture, the ether phase was dried over $MgSO_4$, filtered, and evaporated to give a crude product. To the solution of the crude product in 50 mL of dry ether, a 1.6 M hexane-solution of *n*-BuLi (24 mL, 39 mmol) was added dropwise at 0 °C, and the solution was stirred at rt for 30 min. DMF (3.58 g, 49 mmol) was then added, and the solution was kept stirring for 1 h. The solution was acidified with 2N HCl, washed with saturated aq. Na_2CO_3, dried over Na_2SO_4, and concentrated to give a crude product of 4-(2-trimethylsilylethynyl)benzaldehyde. Into a solution of the crude product in toluene (100 mL) was added molecular sieves (3A) (ca, 15 g), aniline (52.0 mg, 70 mmol) and acetic acid (0.5 mL), and the mixture was kept stirring at rt for 24 h. After the mixture was filtered, the solution was washed with saturated solution of Na_2CO_3, water and then brine. The solution was dried over $MgSO_4$, filtered, and concentrated to give a crude material, which was treated with 1.1 equiv of KOH (4.0 g, 100 mmol) in methanol (100 mL) at rt for 1 h. Purification was carried out by recrystallization from hexane or Al_2O_3-column chromatography (eluent, hexane/ethyl acetate). Spectroscopic data for the monomers are as follows.

1; Mp. 65-66 °C. ^1H NMR ($CDCl_3$) δ 3.21 (s, 1H), 7.20-7.42 (m, 5H), 7.58 (d, 2H, *J* = 8.3 Hz), 7.86 (d, 2H, *J* = 8.3 Hz), 8.44 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 79.63, 83.45, 121.07, 125.13 126.43, 128.79, 129.38, 132.67, 136.55, 151.91, 159.41; IR (KBr) 3291, 3090, 2100, 1618 cm^{-1}; Anal. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.58; H, 5.60; N, 6.78. **2**; ^1H NMR ($CDCl_3$) δ 3.12 (s, 1H), 7.20-7.45 (m, 6H), 7.59 (d, 1H, *J* = 8.0 Hz), 7.89 (d, 1H, *J* = 8.0 Hz), 7.90 (s, 1H), 8.42 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 78.15, 83.07, 121.06, 123.01, 126.41, 128.99, 129.07, 129.38, 132.67, 134.88, 136.60, 151.87, 159.33; IR (neat) 3292, 3063, 2100, 1628 cm^{-1}; Anal. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.13; H, 5.80; N, 6.35. **3**; Mp. 106-107°C. ^1H NMR ($CDCl_3$) δ 1.17 (d, 12H, *J* = 6.8 Hz), 2.93 (m, 2H), 3.14 (s, 1H), 7.13-7.20 (m, 3H), 7.46 (t, 1H, *J* = 7.8 Hz), 7.62 (d, 1H, *J* = 7.8 Hz), 7.91 (d, 1H, *J* = 7.8 Hz), 8.02 (s, 1H), 8.16 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.32, 27.80, 77.95, 82.72, 122.76, 122.90, 124.13, 128.52, 128.75, 132.08, 134.64, 136.05, 137.35, 148.82, 160.85; IR (KBr) 3260, 3065, 3026, 2964, 2924, 2865, 2100, 1636 cm^{-1}; Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84. Found: C, 87.33; H, 8.06; N, 4.67. **4**; Mp. 47-48°C. ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, *J* = 7.3 Hz), 1.28-1.36 (m, 6H), 1.58-1.64 (m, 2H), 2.62 (t, 2H, *J* = 8.3 Hz), 3.20 (s, 1H), 7.15-7.25 (m, 5H), 7.58 (d, 2H, *J* = 8.3 Hz), 7.85 (d, 2H, *J* = 8.3 Hz), 8.46 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.29, 22.81, 29.16, 31.68, 31.92, 35.72, 79.49, 83.51, 121.04, 124.91, 128.68, 129.34, 132.65, 136.75, 141.54, 149.42, 158.53; IR

(KBr) 3295, 2951, 2924, 2853, 1622 cm^{-1}; Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84. Found: C, 87.07; H, 8.04; N, 4.73. **5**; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3H, *J* = 7.3 Hz), 1.36-1.70 (m, 4H), 3.16 (s, 1H), 3.59-3.63 (m, 2H), 7.51 (d, 2H, *J* = 7.3 Hz), 7.67 (d, 2H, *J* = 7.3 Hz), 8.24 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.05, 20.62, 33.11, 61.67, 78.96, 83.51, 124.18, 127.99, 132.49, 136.71, 159.97; IR (neat) 3301, 2959, 2930, 2872, 2110, 1686 cm^{-1}; Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 83.50; H, 7.94; N, 6.01. **6**; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H, *J* = 6.8 Hz), 1.15-1.32 (m, 10H), 1.68 (m, 2H), 3.16 (s, 1H), 3.58 (m, 2H), 7.52 (d, 2H, *J* = 8.3 Hz), 7.87 (d, 2H, *J* = 8.3 Hz), 8.24 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.25, 22.81, 27.53, 29.41, 29.56, 31.04, 32.01, 62.02, 78.94, 83.51, 124.20, 128.00, 132.30, 136.71, 159.95; IR (neat) 3301, 2955, 2928, 2855, 2100, 1646 cm^{-1}; Anal. Calcd for $C_{17}H_{23}N$: C, 84.58; H, 9.61; N, 5.81. Found: C, 83 .44; H, 9.73; N, 5.35.

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