Synthesis and Properties of Polyacetylenes Having Azobenzene Pendant Groups

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Azobenzene is a well-known photosensitive chromophore, which undergoes photoinduced and thermal geometric isomerizations.[1] A variety of polymers having azobenzene moieties in the main chain or side chain have been synthesized, and their properties have been investigated because of their photoactivities which may lead to various photonic applications.[2] The following polymers which contain azobenzenes in the main chain have been reported: a poly(phenyleneethynylene) having azobenzene moieties[3a] synthesized via Pd-catalyzed coupling reaction and a polyurea[3b] prepared by polycondensation of diisocyanate and 4,4′-diaminoazobenzene. On the other hand, there have been many examples of polymers carrying azobenzene moieties in the side chain. Thus, poly(4-vinylazobenezene),[4a] poly(methacrylates),[4b] poly(acrylates),[4c] polythiophenes,[4d,e] and poly(isocyanates)[4f−h] have been intensively investigated. Interestingly, UV irradiation of poly(isocyanates) having optically active azobenzene moieties causes trans-to-cis isomerization of azobenzene moieties, which induces inversion of the helical structure of the main chain.[4f−h] Some of these polymer films generate holographic surface relief gratings by photoirradiation.[5] Recently, the synthesis and photoisomerization behavior of azobenzene-containing dendrimers have been reported.[6]

Polyacetylenes possess alternating double bonds along the main chain, which brings about unique electrical and optical properties.[7] There have, however, been a few reports regarding azobenzene-containing polyacetylenes. For instance, a 1,6-heptadiyne, to which an azobenzene group is tethered through an alkylene spacer at the 4-position, polymerizes with WCl_6- and $MoCl_5$-based catalysts in a ring-forming metathesis manner to afford a soluble polymer in moderate yields.[8] Polymerization of acetylenes that are connected with an azobenzene through alkylene spacing groups also proceeds with Rh and Fe catalysts, and the formed polymers show a smectic liquid-crystalline phase according to DSC analyses.[9] An acetylene with a ferrocenylazo group has been polymerized with a Schrock catalyst in a living fashion.[10]

Thus, there has been no example of the polymerization of acetylenes that have a directly bonded azobenzene moiety. The resulting polymers are expected to have a conjugation between the main chain and the azobenzene, which may endow novel optical and electronic properties. It is hence very interesting to synthesize polyacetylenes that possess directly connected azobenzene moieties and further study their properties. Here we report on the polymerization of 3-ethynylazobenzene and 4-ethynylazobenzene (3EAB and 4EAB, respectively). Polymers have been successfully obtained with use of suitable transition-metal catalysts, and properties of the formed polymers have been clarified.

Table 1. Polymerization of 3EAB and 4EAB by Various Catalysts [a]

			polymer [b]		
run	catalyst	monomer conv, %	yield, %	$M_n/10^3$ [c]	$M_w/10^3$ [c]
	Monomer: 3EAB				
1	$[(nbd)RhCl]_2-Et_3N$ (1:2)[d]	100	99	80	350
2	$[(nbd)RhCl]_2-Et_3N$ (1:2)[e]	100	80	110	490
3	$Fe(acac)_3-Et_3Al$ (1:3)[f]	47	36	*j*	*j*
4	Schrock carbene[g]	100	76	5.2	16
5	Schrock carbene[h]	0	0		
6	$MoCl_5-n$-Bu_4Sn (1:1)[i]	0	0		
7	WCl_6-Ph_4Sn (1:1)[i]	0	0		
	Monomer: 4EAB				
8	$[(nbd)RhCl]_2-Et_3N$ (1:2)[e]	100	100	*j*	*j*
9	$Fe(acac)_3-Et_3Al$ (1:3)[f]	81	69	*j*	*j*
10	Schrock carbene[g]	100	75	6.8	14
11	Schrock carbene[h]	0	0		

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 0.20$ M, [cat.] = 2.0 mM. [b] Hexane-insoluble product. [c] Measured by GPC. [d] For 3 h, $[M]_0 = 0.10$ M. [e] For 3 h, $[M]_0 = 0.25$ M. [f] $[Fe(acac)_3] = 10$ mM. [g] $\{Mo[OC(Me)(CF_3)_2]_2{=}N(2,6\text{-}i\text{-}Pr_2C_6H_3){=}CH-CMe_2Ph\}$. [h] $\{Mo(O\text{-}t\text{-}Bu)_2{=}N(2,6\text{-}i\text{-}Pr_2C_6H_3){=}CHCMe_2Ph\}$. [i] [Cat.] = 20 mM. [j] Insoluble.

The two monomers were prepared with reference to the literature.[11,12] $[(nbd)RhCl]_2$ (Aldrich), other transition-metal catalysts (Strem), and organometallic cocatalysts (Aldrich or Kanto Chemicals) were used as purchased.

Table 1 shows the results for the polymerization of 3EAB and 4EAB by various catalysts.[14] The $[(nbd)RhCl]_2-Et_3N$ catalyst exhibited high activity in the polymerization of 3EAB; the monomer was completely consumed to afford polymer in 80% or higher yield. The polymer was an orange-colored solid soluble in low-polarity solvents such as toluene and $CHCl_3$. Though the $Fe(acac)_3-Et_3Al$ catalyst also induced polymerization, its activity was lower. The polymer obtained with the Fe catalyst was a vermilion solid insoluble in any solvent; the insolubility seems to be attributable to the cis-cisoidal geometric structure like the case of poly(phenylacetylene).[15] No polymer was obtained with classical metathesis catalysts such as WCl_6-Ph_4Sn and $MoCl_5-n$-Bu_4Sn, which is attributable to catalyst deactivation by the azo group. On the other hand, a Schrock carbene, which is relative tolerant to functional groups, afforded a soluble polymer in good yield, but the M_n was no more than 5000. The other monomer, 4EAB, also polymerized with $[(nbd)RhCl]_2-Et_3N$ and $Fe(acac)_3-Et_3Al$, but the formed polymers were insoluble in any solvents. This suggests that the rigid planar *p*-azobenzene groups take a stacked structure. A Schrock carbene polymerized also 4EAB into a low molecular weight polymer.

The structure and properties of poly(3EAB) were examined with the Rh-based sample (Table 1, run 2). The IR spectrum of poly(3EAB) exhibited no absorption at 3285 cm^{-1} ($\nu_{H-C\equiv}$) that is seen in the monomer. Otherwise, similar bands were observed in the polymer and the monomer. The ^1H NMR spectrum of poly(3EAB) (Figure 1) exhibits a relatively sharp signal due to main-chain cis-vinyl protons (5.87 ppm), indicating a high content of stereoregular cis-transoidal structure.[16] Since the vinyl-proton signal of the trans structure is overlap-

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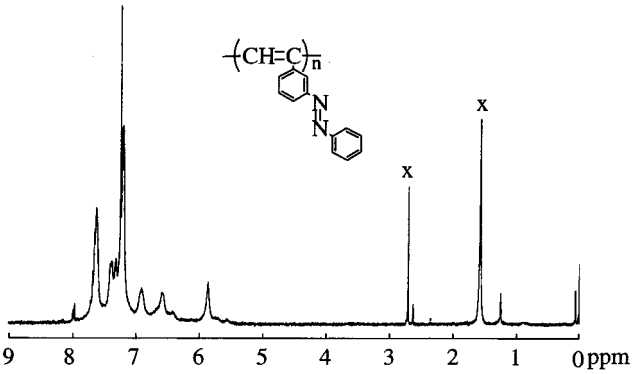

Figure 1. ^{1}H NMR spectrum of poly(3EAB) (sample from run 2, Table 1, measured in $CDCl_3$).

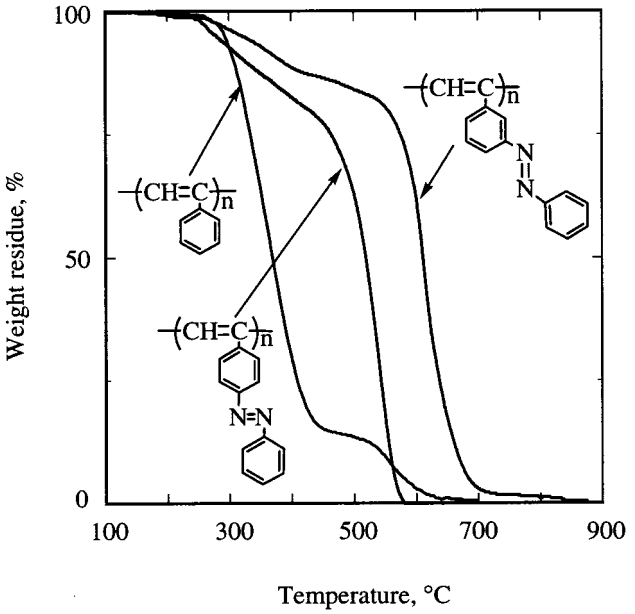

Figure 2. TGA curves of poly(3EAB) and poly(4EAB) (the samples prepared with Rh catalyst; heating rate 10 °C/min, in air).

ping with the aromatic region, the percent cis content of poly(3EAB) is determined to be 88% from the relative intensity of the signals at 5.87 ppm and that of the aromatic region.

Poly(3EAB) was soluble in toluene, benzene, THF, anisole, and $CHCl_3$ and insoluble in hexane, ethyl acetate, DMF, DMSO, and methanol. Poly(3EAB) provided a tough film by casting it from toluene solution. This polymer was stable enough in the solid state in air over a long period of time, while the molecular weight of the polymer decreased rapidly in $CHCl_3$. The M_w quickly decreased even during GPC measurement when chloroform was used as eluent. On the other hand, poly(3EAB) was relatively stable in THF, and the polymer degradation was rather slow; e.g., the M_w decreased to ca. $^4/_5$ the initial value when THF solution of the polymer was left for 1 h.

The thermal stability of poly(3EAB) was examined by TGA in air (Figure 2). The weight loss began at 230 °C, which is higher than the temperature (ca. 200 °C) for poly(phenylacetylene). Thus, the introduction of azobenzene moieties in polyacetylene side groups exhibits no significant adverse effect on thermal stability.

The isomerization behavior of azobenzene moieties of the polymer in solution was investigated by UV−vis

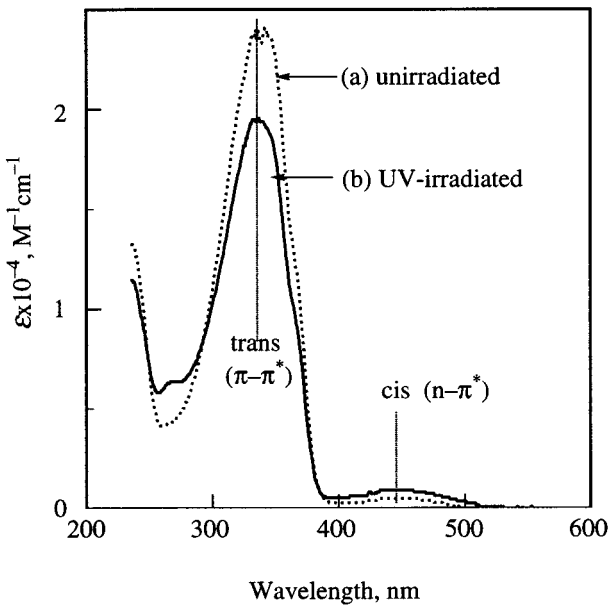

Figure 3. UV−vis spectra of poly(3EAB) in THF (a) before and (b) after UV irradiation at 300−400 nm for 2 h (with 200 W, high-pressure Hg lamp).

spectroscopy (Figure 3). The absorption maximum of the trans form was observed at 340 nm ($\epsilon_{max} = 2.3 \times 10^4$ M^{-1} cm^{-1}). When a solution of poly(3EAB) in THF was irradiated with UV light of wavelength 300−400 nm, the azobenzene moieties isomerized, resulting in the decrease of the absorption at 340 nm and in the increase of the absorption at 450 nm.

In conclusion, polyacetylenes having azobenzene moieties [poly(3EAB) and poly(4EAB)] were obtained by the polymerization using $[(nbd)RhCl]_2-Et_3N$. These results are the first example of synthesis of polyacetylenes having azobenzene moieties directly connected to the main chain. Though poly(4EAB) was insoluble in any solvents, poly(3EAB) was soluble in common solvents, had high molecular weight up to 4.9×10^5, and provided free-standing film by solution casting. Trans-to-cis photoisomerization of azobenzene moieties in poly(3EAB) was observed upon UV irradiation.

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(11) Synthesis of 3EAB: To a solution of nitrosobenzene (5.4 g, 50 mmol) in acetic acid (320 mL) was added 3-iodoaniline (10 g, 46 mmol), and the reaction mixture was stirred for 45 h at a reflux temperature. The solvent was evaporated, and the residue was diluted with diethyl ether. Then the ether solution was washed with water and dried over anhydrous Na_2SO_4. The ether was evaporated, and the crude product was purified by flash column chromatography (eluent: a gradient from 4:1 hexane/benzene to 1:1 hexane/benzene was applied) to give 3-iodoazobenzene (12 g; yield, 87%) as an orange solid. The iodide (9.2 g, 30 mmol), $(Ph_3P)_2PdCl_2$ (98 mg, 0.14 mmol), CuI (154 mg, 0.81 mmol), Ph_3P (142 mg, 0.54 mmol), and triethylamine (100 mL) were placed in a three-necked flask. Then, trimethylsilylacetylene (6.4 mL, 45 mmol) in triethylamine (30 mL) was gradually added, and stirring was continued for an additional 2 h (until TLC indicated no starting iodide). After triethylamine was evaporated, diethyl ether (ca. 200 mL) was added, and the insoluble salt was filtered off. The solution was washed with 2 N hydrochloric acid and then water, and dried over anhydrous Na_2SO_4. After evaporation of the ether, the crude product was purified by flash column chromatography (eluent: a gradient from 40:1 hexane/benzene to 1:1 hexane/benzene was applied) to give the coupling product (yield 8.2 g, 98%) as a red oil. To a solution of the coupling product (8.2 g, 29 mmol) in ethanol (80 mL) was added KOH powder (8 g, 0.14 mol), and the mixture was stirred for 2 h at room temperature. Then the reaction mixture was diluted with diethyl ether, and the ether solution was washed with water. The ether was evaporated, and the crude product was purified by flash column chromatography (eluent: a gradient from 40:1 hexane/benzene to 1:1 hexane/benzene was applied) to give 3EAB (5.5 g; yield, 88%) as an orange solid. Overall yield 76%, mp 64.0−65.0 °C. IR (KBr): 3285, 3061, 1593, 1568, 1479, 1469, 1261, 1074, 897, 806, 770, 687, and 661 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.05−7.41 (9H, aromatic) and 3.14 (1H) ppm. ^{13}C NMR ($CDCl_3$): δ 152.4, 152.3, 134.2, 131.3, 129.0, 126.2, 123.4, 123.0, 122.9, 122.8, 82.8, and 77.9 ppm. Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.80; H, 5.00; N, 13.47. No impurities were detected in ^1H NMR.

(12) Synthesis of 4EAB: 4EAB was prepared by another method before.[13] Here, at first, 4-iodoazobenzene was prepared from 4-aminoazobenzene by the Sandmeyer reaction. Then, the coupling and desilylation reactions were carried out in the same way as for 3EAB. Overall yield 61.0%; mp 81.0−82.0 °C. IR (KBr): 3260, 3040, 1587, 1572, 1483, 1466, 1 441, 1153, 1102, 1069, 843, 760, and 679 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.95−7.48 (9H, aromatic) and 3.23 (1H) ppm. ^{13}C NMR ($CDCl_3$): δ 152.5, 152.1, 132.9, 131.3, 129.0, 124.6, 122.9, 122.8, 83.2, and 79.4 ppm. Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.67; H, 4.99; N, 13.76. No impurities were detected in ^1H NMR.

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(14) A typical example of the polymerization procedure is as follows: A toluene solution of 3EAB and eicosane was placed in a Schlenk tube equipped with a three-way stopcock under a nitrogen atmosphere. To the monomer solution was added a solution of $[(nbd)RhCl]_2$ and Et_3N (mole ratio 1:2) in toluene at 30 °C. After 3 h, the polymerization was quenched by the addition of a mixture of toluene and acetic acid (4:1, volume ratio). The monomer conversion was determined by gas chromatography (GC). The formed polymer was isolated by precipitation in a large amount of hexane, and its yield was determined by gravimetry.

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