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Notes

Preparation of Head-to-Head Type Substituted Polyacetylenes by Organometallic Polycondensation

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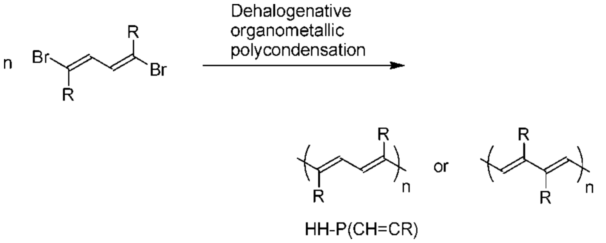
Introduction

Various substituted polyacetylenes have been prepared by addition polymerization of substituted acetylenes.[1−3] They are considered to have a head-to-tail type HT-P(CH=CR) structure. We previously reported synthesis of polyacetylene and a substituted polyacetylenes by dehalogenative organometallic polycondensation from the corresponding dihalo-monomers.[4]

We have expanded the dehalogenative organometallic polycondensation, and herein report synthesis of several new substituted polyacetylenes by organometallic polycondensation. For example, synthesis of head-to-head substituted polyacetylenes, HH-P(CH=CR), becomes possible by the polycondensation.



(1)

HT-P(CH=CR)s show interesting nature and functionalities such as helix-forming nature, functions as gas-permeable membranes, and photoelectronic functionalities.[1−3] Obtaining the new type of substituted polyacetylenes, HH-P(CH=CR)s, is expected to expand the scope of substituted polyacetylenes.

Experimental Section

Materials and Measurements. Bis(1,5-cyclooctadiene)nickel(0), Ni(cod)$_2$, was prepared according to the literature.[5] Substituted acetylenes, $Me_3SnSnMe_3$ and bis(pinacolato)diboron were used as purchased. Cyclic voltammetry (CV) was carried out with a Hokuto HSV-100 system. MALDI-TOF mass spectra of polymers were obtained with a Shimadzu AXIMA-CFR Plus MALDI-TOF MS system. ^{1}H NMR spectra were recorded on a JEOL JNM-LA300 spectrometer. Gel permeation chromatography (GPC) was carried out using a Shimadzu LC-20AD GPC system and polystyrene standards. ICP (inductively coupled plasma) analysis of Ni in polymers was carried out by Mr. S. Nakamura and Dr. M. Hirai of Center for Advanced Materials Analysis (Suzukakedai) at our university using a Shimadzu ICPS-8100 analyzer.

Table 1. Results of Polymerization

polymer[a]	monomer	yield/ %	M_n[b]	M_w[b]	λ_{max}/ nm[d]
HH-P(CH=CPh-Hex)-Ni	**monomer-a**	92	2290 2230[c]	2620	440
HH-P(CH=CPh-Hex)-Ni-mw	**monomer-a**	60	4470	4710	440
HH-P(CH=CTh-Hex)-Ni	**monomer-b**	80	2760	3210	450
HH-P(CH=CDod)-Ni	**monomer-c**	91	2370	2630	400
HH-P(CH=CPh-Hex)-Pd	**monomer-a**	91	2400	3320	430

[a] Polymers with "-Ni" and "-Pd" were prepared according to eqs 2 and 3 in Scheme 1, respectively. The polymer with "-mw" was prepared under microwave irradiation. [b] Molecular weights were determined by GPC (vs polystyrene standards) unless otherwise noted. [c] M_n estimated from a MALDI-TOF mass method. [d] Position of the shoulder peak assigned to $\pi-\pi^*$ transition along the polymer main chain (cf. the text and Figure 2).

Synthesis of Monomers and Polymers. 1,4-Dihalo-1,4-disubstituted-1,3-butadienes used in this work were prepared by applying a recently reported method using the corresponding substituted acetylenes, PdX_2, and CuX_2,[6] and details of the synthetic procedure are shown in the Supporting Information. Polycondensation and workup were carried out in manners similar to those reported previously[4] and details are shown in the Supporting Information. Microwave-assisted polymerization of 1,4-dibromo-1,4-bis(4-hexylphenyl)-1,3-butadiene (**monomer-a**) was carried out using a CEM Discover apparatus.

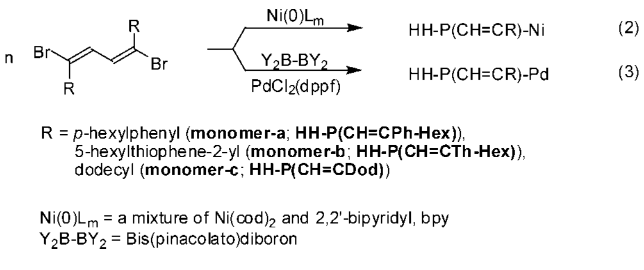
Results and Discussion

Preparation of Polymers. Dehalogenative polycondensation of 1,4-disubstituted-1,4-dibromo-1,3-butadienes gave the corresponding HH-P(CH=CR) in high yields.

Use of (i) the Ni(0)L$_m$ complex[4] or (ii) the diboron compound[7] in the presence of PdCl$_2$(dppf)[8] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) catalyst as the condensing agent gave the polymers in good yields (60−92%). On the other hand, use of a ditin compound[9] in the presence of Pd(PPh$_3$)$_4$ did not give the polymer. Results of polymerization are summarized in Table 1.

The obtained polymers were soluble in chloroform, dichlo-

Scheme 1. Preparation of HH-P(CH=CR)s[a]



[a] Abbreviations for the monomers and obtained polymers are shown in parentheses.

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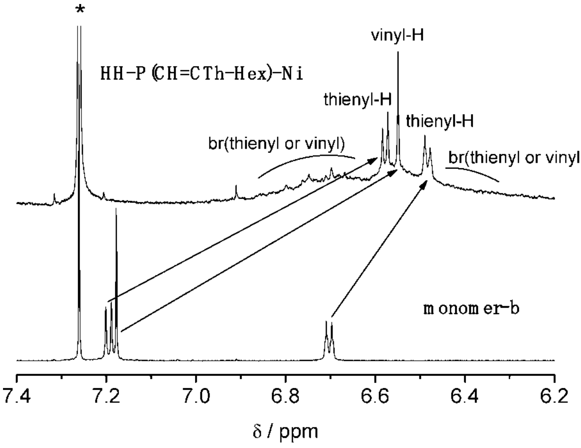


Figure 1. ^1H NMR spectra of (top) **HH-P(CH=CTh-Hex)-Ni** and (bottom) **monomer-b** in $CDCl_3$. The peak with * is due to the solvent impurity ($CHCl_3$).

romethane, hexane, and THF. However, they were not soluble in polar solvents such as DMF and acetonitrile. The polymers were characterized by GPC, ^1H NMR, MALDI-TOF mass, and elemental analysis. GPC analysis using polystyrene standards indicated that the polymers had number average molecular weights M_n of 2290−4470 and weight average molecular weights M_w of 2620−4710. **HH-P(CH=CR)-Ni** and **HH-P(CH=CR)-Pd** showed similar M_n and M_w each other. MALDI-TOF mass data of **HH-P(CH=CPh-Hex)-Ni** gave M_n (2230) similar to M_n (2290) estimated from GPC. Although M_n was not high, ^1H NMR and UV−vis data revealed structural and optical features of HH-P(CH=CR)s. **HH-P(CH=CPh-Hex)-Ni-mw** synthesized under irradiation with microwave[10] showed a somewhat larger M_n of 4470 and M_w of 4710 as shown in Table 1, however, the polymer gave essentially the same ^1H NMR and UV−vis spectra as those of **HH-P(CH=CPh-Hex)-Ni** prepared without irradiation of microwave and having M_n of 2290. Because the obtained polymers did not contain Br (cf., Supporting Information), the polymers obtained after the polycondensation are considered to have a polymer−metal (metal = NiL_m (L = ligand), etc.) terminal group as the major polymer end, similar to polymers synthesized by analogous dehalogenative organometallic polycondensation, and the polymer−metal terminal group is considered to be converted to a polymer-H terminal group during workup.[11] Ni was not detected in ICP analysis of **HH-P(CH=CPh-Hex)-Ni** and **HH-P(CH=CTh-Hex)-Ni**. Use of a dichloro analogue of **monomer-a** in the polymerization using the Ni(0) complex gave **HH-P(CH=CPh-Hex)-Cl-Ni** with a somewhat smaller M_n of 2000.

NMR and UV−Vis Data. Figure 1 shows ^1H NMR spectra of **HH-P(CH=CTh-Hex)-Ni** and **monomer-b** in the aromatic and vinylic region.

For **monomer-b**, the vinylic C*H* signal appears as a sharp singlet at δ 7.18. However, the vinylic C*H* signal in the polymers seems to appear as an overlapped signal of a sharp singlet at δ 6.55 and a broad signal in a region of δ 6.9−6.2, similar to the case of usual HT-P(CH=CR) synthesized by addition polymerization.[3] The reported HT-P(CH=CR) gives a sharp vinylic C*H* signal and a broad vinylic C*H* signal for cis- and trans-sequences, respectively, in its ^1H NMR spectrum, and the cis/trans content has been estimated from areas of the two signals.[3]

The AB quartet of the thiophene protons (Th-*H*s) of **monomer-b** at δ 7.19 and δ 6.70 seems to be changed to a sharp AB quartet at δ 6.58 and δ 6.48 and a broad peak in a range of δ 6.9−6.2 for the ^1H NMR spectrum of **HH-P(CH=CTh-Hex)-Ni**. The peak area ratio between the sharp vinylic C*H* signal at δ 6.55 and the AB quartet of Th-*H*s at δ 6.58 and δ 6.48 is roughly 1:2, suggesting that the sharp AB quartet at δ 6.58 and δ 6.48 is assigned to Th-*H*s in the cis-sequence; whereas the Th-*H*s signals in the trans-sequence is considered to appear a broad signal in the range of δ 6.9−6.2 overlapped with the broad vinylic C*H* signal in the trans-sequence. The total area of all the overlapped broad and sharp peaks in the range of δ 6.9−6.2 corresponds to 6H (relative to aliphatic signals) in agreement of the polymer structure.

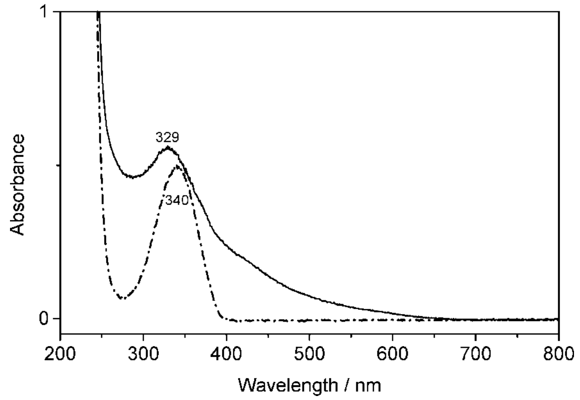
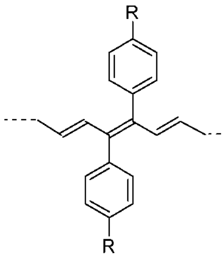


Figure 2. UV−vis spectra of **HH-P(CH=CPh-Hex)-Ni** (solid line) and **monomer-a** (broken line) in $CHCl_3$.

If the ^1H NMR peaks of **HH-P(CH=CTh-Hex)-Ni** are assigned as described above, similarly to the case of HT-P(CH=CR),[3] the cis/trans ratio is estimated at about 1/8. **HH-P(CH=CTh-Hex)-Pd** and **HH-P(CH=CPh-Hex)-Ni** also gave the vinylic C*H* and aromatic-*H*s signals mainly as a broad signal (cf., Figures S1 and S2 in Supporting Information), suggesting that the obtained polymers contained the trans-sequence as a main sequence. The sharp vinylic H signal of **monomer-c** at δ 6.54 was also broadened in **HH-P(CH=CDod)-Ni**, and appeared as a broad signal in a range of δ 5.4−6.4.

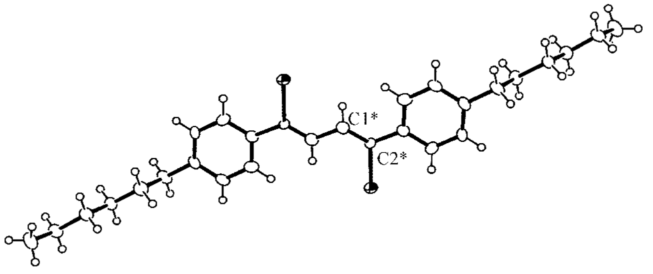
In the trans-sequence of HH-P(CH=CR), the polymer main chain has the following structure, e.g.,



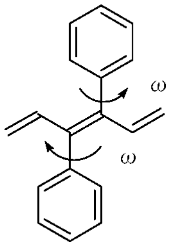
The HH-unit of **HH-P(CH=CPh-R)**.

Single crystal X-ray crystallography revealed that **monomer-a** has essentially a coplanar structure. However, an energy vs rotation angle (ω) profile of the following 3,4-diphenyl-1,3,5-hexatriene, which is shown in Figure S5, indicates that it is difficult for the molecule to form a coplanar structure.

Steric repulsion between the *o*-hydrogen of the phenyl group and the hydrogen in the π-conjugated 1,3,5-hexatriene seems to prevent the coplanar structure from being formed. The polymers have larger carbon main chain groups at the two ends of the 1,3,5-hexatriene unit and will receive a stronger steric



Molecular structure of **monomer-a** (CCDC 707337). Cf., Figure S3.



repulsion to prevent the coplanar structure from being formed. Similar calculation results were obtained for 3,4-di(2-thienyl)-1,3,5-triene as shown in Figure S6, and these results suggest that HH-P(CH═CR) has a twisted main chain, similar to HT-P(CH═CR).

The UV−vis spectra of HH-P(CH═CR)s revealed that HH-P(CH═CR)s have an effective π-conjugation length similar to that of HT-P(CH═CR)s. Figure 2 shows UV−vis spectra of **HH-P(CH═CPh-Hex)-Ni** and **monomer-a**.

As shown in Figure 2, **HH-P(CH═CPh-Hex)-Ni** gives a peak at 329 nm and a shoulder peak at about 440 nm. The former peak is considered to originate basically from a π-conjugation system similar to that in **monomer-a**, and the latter seems to come mainly from the π-conjugated main chain system.

HT-P(CH═CPh) and its derivatives show a UV−vis peak near 450 nm.[1−3] **HH-P(CH═CPh-Hex)-Ni-mw** having a higher molecular weight also showed the shoulder peak at about 440 nm, suggesting that the $\lambda_{\max}$ was saturated at a relatively low molecular weight. The UV−vis spectrum of **HH-P(CH═CPh-Hex)-Ni** showed no observable change after compressing its powdery sample at high pressure (in a molding cell for IR KBr pellet), suggesting that **HH-P(CH═CPh-Hex)-Ni** contained the trans unit as the major unit and pressure-induced cis−trans isomerization[3a] did not take place. UV−vis spectrum of a cast film of **HH-P(CH═CPh-Hex)-Ni** essentially agreed with that in the chloroform solution.

The UV−vis spectrum of **HH-P(CH═CTh-Hex)-Ni** showed a similar shoulder peak as that of **HH-P(CH═CPh-Hex)-Ni**. **Monomer-b** showed a peak at 395 nm, and **HH-P(CH═CTh-Hex)-Ni** gave a shoulder peak at about 450 nm. **Monomer-c** did not show UV−vis absorption in a range longer than 280 nm, whereas **HH-P(CH═CDod)-Ni** showed a shoulder peak at about 400 nm. **HH-P(CH═CPh-Hex)-Pd** gave rise to a UV−visible spectrum essentially agreeing with that of **HH-P(CH═CPh-Hex)-Ni**. HH-P(CH═CR)s did not have high stability under air. For example, dark brown-black color of **HH-P(CH═CPh-Hex)-Ni** became somewhat faded after exposure of the polymer to air for 3 days, and the UV−vis peak became weaker. The polymers were electrochemically active. For example, CV charts of cast films of **HH-P(CH═CPh-Hex)-Ni** and **HH-P(CH═CTh-Hex)-Ni** on Pt plates showed electrochemical oxidation (or p-doping) peaks at about 1.4 and 1.2 V vs Ag$^+$/Ag, respectively, when immersed in an acetonitrile solution of [NBu$_4$]BF$_4$ (0.10 M) (cf., Figures 3 and S7). Their corresponding p-dedoping peaks, however, were not clearly observed. The p-doping potential of **HH-P(CH═CPh-Hex)-Ni** seems to be higher than those of HT-poly(phenylacetylene)s.[12]

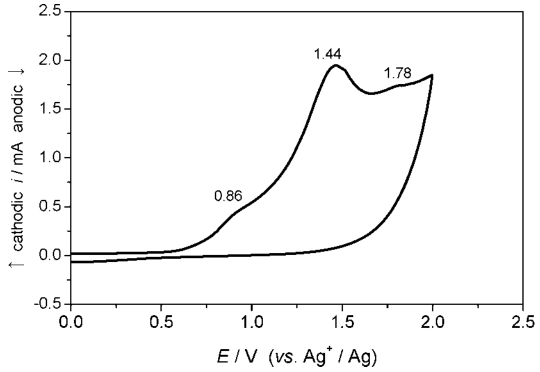
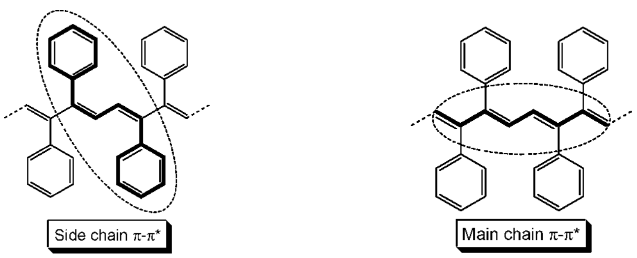


Figure 3. CV chart of **HH-P(*C*═CPh-Hex)-Ni** film on a Pt plate immersed in an CH$_3$CN solution of [(*t*-Bu$_4$)N]BF$_4$ (0.10 M) under N$_2$. Scan rate = 50 mV s^{-1}.

Chart 1. Two Types of π-Conjugation Systems Assumed in the HH-P(CH═CPh) Type Polymer



Exposure of powdery **HH-P(CH═CPh-Hex)-Ni** to an iodine vapor gave an iodine-doped sample showing electrical conductivity of 5 × 10^{-6} S cm^{-1}, which was comparable to that of HT-poly(phenylacetylene).[13] Iodine-doped polymer films showed new UV−vis peaks in a range of 600−1000 nm.

As described above, HH-P(CH═CR) type polyacetylenes were synthesized by organometallic polycondensations. Although the polymers seemed to have a twisted main chain similar to that of HT-P(CH═CR)s prepared by addition polymerization, obtaining the HH-P(CH═CR) type polymers is expected to expand the scope of chemistry of substituted polyacetylenes.

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Supporting Information Available: Figures showing ^{1}H NMR data of polymers, tables of crystallographic data of **monomer-a** and its chloride analogue and figures showing their structures, figures of profiles of relative energy vs rotation angle of 3,4-diphenyl-1,3,5-triene and its 2-thienyl analogue, CV, and UV−vis data, and text giving synthetic details of the monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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