Polymer Bulletin 52, 315–319 (2004)
DOI 10.1007/s00289-004-0291-z

Polymer Bulletin

Preparation of Polyacetylenes via Organometallic C-C Coupling Reactions

Takakazu Yamamoto (✉),[1] Kazuaki Kobayashi,[1] Takuma Yasuda,[1] Zhen-Hua Zhou,[1] Isao Yamaguchi,[1] Tadahiko Ishikawa,[2] and Shin-ya Koshihara[2]

[1]Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
[2]Department of Chemistry and Materials Science, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

e-mail: tyamamot@res.titech.ac.jp, Fax: +81-45-924-5976

Received: 17 August 2004 / Revised version: 17 August 2004 / Accepted: 17 August 2004

Summary

Dehalogenative polycondensation of 1,2-dibromoethylene, *trans*-1,2-dichloroethylene, and *cis*-1,2-dichloroethylene with a Ni(0) complex gave a black polymer whose IR spectrum essentially agreed with that of *trans*-polyacetylene. Suzuki-Miyaura coupling between 1,2-dibromoethylene and vinylene diboronic compounds was applied to synthesis of π-conjugated polymers.

Introduction

Polyacetylene is the most fundamental π-conjugated polymer, and very active researches have been carried out since the discovery of highly electrically conducting doped film of polyacetylene [1-3]. Investigation of other π-conjugated polymers such as π-conjugated aromatic (e.g., poly(*p*-phenylene)) and heteroaromatic (e.g., poly(thiophene-2,5-diyl)) polymers has also been carried out actively [4-7].

For the π-conjugated aromatic and hetroaromatic polymers, organometallic polycondensations of dihalogenated monomers have been used for their synthesis; e.g., [5,7]

$$n\ \mathrm{X{-}Ar{-}X} + n\ \mathrm{Ni(0)Lm} \longrightarrow \mathrm{-\!\!(Ar)\!\!-}_n + n\ \mathrm{NiX_2Lm} \qquad (\mathbf{1})$$

Ar: aromatic or heteroaromatic unit
Ni(0)Lm: zerovalent nickel complex (e.g., a mixture of
bis(1,5-cyclooctadiene)nickel(0), Ni(cod)$_2$, and neutral ligands
such as triphenylphosphine (PPh$_3$) and 2,2'-bipyridyl (bpy))

$$n\ \mathrm{X{-}Ar{-}X} + n\ \mathrm{(RO)_2B{-}Ar'{-}B(OR)_2} \xrightarrow[\text{base}]{\text{Pd-catalyst}} \mathrm{-\!\!(Ar{-}Ar')\!\!-}_n \qquad (\mathbf{2})$$

However, utilization of analogous polycondensation to the synthesis of polyacetylenes from dihaloolefinic compounds has not received much attention. Polyacetylenes have usually been prepared with Ziegler-Natta type catalyst [1,8,9], although the ring-opening metathesis polymerization (ROMP) of 1,3,5,7-cyclooctatetraenes can also give polyacetylenes [10-13]. We now report preparation of polyacetylenes by the organometallic polycondensation.

Experimental

Materials and Measurements

1,2-Dibromoethylene, *cis*-1,2-dichloroethylene, and *trans*-1,2-dichloroethylene were used as purchased. Bis(1,5-cyclooctadiene)nickel(0) [14], Ni(cod)$_2$, *cis*-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-octene [15], comonomer-1, and tetrakis(triphenylphosphine)palladium(0) [16], Pd(PPh$_3$)$_4$, were prepared according to the literature. *Cis*-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-1,2-diphenyl-ethene, comonomer-2, was purchased from Sigma-Aldrich Co. Ltd. IR spectra were measured with a JASCO IR 810 spectrometer with a KBr pellet. Reflection spectrum was measured with a disk (ϕ = 13 mm) obtained by compressing powdery polymer-1 at 2000 kg cm^{-2}.

Polymerization of 1,2-Dihaloethylene

To a dry DMF (20 mL) solution of Ni(cod)$_2$ (1.1 g, 3.9 mmol) were added 1,5-cyclooctadiene (0.8 mL) and PPh$_3$ (0.92 g, 3.5 mmol or 0.90 mol/1 mol of Ni(cod)$_2$) under N$_2$. After stirring for 30 min, a dry DMF (10 mL) solution of 1,2-dibromoethylene (700 mg, 3.8 mmol) was added dropwise under N$_2$. The solution was stirred at 60 ˚C for 20 h to obtain a black suspension. After cooling to room temperature, the black powdery product was collected by filtration under N$_2$. The black powder was washed with DMF, water, diluted ammonia water, water, diluted hydrochloric acid, water, methanol, and diethyl ether under N$_2$, and dried under vacuum to obtain 59 mg (48% yield, based on the amount of carbon recovered) of black polymer. The medium yield of the polymer seemed to be due to loss of the polymer in repeated washing of the polymer. Dehalogenative polymerization of *cis*-1,2-dichloroethylene and *trans*-1,2-dichloroethylene with Ni(cod)$_2$ was carried out analogously.

Copolymerization of 1,2-dibromoethylene and the comonomer-1 was carried out by using Pd(PPh$_3$)$_4$ as the catalyst. A mixture of 1,2-dibromoethylene (0.93 g, 5.0 mmol), comonomer-1 (1.8 g, 5.0 mmol), Pd(PPh$_3$)$_4$ (0.17 g, 0.15 mmol), and Cs$_2$CO$_3$ (4.9 g, 15 mmol) in 15 mL of NMP was stirred at 80 ˚C for 72 h under N$_2$. The black precipitate was separated by filtration, washed with methanol and water under N$_2$, and dried under vacuum. Copolymerization of 1,2-dibromoethylene and comonomer-2 was carried out analogously.

Results and discussion

Dehalogenative polycondensation of 1,2-dibromoethylene (a 6:4 mixture of cis- and trans-isomers, as estimated from the ^{1}H-NMR spectrum) with the zerovalent nickel complex proceeded smoothly to produce a black powdery polymer.

$$\mathrm{BrHC{=}CHBr + Ni(0)Lm \longrightarrow \left(HC{=}CH \right)_n}$$

The IR spectrum of the polymer exhibited in Fig. 1 essentially agrees with the IR spectrum of *trans*-polyacetylene reported by Shirakawa and Ikeda [8] (cf. the inset in Fig. 1), showing a characteristic ν(C-H) and δ(C-H) peaks at 3010 and 1010 cm^{-1}, respectively. Observation of IR peaks at about 3400 and 1650 cm^{-1} suggests partial hydration of the polymer during work-up, which includes repeated washing in aqueous media. The polymerization proceeded both in the presence of PPh_3 (about 1 mol/1 mol of $Ni(cod)_2$) and bpy (about 1 mol/1 mol of $Ni(cod)_2$) as the neutral ligand for the Ni(0) complex (cf. eq. 1 [17]), and the obtained polymers exhibited essentially the same IR spectrum. In the case of polyacetylene obtained by the ROMP of 1,3,5,7-cyclooctatetraene, it was reported that the obtained polymer showed IR peaks at 930 and 980 cm^{-1} assigned to *trans*-polyacetylene and 765 cm^{-1} assigned to *cis*-polyacetylene [10]. When bpy was used, the yield (23%) of the polymer was lower. Without addition of the neutral ligand to $Ni(cod)_2$, polyacetylene was not obtained.

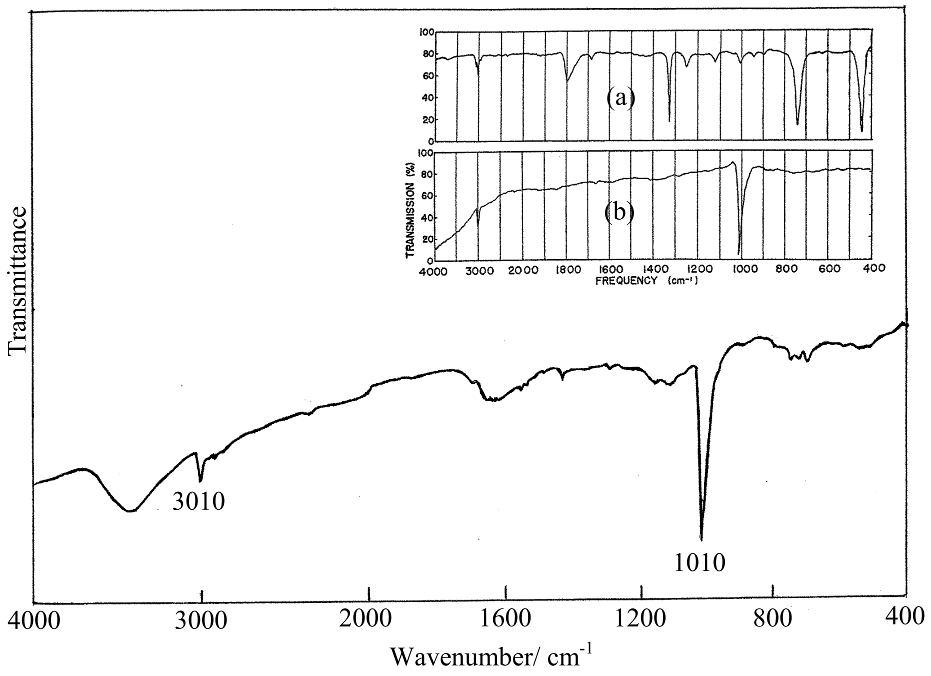
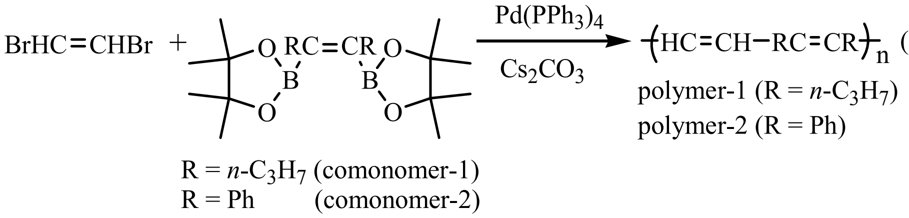


Figure 1. IR spectrum of polyacetylene prepared by dehalogenative polycondensation of 1,2-dibromoethylene using a zerovalent nickel complex. The inset exhibits IR spectra of (a) *cis*-polyacetylene and (b) *trans*-polyacetylene reported by Shirakawa and Ikeda [8].

Use of *trans*-1,2-dichloroethylene and *cis*-1,2-dichloroethylene, instead of 1,2-dibromoethylene, also gave a black powdery polymer (in 12% yield for the both monomers), whose IR spectrum was almost identical to that of *trans*-polyacetylene obtained from dibromoethylene. These results indicate that isomerization of the *cis* –CH=CH– unit to the *trans* –CH=CH– unit took place during the polymerization at 60 ºC. Similar isomerization from *cis*-polyacetylene, prepared at -78 ºC using a Ziegler-type catalyst, to *trans*-polyacetylene at higher temperatures was reported by Shirakawa and Ikeda [9]. However, the reported cis to trans isomerization seems to require somewhat higher temperature; e.g., at 50 ºC the polyacetylene had 32% cis content [9]. In the present polycondensation, the presence of the Ni complex may assist the cis to trans isomerization. The polymer obtained in this study was reactive to air, similar to the reported polyacetylene [8,18]. After exposure to air for 20 days, the IR spectrum of the polymer showed new strong and broad peaks at 1720 and 1670 cm^{-1} characteristic of oxidized polyacetylene [8,18]. The polymer itself was essentially an insulator with low electrical conductivity of 10^{-12} S cm^{-1}. When exposed to vapor of iodine, the powdery polymer formed an adduct with iodine, similar to the film of polyacetylene [1-3], however, electrical conductivity (1 x 10^{-4} S cm^{-1}) was not so high as that observed with the iodine adduct of the film of polyacetylene [1-3].

Copolymerization of 1,2-dibromoethylene with the following cis-monomers, comonomer-1 and comonomer-2, according to Suzuki-Miyaura coupling [19,20] gave



(3)

polymer-1 (R = n-C_3H_7)
polymer-2 (R = Ph)

R = n-C_3H_7 (comonomer-1)
R = Ph (comonomer-2)

black polymer-1 and brown polymer-2 in 56 and 31% yields, respectively, and their color suggested the presence of an expanded π-conjugation system in the polymer. Without the $Pd(PPh_3)_4$ catalyst, the polymer was not obtained. Both the polymers showed only low solubility in organic solvents. The UV-vis spectrum of a toluene-soluble part of polymer-1 showed a broad absorption tail ranging from 250 nm to 700 nm. Similar UV-vis absorption patterns are sometimes observed with π-conjugated polymers. The absorption of light covering the visible region made the solution and the solid of polymer-1 black. The reflection spectrum of the compressed powder of polymer-1 exhibited a reflection peak at about 660 nm, the position being comparable to that of the reflection peak observed with a film of polyacetylene (λ_{max} = 600-800 nm depending on measurement conditions and specimen [21,22]).

The IR spectrum of polymer-2 showed a sharp peak at 983 cm^{-1} which was characteristic of *trans*-vinylene unit [23,24], however, appearance a weak peak at 752 cm^{-1} (cf. the inset in Figure 1) suggested the presence of *cis*-vinylene unit, too. Expansion of the polymer synthesis by choosing appropriate R group in eq. 3 is expected to give new soluble π-conjugated polymers.

As described above, the organometallic polycondensation can give *trans*-polyacetylene type polymers.

References

1. Shirakawa H (2001) Angew Chem Int Ed 40:2575
2. MacDiarmid AG (2001) Angew Chem Int Ed 40:2581
3. Heeger AJ (2001) Angew Chem Int Ed 40:2591

4. Skotheim TA, Elsenbaumer Ri, Reynold JR (1997) Handbook of Conducting Polymers 2nd ed., Marcel Dekker, New York
5. Nalwa HS (1998) Handbook of Organic Conductive Molecules and Polymers, John Wiley, Chichester
6. Takayama Y, Delas C, Muraoka K, Uemura M, Sato F (2003) J Am Chem Soc 125:14163
7. Yamamoto T (2003) Synlett 425
8. Shirakawa H, Ikeda S (1971) Polym J 2:231
9. Ito T, Shirakawa H, Ikeda S (1974) J Polym Sci: Polym Chem Ed 12:11
10. Klavetter FL, Grubbs RH (1988) J Am Chem Soc 110:7807
11. Scherman OA, Rutenberg IM, Grubbs RH (2003) J Am Chem Soc 125:8515
12. Langsdorf BL, Zhou X, Adler DH, Lonergan MC (1999) Macromolecules 32:2796
13. Lonergan MC, Cheng CH, Langsdorf BL, Zhou X (2002) J Am Chem Soc 124:690
14. Bogdanovic B, Kroner M, Wilke G (1966) Justus Liebigs Ann 699:1
15. Ishiyama T, Matsuda N, Miyaura N, Suzuki A (1993) J Am Chem Soc 115:11018
16. Coulson D (1972) Inorg Synth 13:121
17. Yamamoto T, Morita A, Miyazaki Y, Maruyama T, Wakayama H, Zhou ZH, Nakamura Y, Kanbara T, Sasaki S, Kubota K (1992) Mocromolecules 25:1214
18. Gibson HW, Pochan JM (1982) Mocromolecules 15:242
19. Suzuki A (2002) J Organomet Chem 653:83
20. Miyaura N, Suzuki A (1995) Chem Rev 95:2457
21. Fincher CR Jr, Peebles DL, Heeger AJ, Druy MA, Matsumura Y, MacDiarmid AG, Shirakawa H, Ikeda S (1978) Solid State Commun 27:489
22. Tanaka M, Watanabe A, Tanaka J (1980) Bull Chem Soc Jpn 53:3430
23. Silverstein RM, Bassler GC, Morill TC (1974) Spectrometric Identification of Organic Compounds, John Wiley, New York, p.144
24. Pouchert CJ (1975) The Aldrich Library of Infrared Spectra Second Edt., Aldrich Chemical Co. Inc., Milwaukee, Wisconsin, p.511