Polymer Bulletin 29, 597–603 (1992)

Polymer Bulletin

Poly(1,3-cyclohexadiene-1,4-diyl)

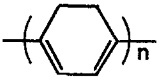
A new π-conjugated polymer

Takakazu Yamamoto[1,*], Hirokazu Saito[1], Kohtaro Osakada[1], Isao Ando[2], and Mizuyo Kikuchi[2]

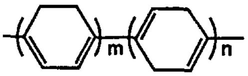
[1]Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan
[2]Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan

Summary

Dehalogenation polycondensation of 1,4-diiodo-1,3-cyclohexadiene with zero-valent nickel complex gives a new π-conjugated polymer, poly(1,3-cyclohexadiene-1,4-diyl) PCyh. A copolymer constituted of 1,3-cyclohexadiene-1,4-diyl and 1,4-cyclohexadiene-1,4-diyl is also obtained by a similar method. The black color of PCyh indicates the presence of extensive π-conjugation along the polymer chain presumably due to taking *s-trans* conformation of PCyh. PCyh is unstable and oxidized under air. IR and CP-MAS ^{13}C-NMR spectra of PCyh are reasonable for the structure.



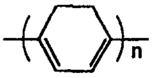
PCyh



Copolymer

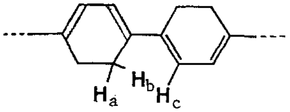
Introduction

Preparation and properties of electrically conducting π-conjugated polymers are subjects of recent interest (1). Now we report synthesis and preparation of a new π-conjugated polymer, poly(1,3-cyclohexadiene-1,4-diyl),



PCyh

The objectives of the present study are twofold. First, it is interesting to reveal whether PCyh can form a full π-conjugation system by making a coplanar structure between the six-membered rings. If PCyh takes the following *s-trans* structure H_c of the diene unit can get between the two CH_2 hydrogens of the $-CH_2CH_2-$ unit to form the planar polymer chain.

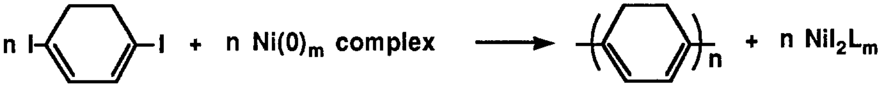


Scheme I *s-trans* conformation of PCyh

---

[*] Corresponding author

In the case of poly(*p*-phenylene) PPP (1, 2), a steric repulsion between the *o*-hydrogens is considered to prevent PPP from taking such a coplanar structure and thus the full π-conjugation is considered to be destroyed.
Second, if PCyh forms the full π-conjugated system, what is the chemical reactivity of the polymer against oxygen.
As for the preparation method of PCyh, a dehalogenation polycondensation of dihaloorganic compounds with zero-valent nickel complex (3) based on organonickel chemistry (4) was chosen.



PCyh

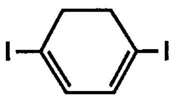
(1)

As the zero-valent nickel complex, a mixture of bis(1,5-cyclooctadiene)nickel (Ni(cod)$_2$) and 2,2'-bipyridine (bpy) was used (3). Tsuchida and his coworkers reported electro-oxidative polymerization of 1,3-cyclohexadiene (5), however, the polymer prepared is considered to have a structure different from that of PCyh.

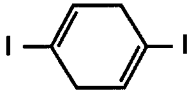
Experimental

Materials

Preparative methods of 1,4-diiodo-1,3-cyclohexadiene, the monomer, were reported by two groups (6), however, the compound had been obtained as mixtures with its isomer, 1,4-diiodo-1,4-cyclohexadiene,



1,3-monomer



1,4-isomer

In this research, the 1,3-monomer was isolated by careful column chromatography and recrystallization. Anal. Found: C, 21.75; H, 1.80; I. 76.5%. Calcd.: C, 21.71; H, 1.82; I, 76.47. Mp. (decomp.) = 97-98 °C. ^{1}H-NMR: 6.23 ppm (s, 2H) and 2.70 ppm (s, 4H). IR(KBr): 1625, 1613, 821, 715, 517 cm^{-1}. Preliminary X-ray crystallographical data: Mr = 319.90, P2$_1$/a, a = 14.532(2), b = 6.319(1), c = 4.529(1) Å, β = 95.05(2)°, R = 0.041.
Ni(cod)$_2$ was prepared as previously reported (3).

Polymerization

Stirring the diiodo compound(s) with a mixture of Ni(cod)$_2$ (molar ratio to the diiodo compound(s) r = 1.4), bpy (r = 1.5), and 1,5-cyclooctadiene (r = 6) in dry DMF under nitrogen at 50 °C for 15 h gave deep black precipitates of PCyh and the copolymer. The polymers were washed with ammonia water, an aqueous solution of ethylenediaminetetraacetic acid disodium, dil. HCl, and water in this order under N$_2$ and dried under vacuum to give deep real black PCyh (yield = 65%) and the copolymer (yield = 72%), respectively.
PCyh. Anal. Found: C, 86.94; H, 7.72; N, 0.28; I, 0%. Calcd. C, 92.26; H, 7.74%. The difference between the found and calculated values seems to be attributable to high thermal stability (see text) of the polymer, content of ash (2.6%), and high reactivity of the polymer toward oxygen in air. Contamination with 0.016

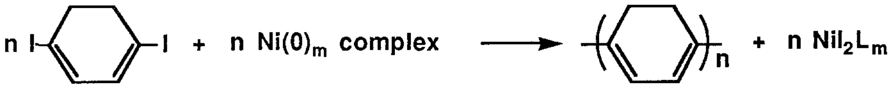
DMF per monomer unit explain the nitrogen content. Air sensitive π-conjugated polymers like poly(acetylene) are reported to show lower content of carbon than the calculated value (7).

Measurements

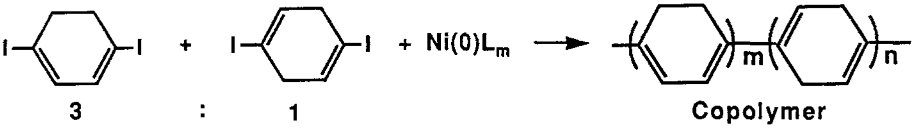
IR spectra and ^{13}C-NMR spectra were recorded on a JASCO IR-810 spectrometer and a JEOL GSX-270 spectrometer, respectively. Elemental analysis was carried out by Mrs. Tanaka of our laboratory with a Yanagimoto CHN Autocorder Type MT-2 and a Mitamura Riken Kogyo Micro Elemental Analyzer.

Results and Discussion

The polymerization was carried out with the pure monomer (Eq. 1) as well as with a 3:1 mixture of 1,4-diiodo-1,3-cyclohexadiene and 1,4-diiodo-1,4-cyclohexadiene (Eq. 2),



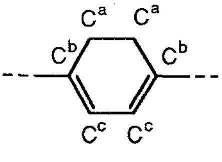
(1)



(2)

The deep black color of PCyh strongly suggests that PCyh takes a coplanar conformation and there exists an extensive π-conjugation along the polymer chain. Although determination of the degree of polymerization was not possible due to very low solubility of the polymer, the color of PCyh suggests an extensive π-conjugation participated by at least about 20 C=C double bonds (8). In the case of poly(pyridine-2,5-diyl) prepared by analogous method (dehalogenation polymerization of 2,5-dibromopyridine with the mixture of Ni(cod)$_2$ and bpy) and having analogous low solubility in the polymerization solvent, the polymer is reported to have degree of polymerization of about 50 (9). The IR spectrum of PCyh is reasonable for the structure shown above. Copolymer was prepared in an analogous way and its color was also deep black.

Figs. 1a and 1b compare CP-MAS ^{13}C-NMR (67.9 MHz) spectra of PCyh and Copolymer. As shown in Fig. 1a, PCyh gives rise to only one signal for the sp^3-carbon C^a.



Cyh unit

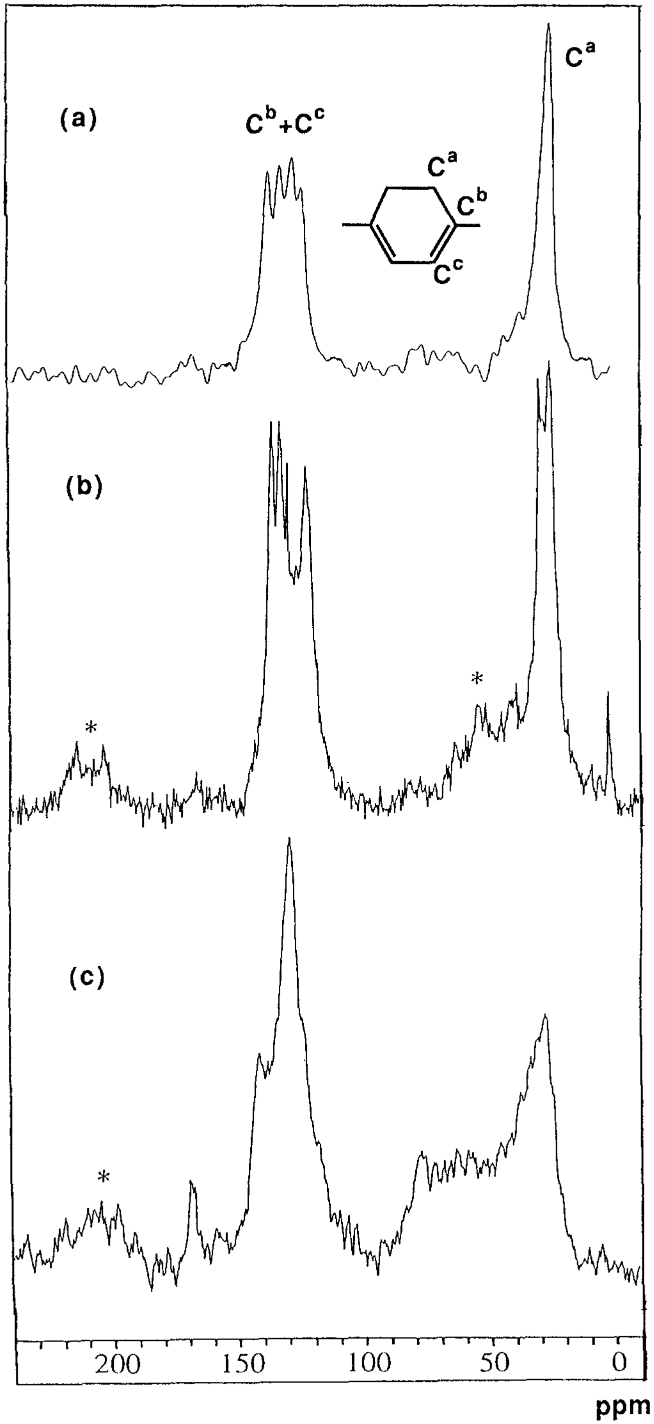
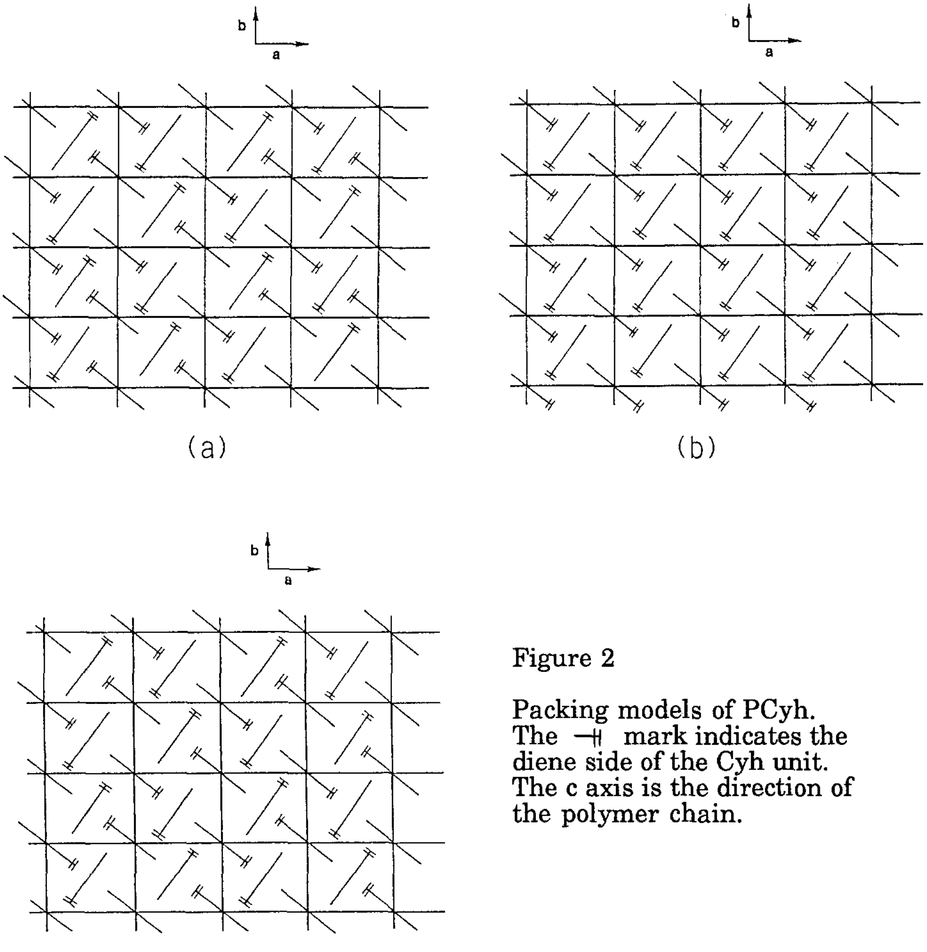


Figure 1

CP-MAS ^{13}C-NMR spectra(67.9 MHz) of (a) PCyh, (b) Copolymer, and (c) PCyh after leaving the sample under air for 48 h at 24 °C
* : side band.

The appearance of four peaks for C^b and C^c olefinic carbon may be due to partial taking of *s-cis* conformation in addition to the *s-trans* conformation (Scheme I) or the presence of the 1,3-cyclohexadiene-1,4-diyl units (the above Cyh units) under various magnetic circumstances in the solid packing as shown in Fig. 2. Powder X-ray diffraction of PCyh gives rise to a diffraction pattern similar to those of poly(*p*-phenylene) PPP (10) and poly(thiophene-2,5-diyl) PTh (11), although the diffraction peaks are considerably broadened. The X-ray diffraction pattern of PCyh suggests that PCyh also takes an orthorhombic packing similarly to PPP, PTh, poly(ethylene) and poly(acetylene). At the moment, we do not have evidence to judge whether PCyh takes the irregular packing as shown in Fig. 2a or makes a mixture of regularly packed orthorhombic-like microcrystals as shown in Figs. 2b and 2c to give rise to the four sp^2-carbon peaks in the CP-MAS ^{13}C-NMR spectrum.



(a)

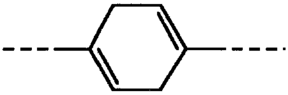
(b)

(c)

Figure 2

Packing models of PCyh. The —ǂ mark indicates the diene side of the Cyh unit. The c axis is the direction of the polymer chain.

PCyh has good thermal stability, its TGA curve showing start of the thermal decomposition at about 210 °C under N_2 and residual weight of 55% at 800 °C. Annealed PCyh showed essentially the same X-ray diffraction pattern.
The CP-MAS ^{13}C-NMR spectrum of Copolymer (Fig. 1b) shows a new -CH_2- carbon peak at 29 ppm in addition to the -CH_2- carbon peak of the Cyh unit (C^a) at 25 ppm. Signals of =CH_2- carbons of Copolymer also show a peak pattern different from that of PCyh. The difference in the CP-MAS ^{13}C-NMR spectrum between PCyh and Copolymer is reasonably explained by the presence of 1,4-cyclohexadiene-1,4-diyl unit in Copolymer.



PCyh shows considerably high sensitivity toward air. Although no apparent changes in color and IR were observed after leaving the sample for 2 h in air, leaving the sample in air for several hours (e.g., 5 h) caused some color and IR changes. After 48 h, the color of the polymer changed to brown or brownish yellow. Figure 3 shows change of the IR spectrum of PCyh on leaving the sample in air for 48 h at 24 °C. The IR spectrum after oxidation (Fig. 3b) shows new peaks, which are considered to be originated from OH group, OOH group, epoxide, and/or ether group. The CP-MAS ^{13}C-NMR spectrum of the air-oxidized PCyh (Fig. 1c) also shows profound change of the chemical structure of PCyh. The air-oxidized PCyh contains 66.15 and 5.70% of C and H, respectively, indicating taking of oxygen by the polymer. However, the C/H ratio was essentially unvaried after the oxidation.

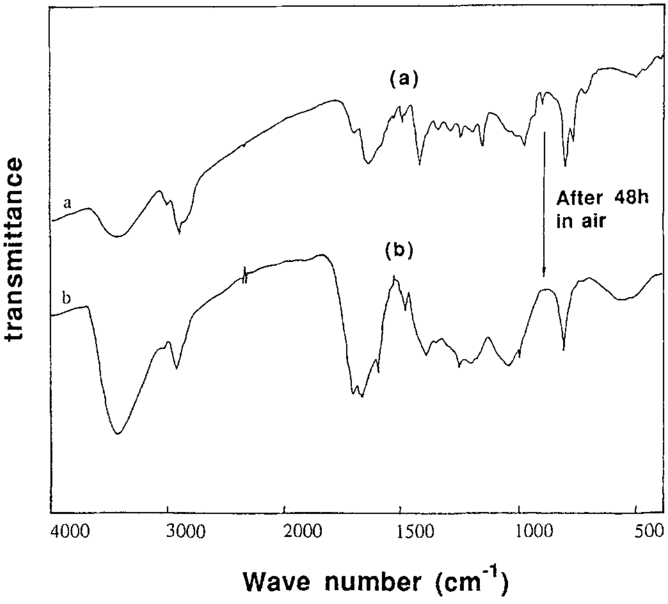


Figure 3 IR spectra of (a) PCyh and (b) PCyh after leaving the sample under air

The changes of color, IR spectrum, and analytical data on the air-oxidation are similar to those (7b, 12) observed during similar air-oxidation of poly(acetylene). Thus, the results described above strongly suggest that the high air sensitively of PCyh is related to the extensive π-conjugation along the polymer chain of PCyh, similarly to the case of poly(acetylene). The extensive π-conjugation seems to be due to taking the *s-trans* conformation shown in Scheme I.

Both PCyh and Copolymer themselves have electrical conductivity (σ) of about 10^{-7} S cm^{-1} at room temperature under N_2. Exposure of the polymers to the vapor of iodine gives iodine adducts, which show the σ value of 2.0×10^{-4} and 2.8×10^{-6} S cm^{-1} for the PCyh-iodine (76 wt% of iodine/PCyh) and Copolymer-iodine adducts, respectively, as measured with pressed powder samples.

References

(1) (a) T. A. Skotheim, ed. *Handbook of Conductive Polymers* , Vols. I and II.; Marcel Dekker, New York; 1986. (b) A. G. MacDiarmid and A. J. Heeger, *NRL Memo. Rep., Proc. Mol. Electron Devices Workshop,* **1981,** AD-A 105816, 208. (c) W. R. Salaneck, D. T. Clark, and E. J. Samuelsen, ed. *Science and Applications of Conducting Polymers*; Adam Hilger, New York; 1990. (d) J. -M. Andre, J. Delhalle, and J. -L. Bredas, *Quantum Chemistry Aided Design of Organic Polymers*; World Scientific, London; 1991; (e) E. Tsuchida, ed., "*Macromolecular Complexes*", VCH Publishers, New York (1991); (f) N. Ogata, ed., "*Dodensei Kobunshi*", Kodansha, Tokyo (1990); (g) H. Shirakawa and T. Yamabe, ed. "Gosei Kinzoku", Kagaku Dojin (1980).

(2) (a) P. Kovacic, M. B. Feldman, J. P. Kovacic, and J. B. Lando, *J. Appl. Polym. Sci.,* **12,** 1735 (1968); (b) T. Yamamoto, Y. Hayashi, and A. Yamamoto, Bull. chem. Soc. Jpn., **51,** 2091 (1978); (c) N. Toshima, K. Tanaka, A. Koshirai, and H. Hirai, Bull. Chem. Soc. Jpn., **61,** 2251 (1988); (d) E. Tsuchida, K. Yamamoto, T. Asada, and H. Nishide, Chem. Lett., 1541 (1988).

(3) T. Yamamoto, Y. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules,* **25,** 1214 (1992); T. Yamamoto, Y. Morita, T. Maruyama, Z. -H. Zhou, and T. Kanbara, *Polym. J.* **22,** 187 (1990).

(4) (a) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.* **93,** 3350 and 3360 (1971); (b) T. Kohara, T. Yamamoto, and A. Yamamoto, *J. Organomet. Chem.*, **192,** 265 (1980); (c) T. Yamamoto, S. Wakabayashi, and K. Osakada, *ibid.*, **428**, 223 (1992); (d) M. F. Semmelhack, P. M. Helquist, and J. D. Jones, *J. Am. Chem. Soc.*, **97,** 5903 (1975).

(5) K. Yamamoto, T. Asada, H. Nishide, and E. Tsuchida, *Polym. Adv. Tech.,* **1,** 207 (1990).

(6) (a) J. R. Wiseman and J. J. Vanderbilt, *J. Am. Chem. Soc.* **100,** 7730 (1978); (b) D. H. R. Barton, G. Bashiardes, and J. -L. Fourrey, *Tetrahedron,* **44,** 147 (1988).

(7) (a) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.* **12,** 11 (1974); (b) M. Hatano, S. Kanbara, and S. Okamoto, *J. Polym. Sci.* **51,** S26 (1961).

(8) (a) J. L. Bredas, R. Silbey, D. S. Boudreaux, and R. R. Chance, *J. Am. Chem. Soc.* **105,** 6555 (1983); (b) J. -L.Bredas, *Handbook of Conducting Polymers Vol. 2,* ed. T. A. Skotheim, pp.859; Marcel Dekker, New York; 1986. (c) J. Tanaka and M. Tanaka, *ibid.* pp. 1269.

(9) T. Yamamoto, T. Maruyama, and K. Kubota, *Chem. Lett.* **1989,** 1951.

(10) G. Froyer, F. Maurice, J. P. Mersior, D. Riviere, M. Le Cun, and P. Auvray, *Polym.* **22,** 992 (1981).

(11) S. Bruckner and W. Porzio, *Makromol. Chem.* **189,** 961 (1988).

(12) H. W. Gibson and J. M. Pochan, *Macromolecules,* **15,** 242 (1982).

Accepted October 28, 1992 S