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Polymerizations of nitrogen-containing heterophanes by vapor deposition method, transformation to polymeric films bearing a conjugated structure, and their properties

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Summary

The polymerizations of three nitrogen-containing heterophanes such as [2.2](2,5)pyridinophane (**1**), [2.2](2,5)pyrazinophane (**2**) and N, N'-dimethyl-[2.2](2,5)pyrrolophane (**3**) by the vapor deposition method were carried out. Compounds **1**, **2**, and **3** gave poly(2,5-pyridinediyl-ethylene), poly(2,5-pyrazinediyl-ethylene), and poly(N-methyl-2,5-pyrrolediyl-ethylene) as tough films, respectively. The transformation of the ethylene unit in the polymer films to the vinylene one by the dehydrogenation reaction using 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) failed in the former two polymeric films and succeeded to a certain extent in the latter one. The electrical conductivity of a poly(N-methyl-2,5-pyrrolediyl-vinylene) film obtained by the dehydrogenation reaction was measured to be 4×10^{-4} S/cm at room temperature and increased up to 1×10^{-2} S/cm on doping with iodine.

Introduction

Gorham *et al.* reported that a strained [2.2]paracyclophane is converted by vacuum pyrolysis at 600 °C to a reactive intermediate p-xylylene, stable in the vapor phase, which spontaneously polymerizes upon condensation to form a poly(p-xylylene) (poly(p-phenylene-ethylene)) film (1,2). This was a very useful method to obtain a film free from contaminant and cross-linking because of using no solvent. However, this vapor deposition method has been applied to only [2.2]paracyclophane and substituted [2.2]paracyclophanes bearing substituents on their aromatic rings so far (1,2). Recently, we applied this method to a [2.2](2,5)thiophenophane to obtain successfully a poly(2,5-thienylene-ethylene) (poly(2,5-thiophenediyl-ethylene)) film free from cross-linking (3).

Polymers with a fully conjugated structure such as poly(2,5-thienylene-vinylene)s and poly(p-phenylene-vinylene)s are currently attracting much interest as materials for their high electrical conductivity and nonlinear optical property (4-12). However, fully conjugated polymers were intractable due to their nonfusibility or insolubility in any solvents. In order to improve their processibilities, a water-soluble precursor route has been designed and a modification of the arylene unit such as thienylene and phenylene groups has been carried out by introducing long alkyl and alkoxy chains (7-12). We found that a poly(2,5-thienylene-ethylene) film could be converted easily to a poly(2,5-thienylene-vinylene) one by the dehydrogenation reaction with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) in p-dioxane at reflux and also the polymeric film doped with iodine exhibited an electrical conductivity of 160 S/cm (13). The process, which involves the preparation of a tough film by the

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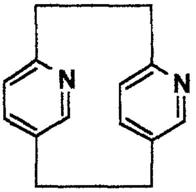
vapor deposition method followed by the dehydrogenation reaction, is considered to be an advantageous method for preparing a fully conjugated film. We are interested in applying this process to other cyclophanes to prove its usefulness.

In this work were described the application of this process to nitrogen-containing heterophanes such as [2.2](2,5)pyridinophane (**1**), [2.2](2,5)pyrazinophane (**2**) and N, N'-dimethyl[2.2](2,5)pyrrolophane (**3**) and some properties of polymeric films obtained.



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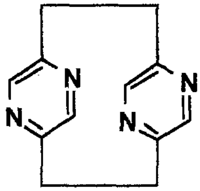

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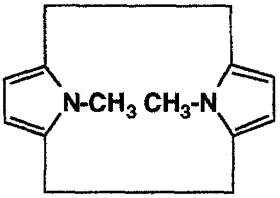

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Experimental

Materials

[2.2](2,5)Pyridinophane (**1**) was prepared in 2.2 % yield via seven steps from 5-ethyl-2-picoline as a starting material according to the method reported by Bruhin *et al.* (14): mp 192 °C ; IR(KBr): 2988, 2930, 2850, 1577, 1552, 1470, 1433, 1390 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ7.22-6.52 (m, 4H), 3.31-3.08 (m, 8H). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.81; H, 6.85; N, 13.34. [2.2](2,5)Pyrazinophane (**2**) was prepared in 1.4 % yield via four steps from 2,5-dimethylpyrazine as a starting material according to the method reported by Eiermann *et al.* (15): mp 255-256 °C ; IR(KBr): 3050, 2938, 2856, 1547, 1505, 1471, 1450, 1434 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ7.83 (s, 4H), 3.31 (s, 8H). Anal. Calcd for $C_{12}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.10; H, 5.22; N, 23.68. N, N'-Dimethyl-[2.2](2,5)pyrrolophane (**3**) was prepared in 15 % yield via four steps from [2.2](2,5)furanophane (16) as a starting material according to the method reported by Wasserman *et al.* (17): mp 143-145 °C ; IR(KBr): 3080, 3018, 2986, 2926, 1482, 1444, 1396, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ5.98 (s, 4H), 2.95 (s, 6H), 2.73 (s, 8H). Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.65; H, 8.40; N, 12.95. Commercial 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) was used without further purification. p-Dioxane (bp 101 °C) was refluxed over metal sodium for 24 h and then distilled.

Polymerization by the vapor deposition method

The apparatus for polymerization by the vapor deposition method is shown in Figure 1. The apparatus is composed of a vaporization section, a pyrolysis section, a deposition section, a cold trap, and a vacuum pump. A Pyrex glass tube of 8 mm in inside diameter was used as the pyrolysis tube. The system was evacuated to the pressure of 0.1 mmHg. The pyrolysis tube was heated externally by an electric furnace and the temperature was measured by the thermocouple in the middle of the furnace on the outside of the tube. The deposition section was cooled to the temperature of -18 °C by using a cooling bath of carbon tetrachloride-dry ice. When the temperature of a pyrolysis section reached to 580 °C, heterophane compound present at a vaporization section was heated externally by using a heat gun or a band heater. The use of a heat gun allowed the heterophane to vaporize in a few minutes and the use of a band heater allowed it to vaporize in about 30 minutes. The vaporization section was then cooled and the system was returned to atmospheric pressure. The polymeric film was recovered from the wall of the Pyrex tube at the deposition section. The film was washed in a Soxhlet apparatus with dichloromethane, dried, and weighed to determine the conversion.

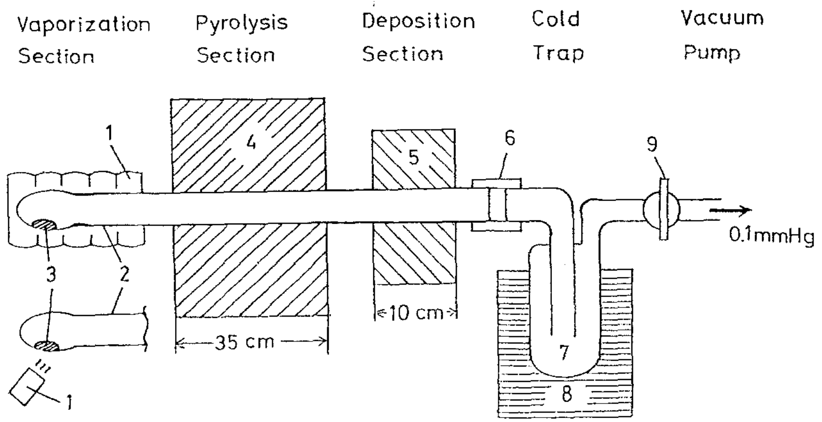


Figure 1. The apparatus for the polymerization by the vapor deposition method. 1: band heater or heat gun; 2: Pyrex glass tube; 3: heterophane compound; 4: electric furnace; 5: cooling bath; 6: rubber tube; 7: cooling trap; 8: Dewar jar (liquid nitrogen); 9: two way stopcock.

Dehydrogenation reaction

DDQ as an oxidizing reagent was dissolved in 30 mL of p-dioxane and a piece of film (about 10 mg) was added. The mixture was refluxed under nitrogen for 10 h. Then the reacted films were picked up from the reaction mixture and extracted for purification in a Soxhlet apparatus with p-dioxane for 3 h.

Electrical conductivity

The electrical conductivity of undoped and doped polymeric films was measured by using the conventional four-probe d.c. technique at room temperature. Four silver wires were connected on the film by using a silver paste. For the electrical conductivity measurement of a doped polymeric film, after connecting silver wires on the film and then exposing to iodine vapor for 24 and 48 h, the measurement was carried out. The film thickness was measured by using a micrometer.

Results and discussion

Polymerizations of heterophanes (1-3) by the vapor deposition method

Although compounds **1** and **2** except for **3** are usually prepared as a mixture of isomers (14, 15), their polymerizations by the vapor deposition method were carried out without isolation of the isomers. The results of polymerizations of **1-3** by the vapor deposition method are summarized in Table 1. For all **1-3,** the polymers were obtained as thin films in low yields for fast vaporization using a heat gun (run nos. 1, 3, and 5) and also unreacted heterophanes were recovered in substantial quantity from

Table 1 Preparation of polymeric films from **1-3** by the vapor deposition method

Run no.	Compound **1-3** / mg	Vaporizing Method	Vaporizing Time/ min	Pyrolysis Temp./ °C	Deposition Temp./ °C	Polymer Yield/ mg	Conversion / %
1	**1** 30.7	a)	2	580	-18	5.3	17.3
2	**1** 50.5	b)	30	580	-18	32.6	64.6
3	**2** 30.5	a)	2	580	-18	1.5	4.9
4	**2** 45.4	b)	30	580	-18	11.7	25.8
5	**3** 30.3	a)	2	580	-18	13.2	43.6
6	**3** 56.1	b)	30	580	-18	48.4	86.3

a) By using a heat gun.
b) By using a band heater.

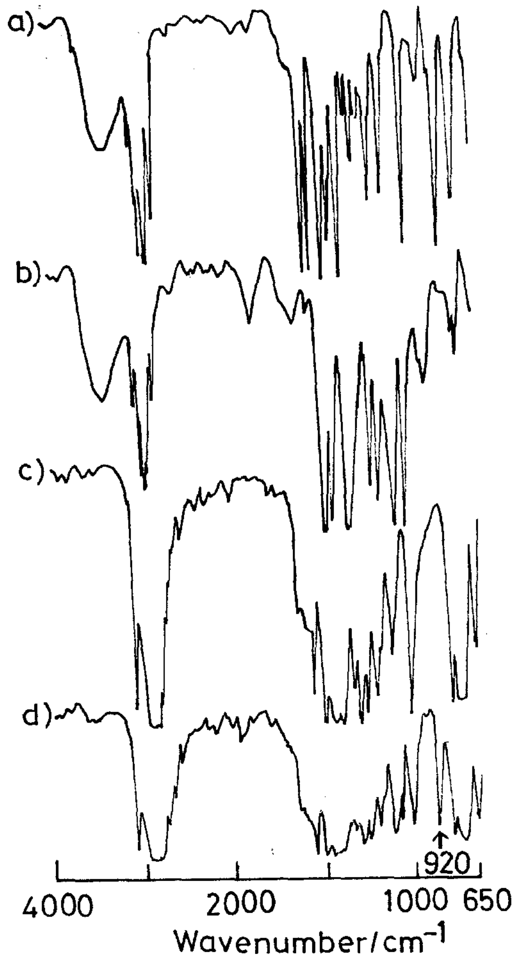
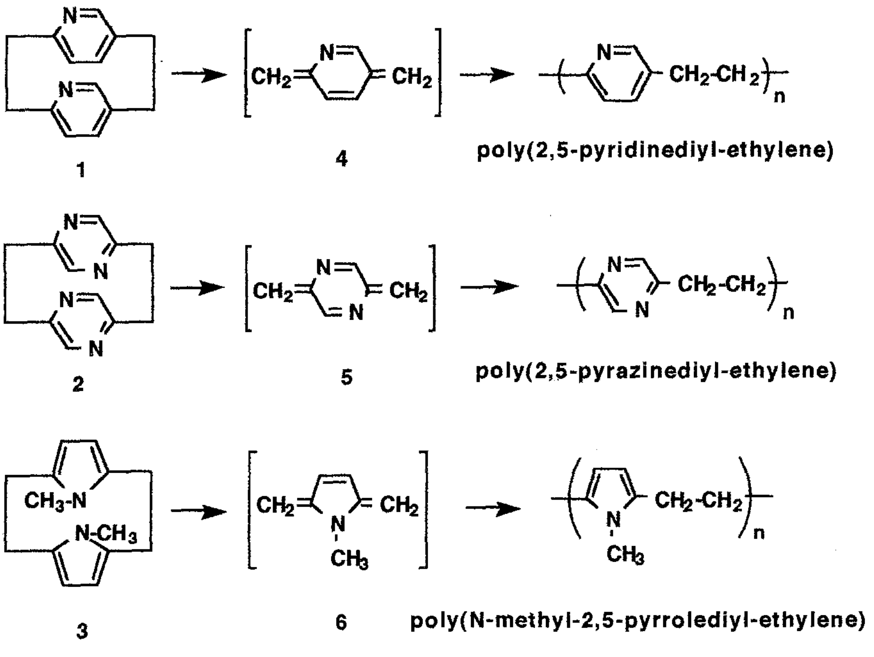


Figure 2. The IR spectra of the polymeric films obtained from (a) **1**, (b) **2**, and (c) **3**, and of (d) poly(N-methyl-2,5-pyrrolediyl-ethylene) film obtained after the dehydrogenation reaction.

the dichloromethane extracts, but they were obtained as thick films in relatively high yields for slow vaporization using a band heater (run nos. 2, 4, and 6), indicating that fast vaporization makes decomposition of heterophanes incomplete. Compounds **1** and **2** gave clear colorless transparent films and **3** gave clear pale yellow transparent one.

The IR spectra of the films obtained from **1**, **2**, and **3** are shown in the parts a, b, and c, respectively, in Figure 2. The absorption peaks due to the stretching vibration of the methylene group were observed at around 2900 and 2850 cm^{-1} for all polymeric films. The absorption peaks at 1600, 1565, 1450, and 1390 cm^{-1} in part a, at 1450 and 1360 cm^{-1} in part b, and at 1565, 1500, and 1300 cm^{-1} in part c were assigned well to the pyridine, pyrazine, and pyrrole rings, respectively. The elemental analysis values for the polymeric film (Found: C, 80.14; H, 6.67; N, 13.19) obtained from **1**, for the polymeric film (Found: C, 71.40; H, 5.01; N, 23.59) from **2** , and for the polymeric film (Found: C, 78.19; H, 8.53; N, 13.27) from **3** were in good agreement with the calculated ones for poly(2,5-pyridinediyl-ethylene) (Calcd for $(C_7H_7N)_n$: C, 79.97; H, 6.71; N, 13.32), for poly(2,5-pyrazinediyl-ethylene) (Calcd for $(C_6H_6N_2)_n$: C, 71.17; H, 5.12; N, 23.71), and for poly(N-methyl-2,5-pyrrolediyl-ethylene) (Calcd for $(C_7H_9N)_n$: C, 78.46; H, 8.47; N, 13.07), respectively. This indicates that **1**, **2**, and **3** are converted by vacuum pyrolysis to reactive intermediates 2,5-dimethylene-2,5-dihydropyridine (**4**), 2,5-dimethylene-2,5-dihydropyrazine (**5**), and N-methyl-2,5-dimethylene-2,5-dihydropyrrole (**6**), which spontaneously polymerize upon condensation on a glass surface to form poly(2,5-pyridinediyl-ethylene), poly(2,5-pyrazinediyl-ethylene), and poly(N-methyl-2,5-pyrrolediyl-ethylene) films (Scheme), respectively, like the cases of a [2.2]paracyclophane (1) and a [2.2](2,5)thiophenophane (3).

Scheme



Dehydrogenation reaction with DDQ and properties of polymeric films

All polymeric films obtained by the vapor deposition method were tough and insoluble in conventional organic solvents such as chloroform, tetrahydrofuran, dimethylsulfoxide, and N,N-dimethyl formamide at room temperature, but soluble in m-cresol at boiling, suggesting that they are linear polymers without cross-linking. However, an exposure of a poly(N-methyl-2,5-pyrrolediyl-ethylene) film to air for one day made it insoluble in m-cresol, indicating that a cross-linking took place, probably due to a lower ionization potential of a pyrrole ring as described later.

All polymeric films were subject to the dehydrogenation reaction with DDQ in p-dioxane at reflux under nitrogen. The reaction was carried out in liquid-solid phase. A poly(N-methyl-2,5-pyrrolediyl-ethylene) film changed in color with the reaction time from pale yellow to black with a golden luster, but poly(2,5-pyridinediyl-ethylene) and poly(2,5-pyrazinediyl-ethylene) films did not change in color. The IR spectra of the poly(2,5-pyridinediyl-ethylene) and poly(2,5-pyrazinediyl-ethylene) films were exactly same as those of the respective starting polymeric films. While, the IR spectrum of the poly(N-methyl-2,5-pyrrolediyl-ethylene) film was different from that of the starting polymeric film. The IR spectrum of the poly(N-methyl-2,5-pyrrolediyl-ethylene) film obtained in a reaction time of 10 h is shown in the part d in Figure 2. A new strong peak appears at 920 cm^{-1}, assigned to the carbon-hydrogen out-of-plane bending of the trans vinylene, indicating the conversion of the ethylene unit to vinylene one. However, peaks at 2900-2850 cm^{-1}, assigned to the stretching vibration of the methylene group, did not disappear completely even in the reaction time more than 10 h, contrast to the case of poly(2,5-thienylene-ethylene) film, where the corresponding peaks disappeared completely in 4 h (13). The extent of the dehydrogenation reaction of the polymeric film in a reaction time of 10 h was estimated on the basis of the amount of 2,3-dichloro-5,6-dicyanohydroquinone obtained from the reaction mixture to be about 55 %. A poly(N-methyl-2,5-pyrrolediyl-ethylene) film could be converted to a conjugated poly(N-methyl-2,5-pyrrolediyl-vinylene) film even though incomplete, but both poly(2,5-pyridinediyl-ethylene) and poly(2,5-pyrazinediyl-ethylene) films could not. Previously, it was reported that a poly(p-phenylene-ethylene) film was hardly converted to a poly(p-phenylene-vinylene) one (18). The ionization potentials of heteroaromatic rings such as pyridine, pyradine, thiophene, and pyrrole are reported to be 9.28, 9.28, 8.87, and 7.95 eV, respectively, and that of the benzene ring is to be 9.24 eV (19). The transformation of the ethylene units in the polymeric films to the vinylene one by the dehydrogenation reaction was possible for only the cases of the polymeric films bearing the thiophene and pyrrole rings, which have lower ionization potentials than benzene ring. It is considered that as the course of the dehydrogenation reaction by quinones involves the initial abstraction of a hydride ion (20), only the polymeric films with a more electron-donating ring, that is, a ring of a lower ionization potential could be easily oxidized.

The electrical conductivity of a poly(N-methyl-2,5-pyrrolediyl-vinylene) film obtained by the dehydrogenation reaction was measured by a conventional four-probe d.c. technique to be 4×10^{-4} S/cm, and also on exposure to iodine vapor at room temperature, its conductivity increased up to 1×10^{-2} S/cm in 24 h, whose value did not change in 48 h. However, the electrical conductivity of the poly(N-methyl-2,5-pyrrolediyl-vinylene) film was lower than those of a poly(thiophenediyl-vinylene) film (0.2 S/cm for an undoped film and 160 S/cm for a doped film with iodine) prepared by the same procedure (13). The difference in the electrical conductivity between the former film and the latter one is probably due to that in the vinylene unit content.

In conclusion, the process, which involves the preparation of a polymeric film by the vapor deposition method followed by the dehydrogenation reaction, were successfully applicable to the nitrogen-containing heterophanes such as **1**, **2**, and **3** to afford linear, tough films. It was found that the transformation to the polymeric films with a conjugated structure by the dehydrogenation reaction with DDQ was successful in only the polymeric films with the heteroaromatic rings such as thiophene and pyrrole of lower ionization potentials. The electrical conductivity of a poly(N-methyl-2,5-pyrrolediyl-vinylene) film obtained by the dehydrogenation reaction was measured to be 4 x 10^{-4} S/cm at room temperature and increased up to 1 x 10^{-2} S/cm on doping with iodine.

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