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Vapor Deposition Polymerization of Dispiro[2.2.2.2]deca-4,9-diene

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ABSTRACT: Dispiro[2.2.2.2]deca-4,9-diene was sublimed under a pressure of 0.1 mmHg and was pyrolyzed at 500 °C. When condensed on a glass surface at 20 °C, the pyrolyzed gas underwent spontaneous polymerization to give poly(1,4-phenylene-1,2-dimethylethylene) as a film ($\bar{M}_n = 3 \times 10^4$) in 10–20% yield and oligo(1,4-phenylenetetramethylene-*co*-1,4-phenylene-1,2-dimethylethylene) as an oil ($\bar{M}_n = (2\text{–}4) \times 10^2$) in 50–70% yield. It was proposed for the formation of the polymer film that the diradical intermediate generated in the pyrolysis of dispiro[2.2.2.2]deca-4,9-diene undergoes an isomerization reaction to form 7,8-dimethyl-1,4-benzoquinodimethane which polymerizes spontaneously to give a poly(1,4-phenylene-1,2-dimethylethylene) film.

Introduction

[2.2]Paracyclophane undergoes vapor-phase pyrolysis under reduced pressure at 600 °C to give 1,4-benzoquinodimethane in a gas state which condenses on a cold surface below 30 °C and simultaneously and spontaneously polymerizes to give linear poly(1,4-phenyleneethylene) as a colorless transparent film (Scheme I).[1] This polymerization technique is called the vapor deposition polymerization method which has been effectively applied to a limited range of highly strained compounds such as [2.2]paracyclophane,[1] its ring-substituted derivatives,[1] [2.2](2,5)thiophenophane,[2] and 1,9-dichloro[2.2]paracyclophane[3] to afford poly(1,4-phenyleneethylene), poly(2,5-substituted 1,4-phenyleneethylene), poly(2,5-thienyleneethylene), and poly(1,4-phenylenechloroethylene) films, respectively.

Dispiro[2.2.2.2]deca-4,9-diene (1) with a highly strained dispiro structure of two cyclopropane rings and 1,4-cyclohexadiene was first synthesized by Tsuji et al. in 1972.[4] When heated in diglyme at 160 °C, 1 turned to *p*-diethylbenzene (3),[5] indicating that the cyclopropane ring was cleaved to generate a 2,2′-(1,4-phenylene)diethyl diradical (2) which abstracted hydrogen from a solvent to give 3 (Scheme II).[5] If 1 can be readily subjected to pyrolysis at such a low temperature to afford a compound stable in a gas state but spontaneously polymerizable in a condensed state, then 1 can be a compound suitable for the vapor deposition polymerization to obtain a poly(1,4-phenylenetetramethylene) film.

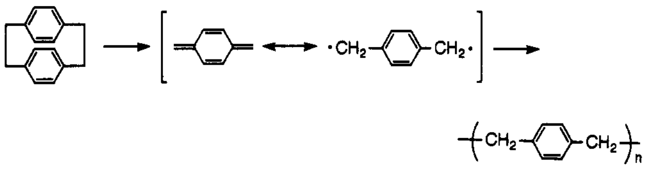
In this work were studied the vapor deposition polymerization of 1 and the chemical structure of the products obtained. Furthermore, the addition reaction of the pyrolyzed gas of 1 with chlorine was carried out to obtain information about the chemical structure of the intermediates.

Experimental Section

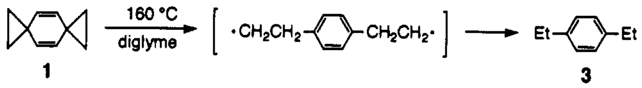
Dispiro[2.2.2.2]deca-4,9-diene (1). Compound 1 was prepared according to the method of Tsuji et al.:[5] mp 119 °C (lit.[5] mp 121–122 °C); ^{1}H NMR ($CDCl_3$) δ 5.0 (s, 4 H), 0.77 (s, 8 H); IR (KBr) 1585, 1032 cm^{-1}.

Diethyl 1,4-Phenylenediacetate (5). To the suspension of 5.8 g (30 mmol) of 1,4-phenylenediacetic acid (4) in 30 mL of benzene were added 8.3 g (70 mmol) of thionyl chloride and 1 mL of *N,N*-dimethylformamide (DMF). The mixture was refluxed for 3 h and placed under reduced pressure to remove volatile materials. The remaining solid was dissolved in a mixture of 40 mL of ethyl acetate and 5 mL of ethanol. After 7.1 g (70 mmol) of triethylamine was added dropwise into the resulting solution, the mixture was stirred at room temperature for 10 h. The mixture was washed three times with 50-mL portions of water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The remaining solid was recrystallized from hexane to give 4.9 g of 5 (in 59% yield) as pale-orange needles: mp 57.0 °C (lit.[6] mp 57.5–58.0 °C); ^{1}H NMR ($CDCl_3$) δ 7.24 (s, 4 H), 4.2–4.1 (m, 4 H), 3.59 (s, 4 H), 1.25 (t, *J* = 6.9 Hz, 6 H); IR (KBr) 1696 cm^{-1}.

Scheme I



Scheme II



1,4-Bis(2-hydroxyethyl)benzene (6). To the suspension of 0.7 g (18 mmol) of lithium aluminum hydride in 150 mL of ethyl ether was added 3.0 g (12 mmol) of 5, and the mixture was refluxed for 2 h. The reaction mixture was cooled to 0 °C, and then 100 mL of a saturated magnesium sulfate aqueous solution was added dropwise to it. The ether layer was separated, washed with water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The remaining solid was recrystallized from a mixture of dichloromethane and hexane to give 1.1 g of 6 (in 60% yield) as white needles: mp 84.3–85.0 °C (lit.[7] mp 85–86 °C); ^{1}H NMR ($CDCl_3$) δ 7.18 (s, 4 H), 3.85 (t, *J* = 6.0 Hz, 4 H), 2.85 (t, *J* = 6.0 Hz, 4 H), 1.55 (br s, 2 H); IR (KBr) 3340 cm^{-1}.

1,4-Bis(2-chloroethyl)benzene (7). To the suspension of 1.7 g (10 mmol) of 6 in 30 mL of carbon tetrachloride was added 5.2 g (25 mmol) of phosphorus pentachloride. After the mixture was refluxed for 2 h, the mixture was washed with three 50-mL portions of water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The remaining solid was recrystallized from a mixture of ethanol and water to give 1.4 g (in 68% yield) of 7 as white fine needles: mp 45.0–46.0 °C (lit.[7] mp 46–47 °C); ^{1}H NMR ($CDCl_3$) δ 7.17 (s, 4 H), 3.70 (t, *J* = 7.0 Hz, 4 H), 3.04 (t, *J* = 7.0 Hz, 4 H), 1.55 (br s, 2 H); IR (KBr) 763 cm^{-1}.

Poly(1,4-phenylenetetramethylene) (8). The polymer 8 was prepared in a way similar to that for the preparation of poly(1,4-phenyleneethylene) from *p*-xylylene dichloride.[8] The mixture of 0.50 g (2.5 mmol) of 7, 0.14 g (6.2 mmol) of sodium, and 5 mL of *p*-xylene was heated under reflux for 2 h. It was poured into 30 mL of methanol to deposit a solid which was removed by filtration, washed with methanol, stirred with water for 48 h, and dried under reduced pressure to give 0.17 g of 8 (in 53% yield)

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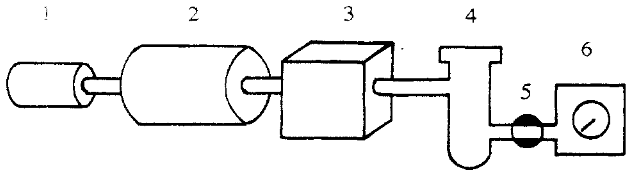


Figure 1. Apparatus for the vapor deposition polymerization of 1: 1, vaporizer; 2, 800-W furnace; 3, deposition chamber; 4, liquid nitrogen trap; 5, stopcock; 6, vacuum pump.

as a pale-yellow powder: ^{1}H NMR ($CDCl_3$) δ 7.1 (s, 4 H), 2.6 (s, 4 H), 1.2 (s, 4 H); IR (KBr) 3400, 2900, 2830, 1485, 1431, 817 cm^{-1}; $\bar{M}_n$ (GPC) 900. Anal. Calcd for $(C_{10}H_{12})_n$: C, 90,85; H, 9.15. Found: C, 90.63; H, 8.87.

1,4-Bis(1-hydroxyethyl)benzene (10). Sodium borohydride (2.0 g, 53 mmol) was added to the solution of 6.5 g (40 mmol) of *p*-diacetylbenzene (**9**) in 40 mL of methanol. The mixture was stirred at room temperature for 24 h and then poured into 200 mL of a 1 N hydrochloric acid solution. The resulting mixture was extracted with three 50-mL portions of dichloromethane. The combined extract was washed with two 100-mL portions of water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The remaining solid was recrystallized from isopropyl ether to give 3.1 g of **10** (in 46% yield) as white needles: mp 77.5–78.0 °C (lit.[9] mp 78.4–80 °C); ^{1}H NMR ($CDCl_3$) δ 7.33 (s, 4 H), 4.87 (q, J = 6.0 Hz, 2 H), 2.08 (br s, 2 H), 1.47 (d, J = 6.0 Hz, 6 H); IR (KBr) 3280, 1070 cm^{-1}.

1,4-Bis(1-chloroethyl)benzene (11). To the suspension of 3.3 g (20 mmol) of **10** in 50 mL of carbon tetrachloride was added 10.4 g (50 mmol) of phosphorus pentachloride, and the mixture was stirred for 6 h. The reaction mixture was then washed with three 50-mL portions of water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to obtain a residual solid which was recrystallized from hexane to give 3.0 g of **11** (in 73% yield) as white needles: mp 85.0–86.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.41 (s, 4 H), 5.09 (q, J = 7.0 Hz, 2 H), 1.84 (d, J = 7.0 Hz, 6 H); IR (KBr) 710 cm^{-1}. Anal. Calcd for $C_{10}H_{12}Cl_2$: C, 59.14; H, 5.95; Cl, 34.91. Found: C, 59.09; H, 6.04; Cl, 34.88.

Poly(1,4-phenylene-1,2-dimethylethylene) (12). The polymerization procedure was similar to that for the preparation of **8**. A mixture of 0.50 g (2.5 mmol) of **11**, 0.14 g (6.2 mmol) of sodium, and 5 mL of *p*-xylene was refluxed for 2 h and then poured into 30 mL of methanol to precipitate a solid product which was filtered off, washed with methanol, stirred with water for 48 h, and dried under reduced pressure to give 0.09 g of **12** (in 73% yield) as a white powder: ^{1}H NMR ($CDCl_3$) δ 7.2–6.7 (m, 4 H), 2.9–2.6 (m, 2 H), 1.4–0.8 (m, 6 H); IR (KBr) 3400, 2924, 2890, 1484, 1429, 1395, 1360, 827 cm^{-1}; $\bar{M}_n$ (GPC) 1500. Anal. Calcd for $(C_{10}H_{12})_n$: C, 90.85; H, 9.15. Found: C, 90.72; H, 8.95.

Vapor Deposition Polymerization of 1. Vapor deposition polymerization was carried out according to the method of Gorham.[1] The outline of the apparatus employed is shown in Figure 1. A glass tube with a diameter of 1 cm and a length of 50 cm was employed with one end connected to a mechanical vacuum pump through a liquid-nitrogen trap. A given amount of **1** was set in the other end, and the system was evacuated to 0.1 mmHg. Compound **1** was sublimed by heating the vaporization zone at 80 °C. The sublimed vapor was introduced into the pyrolysis part kept at a given temperature of 400–620 °C. The pyrolyzed gas was led to a deposition chamber held at 20 °C, where polymerization occurred on the gas–solid interfaces. After completion of this pyrolytic conversion, the system was equilibrated to atmospheric pressure and the polymeric film formed at the deposition chamber was peeled from the wall. The inside of the glass tube in the pyrolysis zone was washed with dichloromethene, and the wash solutions were collected and evaporated under reduced pressure to give a colorless oily material.

Reaction of Pyrolyzed Product of 1 with Chlorine. The reaction of the pyrolyzed product of **1** with chlorine was carried out according to the method of Errede and Landrum.[10] Compound **1** (50 mg) was pyrolyzed at 500 °C under a pressure of 0.1 mmHg, and the pyrolyzed gas was absorbed in 40 mL of hexane kept at −78 °C. Excess chlorine gas was bubbled into 30 mL of carbon tetrachloride, and the resulting solution was added into the above-mentioned hexane solution under nitrogen at −78 °C. The reaction mixture was allowed to warm to room temperature, and then the mixture was evaporated under reduced pressure to remove volatile materials. The solid residue obtained thereby was purified by preparative thin layer chromatography (plate, Merck Art. 5735; eluent, hexane) to give 3 mg of a white solid (mp 74–76 °C), which was identified as 1,4-bis(1-chloroethyl)benzene (**11**) as described in the text.

Instruments for Measurement. ^{1}H NMR spectra were measured with a JEOL EX-270 (270-MHz) spectrometer using tetramethylsilane as an internal standard. IR spectra were measured with a Jasco IR-700 infrared spectrophotometer. Gel permeation chromatography (GPC) was performed with a Tosoh TSK-gel GMHXL column using chloroform and standard polystyrenes as an eluent and references, respectively. High-performance liquid chromatography (HLC) was performed with a Tosoh Si-150 column using hexane as an eluent.

Table I
Vapor Deposition Polymerization of 1[a]

run	1, mg	temp, °C			yield, %		
		vaporzn	pyrolysis	deposn	film	oil	total
1	50	80	400	20	0	0	0
2	50	80	450	20	10	46	56
3	30	80	450	20	9	57	66
4	30	80	500	20	17	55	72
5	30	80	620	20	12	68	80

[a] Pressure, 0.1 mmHg.

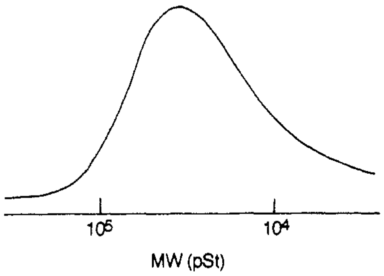


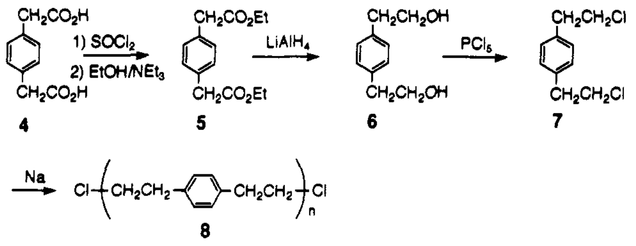
Figure 2. GPC chromatogram of the polymer film obtained in run 4 of Table I.

Results and Discussion

Vapor Deposition Polymerization of 1. Vapor deposition polymerization of **1** was carried out under a pressure of 0.1 mmHg at temperatures of 400, 450, 500, or 620 °C. The experimental results are summarized in Table I. When pyrolyzed at 400 °C, **1** was unreacted and was quantitatively recovered (run 1). When the temperature was raised to 450 °C, a colorless transparent film was obtained in the deposition chamber in 10–20% yield along with a colorless, oily material (in 50–70% yield) deposited on the glass tube wall located between the pyrolysis zone and deposition chamber (runs 2–5). The total conversion to products increased monotonically with temperature from 450 to 620 °C, but the yield of the solid polymer looked maximal at 500 °C. Thus, it was assumed that pyrolysis of **1** sufficiently took place at 450 °C.

The film obtained in the deposition chamber was not soluble in benzene, methanol, tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) but was soluble in chloroform and *m*-cresol at room temperature. Its number-average molecular weight ($\bar{M}_n$) was determined by gel permeation chromatography (GPC) to be 3 × 10^4 using chloroform and standard polystyrenes as an eluent and references, respectively (Figure 2). Anal. Found: C, 90.77; H, 9.33. Experimental values were also in agreement with the calculated ones for poly(1) (calcd for $(C_{10}H_{12})_n$: C, 90.85; H, 9.15). It was concluded that the film is a high molecular weight polymer of **1**.

Scheme III



Scheme IV

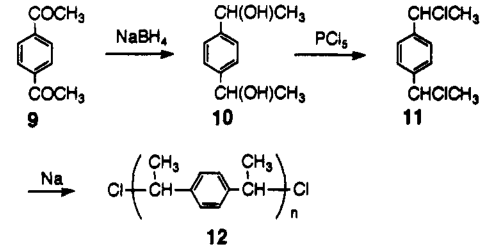


Table II
Solubilities[a] of 8, 12, and the Film of Poly(1)

	polymer		
solvent	8	12	film of poly(1)
chloroform	–	+	+
benzene	–	–	–
THF	–	–	–
MeOH	–	–	–
DMF	–	±	–
m-cresol	–	+	+

[a] +, soluble; ±, swelling; –, insoluble.

On the other hand, the oily material was soluble in THF and chloroform. Its $\bar{M}_n$ was determined to be 200–400. Anal. Found: C, 91.29; H, 8.85. Experimental values were in agreement with the calculated ones for poly(1) (calcd for $(C_{10}H_{12})_n$: C, 90.85; H, 9.15). It was concluded therefore that the oily material is a mixture of lower molecular weight oligomers of 1.

Chemical Structure of the Film. The chemical structure of the film was determined by comparing solubility in various solvents, IR, and ^1H NMR spectra with two model polymers. Two model polymers, poly(1,4-phenylenetetramethylene) (8) and poly(1,4-phenylene-1,2-dimethylethylene) (12) were prepared according to Schemes III and IV, respectively. The former polymer is presumed to be formed by a radical coupling of 2,2′-(1,4-phenylene)diethyl diradical (2) which was considered to be generated by cleavage of the cyclopropane rings of 1. The latter polymer is presumed to be formed by spontaneous polymerization of 7,8-dimethyl-1,4-benzoquinodimethane (13), which was produced via intramolecular hydrogen rearrangement of 2. Solubilities of 8, 12, and the film of poly(1) are summarized in Table II. The solubility of the film of poly(1) was much closer to that of 12 than that of 8. IR spectra of 8, 12, and the film of poly(1) are shown in Figure 3. Both the film of poly(1) and 12 exhibited absorption bands at 2924 and 2890 cm^{-1} due to CH_3 stretching and at 1360 cm^{-1} due to CH_3 bending (Figure 3b,c). On the other hand, 8 showed bands at 2900 and 2830 cm^{-1} due to CH_2 stretching (Figure 3a). The band at 3400 cm^{-1} for 8 and 12 in parts a and b of Figure 3, respectively, was thought to be assignable to moisture as a common contaminant in potassium bromide powder or a possible hydroxy group as terminals of these oligomers, but it apparently did not interfere with the above-mentioned absorption bands below 3000 cm^{-1}. ^1H NMR spectra of 8, 12, and the film of poly(1) are shown in parts a–c of Figure 4, respectively. The peaks in parts a and b of Figure 4a, were assignable to the respective protons in the chemical structures illustrated herein. Polymer 12 carried two multiplet peaks at 3.0–2.5 ppm (2 H) due to the methine proton of H_e and two multiplet peaks at 1.5–0.8 ppm (6 H) due to the methyl proton of H_f. Polymer 8 showed two singlet peaks at 2.6 (4 H) and 1.2 ppm (4 H) due to the methylene protons of H_b and H_c, respectively. In addition, 12 exhibited three peaks in the range of 7.0–6.5 ppm due to the protons on benzene rings, whereas 8 showed a single peak at 7.1 ppm. It is obvious that the spectrum of poly(1) is comparable to that of 12. It was concluded therefore that the film of poly(1) consists of the same structure of 12 rather than that of 8.

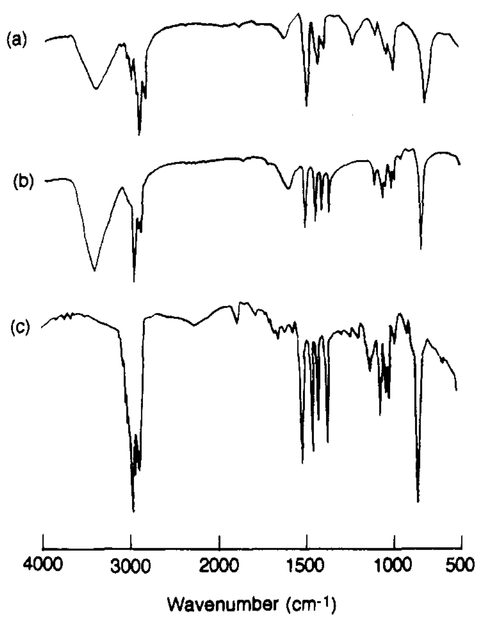


Figure 3. IR spectra of (a) 8, (b) 12, and (c) the polymer film obtained in run 4 of Table I.

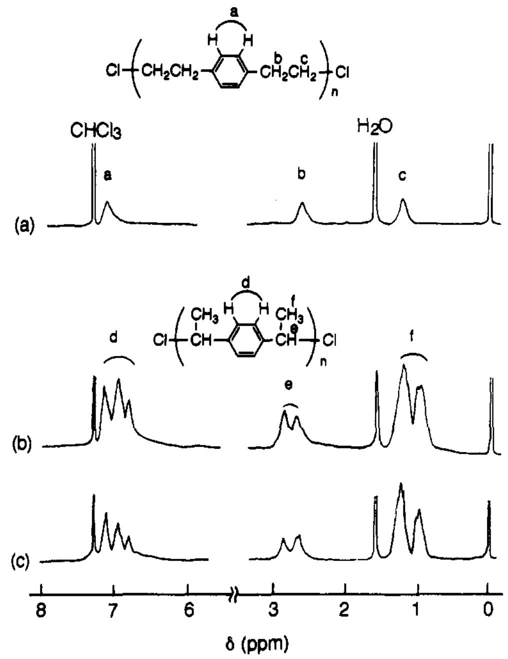


Figure 4. 270-MHz ^1H NMR spectra in chloroform-*d* of (a) 8, (b) 12, and (c) the polymer film obtained in run 4 of Table I.

The IR spectrum of the oily material is shown in Figure 5. It exhibited absorption bands at 2900 and 2830 cm^{-1} observable for 8 in addition to bands at 2924, 2890, and 1360 cm^{-1} observable for the film of poly(1) or 12. Its ^1H NMR spectrum exhibited not only peaks at 3.0–2.5 and

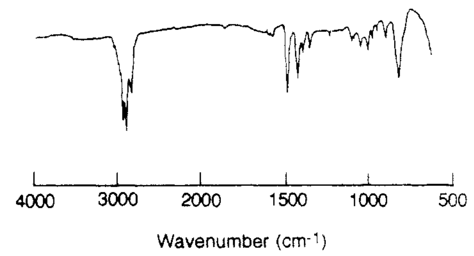


Figure 5. IR spectrum of the oily material obtained in run 3 of Table I.

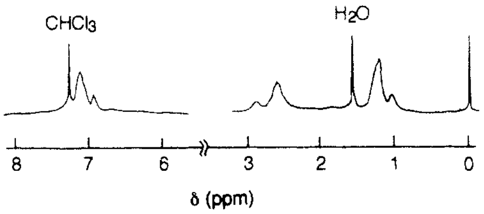


Figure 6. 270-MHz ^1H NMR spectra in chloroform-*d* of the oily material obtained in run 3 of Table I.

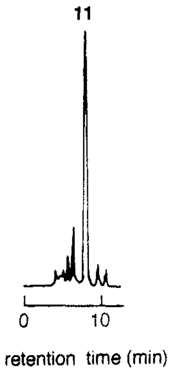


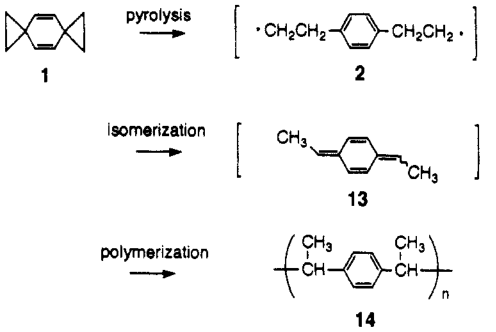
Figure 7. HLC chromatogram of the reaction product of the pyrolyzed gas of 1 with chlorine.

1.5–0.8 ppm observable for the film of poly(1) or 12 but also peaks at 2.6 and 1.2 ppm for 8 as shown in Figure 6. It was concluded that the oligomer of 1 was composed of both structures of 8 and 12. The area ratio of peaks at 2.6 ppm to that at 1.5–0.8 ppm was evaluated to be about 2–3, indicating that the oily material approximately consisted of 8 parts of the 8 unit and 2 parts of the 12 unit.

Addition Product of Pyrolyzed Gas of 1 with Chlorine. Compound 1 was pyrolyzed at 500 °C, and the pyrolyzed gas was absorbed in hexane at −78 °C. To the solution was added chlorine dissolved in carbon tetrachloride at −78 °C. The HLC chromatogram of the reaction product is shown in Figure 7. It exhibits a peak at the same retention time of authentic 1,4-bis(1-chloroethyl)benzene (11). Further, 3 mg of white solid (mp 74–76 °C) was separated by preparative thin layer chromatography using hexane as an eluent ($R_f = 0.7$). Its IR and ^1H NMR spectra were in agreement with those of 11, respectively. It was concluded therefore that 1 was subject to pyrolysis to give 7,8-dimethyl-1,4-benzoquinodimethane even though in poor yield.

Polymerization Mechanism. Cleavage of the spirocyclopropane rings of 1 by vapor phase pyrolysis above 450 °C was expected to generate 2,2′-(1,4-phenylene)diethyl diradical (2) which then underwent isomerization via 1,2-migration of hydrogen to give more stable 7,8-dimethyl-1,4-benzoquinodimethane (13). When condensed, it spontaneously polymerized to afford a poly(1,4-phenylene-1,2-dimethylethylene) (14) film. The fact that the addition reaction of the pyrolyzed product of 1 with chlorine at −78 °C afforded 11 positively suggested the isomerization of 2 to 13 (Scheme V).

Scheme V



The structure of the oily material was somewhat different from that of the film. From its IR and ^1H NMR spectra it corresponded to the copolymer or the cooligomer of 2 with 13, indicating that the isomerization of 2 to 13 took place neither effectively nor selectively under the experimental conditions and that 2 reacted with itself and also with 13 to give the oligomer and cooligomer, respectively, before reaching the deposition chamber because 2 must be less stable and more reactive than 13. The more stable 13 could proceed to the deposition chamber unless it reacted with 2.

Conclusions

Dispiro[2.2.2.2]deca-4,9-diene (1) was subjected to vapor phase pyrolysis above 450 °C, and the pyrolyzed gas was condensed on a glass surface at 20 °C to give poly(1,4-phenylene-1,2-dimethylethylene) (14) as a colorless transparent film. The pyrolyzed product of 1 was absorbed in hexane at −78 °C, and the solution was reacted with chlorine at −78 °C to yield 1,4-bis(1-chloroethyl)benzene (11), supporting that diradical intermediate 2 generated in the vapor phase pyrolysis of 1 is subject to isomerization to give 7,8-dimethyl-1,4-benzoquinodimethane (13) which, when condensed, polymerized spontaneously to give the film of 14. This result was thought to be the first case for ring-opening and isomerization polymerization of dispiropropane compound.

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