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Poly(2-diphenylamino-1,4-phenylenevinylene): Its preparation via chemical vapor deposition polymerization

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Abstract

2,5-Bis(chloromethyl)triphenylamine 1 was prepared and polymerized via the Gilch reaction to give poly(2-diphenylamino-1,4-phenylenevinylene) 2G as a solvent-soluble F-conjugated polymer. 1 was also polymerized via the chemical vapor deposition to yield the precursor polymer of 2C, which was heated under vacuum to yield a yellow or brown thin film of 2C on substrates such as glass and a silicon wafer. Spectroscopies of the film supported the formation of the poly (2-diphenylamino-1,4-phenylenevinylene) 2C. The arylamine moiety of the 2C film worked as a functional group like a redox site.

Keywords: Poly(phenylenevinylene); Triphenylamine; Chemical vapor deposition polymerization; Carbonization

1. Introduction

Poly(p-phenylenevinylene) (PPV) derivatives have been extensively studied as a π-conjugated polymer for their electroluminescence, optical, and electronic properties [1–4]. For example, a PPV derivative emits a yellow fluorescence, and its maximum wavelength and photoluminescence efficiency depend on the substituent species on the PPV backbone. The PPV backbone has also been utilized as a π-conjugated molecular pathway for the spin-alignment of the substituent radical groups’ unpaired electrons or for the formation of purely organic ferromagnetic polymers [5–9].

PPVs have been synthesized via polycondensation using reactions such as the Gilch reaction [10], Wittig reaction, and the reaction of sulfonium derivatives [2,11]. On the other hand, as one of the preparation routes of PPVs, the chemical vapor deposition (CVD) polymerization of dihalogenated xylene derivatives has been reported by Iwatsuki et al. [12] and the present authors at Korea University [13]. On the CVD polymerization, the dihalogenated xylene monomer is first sublimed under vacuum, then the vaporized and flown monomer is activated by heat and adsorbed on a substrate, and polymerized through a chemical reaction. The CVD polymerization, as the preparation method of PPVs, has some advantages over the other chemical reactions [13–16]. During the CVD polymerization, the monomer is directly polymerized on a substrate and the film formation occurs at the same time. This makes it possible to fabricate PPVs directly on a substrate without any other chemicals even when the PPVs lack solvent-solubility. The PPV films prepared via the CVD polymerization could also be converted into the corresponding carbon materials through the following high temperature treatment [14,17–19]. For example, the authors at Korea University reported the carbon nanotube preparation by the carbonization of PPV and its application as a field emission device [17].

However, to the best of our knowledge, there has been no report on the CVD polymerization that produces a PPV derivative bearing a functional side-chain group. We selected, in this paper, a triphenylamine group as the side-chained functional group, because arylamine groups

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often show a redox, hole-transporting, and magnetic activities. We prepared 2,5-bis(chloromethyl)-N,N-di-phenylaminobenzene I as the CVD polymerization dihalogenated xylene monomer, to yield poly(2-diphenylamino-1,4-phenylenevinylene) 2C. The CVD polymerization of a dihalogenated xylene monomer bearing a sterically bulky group is also produced for the first time, and discussed in this paper.

2. Experimental

2.1. Preparation of 2,5-diformyl-N,N-di-phenylaminobenzene 3

To 60 mL of a dried tetrahydrofuran solution of 2,5-dibromo-N,N-di-phenylaminobenzene (2.41 g, 6 mmol), tert-butyllithium in n-pentane (26 mL, 36 mmol) was added under a nitrogen atmosphere at −78 °C and then stirred for 0.5 h. To the mixture, N,N-dimethylformamide (2.8 mL, 36 mmol) was added and the mixture was stirred for 12 h at room temperature. A saturated solution of ammonium chloride was added and the mixture was stirred for 0.5 h. The color of the organic layer turned to orange. To the solution, diethylether was added and extracted. The organic layer was dried over anhydrous sodium sulfate and evaporated. The crude product was purified using a silica gel column with a hexane/chloroform (1/3) eluent (R_f = 0.26). Recrystallization from hexane gave a red solid (0.80 g). The yield was 45%. mp 110 °C. IR (NaCl, cm^{-1}): 1692: \textsuperscript{1}H-NMR (500 MHz, CD_{2}Cl_{2}) \textit{d}: 10.20 (s, 1H, CHO), 9.94 (s, 1H, CHO), 7.95 (d, J = 8.0 Hz, 1H, Ph), 7.71 (d, J = 8.0 Hz, 1H, Ph), 7.61 (s, 1H, Ph), 7.30–7.26 (m, 4H, Ph), 7.10–7.03 (m, 6H, Ph). \textsuperscript{13}C-NMR (500 MHz, CD_{2}Cl_{2}) \textit{d}: 191.5, 190.1, 151.2, 148.9, 141.6, 135.7, 130.4, 130.1, 129.8, 125.5, 124.0, 123.7, 120.3, MS m/z: 301 (calculated, M 301.3). Analytically calculated for C_{20}H_{17}Cl_{2}N: C 70.2, H 5.0, N 4.1, Cl 20.7; found: C 70.6, H 4.9, N 4.5.

2.2. Preparation of 2,5-bis(hydroxymethyl)-N,N-di-phenylaminobenzene 4

A dried tetrahydrofuran solution (6 mL) of 3 (0.66 g, 2.2 mmol) was added dropwise to a mixture of lithium aluminum hydride (0.21 g, 5.5 mmol) and dried tetrahydrofuran (5 mL) under a nitrogen atmosphere at 0 °C, and the solution was then stirred for 3 h at room temperature. The red color of the solution disappeared as 3 reacted. The mixture was extracted with diethylether, washed with water and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and recrystallization from hexane and tetrahydrofuran gave white crystals (0.47 g). The yield was 68%. mp: 147 °C. IR (NaCl, cm^{-1}): 3360; \textsuperscript{1}H-NMR (500 MHz, CD_{2}CN) \delta: 7.54 (d, J = 8.0 Hz, 1H, Ph), 7.26–7.21 (m, 5H, Ph), 7.05 (s, 1H, Ph), 6.95 (t, J = 7.5 Hz, 2H, Ph), 6.91 (d, J = 7.6 Hz, 4H, Ph), 4.51 (d, J = 4.0 Hz 2H, CH_{2}), 4.30 (d, J = 4.6 Hz, 2H, CH_{2}), 3.12 (s, 1H, OH), 2.94 (s, 1H, OH); \textsuperscript{13}C-NMR (500 MHz, CD_{2}CN) \textit{d}: 148.7, 144.7, 143.7, 139.4, 130.2, 129.3, 128.4, 125.6, 122.8, 122.6, 64.1, 61.1; MS m/z: 305 (calculated, M 305.4). Analytically calculated for C_{20}H_{19}NO_{2}: C 78.7, H 6.3, N 4.6; found: C 78.4, H 6.2, N 4.3.

2.3. Preparation of 2,5-bis(chloromethyl)-N,N-di-phenylaminobenzene 1

Triphenylphosphine (1.36 g, 5.2 mmol) and carbon tetrachloride (0.58 mL) were mixed and stirred at room temperature for 24 h. A toluene mixture of 4 (0.31 g, 1 mmol) was added to the suspension under flowing nitrogen and the mixture was stirred for 12 h at 100 °C. The solvent was removed and the reaction mixture was extracted with chloroform. The organic layer was dried and evaporated in vacuo. The residue was purified using a silica gel column with a hexane/chloroform (3/1) eluent (R_f = 0.47). Recrystallization from hexane gave white needle-like crystals (82 mg). The yield was 24%. mp: 102 °C. \textsuperscript{1}H-NMR (500 MHz, CD_{2}Cl_{2}) \textit{d}: 7.50 (d, J = 7.9 Hz, 1H, Ph), 7.30 (d, J = 8.0 Hz, 1H, Ph), 7.25–7.21 (m, 4H, Ph), 7.17 (s, 1H, Ph), 7.0–6.96 (m, 6H, Ph), 4.52 (s, 2H, CH_{2}), 3.42 (s, 2H, CH_{2}); \textsuperscript{13}C-NMR (500 MHz, CD_{2}Cl_{2}): 147.8, 146.2, 140.2, 135.6. 132.2, 130.1, 129.6, 126.6, 122.7, 45.8, 42.9; MS m/z: 341, 343 (calculated, M 342.3). Analytically calculated for C_{20}H_{17}Cl_{2}N: C 70.2, H 5.0, N 4.1, Cl 20.7; found: C 69.8, H 5.1, N 4.8, Cl 20.0.

2.4. Gilch reaction

To the 1.5 mL tetrahydrofuran solution of 1 (20.6 mg, 0.06 mmol), a 0.24 mL tetrahydrofuran solution of potassium tert-butoxide (27 mg, 0.24 mmol) was dropwise added under an argon atmosphere and the solution was then stirred at 50 °C for 24 h. The mixture was next poured into methanol. The precipitate was filtered, extracted using a Soxhlet extractor (CH_{2}Cl_{2}) and freeze-dried to yield 2G as a bright yellow powder.

Poly-(2-diphenylamino-1,4-phenylenevinylene) 2G was oxidized to form the aminium cationic radical. To a dichloromethane solution (2.1 mL) of 2G (3.3 mg, 12.4 unit mmol, M_w = 1100, M_w/M_n = 1.0) a dichloromethane solution (5 mL) of nitrosonium hexafluorophosphate (26 mg, 0.149 mmol) and 18-crown-6 (0.20 g, 0.758 mmol), trifluoroacetic acid (0.3 mL) and trifluoroacetic anhydride (1.2 mL) were added under a nitrogen atmosphere in a glove box, and the mixture was vigorously stirred at room temperature for 5 min.

2.5. CVD polymerization of 1

After being sublimed at 120 °C under vacuum, the monomer was transferred by argon gas and activated by heating the pyrolysis tube at 700 °C. The activated monomer was adsorbed onto the surface of the substrate and chemical polymerization occurred. The obtained
precursor polymer of 2C was heated to 250 °C under vacuum for 12 h and the residual chloromethyl groups of the precursor polymer were converted into a vinyl group. IR (NaCl, cm⁻¹): 1325, 960; ¹H-NMR (500 MHz, CD₂Cl₂) δ: 8.5–6.2 (m, Ph), UV–vis and PL (in a film state): λ_max = 295 nm, λ_shoulder = 360 nm.

The polymer film of 2C on a silicon substrate was gradually heated in the pyrolysis tube same as used in CVD polymerization. A dark black, insoluble solid was obtained.

2.6. Measurements

Cyclic voltammetry (CV) was performed on a BAS 660B electrochemical analyzer with a three-electrode cell in a solution of Bu₄NPF₆ (0.1 M) in dichloromethane. A platinum disk and wire were used as the working and counter electrodes, respectively. An Ag/AgCl electrode was used as the reference electrode. The ESR spectra were measured using a JEOL JES-2XG and a Bruker EMX ESR spectrometer. The IR and NMR spectra were measured using a JASCO FT/IR-410, a JEOL NMR 500L.

3. Results and discussion

3.1. Monomer synthesis

The monomer, 2,5-bis(chloromethyl)-N,N-diphenylamine 1, was prepared via the 5-step reaction shown in Scheme 1. 1,4-Dibromo-2-iodobenzene was obtained from 2,5-dibromoaniline, and its coupling with diphenylamine using tris(dibenzyldieneacetone)dipalladium(0) gave 2,5-dibromo-N,N-diphenylaminobenzene as similarly reported. The two bromide groups of 2,5-dibromo-N,N-diphenylaminobenzene were converted into the formyl groups to yield 2,5-diformyl-N,N-diphenylaminobenzene 3. The two formyl groups of 3 were reduced to the hydroxy groups to yield 2,5-bis(hydroxymethyl)-N,N-diphenylaminobenzene 4. The two hydroxymethyl groups of 4 were treated with triphenylphosphine and carbon tetrachloride to be converted to the chloromethyl groups, yielding 2,5-bis(chloromethyl)-N,N-diphenylaminobenzene 1. This chlorination process to produce 1 was preferable in comparison with the chlorination of 4 using thionyl chloride, from the standpoint of purification to remove the byproducts. The obtained 1 was stable below 200 °C and suitable as the monomer for the CVD polymerization.

3.2. Gilch reaction and its polymer

As a control of the CVD polymerization, 1 was polymerized via the Gilch reaction using potassium t-butoxide to yield poly(2-diphenylamino-1,4-phenylenevinylene) 2G. The polymerization rate of 1 was slower in comparison to those of 1,4-bis(chloromethyl)benzene 5 and 1,4-bis(chloromethyl)-2-diphenylaminophenyl-5-(2'-ethylhexyloxy)benzene 6 (Chart 1). The molecular weight of the polymerized 1 reached 2300 (degree of polymerization = 8), while the polymer was solvent-soluble. This is probably because the steric hindrance of the diphenylamine moiety directly substituted on the 1,4-benzene core Table 1.
The obtained polymer 2G via the Gilch reaction was a yellowish powder, and surprisingly soluble in common solvents such as chloroform, dichloromethane and tetrahydrofuran. This high solvent-solubility enabled the good characterization of 2G. The 1H-NMR spectrum of 2G (Fig. 1(b)) showed complete disappearance of the protons of the chloromethyl groups of 1 and a new absorption at ca. 6.2–8.2 ppm assigned to the vinylene groups. The 1H-NMR and elemental analysis data of the 2G polymer supported the formation of poly(2-diphenylamino-1,4-phenylenevinylene) via the Gilch reaction of 1.

The UV–vis spectrum of the 2G polymer (as a film state) showed an absorption maximum at ca. 300 nm and a shoulder at ca. 420 nm (Fig. 2). The photoluminescence

![Chart 1.](image)

**Table 1**

| Monomer | [M]₀ (mM) | [Monomer]/[base] | Temp (°C) | Time (h) | Yield (wt%) | Mₙ | Mₙ/Mₜ |
|---------|-----------|------------------|-----------|----------|-------------|----|-------|
| 1       | 25        | 0.5              | r. t.     | 24       | 15          | 1100 | 1.1   |
| 1       | 40        | 0.25             | 50        | 24       | 70          | 2300 | 1.1   |
| 1       | 40        | 0.25             | 55        | 96       | 45          | 1900 | 1.1   |
| 5       | 40        | 0.25             | r. t.     | 5        | 50 b        | —   | — b   |
| 6c      | 53        | r. t.            | 0.08      | —0.15    | 44          | 650,000 | 2.2 |

aChloroform solution.
bThe product was insoluble in any solvents.
cRef. [3].
spectrum of 2G displayed a strong fluorescence under the excitation at 420 nm with the maximum at ca. 520 nm. These spectra indicated that the polymer 2G had a developed π-conjugated backbone almost comparable to that of a typical PPV, poly(2,3-diphenyl-1,4-phenylenevinylene) (λ_max = 390 nm, shoulder = 410 nm, Emission = 510 nm, in solid state [20]).

Fig. 3 shows the cyclic voltammogram of the polymer 2G. The onset of the first redox appeared at 0.24 V (vs. Fc/Fc^+) ascribed to the redox of the triphenylamine moiety of the polymer 2G. The second oxidation process occurred at 0.64 V (vs. Fc/Fc^+) probably derived from the PPV backbone. The oxidation current was reasonable compared to that of the dianysylamine-substituted PPV derivatives [9]. The highest occupied molecular orbital (HOMO) level was electrochemically estimated using the redox potential of ferrocene as a standard (Fig. 3). The bandgap of PPV was obtained from the band edge of the UV–vis spectrum in Fig. 2 and these data are summarized in Table 2. It is reported that triarylamine-containing polymers are applicable to hole-injection layers for organic light-emitting diodes (OLEDs) [21]. These results suggest our polymer 2G is a potential candidate for a hole-injection layer in OLEDs.

The aminium cationic radical of the 2G polymer was generated via the chemical oxidation using nitrosonium hexafluorophosphate in dichloromethane. The color of the reaction solution changed into dark blue soon after the addition of the oxidant. The ESR spectrum of the solution (Fig. 4) gave an absorption with a g-value of 2.003 and hyperfine coupling parameter of ca. 0.6 mT, which was ascribed to the N-centered radical or the aminium cationic radical. The spin concentration was determined as 3% from ESR measurement. The aminium cationic radical of 2G was stable in the time-scale of CV but not stable at least in solution state. These results supported the formation of the aminium cationic radical from the side-chained triphenylamine group of the 2G polymer prepared via the Gilch reaction.

3.3. CVD polymerization and its polymer

We carried out the thermal analysis of 1 to evaluate the thermal stability enabling the CVD polymerization under reduced pressure. The TGA thermograms of 1 showed no remarkable degradation below 200 °C.

The CVD polymerization and the thermal treatment of 1 yielded a brownish-yellow film of 2C. The obtained 2C prepared via the CVD polymerization was surprisingly soluble in common solvents such as chloroform, dichloromethane, tetrahydrofuran, N,N-dimethylformamide and toluene. The solvent-solubility of the polymer 2C was as high as poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene-

| Compound | E_{ox}(V) | E_{red}(V) | HOMO (eV) | E_G(eV) |
|----------|-----------|------------|-----------|---------|
| 2G       | 0.88      | 0.96       | -5.12     | 2.5     |
| 2C       | 0.71      | 1.05       | -4.91     | 2.7     |

Onset of oxidation peak.

Estimated from the edge of UV–vis absorption.

![Fig. 4. ESR spectra of the oxidized 2G.](image)

![Fig. 5. (a) SEM and (b) AFM images of the polymer 2C.](image)
vinylene] [22]. The weight average molecular weight of 2C was 3800 (degree of polymerization = 13). The UV–vis spectrum of the 2C polymer (as a film state) showed an absorption maximum at 295 nm and a shoulder at ca. 360 nm, similar to the polymer 2G. The chemical structure of the 2C polymer was identified as poly(2-diphenylamino-1,4-phenylenevinylene) based on the $^1$H-NMR and IR spectroscopic data.

A scanning electron microscopy (SEM) image of the polymer 2C on a silicon substrate showed a plane film (thickness: 110 nm) formation. In the atomic force microscopy (AFM) image of the polymer 2C, the surface was fairly smooth ($R_{\text{rms}} = 0.56 \text{ nm}$). The carbonization of 2C by thermal treatment under argon gas yielded a black, fragile solid. The ESR spectrum of the carbonized 2C gave a signal at $g = 2.003$ ascribed to the N-centered radical or the aminium cationic radical. Further studies on forming mechanism of radicals in the carbonized film are now under going (Fig. 5).

### 4. Conclusion

We synthesized 2,5-bis(chloromethyl)-N,N-diphenylaminobenzene. We then successfully polymerized this monomer to afford poly(2-diphenylamino-1,4-phenylenevinylene) by via both the Gilch reaction and the CVD polymerization. The arylamine moiety of poly(2-diphenylamino-1,4-phenylenevinylene) showed redox activity as a functional group.

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### References

[1] A. Kraft, A.C. Grimsdale, A.B. Holmes, Angew. Chem. Int. Ed. 37 (1998) 402.
[2] T.A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds, Handbook of Conjugating Polymers, Marcel Dekker, New York, 1998.
[3] Y.-J. Pu, T. Kurata, M. Soma, J. Kido, H. Nishide, Synth. Met. 143 (2004) 207.
[4] Y.-J. Pu, M. Soma, J. Kido, H. Nishide, Chem. Mater. 13 (2001) 3817.
[5] H. Nishide, T. Ozawa, M. Miyasaka, E. Tsuchida, J. Am. Chem. Soc. 123 (2001) 5942.
[6] H. Nishide, M. Nambo, M. Miyasaka, J. Mater. Chem. 12 (2002) 3578.
[7] H. Murata, M. Takahashi, K. Namba, N. Takahashi, H. Nishide, J. Org. Chem. 69 (2004) 631.
[8] H. Nishide, M. Miyasaka, R. Doi, T. Araki, Macromolecules 35 (2002) 690.
[9] E. Fukuzaki, H. Nishide, J. Am. Chem. Soc. 128 (2006) 996.
[10] H.G. Gilch, W.L. Wheelwright, J. Polym. Sci. Part A-1 4 (1966) 1337.
[11] R.A. Wessling, J. Polym. Sci. Polym. Symp. 72 (1985) 55.
[12] S. Iwatsuki, M. Kubo, T. Kumeuchi, Chem. Lett. (1991) 1071.
[13] K. Kim, J.-I. Jin, Nano Lett. 1 (2001) 631.
[14] K.M. Vaeth, K.F. Jensen, Macromolecules 31 (1998) 6789.
[15] J.H. Park, T.S. Sudarshan, Chem. Vapor Deposition—Surf. Eng. Ser. 2 (2001) 243.
[16] E.G.J. Staring, D. Braun, G.L.J.A. Rikken, R.J.C.E. Demandt, Y.A.R.R. Kessener, M. Bouwmans, D. Broer, Synth. Met. 67 (1994) 71.
[17] K. Kim, S.H. Lee, W. Yi, J. Kim, J.W. Choi, Y. Park, J.-I. Jin, Adv. Mater. 15 (2003) 1618.
[18] K. Kim, S.-C. Jeoung, J. Lee, T. Hyeon, J.-I. Jin, Macromol. Symp. 201 (2003) 119.
[19] K. Kim, G. Zhong, J.-I. Jin, Macromol. Symp. 195 (2003) 217.
[20] W.C. Wan, H. Antoniadis, V.E. Choong, H. Razaafirimo, Y. Gao, W.A. Feld, B.R. Hsieh, Macromolecules 30 (1997) 6567.
[21] M.C. Suh, B.D. Chin, M.-H. Kim, T.M. Kang, S.T. Lee, Adv. Mater. 15 (2003) 1254.
[22] N.N. Barashkov, D.J. Guerrero, H.J. Olivos, J.P. Ferraris, Synth. Met. 75 (1995) 153.