Synthesis and Thermal Polymerization of Phenylbutadiynylphenoxy Group Substituted 1,3,5-Tricarbonylbenzene, Cyclotriphosphazene and 1,3,5-Triazine

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ABSTRACT: Phenylbutadiynylphenoxy group substituted 1,3,5-tricarbonylbenzene (3), cyclotriphosphazene (4), and 1,3,5-triazine (5) were synthesized and their thermal transitions and polymerizations were investigated by using DSC, polarizing optical microscopy, wide angle XRD, and TGA. Compound 3 had a disc-like structure and exhibited polymorphism by heating. Compounds 3 and 4 showed melt transitions followed by thermal polymerization, while compound 5 was thermally polymerized in the solid state. The IR spectrum of the polymer of compound 5 showed that the polymerization proceeded by 1,4-addition. All polymers, particularly the polymer of compound 4 exhibited excellent thermal stabilities. Compound 4 retained 70% weight even at 800 °C.

Introduction

Diacetylenes were polymerized thermally or photochemically in a solid state,\(^{1,2}\), a liquid crystalline state,\(^{3,4}\), or a liquid state to yield polydiacetylenes. Polydiacetylenes have conjugated backbones and their physical properties such as electric conductivity and nonlinear optical property attracted great attention. In a solid state, it was known that the topochemical polymerization proceeded by 1,4-addition. The solid state polymerization of diacetylenes by irradiation or thermal annealing has been widely used to obtain the organized macromolecules. A diacetylene single crystal was polymerized to give a single crystal of a polymer when a crystal structure satisfied the criteria for the topochemical polymerization. Such criteria can also be met by Langmuir–Blodgett films,\(^{5,6}\) self-assembling monolayers,\(^{7,8}\) and vesicles,\(^{9,10}\). In a liquid crystalline state, molecules were oriented and the topochemical polymerization was expected to give highly ordered polymers. The polymerization of diacetylenes in a liquid state usually yields amorphous polymers.

In this paper, we described the synthesis of planar six membered cyclic compounds containing three or six diphenyl diacetylene groups. Benzene, cyclotriphosphazene and 1,3,5-triazine were used as planar cores. In contrast to that most diacetylenes reported so far for the topochemical polymerization had linear structures,\(^{11}\) the compounds prepared in this study have disc-like or sphere-like structures. Thus they were expected to show unusual molecular packings and thermal behaviors. By using DSC, polarizing optical microscopy, wide angle XRD, and TGA we investigated thermal transitions and polymerizations of the compounds.

Experimental

Materials and Instrumentation. 4-Iodophenol, trimethylsilylacetylene, bis(triphenylphosphine) palladium (II) chloride, copper iodide, phenylacetylene, copper acetate, 1,3,5-benzenetricarbonyl trichloride, hexafluorocyclotriphosphazene and 2,4,6-trichloro-1,3,5-triazine were purchased from Al-
drich and used as they were. Reagent grade solvents were dried and purified as follows. DMF was dried over anhydrous P₂O₅ and purified by distillation. Triethylamine and pyridine were distilled over potassium hydroxide. Methanol was dried over molecular sieves 4 Å and distilled. Tetrahydrofuran and 1,4-dioxane were dried over sodium metal and distilled. H and ¹³C NMR spectra were recorded on a Varian-Gemini 200 spectrometer. Proton-decoupled ³¹P NMR spectra were obtained with the use of a Varian EM-300 spectrometer. Chemical shifts were reported in ppm relative to 85% H₃PO₄ at 0 ppm. IR spectra were obtained with the use of a Nicolet Magna-IR 550 spectrometer. Thermal analyses were performed by a Dupont 2010 differential scanning calorimeter and a 2050 thermogravimetric analyzer. Powder X-ray diffractograms were obtained by using Mac Science Mpx 3 (Cu Kα, radiation, λ=1.54 Å). Optical microscopy study was performed by a Carl Zeiss optical polarizing microscope equipped with a Linkam heating stage and a Linkam TP92 controller. Elemental analyses were performed by a Carlo Erba 1108 or Perkin Elmer 240C elemental analyzer at Korea Research Institute of Chemical Technology and Korea Basic Research Center.

**Synthesis of 4-Trimethylsilylphenylphenol.** This compound was prepared according to our previous report. Dichlorobis(triphenylphosphine)palladium (1.8 g, 2.56 mmol) and copper iodide (0.3 g, 1.58 mmol) were added to a solution of 4-iodo-phenol (10 g, 45.5 mmol) and (trimethylsilyl)acetylene (9.6 mL, 68.1 mmol) in triethylamine (200 mL) in nitrogen at -4 °C. The reaction mixture was stirred at the same temperature for 2 h. After stirring at room temperature for additional 10 h, the reaction mixture was concentrated to dryness by evaporation under reduced pressure. The crude product was isolated by sublimation (35–45 °C, 0.1 mmHg) and further purified by column chromatography on silica gel (20% ethyl acetate in hexane) to yield 6.6 g (76%), mp 60–62 °C.

**Synthesis of Ethynylphenol (1).** 4-Trimethylsilylphenylphenol (2.57 g, 13.5 mmol) was dissolved in methanol (100 mL) in the presence of KOH (1.45 g, 25.8 mmol). The solution was stirred at room temperature for 4 h in nitrogen. After filtration of undissolved KOH, the solvent was removed by evaporation. The product (1.13 g, 957 mmol, yield 71%) was isolated by column chromatography on silica gel (25% ethyl acetate in hexane), mp 129–130 °C.

IR (KBr, cm⁻¹): 3388, 3285, 2966, 2923, 2846, 2105, 1607, 1509.

H NMR (acetone-d₆): δ 7.5–6.9 (dd, aromatic, 4H), 3.7 (s, CH, 1H).

**Synthesis of 1-(4-Hydroxyphenyl)-4-phenylbutadiyne (2).** 4-Ethynylphenol (1.13 g, 9.56 mmol) was dissolved in pyridine-methanol (1:1). To the solution were added phenylacetylene (2.1 mL, 19.2 mmol) and copper acetate (5.83 g, 32.1 mmol) and the reaction mixture was refluxed for 12 h in nitrogen. After concentration to 50 mL, copper acetate was removed by filtration through a silica gel column (3 cm). The solvents were removed by evaporation and the product (1.6 g, 7.33 mmol, yield 77%) was isolated by column chromatography on silica gel (17% ethyl acetate in hexane), mp 119–120 °C.


IR (KBr, cm⁻¹): 3263, 3068, 2938, 2213, 1514, 1601, 1515, 1239.

H NMR (DMSO-d₆): δ 10.2 (s, -OH, 1H), 7.65–6.7 (m, aromatic, 9H).

**Synthesis of Tris(4-phenylbutadiynylphenyl)-1,3,5-benzenetricarboxylate (3).** To a solution of compound 2 (1 g, 4.56 mmol) in THF (60 mL) was added NaH (0.11 g, 4.56 mmol). After stirring for 2 h at room temperature, a solution of 1,3,5-benzenetricarboxyl chloride (0.32 g, 1.2 mmol) in THF (30 mL) was added drop by drop. The solution was refluxed for 12 h. After evaporation, the product was isolated by column chromatography on silica gel (methylene chloride/hexane) and further purified by recrystallization from ethyl acetate/hexane to give 0.68 g (mp 198–200 °C, yield 70%).

Anal. Calcd for C₂₅H₁₆O₆: C, 84.43, H: 3.73. Found: C: 83.95, H: 3.96.

IR (KBr, cm⁻¹): 3073, 2925, 2859, 2223, 2151, 1749, 1499.

H NMR (DMSO-d₆): δ 9.13 (s, NH, 3H), 7.79, 7.5 (dd, CH, 12H), 7.64–7.52 (m, CH, 15H).

C NMR (DMSO-d₆): δ 152.7, 151.5, 135.5, 134.1, 132.5, 130.8, 130.2, 129.0, 122.8, 120.4, 118.7, 82.2.
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81.2, 73.8, 73.5.

Synthesis of Hexakis(4-phenylbutadiynylphenoxy)cyclotriphosphazene (4). To a solution of compound 2 (2.9 g, 9.16 mmol) in 1,4-dioxane (100 mL) was added NaH (0.22 g, 9.17 mmol). After stirring for 2 h at room temperature, hexachlorocyclotriphosphazene (0.24 g, 0.7 mmol) was added. The solution was refluxed for 72 h and then passed through a silica gel column (5 cm). After evaporation, the product was isolated by column chromatography on silica gel (25% ethyl acetate in hexane) and further purified by recrystallization from ethyl acetate/hexane to give 0.5 g (mp 208–210°C, yield 50%).

Anal. Calcd for C_{46}H_{34}N_{8}O_{10}P_{5}: C: 80.16, H: 3.78, N: 2.92. Found: C: 79.70, H: 3.79, N: 2.88.

IR (KBr, cm^-1): 3063, 2925, 2854, 2228, 2151, 1601, 1510.

^1H NMR (CDCl_3): 7.48–7.28 (m, C_H, 30H), 7.41, 6.90 (dd, C_H, 24H).

^31P NMR (CDCl_3): δ 8.79.

Synthesis of 2,4,6-Tris(4-phenylbutadiynylphenoxy)-1,3,5-triazine (5). Cyanuric chloride (0.3 g, 1.63 mmol) was added to a solution of compound 2 (1.21 g, 5.56 mmol) in pyridine/ethyl acetate (150 mL, 1:1 v/v). The solution was refluxed for 36 h. After the removal of precipitates by filtration, the filtrate was concentrated to dryness. The product was isolated by column chromatography on silica gel (chloroform) and further purified by recrystallization from chloroform/hexane to give 0.32 g (yield 27%).

Anal. Calcd for C_{46}H_{34}N_{8}O_{10}P_{5}: C: 83.94, H: 3.73, N: 5.76. Found: C: 83.60, H: 3.68, N: 5.44.

IR (KBr, cm^-1): 3072, 2934, 2855, 2230, 2151, 1570, 1506, 1366.

^1H NMR (CDCl_3): δ 7.60–7.10 (aromatic, 27H).

^13C NMR (CDCl_3): δ 173.4, 151.8, 133.8, 132.5, 129.4, 121.7, 120.1, 81.9, 80.4, 74.5, 73.8.

Results and Discussion

Ring compounds 3–5 containing diphenyl diacylene groups were synthesized according to Scheme I. 4-Trimethylsilylhexynylphenol was prepared by coupling reaction of 4-iodophenol with trimethylsilylacetylene in the presence of a palladium catalyst. The addition of all reagents and the initial reaction was carried out below 0°C, otherwise coupling reaction between acetylenes to produce diacylene compounds was the major process. The trimethylsilyl group was removed easily under basic conditions to give 4-ethynylphenol (I). Compound 1 was very susceptible to hydration. Even when stored as solids at room temperature, 4-acytylenol was formed. Oxidative coupling reaction of compound 1 with 4-ethynylbenzene gave three different diacylene products. The desired unsymmetric diacylene (2) was isolated by column chromatography on silica gel. Chloro groups of 1,3,5-benzenetricarbonyl trichloride, hexachlorocyclotriphosphazene and cyanuric chloride were substituted by 4-phenylbutadiynylphenoxy groups to give compounds 3, 4 and 5, respectively. All compounds were characterized by elemental analysis, ^1H and ^13C NMR. In the ^1H NMR spectrum of compound 3 in DMSO-d_6, a singlet peak at 9.13 ppm for the core ring protons was observed, indicating that all chloro groups were replaced. Complete substitution of six chloro groups of hexachlorocyclotriphosphazene was confirmed by ^31P NMR spectroscopy, which showed one peak at 8.79.
ppm in CDCl₃. Compound 5 also showed only one peak at 173.4 ppm for the core ring carbons in the ¹³C NMR spectrum in CDCl₃.

Compounds 3–5 have planar six-membered rings as cores. Rigid diphenyl diacetylene units were linked to the core via ester bonds in compound 3 and -O- linkages in compounds 4 and 5. Simple molecular modeling showed that compound 3 had a flat structure like a disc, while diphenyl diacetylene groups of compound 4 were pointing up or down away from the core ring plane. The diacetylene groups of compound 5 were rotated about C-O bond to release steric repulsions. Morphology change of the compounds by heating was investigated by polarizing optical microscopy, differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD).

Compound 3 showed a very interesting DSC thermogram (Figure 1a). Around 90°C, a small endotherm was observed, corresponding to glass transition or melting of small crystals, followed by a small exotherm for crystallization. A strong exotherm (ΔH=25.1 kJmol⁻¹) appeared at 140°C before a strong endotherm (ΔH=61.2 kJmol⁻¹) at 207°C for melt transition. As IR, 'H, and ¹³C NMR spectroscopy did not show any structural change when compound 3 was heated above 140°C, the endotherm at 140°C was ascribed to crystallization. This was also confirmed by polarizing optical microscopy, which showed a marlile texture at 115°C and rapid crystal growth at 140°C. Crystallization rather than disordering at such a high temperature is very peculiar. The disc-like structure of compound 3 is likely responsible for this unusual result. Compounds 4 and 5 did not show similar transitions.

As seen in the X-ray diffractograms (Figure 2), compound 3 had very low crystallinity at room temperature. When quenched from 115°C to room temperature, sharp peaks with d-spacings of 4.9, 3.9, and 3.4 Å appeared atop the diffuse peak, corresponding to the ordered molecules. The XRD diffractogram of the crystals obtained by heating above 140°C showed sharp peaks with d-spacings of 3.9 and 3.5 Å. The broad and diffuse peaks almost disappeared. The crystal structure is not known at this time, but DSC, polarizing optical microscopy, and XRD results suggest that by heating, molecules in glassy state or small crystals at room temperature were self-organized to solids with two dimensional order and eventually crystals with three dimensional order.

Compounds 3 and 4 were thermally polymerized on melting. DSC in Figure 1 showed strong exotherms near 250°C (compound 3) and 240°C (compound 4). Since compounds 3 and 4 had three and six diphenyl diacetylene units around the core ring, respectively, thermal polymerization in liquid states was expected to yield the highly branched or cross-linked polymers. After polymerization, the characteristic stretching peaks of diacetylene groups at 2223 and 2151 cm⁻¹ of compound 3 and at 2228 and 2151 cm⁻¹ of compound 4 completely
disappeared. The resulting polymers were dark brown and insoluble in common organic solvents.

In contrast to compounds 3 and 4, compound 5 was thermally polymerized in solid state. No melt transition was observed before polymerization. DSC showed a strong and sharp exotherm (ΔH = 393.8 kJ/mol) at 280 °C, which is a little higher than the polymerization temperatures of compounds 3 and 4. The sample turned red at 280 °C. In the IR spectrum, two triple bond stretching peaks of diacetylene groups at 2230 and 2151 cm⁻¹ disappeared at the same time and the peak at 2220 cm⁻¹ corresponding to new acetylene groups showed up after polymerization, indicating that the polymerization proceeded by 1,4-addition. The strong peak at 1631 cm⁻¹ was assigned to stretching vibrations of double bonds which resulted from 1,4-polymerization (Figure 3). Since the polymerization was carried out in the solid state, the topochemical reaction was expected to occur in a way to minimize the change of the crystal structure of the monomer. The topochemical polymerization of diacetylenes was observed only when the crystal structure had the stacking distance of about 5 Å and an appropriate angle between the diacetylene molecule and the stacking axis. Moreover, it is reported that the bulky groups attached to the triple bond should be separated by at least a methylene group to give the monomer the mobility necessary to the polymerization. All diacetylenes of compound 5 were consumed during polymerization. This result suggests that packings of three diacetylene groups of each monomer satisfied the structural requirements mentioned above for the topochemical polymerization which would resulted in the polymer with three dimensional order. The wide angle XRD diffractogram of compound 5 showed sharp peaks at 11.3, 3.8, 3.6, and 3.4 Å. After polymerization, a relatively sharp peak at 7.8 Å in addition to a broad peak at 3.9 Å appeared, probably due to long range ordering of the side groups in the polymer chain. Although the phenyl rings were directly attached to the triple bonds in compound 5, high polymerization temperature seemed to render the monomers mobile during the polymerization.

Thermal stabilities of the polymers were investigated by TGA under nitrogen. All polymers, particularly the polymer of compound 4 exhibited excellent thermal stabilities. The temperatures of 10% weight loss of the polymers of 3, 4 and 5 were 400, 600, and 450 °C, respectively (Figure 4). Compound 4 retained 70% weight even at 800 °C.

**Conclusions**

We investigated thermal behaviours of planar six membered cyclic compounds (3,4,5) containing diphenyl diacetylene groups. Simple molecular modeling showed that diphenyl diacetylene group substituted benzenetricarbonyl compound (3) has a disc-like structure. This compound exhibited very interesting morphological change by heating. A marble texture and rapid crystal growth were observed at 115 and 140 °C, respectively, by the polarizing optical microscopy. It seems that molec-
ules in glass state or small crystals were organized to solids with two dimensional order and eventually crystals with three dimensional order. Compounds 3 and 4 were thermally polymerized on melting, while compound 5 was polymerized in the solid state. The IR spectrum of the polymer of compound 5 indicated that the topochemical polymerization was proceeded by 1,4-addition. All three diacetylene groups of the monomer participated in the polymerization. Although further structural analysis is necessary to draw a conclusion, the resulting polymer likely has a structure of three dimensional order.

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References