Preparation of Ordered Stacked Phthalocyanine Polymers through Olefin Metathesis Reaction

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ABSTRACT: Novel phthalocyanine polymers **2** and **3** were prepared from two phthalocyanine monomers CuPc(−CH═CH_2)$_8$ and CuPc(−CH═CH_2)$_2$ bearing eight and two terminate olefin groups, respectively, through olefin metathesis reaction using a ruthenium initiator. The phthalocyanine moieties were contained in the polymer network and the main chain of the resulting phthalocyanine polymers. The polymerizations of the phthalocyanine monomers were monitored by UV−vis, NMR, MALDI-TOF-Ms, and GPC analyses. The structures of the resulting phthalocyanine polymers were studied in the solid state by X-ray diffraction measurement and transmission electron microscopy. A linear polymer **3** prepared from CuPc(−CH═CH_2)$_2$ produced a rodlike nanostructure, in which the copper phthalocyanine moieties were stacked with the regular stacking distance.

Introduction

Spontaneous self-assembly of functional organic molecules is currently receiving significant attention due to their possibility for development of molecular-based electronic and photonic nanodevices such as molecular wires, switches, and sensors.[1,2] An important step in the development of molecular-based devices is the precise manipulation of molecular arrangements. This precise manipulation allows for the directional transport of electrons, photons, and ions. In this context, a number of designed functional molecules have been assembled into controlled nanoscaled objects through covalent and noncovalent bonds.

Phthalocyanines (Pcs) and metallophthalocyanines (MtPcs) belong to a class of attractive building blocks bearing potential for application in molecular-based devices.[3−7] Their disc-shaped rigid phthalocyanine rings can easily stack through strong $\pi-\pi$ interaction and form one-dimensional rodlike assemblies with interesting electronic and optic properties. Recent studies have reported Pc-based superstructures driven by $\pi-\pi$ interaction.[8,9] Nolte et al. synthesized crown ether-substituted Pcs to create nanoscaled fibrous assemblies possessing an electron conduction wire and ion transport channels.[10,11] O'Brien, Armstrong, and co-workers reported the direct observation of long rodlike stacks of side-chain-modified Pcs on substrates by AFM and STM.[12] However, these ordered stacks, produced through only noncovalent bonds, possess low kinetic stability. Therefore, the covalent linkage of side chains needs to be enhanced to increase the stability of ordered stacks. Only few examples of such polymeric Pc materials have been known to date.[13,14]

Here, we report the synthesis and characterization of polymeric Pcs obtained through the olefin metathesis polymerization of terminal olefin groups in the side chains. The side chain polymerizations were carried out under mild conditions without heating and radical generation by using the ruthenium catalyst $(PCy_3)_2Cl_2Ru(=CHC_6H_5)$ developed by Grubbs et al.[15,16] This highly effective catalyst for olefin metathesis reaction has been utilized in the construction and also in the preservation of supramolecular architectures such as catenanes,[17−19] knots,[20] oligopeptide assemblies,[21,22] discotic columnar assemblies,[23] large macrocycles,[24] polymer brushes,[25] and dendrimers.[26] The polymers resulting from two Pc monomers **2** and **3** bear the Pc rings in the polymeric network and the main polymer chain, respectively, by the intermolecular formation of carbon−carbon double bonds. The solid structures of the polymeric Pc materials were characterized with differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and X-ray diffraction (XRD) measurement.

Experimental Section

General. NMR spectra were recorded on a Bruker AVANCE 400 FT-NMR spectrometer operating at 399.65 MHz for ^{1}H in $CDCl_3$ solution. Chemical shifts were relative to internal TMS. IR spectra were obtained on a JASCO FS-420 spectrometer as KBr pellets. UV−vis spectra were measured on a JASCO V-570. The calorimetric data were obtained on a Seiko DSC 220 at a scanning rate of 10 °C/min under flow of nitrogen. MALDI-TOF mass spectra were obtained on a PerSeptive Biosystems Voyager-DE-Pro spectrometer with dithranol as matrix. GPC analyses were carried out with a JASCO HPLC system (pump 1580, UV detector 1575, refractive index detector 930) with a Showa Denko GPC KF-804L column (8.0 × 300 mm, polystyrene standards, M = 900−400 000 g/mol) in THF as an eluent at 35 °C (1.0 mL min^{-1}). XRD patterns were measured with Cu Kα radiation using a Rigaku Geigerflex. Melting points were recorded using a Shibata MEL-270 melting point apparatus and are corrected.

Electron Microscopy. Droplets of CH_2Cl_2 solutions containing polymer **2** or **3** (ca. 1.0 mM for monomer concentration) were placed onto carbon-coated copper grids (400 mesh). The solvent was evaporated in vacuo for 1 h. Electron micrographs were taken on a JEOL JEM-2010 electron microscope at an acceleration voltage of 200 kV.

Materials. All chemicals were purchased from commercial suppliers and used without purification. Solvents, such as

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toluene, THF, and CH_2Cl_2, were freshly distilled. Column chromatography was performed with silica gel (Wako, 200 mesh). The phthalocyanine precursor 1,2-dicyano-4,5-bis(undecenyloxy)benzene, **1**, was synthesized from 4,5-dibromocatechol and 11-bromo-1-undecene according to the similar method reported by Liberman et al.[27] Tri-*tert*-butylbromosubphthalocyanine was prepared by a literature method at ca. 50% yield.[28−31]

Symmetrical Phthalocyanine 2,3,9,10,16,17,23,24-Octakis-(undecenyloxy)phthalocyaninatocopper Complex CuPc(−CH═CH$_2$)$_8$. A mixture of 1,2-dicyano-4,5-bis(undecenyloxy)benzene (1.0 g, 2.2 × 10^{-3}mol) and $CuCl_2$ (0.073 g, 5.4 × 10^{-4}mol) in 2-(*N*,*N*-dimethylamino)ethanol (10 mL) was stirred and refluxed under N_2 for 45 h. After cooling, methanol was added and the green precipitate was filtered off. The residue was purified by column chromatography (silica gel, $CHCl_3$/methanol (9:1 v/v)). Yield 30%. MALDI-TOF-MS (dithranol): m/z = 1918 ([M + H]$^+$, 100%) calcd for $C_{120}H_{176}N_8O_8Cu$: 1920.3. UV−vis (CH_2Cl_2): λ_{max} (log ϵ) = 678 (4.96) and 340 (4.76).

^{1}H NMR and ^{13}C NMR spectra were obtained by using the corresponding zinc complex ZnPc(−CH═CH$_2$)$_8$. Zn complex ZnPc(−CH═CH$_2$)$_8$ was prepared by the same procedure of CuPc(−CH═CH$_2$)$_8$ from **1** and $ZnCl_2$. Yield 5%. MALDI-TOF-MS (dithranol): m/z = 1918 ([M + H]$^+$, 100%) calcd for $C_{120}H_{176}N_8O_8Zn$: 1920.3. UV−vis (CH_2Cl_2): λ_{max} (log ϵ) = 678 (5.08) and 344 (4.84). ^{1}H NMR ($CDCl_3$): δ = 1.2−2.15 (br, 128H, CH_2), 4.45 (br, 16H, Ar−OCH_2), 5.00 (m, 16H, C═CH_2), 5.85 (m, 8H, CH═C), 8.16 (br, 8H, Ar).^{13}C NMR ($CDCl_3$): δ = 26.6, 29.4, 33.9, 69.0, 105.7, 114.2, 139.2, 152.9.

Unsymmetrical Copper Phthalocyanine 9,16,23-Tri-tert-butyl-2,3-di(undecenyloxy)phthalocyaninatocopper Complex CuPc(−CH═CH$_2$)$_8$ (Statistical Method). A mixture of **1** (0.46 g, 1.0 × 10^{-3}mol), 4-*tert*-butylphthalonitrile (1.0 g, 5.4 × 10^{-3}mol), and $CuCl_2$ (0.2 g, 1.5 × 10^{-3}mol) in 2-(*N*,*N*-dimethylamino)ethanol (5 mL) was stirred and slowly heated. Then the mixture was refluxed under N_2 for 72 h. After cooling, methanol was added and the precipitate was filtered off. The residue was purified by column chromatography (silica gel, toluene/*n*-hexane (5:2 v/v)). TLC: R_f = 0.26 (toluene/*n*-hexane (5:2 v/v)). Yield: 8%. MALDI-TOF-MS (dithranol): m/z = 1080 ([M + H]$^+$, 100%) calcd for $C_{66}H_{80}N_8O_2Cu$: 1079.6. UV−vis (CH_2Cl_2): λ_{max} (log ϵ) = 678 (5.28) and 340 (4.91).

Unsymmetrical Metal-Free Phthalocyanine H$_2$Pc(−CH═CH$_2$)$_8$ (Subphthalocyanine Method). A mixture of tri-*tert*-buthylsubphthalocyanine (0.10 g, 1.78 × 10^{-4} mol) and 5,6-bis(undecenyloxy)-1,3-diiminoisoindoline (0.26 g, 5.33 × 10^{-4} mol) in 2-(*N*,*N*-dimethylamino)ethanol (15 mL) was heated at 80 °C for 12 h under Ar. After cooling, the mixture was diluted with methanol and the precipitate was centrifuged. The solid was purified by the column chromatography (silica gel, CH_2Cl_2). Yield: 15%. MALDI-TOF-MS (dithranol): m/z = 1020 ([M + H]$^+$, 100%) calcd for $C_{66}H_{80}N_8O_2$: 1019.2. ^{1}H NMR ($CDCl_3$): δ = 1.29−1.61 (m, 32H, CH_2), 1.63−2.06 (m, 27H, CH_3), 3.9−4.0 (t, 4H, Ar−O−CH_2), 4.9−5.0 (m, 4H, −C═CH_2), 5.7−5.8 (m, 2H, CH═C), 7.0 (s, 2H, Ar).^{13}C NMR ($CDCl_3$): δ = 26.2, 29.5, 34.2, 69.9, 114.5, 117.6, 139.5, 148.7, 153.8.

Olefin Metathesis Polymerizations of Pc Monomers. Pc monomer (72 mg, 3.75 × 10^{-5} mol) and ruthenium catalyst (PCy_3)$_2$$Cl_2$Ru(═$CHC_6H_5$) (3.3 mg, 5% mol per Pc monomer) were dissolved in freshly distilled and degassed CH_2Cl_2 (1.0 mL). The solution was stirred at room temperature for 12 h under N_2. The reaction mixture was poured into methanol to precipitate the polymer. The linear polymer **3** prepared from CuPc(−CH═CH$_2$)$_2$ was purified by gel permeation chromatography (Biorad Biobeads SX-1, CH_2Cl_2) to remove oligomeric products (M_w < 10 000) and reprecipitation from CH_2Cl_2 and methanol.

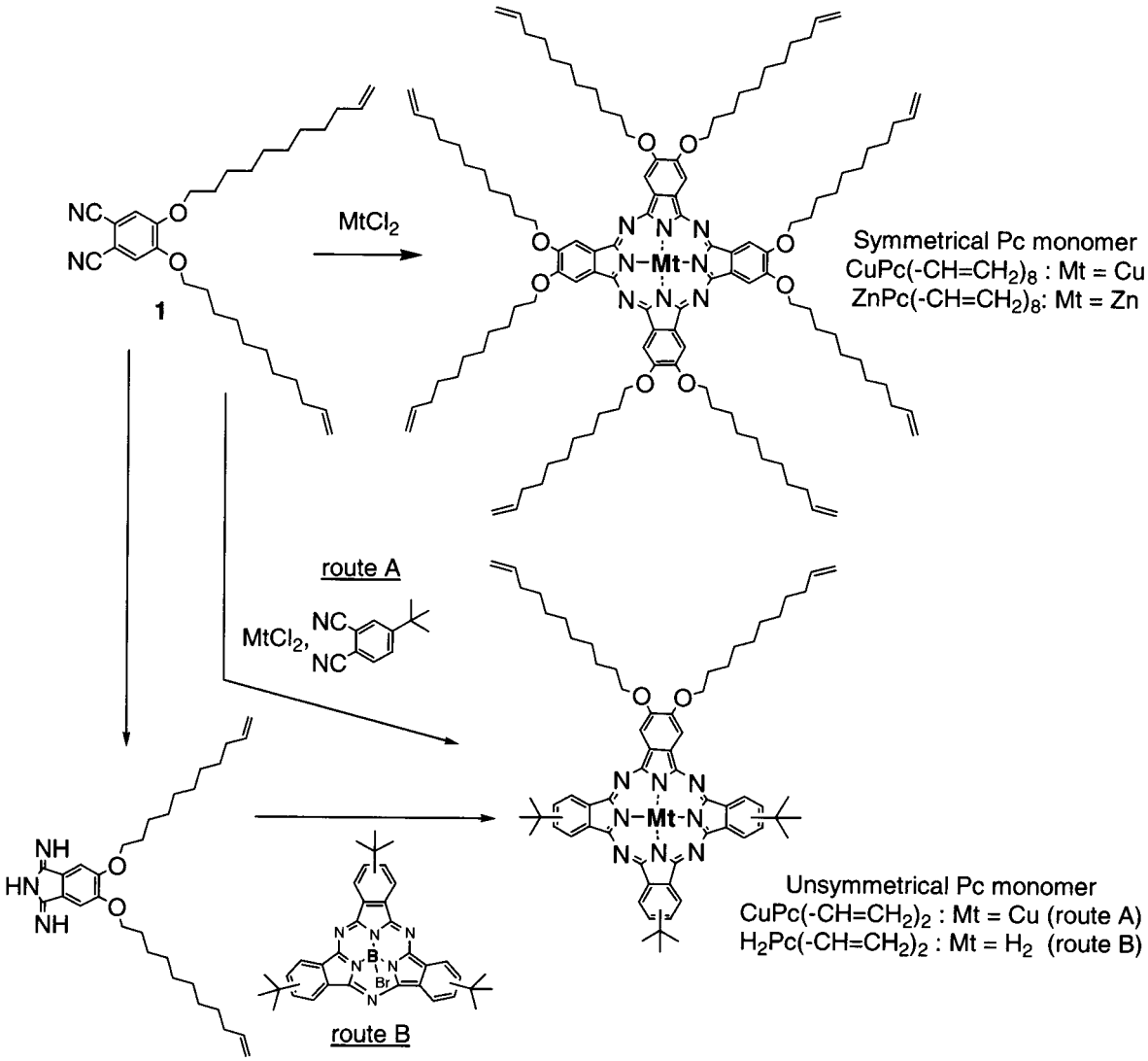
Results and Discussion

Monomer Synthesis. Novel phthalocyanine monomers were prepared from 4,5-dibromocatechol and 11-bromo-1-undecene as shown in Scheme 1.[27] We prepared symmetrical and unsymmetrical phthalocyanines possessing eight and two terminal olefins in the side chains, respectively. Refluxing the phthalocyanine precursor **1** in 2-(*N*,*N*-dimethylamino)ethanol with metals salts provided the symmetrical copper and zinc phthalocyanines CuPc(−CH═CH$_2$)$_8$ and ZnPc(−CH═CH$_2$)$_8$. The synthesis of unsymmetrical phthalocyanine was carried out by two synthetic methodologies: a conventional statistical method and a subphthalocyanine method. The copper unsymmetrical phthalocyanine CuPc(−CH═CH$_2$)$_2$ was prepared by the reaction of 4-*tert*-butylphthalonitrile and **1** in a 3:1 molecular ratio in the presence of $CuCl_2$. After the tetracyclization of two different precursors, the resulting reaction mixture contained four phthalocyanine products. The expected unsymmetrical CuPc(−CH═CH$_2$)$_2$ can be isolated from the reaction mixture by column chromatography. The purity of CuPc(−CH═CH$_2$)$_2$ was checked by the MALDI-TOF-Ms spectrum and HPLC. The MALDI-TOF-Ms spectrum of CuPc(−CH═CH$_2$)$_2$ exhibits only an expected parent molecular ion peak at 1080 g/mol, and the HPLC elution pattern also shows its high purity. However, it is difficult to separate the unsymmetrical metal-free Pc H$_2$Pc(−CH═CH$_2$)$_2$ from the reaction mixture by column chromatography after the statistical reaction of 4-*tert*-butylphthalonitrile and **1** in a 3:1 molecular ratio. During the past decade, several unsymmetrical Pc derivatives were prepared selectively through ring enlargement of subphthalocynines by the reaction of substituted diiminoisoindolines.[28−31] This reaction produced only one unsymmetrical Pc derivative in relatively high yields compared with the statistical reaction. The synthesis of H$_2$Pc(−CH═CH$_2$)$_2$ was carried out by the reaction of tri-*tert*-buthylsubphthalocyanine and diiminoisoindoline derivative obtained from **1**. After the reaction, the expected unsymmetrical H$_2$Pc(−CH═CH$_2$)$_2$ could be isolated as a pure compound by chromatographic techniques. This compound was fully characterized by NMR, MALDI-TOF-Ms, and UV−vis analyses. All of the phthalocyanine monomers were dissolved in CH_2Cl_2, toluene, DMSO, and DMF.

Polymerization of Phthalocyanine Monomers through Olefin Metathesis Process. Olefin metathesis reaction with initiator (PCy_3)$_2$$Cl_2$Ru(═$CHC_6H_5$) was performed in dichloromethane at room temperature with Pc monomers at different concentrations (Scheme 2). During the polymerization of all of the Pc monomers with the initiator, it was observed that polymerized Pc products were still soluble in dichloromethane and there was no precipitate. After the polymerization, the resulting reaction solutions were poured into methanol to remove the initiator. The collection of the precipitates yielded polymers **2** and **3** as green solids in a quantitative yield. Precipitated polymer **2** hardly dissolved in any of the organic solvents employed, and this indicated the formation of a three-dimensional polymeric network. In contrast, the isolated product **3** was soluble in common organic solvents such as CH_2Cl_2 or THF and was purified by gel permeation chromatography to remove the unreacted monomer and oligomeric products.

The UV−vis spectra of CuPc(−CH═CH$_2$)$_8$ and CuPc(−CH═CH$_2$)$_2$ feature a strong sharp peak at 678 nm, which is attributed to the Q-band of the copper Pc moiety (Figure 1). The spectral shape in CH_2Cl_2 indicates that the copper Pc moiety is in a monomeric condition.[32,33] When the initiator was added to the CH_2Cl_2 solution of CuPc(−CH═CH$_2$)$_8$ ([CuPc(−CH═

Scheme 1



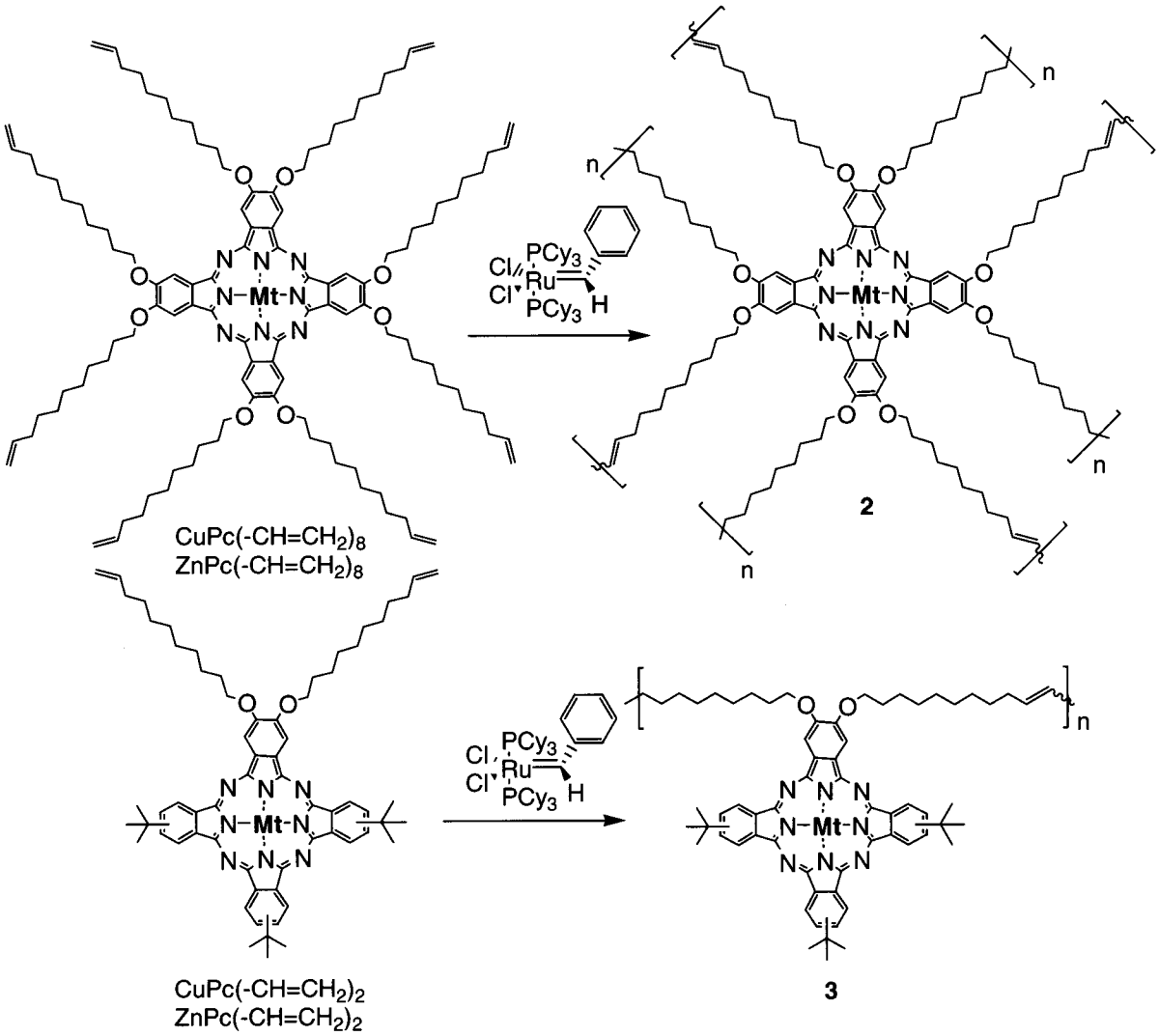
$CH_2)_8$] = 37.5 mM, [CuPc(−CH═$CH_2)_8$]/[initiator] = 20.0), the broadening and the blue shift of the Q-band were observed (Figure 1a). Figure 1b shows the visible spectrum of **3**. The intensity of the Q-band decreased compared to the monomer CuPc(−CH═$CH_2)_2$, and a new peak appeared at 646 nm. These spectral changes could be ascribed to the formation of phthalocyanine aggregates. By the covalent linkage of side chains through the olefin metathesis reaction, the planar phthalocyanine cores came closer and formed phthalocyanine aggregates in CH_2Cl_2.

The olefin metathesis reaction was also monitored by the ^{1}H NMR spectrum. In the ^{1}H NMR spectrum of Pc monomers ZnPc(−CH═$CH_2)_8$ and H_2Pc(−CH═$CH_2)_2$, the terminal olefin protons were present at 5.00 and 5.85 ppm. The ^{1}H NMR spectrum of ZnPc(−CH═$CH_2)_8$ and H_2Pc(−CH═$CH_2)_2$ in $CDCl_3$ broadened after the addition of the initiator, indicating the restriction of motion due to the formation of Pc aggregates and the production of many isomers. The peaks corresponding to the terminal olefins were diminished, and a new broad peak around 5.50 ppm appeared. These ^{1}H NMR spectral changes suggest the formation of disubstituted alkenes between the two olefins by the olefin metathesis reaction.[26]

To evaluate the exact mass of the polymer, MALDI-TOF-Ms spectroscopy was applied to **2** (Figure 2). At different concentrations, the polymerization reaction was found to yield different product distributions. At a concentration of 60.0 μM, only one product could be detected at 1810 g/mol (Figure 2a). This result indicated that all of the olefin groups were intramolecularly linked through the olefin metathesis reaction at a high-diluted condition. On the other hand, all ionized oligomers with up to 10 repeat units could be resolved for a sample prepared at a higher concentration ([ZnPc(−CH═$CH_2)_8$] = 7.5 mM), differing by the monomer mass of ca. 1800 g/mol (Figure 2b). The molecular weight of the linear product **3** was investigated by gel permeation chromatography (GPC). The GPC analysis of **3** revealed a high molecular weight M_n = 55 000 with a wide polydispersity PDI = 3.0 (relative to monodispersed polystyrene standards). The intermolecular formation of carbon−carbon double bonds through the olefin metathesis reaction gave a high molecular weight polymer material containing a Pc moiety.

Solid Structure of Polymerized Pcs. A slow evaporation of the CH_2Cl_2 solution of CuPc(−CH═$CH_2)_8$ in the presence of the initiator (([CuPc(−CH═$CH_2)_8$] = 37.5 mM, [CuPc(−CH═$CH_2)_8$]/[initiator] = 20.0) gave a green film on a glass plate. After drying at 50 °C, the film was washed with methanol and CH_2Cl_2 to remove the initiator and low-molecular-weight products. Before polymerization, Pc monomer CuPc(−CH═$CH_2)_8$ substi-

Scheme 2



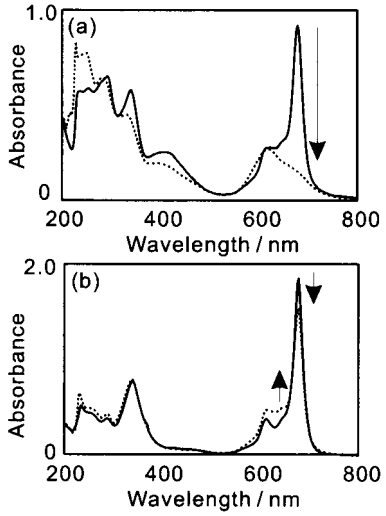


Figure 1. Absorption spectral change of CuPc($-$CH$=$CH$_2$)$_8$ (a) and CuPc($-$CH$=$CH$_2$)$_2$ (b) before (solid line) and after (dotted line) polymerization in CH_2Cl_2. [CuPc($-$CH$=$CH$_2$)$_8$] = 5.0 μM, [CuPc($-$CH$=$CH$_2$)$_2$] = 9.7 μM, and [**3**] = 10.5 mg/L.

tuted with eight hydrocarbon chains forms a thermotropic discotic liquid crystalline phase.[34,35] A first heating cycle of CuPc($-$CH$=$CH$_2$)$_8$ from room temperature to 250 °C resulted in an exothermic peak at 88 °C. The X-ray diffraction patterns (XRD) of CuPc($-$CH$=$CH$_2$)$_8$ were characterized by three Bragg reflection values in the ratio of 1:1/$\sqrt{3}$:1/2 (Figure 3). These diffraction patterns could have been due to the reflections from a two-dimensional hexagonal lattice of columnar stacks with an intercolumnar distance of 3.4 nm. The strong $\pi-\pi$ interaction among Pc cores and van der Waals interaction between hydrocarbon chains led to a highly ordered two-dimensional structure. However, the polymerized film **2** did not show one weak reflection at 2.0 nm by XRD measurement, indicating that the polymer **2** is almost completely amorphous. Furthermore, **2** displayed only a glass transition at -5 °C and no other disordering peaks by DSC measurement, clearly showing that polymer **2** does not exhibit liquid crystalline behavior. These results suggested that the formation of a polymer network hinders the ordered self-assembly of Pc moieties.

The X-ray diffraction pattern of Pc monomer CuPc($-$CH$=$CH$_2$)$_2$ displays a high-intensity reflection at a low Bragg angle and a weak secondary reflection in a small-angle region in the proportion of 1:1/2 (Figure 4). The intense reflection corresponding to a spacing of 1.88 nm can be attributed to the (001) reflection of a discotic lamellar structure. The second peak around 0.96 nm results from the (002) reflection. This observed spacing almost agrees with the molecular dimension of Pc

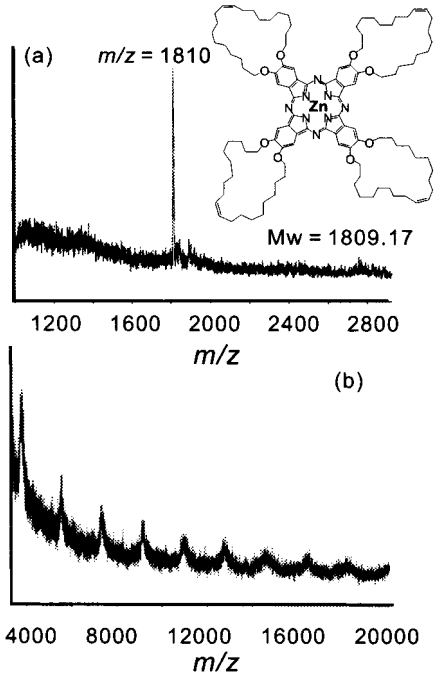


Figure 2. MALDI-TOF-Ms spectra of polymerized samples from ZnPc(−CH═CH_2)$_8$ at the two initial concentrations: [ZnPc(−CH═CH_2)$_8$] = 60.0μM (a) and [ZnPc(−CH═CH_2)$_8$] = 7.5 mM (b).

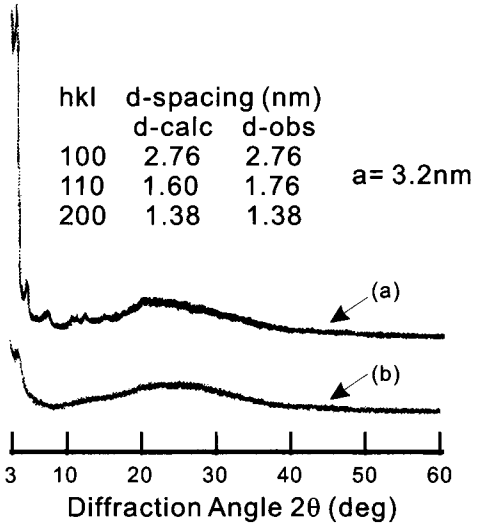


Figure 3. Diffraction patterns of X-ray reflected from a glass surface coated with CuPc(−CH═CH_2)$_8$ (a) and **2** (b).

moiety estimated by the CPK model. The X-ray diffraction pattern of linear polymer **3** is shown in Figure 4b. The regular spacing of 0.34 nm among Pc moieties within the columns can be derived from the oriented reflection in the wide-angle region. This value of 0.34 nm is a common stacking distance in planar aromatic compounds.[34,35] The 0.34 nm spacing value indicates the formation of highly ordered stacks among Pc moieties within **3**. The diffuse halo at around 0.43 nm is characteristic for liquidlike order of the alkyl chains. The small-angle reflection at 2.05 nm is related to ordering of the columns.[23,36−39] The covalent linkage of side chains in CuPc(−CH═CH_2)$_2$ results in the formation of a columnar structure consisting of one-dimensional ordered stacks of numerous Pc moieties.

The morphologies of the aggregates were examined by TEM. Samples were prepared by casting thin films

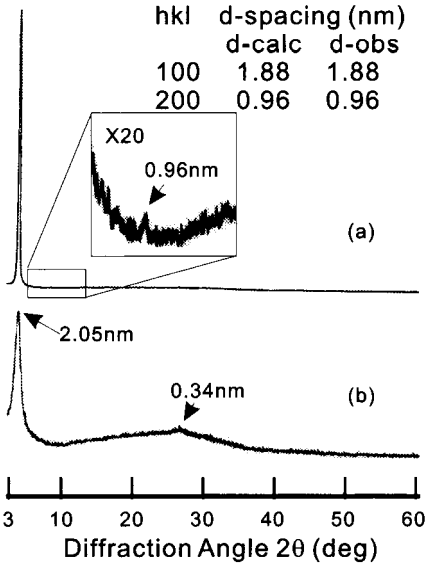


Figure 4. Diffraction patterns of X-ray reflected from a glass surface coated with CuPc(−CH═CH_2)$_2$ (a) and **3** (b).

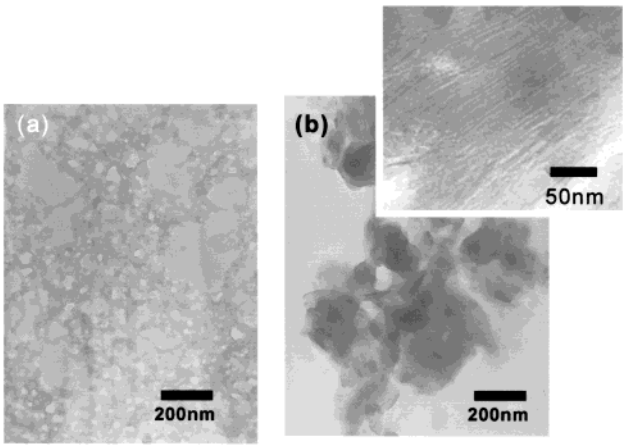


Figure 5. Transmission electron micrographs of **2** (a) and **3** (b). The inset shows the rodlike structure of **3** under magnification.

of **2** and **3** from CH_2Cl_2 solution onto a carbon-coated grid. Pc monomers CuPc(−CH═CH_2)$_8$ and CuPc(−CH═CH_2)$_2$ did not produce the TEM images. On the other hand, polymerized **2** and **3** produced unique TEM images without staining and the dark images ascribed to Pc aggregates (Figure 5). While **2** showed only irregular nanostructures (Figure 5a), linear polymer **3** displayed many domains built up by many rodlike structures with a width of ca. 2.0 nm (Figure 5b).[40] The rods in each domain were almost orientated belong to a regular direction. Therefore, the covalent linkage of side chains in the unsymmetrical Pc monomer allows the direct observation of columnar densely packed Pc stacks bearing 300−500 nm lengths.

Conclusion

We synthesized new Pc polymers by using two different Pc monomers obtained through olefin metathesis reaction. The side chain polymerization of the Pc monomers by a ruthenium catalyst produced high-molecular-weight polymers characterized by MALDI-TOF-Ms and GPC analyses. XRD and TEM measurements indicated that linear polymer **3** prepared from unsymmetrical Pc monomer CuPc(−CH═CH_2)$_2$ displays

an orientation of ordered Pc stacks, while the polymer network from CuPc($-CH=CH_2$)$_8$ does not contain a regular structure. Long ordered Pc stacks should open new possibilities toward the construction of molecular wires.

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