

Nanoscopic Fibrous Assemblies Made of Metallophthalocyanine-Terminated Amphiphilic Polymers

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Abstract: Atom-transfer radical polymerization (ATRP) of acrylates from the initiator-modified zinc phthalocyanine yielded amphiphilic, phthalocyanine-terminated polymers with a narrow molecular-weight distribution. The disklike phthalocyanine moiety was incorporated into one end of the polymer chain. We investigated the aggregation behavior of phthalocyanine-terminated polymers in solution and in the solid state by using UV-visible, FT-IR, differential scanning calorimetry

(DSC), and temperature-controlled powder X-ray diffraction (XRD) measurements. Amphiphilic phthalocyanine-terminated polymers that possess a poly[tri(ethylene glycol)methyl ether acrylate] chain aggregate in methanol to form a physical gel. Images from

atomic force microscopy (AFM) and transmission electron microscopy (TEM) indicate that the physical gel contains a dense fibrous network structure, in which the zinc phthalocyanine groups were stacked into one-dimensional columnar aggregates through intermolecular π - π interactions between the π -conjugated phthalocyanines and through van der Waals interaction of alkyl chains.

Keywords: living polymerization • nanostructures • phthalocyanines • self-assembly • supramolecular chemistry

Introduction

Self-assembly and self-organization of functional molecules into well-defined structures with nanometer dimensions are a highly active area of research in chemistry and material science.^[1] These programmed assemblies of molecular units have great potential for fabricating nanoscale optoelectronic devices, such as light-emitting diodes (LEDs), sensors, photovoltaic cells, and field-effect transistors.^[2] Many approaches have been explored for controlling the organiza-

tion of functional molecules into well-defined large-scale objects.^[3] Block copolymers can be organized into nanostructures that are highly regular in size and shape.^[4] Incompatibility between different blocks within the polymer is used to achieve self-organization on the nanometer scale. Stupp et al. reported the spontaneous generation of mushroom-shaped nanostructures of triblockcopolymers that consisted of a diblock coil of oligostyrene and oligoisoprene or oligobutadiene covalently attached to a rigid rod-like segment.^[5] Incorporating the functional units into a one-block copolymer could lead to unique functional nanostructures.^[6] The creation of nanostructures complies with the requirement for performance enhancement of optoelectronic devices.

π -Conjugated disk-like molecules such as triphenylenes, hexa-*peri*-hexabenzocoronenes, porphyrins, and phthalocyanines have attracted special interest for use in organic electronic devices.^[7] These disklike molecules can be assembled into long one-dimensional columnar aggregates through their strong intermolecular π - π stacking. The columnar aggregates show highly efficient hole mobilities approaching $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[7a] Controlling the self-organization of disklike molecules would enable the construction of supramolecular wires or cables capable of transporting electrons or holes parallel to a columnar axis. In this paper we describe the synthesis and self-organizing properties of metallophthalocyanine-terminated polymers. The introduction of a polymer chain might affect the organization of disklike phthalocya-

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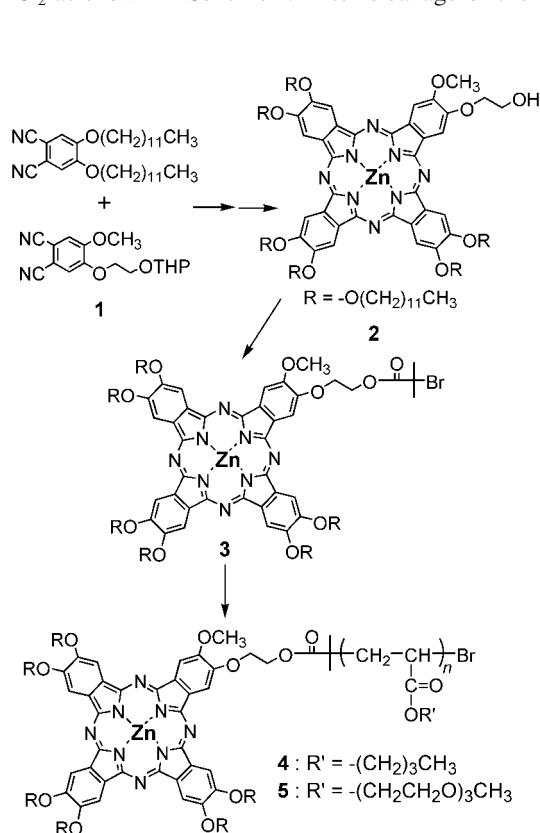
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nine molecules. Phthalocyanines and their metal complexes have been incorporated into macromolecular structures as a side group, in the main chain, and in a polymeric network.^[8] However, there have been few reported examples of the polymers containing a terminal phthalocyanine group.^[9] McKeown and co-workers reported on the liquid crystalline properties of asymmetric phthalocyanines with one poly(ethylene glycol) chain.^[9a] Controlled living-radical polymerization from a terminal phthalocyanine has not been applied to phthalocyanine-containing polymers. Within the living polymerization methods, atom-transfer radical polymerization (ATRP) developed by Matyjaszewski and co-workers is a versatile method for preparing well-defined polymers with a narrow molecular-weight distribution ($1.0 < M_w/M_n < 1.5$).^[10] ATRP has been recently used for synthesizing functional polymers with functional initiators.^[11] We synthesized the amphiphilic polymers by using a phthalocyanine initiator through ATRP. The π - π stacking among the terminal phthalocyanine groups provides a driving force for self-organization of polymers. We report on the formation of nanofibers through self-organization of the phthalocyanine-terminated polymers.

Results and Discussion

Syntheses of phthalocyanine-terminated polymers: Unsymmetrical zinc phthalocyanine (ZnPc) **2** was prepared by using a mixed tetracyclization of 1,2-dicyano-4,5-didodecyloxybenzene and **1**^[12] in a 3:1 molecular ratio in the presence of $ZnCl_2$ as shown in Scheme 1. After cleavage of the tetra-



Scheme 1.

hydropyran (THP) group by *p*-toluenesulfonic acid (TsOH), the required unsymmetrical ZnPc **2** was separated by column chromatography as a second fraction. Reaction of 2-bromoisobutyryl bromide with the hydroxy group in **2** gave the bromo ester (**3**), which acted as an initiator for the ATRP. ZnPcs **2** and **3** were characterized by MALDI-TOF MS, and FT-IR and 1H NMR spectroscopy. The copper-mediated ATRP of butyl acrylate (BA) or tri(ethylene glycol)methyl ether acrylate (TEGA) was carried out with **3** by using the method reported by Matyjaszewski and co-workers.^[13] In this study, we used *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) as a ligand for the ATRP polymerization, starting from the initiator-modified ZnPc **3**. Purification of the reaction mixture by gel permeation chromatography (GPC; Bio-Beads SX-1, 200–400 mesh, eluting with THF) to remove the catalyst and the low molecular-weight products resulted in ZnPc-terminated polymers **4** and **5**. The number-averaged molecular-weights (M_n) of **4** and **5** were estimated by GPC, 1H NMR, and UV-visible analyses. GPC analyses for **4** and **5** yielded values of M_n of 9000 and 6200, respectively. The polydispersity indices (PDI) of **4** and **5** were 1.20 and 1.14, respectively, which is consistent with a controlled/living polymerization of acrylates from the initiator-modified terminal ZnPc group.^[13] The GPC profile detected by the RI detector was in agreement with that detected by the UV-visible detector monitored at 370 nm, indicating that polymers **4** and **5** did not contain free polymers that lacked the terminal ZnPc group. Figure 1

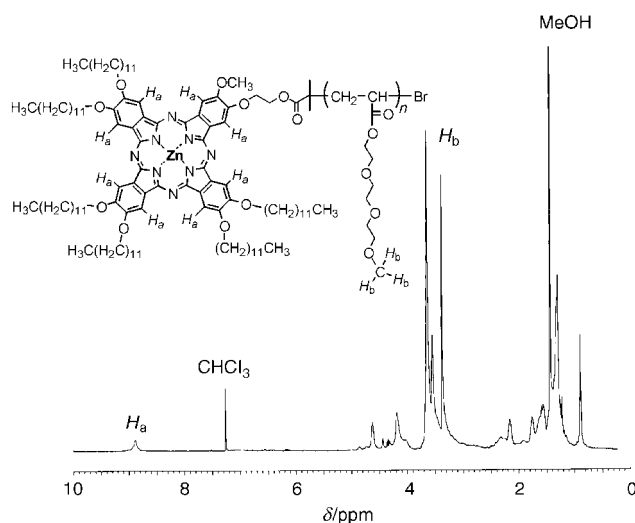


Figure 1. 1H NMR spectrum of the zinc phthalocyanine-terminated polymer **5** in $CDCl_3$.

shows the 1H NMR spectrum of **5** in $CDCl_3$. The weight fractions were obtained from NMR spectroscopic data by comparing the resonance signals in the aromatic part of the terminal ZnPc group ($\delta = 8.8$ ppm) with those of the methyl protons of TEGA ($\delta = 3.3$ ppm). The molecular weights of **4** and **5** determined by the 1H NMR analysis were 9200 and 6900, respectively. The number-average degree of polymerization of TEGA units in **5** was estimated to be about 20 by the 1H NMR analysis. The absorption spectra of **4** and **5** ex-

hibited a sharp Q-band at 678 nm in CH_2Cl_2 . The molecular weights, estimated from the absorbance of the Q-band using a molecular absorption coefficient of **3** ($\log \epsilon = 5.38 \text{ M}^{-1} \text{ cm}^{-1}$), were 9300 and 7200, respectively. The estimated molecular weights of **4** and **5** from the $^1\text{H NMR}$ and UV-visible analyses were in relatively good agreement with those determined by the GPC analysis. The ATRP of acrylates from the initiator-modified ZnPc **3** allowed the construction of disk-coil block copolymers composed of a zinc phthalocyanine (disk) and a flexible poly(acrylate) (coil) block.

Thermal properties: The comparative thermal properties of **2**, **4**, and **5** were investigated by using differential scanning calorimetry (DSC) and temperature-controlled X-ray diffraction (XRD) measurements. Phthalocyanines and their metal complexes substituted with flexible alkyl chains form a major class of discotic liquid crystalline materials.^[14] The DSC trace of **2** exhibited one transition peak at 123 °C, which corresponded to the transition from a crystalline to a liquid crystalline mesophase (Figure 2), in the second heat-

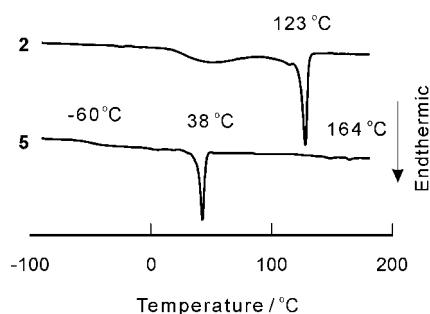


Figure 2. DSC traces for the second heating of **2** and **5** at 10°Cmin^{-1} .

ing run. Since the sample did not form an isotropic liquid, it was impossible to characterize the mesophase structure by using temperature-controlled polarizing optical microscopy. The solid structures of **2** at room temperature and at 150 °C were established from the temperature-controlled XRD measurements. The XRD diagram of **2** at room temperature displayed many deflections in the small angle region, which indicated a crystallization of alkyl chains (Figure 3a). Above the transition point observed in DSC, an intense reflection peak appeared at 2.76 nm, which could be attributed to the (100) reflection of a hexagonal columnar mesophase (Figure 3b). Two small diffractions signals at 1.59, and 1.39 nm were related to the (110) and (200) reflections, respectively. The lattice constant of the hexagonal columnar mesophase was estimated as 3.19 nm from these reflection values. Furthermore, the broad and diffuse halo at around 0.43 nm was ascribed to the liquidlike disorder in the alkyl chains. A peak was also observed at around 0.34 nm due to the average stacking distance among the phthalocyanine rings within the columnar aggregates. These results suggested that the asymmetric zinc phthalocyanine **2** could assemble into one-dimensional columnar aggregates driven by intermolecular π - π interactions.

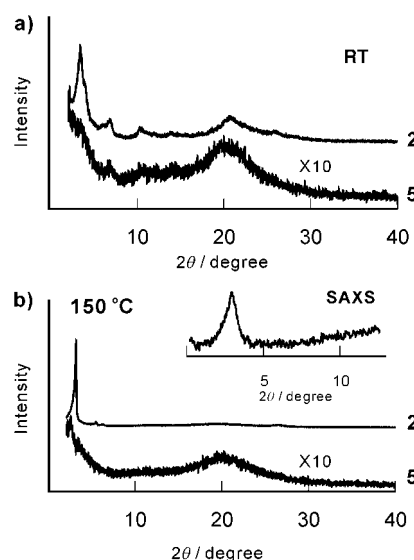


Figure 3. XRD patterns of **2** and **5** at a) room temperature and b) 150 °C. The inset in b) shows the SAXS curve of **5** at 150 °C.

The DSC trace of the disk-coil polymer **4** exhibited only a glass transition temperature (T_g) at -52°C over the range -100 to 250°C , suggesting that **4** was amorphous. In addition to T_g at -60°C of the poly(TEGA) block, polymer **5** shows two other transition points at 38 and 164°C (Figure 2). The XRD pattern of **5** at room temperature showed many reflection peaks in positions similar to those found for **2** (Figure 3a). These peaks disappeared above 38°C , indicating the melting of alkyl side chains in the terminal phthalocyanine group. The FT-IR spectra of the thin film of **5** at various temperatures were measured with a temperature-controlled infrared microscope. The CH_2 antisymmetric $\nu_{\text{as}}(\text{CH}_2)$ and symmetric $\nu_{\text{s}}(\text{CH}_2)$ stretching vibration frequencies reflect the conformation of the alkyl chains,^[15] absorb around 2920 and 2850 cm^{-1} , respectively. Figure 4 shows the temperature dependence of $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ stretching vibration frequencies. Two bands showed a shift to higher frequencies above the transition point, also indicating the conformational change of alkyl chains. From these results, the transition point at 38°C could be ascribed to the transition from a crystalline phase to a mesophase. The transition point was 85°C lower than that for the parent molecule **2**. Furthermore, small-angle X-ray scattering

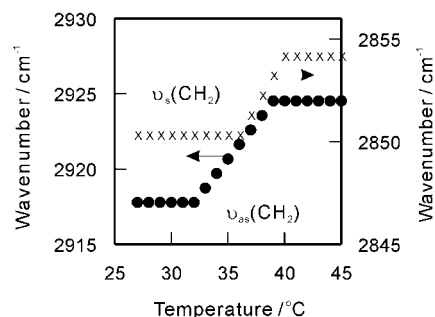


Figure 4. Temperature dependence of the $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ band peak position for **5**.

(SAXS) reflections indicated a d -spacing of 3.40 nm at 150 °C. The observed SAXS reflection was related to the ordering of the columnar aggregates. Polymer **5** appeared as a viscous solid up to 160 °C under the temperature controlled optical microscope, which also suggested that the solid included columnar aggregates. The viscosity was lost above 160 °C due to the dissociation of columnar aggregates. The terminal phthalocyanine groups were phase-segregated within **5**, which has a poly(TEGA) coil, and formed columnar aggregates by non-covalent stacking. The poly(BA) chain in **4**, however, inhibited the assembly of terminal phthalocyanine groups.

Aggregation behavior of phthalocyanine-terminated polymers:

The aggregation behavior of the phthalocyanine-terminated polymer **5** in solution was studied by using UV-visible spectroscopy. Figure 5a shows the UV-visible spectra of

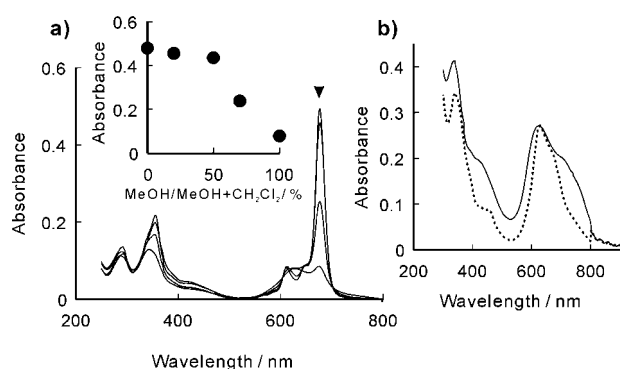


Figure 5. a) Absorption spectra of **5** in CH₂Cl₂, CH₂Cl₂/methanol (6:4 v/v and 3:7 v/v), and methanol. The inset shows the absorbance change of Q bands of **5**. b) Absorption spectra of **5** in methanol at 25 °C (solid line) and 50 °C (dashed line).

a diluted solution of **5** in CH₂Cl₂ (0.1 mg mL⁻¹), and a mixture of CH₂Cl₂ and methanol. The UV-visible spectrum in CH₂Cl₂ had a strong sharp peak at 678 nm that is characteristic of nonaggregated zinc phthalocyanines. When methanol was admixed, the Q-band was broadened, and the maximum was blue-shifted. This spectral change indicated that the aggregates were formed in polar solutions by stacking among terminal zinc-phthalocyanine groups.

Stacking interactions in **5** could result in the formation of large aggregates. To investigate the formation of these aggregates, we prepared several samples of different concentrations in methanol. When **5** was dissolved above a concentration of 10 mg mL⁻¹ in hot methanol (55 °C) and was then allowed to cool at 25 °C, a firm gel was formed. The gelation was found to be thermoreversible. The melting point of the methanol gel of **5** was 48 °C. This melting point almost agrees with the transition temperature, which corresponded to the melting of alkyl side chains of terminal ZnPc group as observed in the DSC analysis of **5** in the solid state. Figure 5b shows the absorption spectra of the methanol gel of **5** recorded at 25 and 50 °C. The gel of **5** at 25 °C showed a broad Q-band at 610 nm with a shoulder peak around 750 nm. When the gel was melted above 50 °C, this shoulder

peak disappeared. The absorption spectrum provided information about the type of aggregated structure, such as cofacial (face-to-face), edge-to-edge, and herringbone conformations.^[16] Compared with the diluted solution spectrum in CH₂Cl₂, the Q-band of the methanol gel was broad and shifted to a shorter wavelength, indicating that the phthalocyanines form columnar aggregates. Furthermore, the conformations of the phthalocyanine stacks were different between 25 and 50 °C. The presence of shoulder peak in the gel state suggested that the phthalocyanines were stacked in an eclipsed conformation, as illustrated in Figure 7. The melting of the alkyl side chain resulted in a change from the eclipsed conformation to the cofacial conformation.

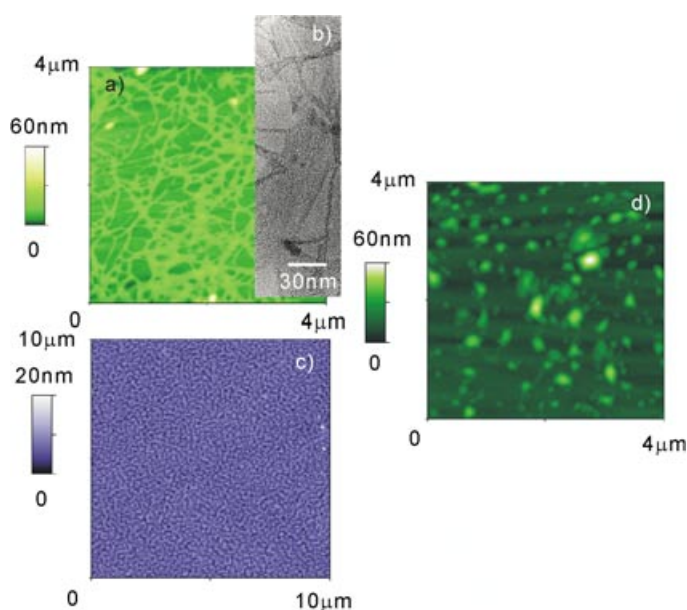


Figure 6. a) AFM image and b) TEM image of a methanol gel of **5** (10 mg mL⁻¹). AFM images of c) **5** and d) **4** prepared from a homogeneous solution in CH₂Cl₂ (10 mg mL⁻¹).

Figure 6a shows the AFM image of the methanol gel, which was transferred onto a mica substrate.^[17] At a concentration of 10 mg mL⁻¹, polymer **5** showed dense fibrous network structures with a length of several micrometers and a height of about 10 nm. Formation of these fibrous structures was not observed in samples with low concentration. Judging from the molecular dimensions of **5**, as estimated from the computer-generated molecular model, fibrous structures observed by AFM would be composed of bundles of numerous columnar aggregates. The morphology of the aggregates was also examined by transmission electron microscopy (TEM). The sample prepared from the methanol gel of **5** displayed a fibrous structure built up of many rod-like structures with a width of approximately 5 nm (Figure 6b). These rods were orientated almost to the fiber axis. By contrast, spreading a solution of **5** in CH₂Cl₂ (10 mg mL⁻¹) onto a mica substrate resulted in the formation of a rough surface (Figure 6c). The mean height of protrusions from the lowest surface was about 15 nm. Further-

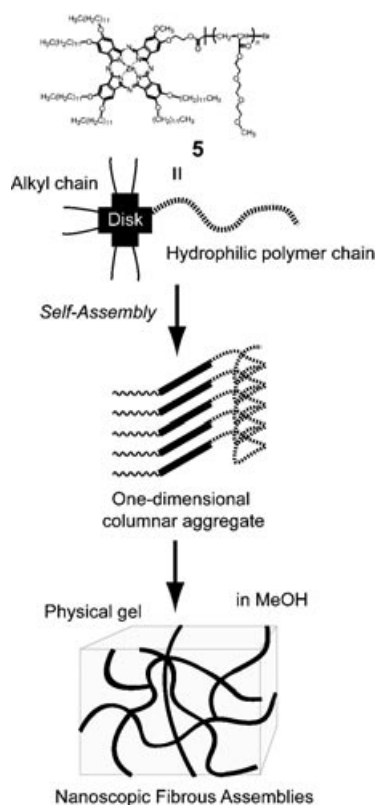


Figure 7. Schematic illustration of the formation of nanoscopic fibrous assemblies of zinc-phthalocyanine-terminated polymer **5** in methanol.

more, polymer **4** gave an AFM image of spherical and ill-defined aggregates (Figure 6d).

Recently it has been shown that many organic compounds can form physical gels through self-assembly processes by using intermolecular hydrogen bonds, π - π interactions, donor-acceptor interactions, and electrostatic interactions.^[18] These molecules are assembled into flexible fibers and partial cross-linking of these fibers results in a physical gelation. Furhop and co-workers succeeded in constructing micellar fibers by spontaneous organization of amphiphilic unsymmetrical porphyrins with chiral carbohydrate groups in aqueous media.^[19] Nolte et al. reported the physical gelation phenomena of phthalocyanine derivatives that possess one central phthalocyanine core, four crown ether rings, and eight hydrocarbon chains.^[20] The rigid porphyrin or phthalocyanine moieties acted as a skeleton for fiber formation.^[21] From the AFM and TEM images, we might conclude that the amphiphilic phthalocyanine-terminated polymer **5** self-assembled into fibrous aggregates, which included the columnar stacks of terminal ZnPc groups.

Conclusion

New ZnPc-terminated amphiphilic polymers have been successfully synthesized through atom-transfer radical living polymerization from initiator-modified ZnPc. Living polymerization produced disk-coil block copolymers with narrow molecular-weight distributions. We also demonstrat-

ed that amphiphilic ZnPc-terminated polymer **5** could form fibrous aggregates in methanol through spontaneous self-assembly processes. The π - π and van der Waals interactions have been shown to be the main driving forces for the organization of amphiphilic polymer, which contained one-dimensional columnar aggregates of terminal ZnPc groups. The mechanistic pathways of the self-organization processes are as postulated in Figure 7. We believe that these nanoscopic fibers, which possess potential energy- and electron-conducting assemblies, will open new possibilities for constructing new molecular devices.

Experimental Section

General: NMR spectra were recorded on a Bruker AVANCE 400 FT-NMR spectrometer operating at 399.65 MHz for ^1H and ^{13}C , respectively, in CDCl_3 . Chemical shifts are reported relative to internal TMS. IR spectra were obtained on a JASCO FS-420 spectrometer as KBr pellets. UV-visible and fluorescence spectra were measured on a JASCO V-570 and a JASCO FP-750. MALDI-TOF MS 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, and refractive index detector 930) and a Showa Denko GPC KF-804 L column ($8.0 \times 300 \times 2$ mm, polystyrene standard $M = 900$ – $400\,000$ g mol^{-1}) in THF as an eluent at 35°C (1.0 mL min^{-1}). X-ray diffraction (XRD) patterns were measured with $\text{Cu K}\alpha$ radiation on a Rigaku Geigerflex diffractometer.

Atomic force microscopy images were acquired in noncontact mode by a Thermomicroscope Explorer AFM system. The samples for AFM were obtained by spin-coating films on a freshly cleaved mica substrate from solutions of **4** and **5** in CH_2Cl_2 (10 mg mL^{-1}). The sample for the gel was prepared by the gel-transfer method. The mica substrate was pressed against the gel surface for 10 min. The substrate was detached from the gel surface and observed by AFM. The specimens for TEM were prepared by freeze-drying a methanol gel of **5** onto amorphous carbon-coated copper grids (400 mesh). The grids were observed in a JEOL JEM-2010 electron microscope at an acceleration voltage of 200 kV without any staining.

Materials: All chemicals were purchased from commercial suppliers and used without purification. All solvents were distilled before each procedure. Adsorption column chromatography was performed using silica gel (Wakogel C-200, 200 mesh). Analytical thin-layer chromatography was performed on commercial Merck plates coated with silica gel 60 F_{254} or aluminum oxide 60 F_{254} .

Compound 2: A mixture of **1** (0.2 g, 0.67 mmol), 1,2-dicyano-4,5-di(dodecyloxy)benzene (1.0 g, 2.0 mmol), and ZnCl_2 (0.18 g, 1.3 mmol) in 2-(dimethylamino)ethanol (10 mL) was stirred and slowly heated. The mixture was refluxed under a nitrogen atmosphere for 72 h. After the mixture was cooled, methanol (50 mL) was added, and the resulting precipitate was filtered off. The residue was treated with *p*-toluenesulfonic acid monohydrate (0.3 g) in mixed solution of methanol and CH_2Cl_2 (10 mL, 1:2 v/v) to remove tetrahydro-2H-pyran. The solvent was removed under reduced pressure, and the residue was washed off with methanol. Compound **2** was purified by column chromatography (silica gel, $\text{CHCl}_3/\text{methanol}$ 9:1 v/v). TLC: $R_f = 0.45$ ($\text{CHCl}_3/\text{methanol}$ 9:1 v/v); yield 12%; $^1\text{H NMR}$ (400.1 MHz): $\delta = 8.19$ (brs, 8H; ArH), 5.74 (brs, 1H; OH), 4.58 (m, 14H; ArOCH_2), 3.98 (t, 2H; CH_2OH), 3.45 (s, 3H; ArOCH_3), 2.18 (br t, 12H; OCH_2CH_2), 1.2–1.7 (m, 108H; CH_2), 0.90 ppm (t, 18H; CH_3); MALDI-TOF MS (dithranol): m/z (%): 1772 (10) [$M^+ + \text{H}$].

Compound 3: 2-Bromo-2-methylpropionyl bromide (0.1 mL, 0.81 mmol) was added drop by drop to a solution of **1** (30 mg, 17.0 μmol) and triethylamine (1.0 mL) in CH_2Cl_2 (20 mL) at 0°C under an argon atmosphere. The solution was stirred for 2 h at 0°C and then at room temperature for one night. The completion of the reaction was checked by TLC (silica gel; $R_f = 1$ (CHCl_3)). Triethylamine hydrobromide was filtered off, and the solution was evaporated. The crude product was purified by

column chromatography (silica gel, CHCl_3). Yield 82%; $^1\text{H NMR}$ (400.1 MHz): δ =8.76 (brs, 8H; ArH), 4.52–4.65 (m, 14H; ArOCH_2), 4.12 (brt, 2H; $-\text{CH}_2\text{OC}(\text{O})-$), 3.46 (s, 3H; ArOCH_3), 2.17 (brt, 12H; OCH_2CH_2-), 1.89 (s, 6H; CH_3), 1.2–1.8 (m, 108H; CH_2), 0.89 ppm (t, 18H; CH_3); FT-IR (KBr): $\tilde{\nu}$ 1740 cm^{-1} (C=O); MALDI-TOF MS (dithranol): m/z (%): 1919 (100) [M^+ +H].

Polymerization: A solution of **2** (20 mg, 10.4 μmol), PMDETA (22 L, 10.4 μmol), and acrylate (BA or TEGA 1.25 mmol) in degassed toluene (3.0 mL) was added to a dry glass tube charged with CuBr (1.5 mg, 10.4 μmol). Three freeze-pump-thaw cycles were performed, and the tube was sealed under vacuum and placed in an oil bath under thermostat control at 70°C for 4 h. After 4 h, the polymerization was stopped by cooling the tube into ice-water. The tube was opened and the contents dissolved in THF. The resulting polymers were purified by gel permeation chromatography (Biorad Biobeads SX-1, THF).

Compound 4: Conversion 38%; M_n =9000, PDI=1.20 (determined by GPC analysis); UV/Vis (CH_2Cl_2): λ_{max} =678, 331 nm; $^1\text{H NMR}$ (400.1 MHz): δ =8.7 (ArH), 4.2–4.6 ($-\text{OCH}_2-$, $-\text{CH}_2\text{OC}(\text{O})-$), 3.7 ($-\text{OCH}_3$), 2.2 ($-\text{OCH}_2\text{CH}_2-$, $-\text{CH}_2-$), 12–1.7 (CH_2), 0.9 ppm (CH_3).

Compound 5: Conversion 30%; M_n =6200, PDI=1.14 (determined by GPC analysis); UV/Vis (CH_2Cl_2): λ_{max} =678, 332 nm; $^1\text{H NMR}$ (400.1 MHz): δ =8.8 (ArH), 4.3–4.6 ($-\text{OCH}_2-$), 4.2 ($-\text{CH}_2\text{OC}(\text{O})-$), 3.7 ($-\text{OCH}_2\text{CH}_2-$), 3.5 ($-\text{OCH}_2\text{CH}_2-$), 3.3 ($-\text{OCH}_3$), 2.2 ($-\text{OCH}_2\text{CH}_2-$, $-\text{CH}_2-$), 12–1.7 (CH_2), 0.9 ppm (CH_3).

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