Synthesis and Solid-State Polymerization of Butadiyne Derivatives with Trialkoxyphenylurethane Groups

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Received July 19, 2011; E-mail: okadas@yz.yamagata-u.ac.jp

3,4,5-Trialkoxyphenyl isocyanate derivatives, in which alkoxy was dodecyloxy or methoxy, reacted with 4,6decadiyn-1,10-diol and 5,7-dodecadiyn-1,12-diol, and four butadiyne derivatives with (*N*-trialkoxyphenyl)urethane groups were successfully synthesized. Their solid-state polymerization stimulated by UV or γ -ray irradiation was investigated. All monomers in crystals were found to be polymerizable. However, conversion was different depending on the compounds. The derivatives from 5,7-dodecadiyn-1,12-diol showed better conversion, suggesting that they have more favorable monomer arrangement for the solid-state polymerization. Polymers of dodecyloxy derivatives could be partially dissolved in chloroform and they showed solvatochromism when hexane was added to the solution. As was expected from the structure of tridodecyloxyphenyl groups introduced, dodecyloxy derivatives gave organogels in various organic solvents in the concentration less than 2 wt %. However, these gels could not be polymerized by UV irradiation, and the monomer alignment was found to be different between crystalline and gel states.

Polydiacetylene (PDA) is one of the most interesting conjugated polymers because it is uniquely prepared by solid-state polymerization of butadiyne monomers.¹ Since this polymerization reaction progresses topochemically, monomer alignment in the crystals should satisfy the following conditions: distance d between adjacent molecules in the stacking axis of approximately 0.5 nm and angle θ between the linear butadiyne moiety and stacking axis of about 45°.² Obviously, substituents of butadiyne derivatives are quite important to determine polymerizability. From the other point of view, variation of butadiyne substituents gives various states of monomers and the resulting PDAs. Usually the solid-state polymerization is performed in crystals, but the reaction environment has been extended to self-organized systems. For example, the solid-state polymerization in Langmuir-Blodgett films of amphiphilic butadiyne derivatives with longalkyl groups has more than three decades of history,³⁻⁶ and that in the nanostructures like nanofibers has recently been pursued.⁷⁻¹⁰ Although most PDAs are insoluble due to high crystallinity, some PDAs with flexible substituents are known to be dissolved in solvent.¹¹⁻¹³ Even in the case of insoluble PDAs, they can be dispersed in solvent by fabricating into nanocrystals.^{14,15} By selecting proper substituents of butadiyne monomers, PDAs in various states can be obtained.

In the present study, we designed butadiyne molecules with solid-state polymerizability, gel formability, and solubility of the corresponding polymers and synthesized **10a** and **11a** (Figure 1) with urethane groups as well as 3,4,5-tridodecyl-oxyphenyl (TDP) groups at both ends. As mentioned above, introduction of proper substituents, which make the butadiyne molecules set in polymerizable stacks, is necessary for the solid-state polymerization. Butadiyne derivatives with urethane

groups like 5,7-dodecadiyn-1,12-diyl bis(N-phenylcarbamate) (TCDU).¹⁶ 4.6-decadiyn-1.10-divl bis[*N*-(butoxycarbonylmethyl)carbamate] (3BCMU),¹⁷ and 5,7-dodecadiyn-1,12-diyl bis[N-(butoxycarbonylmethyl)carbamate] $(4BCMU)^{18}$ are apt to form one-dimensional columns in crystals because of intermolecular hydrogen bonds between adjacent molecules along the column. Actually, we have succeeded to prepare PDAs from the monomers with urethane groups in the crystalline state,^{19–22} and the urethane group is a key structure to increase probability of the solid-state polymerization. The other characteristic group of TDP has an interesting property in that the compounds with TDP often show gel formability.^{10,23–25} There are several reports on butadiyne derivatives forming gels. However, their chemical structures were slightly complicated, e.g., butadiyne derivatives with chiral substituents⁷⁻⁹ and those having two TDP groups together with four amide groups in one molecule.¹⁰ On the other hand, the structures of the butadiyne derivatives in this study were quite simplified to study the effects of the functional groups. For comparison, we also prepared butadiyne derivatives 10b and 11b (Figure 1), in which methyl groups were introduced instead of dodecyl groups in 10a and 11a, respectively, and their polymerization behaviors were investigated.

Results and Discussion

Butadiyne monomers with trialkoxyphenylurethane groups were synthesized according to Figure 1. In order to introduce both trialkoxyphenyl and urethane groups simultaneously into butadiyne monomers, we used trialkoxyphenyl isocyanate²⁶ to react with diols having a butadiyne moiety. Trialkoxyphenyl isocyanates were synthesized starting from methyl gallate (1), and the final step of the series of reactions was Curtius



Figure 1. Scheme on synthesis of butadiyne derivatives with trialkoxyphenylurethane groups and their solid-state polymerization.

rearrangement of 3,4,5-alkoxybenzoyl azide. Over all yields of dodecyl derivative **5a** and methyl derivative **5b** from **1** were 59% and 74%, respectively. The addition reactions of diynediols **8** and **9** to isocyanates **5a** and **5b** successfully progressed in a yield more than 87%.

When compared between the same alkoxy derivatives, compounds with inner methylene number n of 3 have higher melting points than the corresponding compounds with n of 4, i.e., melting points of 10a, 11a, 10b, and 11b are 109, 74, 189, and 161 °C, respectively. This means that 10a and 10b have stronger intermolecular interactions than 11a and 11b, respectively. Considering their molecular structures, hydrogen bonding between urethane groups seemed to be one of the strong interactions. Strength of hydrogen bonding between urethane groups of adjacent monomers can be qualitatively evaluated by the wavenumbers of C=O stretching vibration. They were 1697 and $1699 \,\mathrm{cm}^{-1}$ for dodecyl derivatives **10a** and **11a**, respectively. On the other hand, those of methyl derivatives **10b** and **11b** were observed at 1722 and 1728 cm^{-1} , respectively. Since C=O vibration of dodecyl derivatives was observed at smaller wavenumbers than that of methyl derivatives, dodecyl derivatives have stronger hydrogen bonding than methyl derivatives. However, the strength of hydrogen bonding between compounds with n = 3 was not so different from that of the corresponding compounds with n = 4. Namely, hydrogen bonding is not a unique strong intermolecular interaction of this series of compounds and other interactions such as methylene-chain stacking, phenyl-ring stacking, etc. are also important.

 Table 1. Gelation in Various Solvents and the Minimum Concentration^{a)}

Solvent	10a	11a
Hexane	Gs (1.0)	Gs (1.0)
Cyclohexane	Gs (1.0)	Gs (1.0)
Carbon tetrachloride	Gs (1.0)	Gs (2.0)
Toluene	Gs (2.0)	Gs (2.0)
Diethyl ether	S	S
Chloroform	S	S
Ethyl acetate	Go (1.0)	Go (1.0)
THF	S	S
Acetone	Go (1.0)	Go (2.0)
Ethanol	Go (1.0)	S
Methanol	S	S
Acetonitrile	S	S

a) The symbols for gelation ability: Gs, semitransparent gel formation; Go, opaque gel formation; S, solution even in 5-wt% concentration. Numbers in parentheses are minimum concentration for gel formation in wt%.

Gel formabilities of **10a** and **11a** with TDP groups were investigated in the range of less than 5 wt% solutions of various organic solvents and the results are summarized in Table 1. As was expected from introduction of TDP groups, gel formation was confirmed in various solvents in the concentration less than 2 wt%. In less polar solvents such as hexane, cyclohexane, carbon tetrachloride, and toluene, semitransparent gels were formed. Since hydrogen bonds are



Figure 2. UV-visible diffuse reflectance spectra of (a) 10a, (b) 11a, (c) 10b, and (d) 11b depending on UV irradiation time. Dotted lines are the spectra before UV irradiation. Dashed lines of (a) and (b) are the spectra after UV irradiation for 3 min. Dashed lines of (c) and (d) are the spectra after UV irradiation for 1 min. A solid line of (a) is the spectrum after UV irradiation for 30 min. Solid lines of (b), (c), and (d) are the spectra after UV irradiation for 10 min. Gray solid lines are the spectra after UV irradiation for 60 min.

effectively formed in less polar solvents in general, selfassembling is apt to occur to form gels. In addition, we found that **10a** and **11a** also formed opaque gels even in polar solvents like ethyl acetate and acetone. In these cases, methylene-chain and/or phenyl-ring stackings seemed to play important roles to form gels.

Solid-state polymerization of the monomers was first investigated by UV irradiation. As shown in Figure 2, all the monomer crystals showed characteristic excitonic absorption bands of the PDA backbone structure, indicating that regular 1,4-addition polymerization in Figure 1 occurred. Absorption maxima observed for 10a, 10b, and 11a were about 580 and 540 nm while those for 11b were 563 and 523 nm. On the other hand, the monomer gels of 10a and 11a did not show polymerizability. This fact indicates that monomer arrangements in the gels different from those of the corresponding crystals although the structure analysis of the gel states containing solvent was difficult. Hereafter, discussion is concentrated on polymers obtained from crystalline states. Generally, conversions of UV-irradiated samples are not high because UV cannot penetrate through the samples due to absorption. Thus, γ -ray-induced polymerization was performed. Figure 3 shows conversion of the monomers when



Figure 3. Conversions from monomers to the corresponding polymers: 10a (black triangle), 11a (black square), 10b (gray triangle), and 11b (gray square). The horizontal axis is taken as the logarithm scale.



Figure 4. UV-visible diffuse reflectance spectra of (a) 10a, (b) 11a, (c) 10b, and (d) 11b after γ -ray irradiation. These spectra were taken after monomer extraction.

 γ -ray doses were 10 kGy, 100 kGy, and 1 MGy. Except **10b**, conversions increased depending on dosage, and quantitative conversions were observed for 11a and 11b. From the conversion curves, monomers with methylene number n of 4 seem to have more favorable stacks for solid-state polymerization than those with *n* of 3. Although the conversion of **10b** was only 1.5% even after a 1-MGy γ -ray dose, the hexane filtrate showed red color indicating that the filtrate contained some reacted portions and the conversion might be slightly underestimated. The samples obtained by γ -ray irradiation showed broad absorption with absorption maximum at around 500 nm as shown in Figure 4. Although the spectra of the polymers in Figure 4 were recorded after monomer extraction, those before extraction were essentially the same. The blue shifts of absorption maxima compared with the polymer obtained by UV irradiation are often observed for butadiyne derivatives with alkyl chains. This can be explained as follows: In the initial stage of the solid-state polymerization, the produced polymers were in monomer crystalline lattices and the π -conjugated backbones were extended with strain caused by the structural difference between the monomer and the corresponding polymer. When polymerization progressed, the strain was released with disorder in crystals. This process should be accompanied by undulations of π -conjugated backbone resulting in blue shifts of absorption.

For 10a and 11a, the polymers obtained by γ -ray irradiation followed by hexane extraction of the monomers could be partially dissolved in chloroform. Distribution of molecular weight of the soluble polymer portion measured by gel permeation chromatography (GPC) were very broad from the oligomer level to over the exclusion limit of the GPC columns used, i.e., about 1×10^6 , and the peak was observed around 2×10^5 . Thus, the insoluble polymer portion is considered to have the molecular weight more than 1×10^6 . Since solvatochromism of poly3BCMU and poly4BCMU has been known in chloroform-hexane mixed solvent,11,12 the similar experiments were performed for polymers of 10a and 11a. Figure 5 shows UV-visible spectra of the polymers of 10a and 11a in mixed solvent with different composition ratio. Absorption maximum of both polymers in chloroform was observed at around 465 nm. When volume ratio of hexane in chloroform-hexane mixed solvent increased, the absorption maximum was redshifted. In chloroform-hexane (1:19) mixed solvent, absorption maxima of the polymers of 10a and 11a were 527 and 518 nm, respectively. For the polymer of 10a, additional shoulder appeared around 600 nm, which was almost the same as the wavelength of the absorption maximum at the longest wavelength in the solid state. These solvatochromisms were similar to those of poly3BCMU and poly4BCMU. More polar chloroform broke hydrogen bonding between urethane groups in the



Figure 5. UV-visible spectra of (a) the polymer of 10a and (b) the polymer of 11a in solvent. ε is the molar absorptivity per repeating unit. The mixing ratio of chloroform and hexane were 20:0 (solid line), 4:16 (dashed line), 2:18 (dash-dotted line), and 1:19 (dotted line), respectively.

adjacent side groups and planarity of π -conjugated backbone reduced to show the blue shift of absorption. On the other hand, increase of hexane ratio caused less polarity of the solvent, which promoted hydrogen-bond formation to make π -conjugated backbone planar. Thus, the red shifts of absorption bands were observed. Since **10a** has less methylene number of *n* than 11a, the polymer backbone structure seems to be more affected by the planar hydrogen-bond arrays of the urethane groups resulting that the π -conjugated structure of **10a** became partly similar to that in the crystalline state. Different points of the absorption in solution of 10a and 11a compared with poly3BCMU and poly4BCMU are the maximum wavelengths. Poly3BCMU and poly4BCMU were reported to show absorption maxima around 485 and 470 nm, respectively, in chloroform.¹² In chloroform-hexane mixed solvent, absorption maxima of poly3BCMU were about 570 and 618 nm, and those of poly4BCMU was around 540 nm. The reason of the absorption blue shifts of 10a and 11a compared with poly3BCMU and poly4BCMU in the corresponding states can be explained by the bulkiness of TDP groups at the both side chain ends, which seemed to deform the planarity of the π -conjugated backbone.

Crystallinity of monomers and their γ -ray-irradiated samples before monomer extraction were evaluated by X-ray diffraction. Long spacings of 4.15 and 4.27 nm were observed for 10a and 11a monomers, respectively, and their spacings were lengthened to be 4.29 and 4.31 nm after polymerization, respectively (Figures 6a and 6c). Although the diffraction peak intensity of the long spacing of 10a decreased, that of 11a remained. From the result that conversion of 11a was higher than that of 10a, 11a has more favorable stack for solid-state polymerization, in which crystallinity can be maintained even after polymerization. The other prominent peaks for both monomers and the polymers were at 2θ of around 21° corresponding to the spacing of about 0.42 nm (Figures 6b and 6d) and they can be assigned to the stack of alkyl chains. Diffraction patterns of methyl-substitute monomers were fairly different from those of dodecyl-substituted ones. Many sharp peaks were observed between 7 and 30° for 10b (Figure 7a)



Figure 6. Powder X-ray diffraction patterns of 10a and 11a. Figures (a) and (b) are for 10a, and Figures (c) and (d) are for 11a. Gray and black lines are for the monomers and the polymers obtained after γ -ray irradiation, respectively. Figures (a) and (c) were recorded on a small-angle diffractometer while a wide-angle diffractometer was used to obtain Figures (b) and (d).

and between 3 and 33° for **11b** (Figure 7b). Since conversion of **10b** was found to be low, the diffraction peaks after γ -ray irradiation may be mainly originated not from the polymer but from the monomer. However, in the case of **11b**, there was no



Figure 7. Powder X-ray diffraction patterns of (a) 10b and (b) 11b. Gray and black lines are for the monomers and the polymers obtained after γ -ray irradiation, respectively.

remarkable degradation of crystallinity from the monomer to the corresponding polymer, suggesting topochemical polymeriztion of **11b** in the crystalline state.

Conclusion

Butadivne derivatives 10a and 11a with TDP and urethane groups and the corresponding derivatives 10b and 11b with methyl groups instead of dodecyl groups were prepared and their solid-state polymerization was investigated. All crystalline monomers could be polymerized in the solid state by UV irradiation to show excitonic absorption bands assigned to the PDA backbone structure. Qualitative order of conversion from a monomer to the corresponding polymer obtained by γ -ray irradiation was $11b > 11a > 10a \gg 10b$. Thus, inner methylene number of 4 gave more favorable monomer stack for solidstate polymerization among the compounds prepared. Monomers 10a and 11a could be dissolved in chloroform and their solvatochromism was confirmed when hexane was added to the chloroform solution. Although organogel formation of 10a and 11a was confirmed not only in less polar solvents but also polar solvents like ethyl acetate and acetone, these gels could not be polymerized and difference in monomer stacking structures was found.

Experimental

Apparatus. The melting points were measured using a Yanaco MP-500P micro melting-point apparatus without correction. Differential scanning calorimetry was performed using a SII DSC 220 analyzer. IR spectra were recorded for KBr-pelletized samples on a Horiba FT-210 spectrometer. NMR spectra were obtained using a Jeol ECX-400 spectrometer. Elemental analysis was performed using a Perkin-Elmer 2400II analyzer. UV-vis-NIR diffuse reflectance spectra were measured using a Jasco V-570 spectrophotometer, in which an integrated sphere (ILN-472) was attached. The samples were grounded together with potassium bromide and the mixture was put into a cell with a guartz window. Powder X-ray diffraction patterns were recorded on a Rigaku NANO-Viewer diffractometer for small angles and a Rigaku R-AXIS RAPID diffractometer for wide angles with both $Cu K\alpha$ sources.

GPC was performed using Jasco PU-980 pump and UV-975 UV-vis detector, and two serially-connected Tosoh TSKgel G4500H_{HR} columns. Eluent was chloroform and polystyrene was used as a molecular weight standard.

Methyl 3,4,5-Tridodecyloxybenzoate (2a): Syntheses. To 300 mL of anhydrous N.N-dimethylformamide (DMF), methyl gallate (1) (6.2 g, 34 mmol), 1-bromododecane (25 g, 100 mmol), and potassium carbonate (45 g, 326 mmol) were added, and they were stirred at 85 °C for 30 h. To the reaction mixture, 1-bromododecane (8 mL, 33 mmol) was again added and it was further stirred at 85 °C for 18 h. The mixture was poured into water and the resulting colorless precipitates were filtered off. The filtered solid was recrystallized from ethanol to give 17.0 g (74%) of 2 as colorless crystals: IR (KBr): 2924, 2854, 1689, 1589, 1435, 1334, 1227, 1126, 725 cm⁻¹; ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: $\delta 0.88 (9\text{H}, \text{t}, J = 6.6 \text{ Hz}), 1.20-1.52 (54\text{H}, \text{t})$ m), 1.74 (2H, tt, J = 7.4, 6.4 Hz), 1.81 (4H, tt, J = 7.1, 6.4 Hz), 3.39 (3H, s), 4.007 (4H, t, J = 6.4 Hz), 4.014 (2H, t, J =6.4 Hz), 7.25 (2H, s); $^{13}{\rm C}\,{\rm NMR}$ (400 MHz, CDCl₃): δ 14.03, 22.64, 26.04, 29.27, 29.33, 29.35, 29.53, 29.59, 29.66, 30.30, 31.88, 51.95, 69.09, 73.39, 107.95, 124.60, 142.34, 152.76, 166.82.

Methyl 3,4,5-Trimethoxybenzoate (2b): To 300 mL of anhydrous DMF, methyl gallate (1) (12.5 g, 0.068 mol), iodomethane (12.6 mL, 0.204 mol), and potassium carbonate (28.2 g, 204 mmol) were added, and they were stirred at 85 °C for 48 h. To the reaction mixture, iodomethane (6.30 mL, 102 mmol) was again added and it was further stirred at 85 °C for 10 h. The mixture was poured into water and the resulting colorless precipitates were filtered off. The filtered solid was recrystallized from ethanol to give 13.1 g (85%) of **2b** as colorless crystals: IR (KBr): 2953, 2841, 1716, 1591, 1414, 1337, 1227, 1132 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 3.91 (12H, s), 7.30 (2H, s); ¹³C NMR (400 MHz, CDCl₃): δ 52.13, 56.13, 60.81, 106.68, 125.06, 142.04, 152.83, 166.61.

3,4,5-Tridodecyloxybenzoic Acid (3a): Ester **2a** (1.9 g, 2.8 mmol) was dissolved in 100 mL of ethanol. To this solution, potassium hydroxide (0.35 g, 6.2 mmol) in 5 mL of water was added, and it was refluxed for 3 h. After evaporating ethanol, diluted sulfuric acid was added and the mixture was extracted

with ether. The ether layer was collected and dried over anhydrous magnesium sulfate. After filtration, solvent of the filtrate was removed under reduced pressure to give 1.79 g (96%) of **3a** as colorless solid: IR (KBr): 2923, 2854, 1681, 1589, 1431, 1335, 1225, 1126, 725 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.88 (9H, t, J = 6.8 Hz), 1.20–1.52 (54H, m), 1.75 (2H, tt, J = 7.6, 6.6 Hz), 1.82 (4H, tt, J = 7.3, 6.6 Hz), 4.02 (4H, t, J = 6.6 Hz), 4.04 (2H, t, J = 6.6 Hz), 7.32 (2H, s), a carboxyl proton was not clearly detected; ¹³C NMR (100 MHz, CDCl₃): δ 14.07, 22.68, 26.04, 26.07, 29.28, 29.37, 29.38, 29.56, 29.63, 29.65, 29.69, 30.32, 31.92, 69.15, 73.51, 108.54, 123.72, 143.13, 152.82, 172.02.

3,4,5-Trimethoxybenzoic Acid (3b): Ester **2b** (7.23 g, 3.2 mmol) was dissolved in 100 mL of ethanol. To this solution, potassium hydroxide (0.36 g, 6.4 mmol) in 50 mL of water was added, and it was refluxed for 3 h. After evaporating ethanol, diluted sulfuric acid was added and the mixture was extracted with ether. The ether layer was collected and dried over anhydrous magnesium sulfate. After filtration, solvent of the filtrate was removed under reduced pressure to give 6.45 g (95%) of **3b** as colorless solid: IR (KBr): 2958, 2839, 1687, 1589, 1417, 1329, 1227, 1130 cm⁻¹; ¹HNMR (400 MHz, CDCl₃): δ 3.93 (6H, s), 3.94 (3H, s), 7.38 (2H, s), a carboxyl proton was not clearly detected; ¹³C NMR (100 MHz, CDCl₃): δ 56.21, 60.91, 107.40, 124.09, 142.97, 152.93, 171.80.

3,4,5-Tridodecyloxybenzoyl Chloride (4a): To **3a** (6.81 g, 10 mmol), thionyl chloride (4.0 g, 34 mmol) was added dropwise and the mixture was stirred at 80 °C for 2 h. Thionyl chloride remained in the mixture was removed by distillation to give 6.91 g (99%) of **4a** as colorless solid: IR (KBr): 2924, 2850, 1751, 1581, 1427, 1335, 1126, 771 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.88 (9H, t, J = 6.8 Hz), 1.20–1.52 (54H, m), 1.74 (2H, tt, J = 7.6, 6.5 Hz), 1.82 (4H, tt, J = 7.4, 6.5 Hz), 4.02 (4H, t, J = 6.5 Hz), 4.08 (2H, t, J = 6.5 Hz), 7.33 (2H, s); ¹³C NMR (100 MHz, CDCl₃): δ 14.11, 22.68, 25.97, 26.03, 29.17, 29.36, 29.51, 29.61, 29.65, 29.68, 30.31, 31.92, 69.30, 73.70, 109.92, 127.23, 144.68, 152.83, 167.72.

3,4,5-Trimethoxybenzoyl Chloride (4b): To **3b** (5.04 g, 24 mmol), thionyl chloride (9.57 g, 80 mmol) was added dropwise and the mixture was stirred at 80 °C for 21 h. Thionyl chloride remained in the mixture was removed by distillation to give 5.09 g (93%) of **4b** as colorless solid: IR (KBr): 2969, 2837, 1763, 1591, 1444, 1340, 1132 cm⁻¹; ¹HNMR (400 MHz, CDCl₃): δ 3.93 (6H, s), 3.97 (3H, s), 7.38 (2H, s); ¹³C NMR (100 MHz, CDCl₃): δ 56.19, 60.91, 108.66, 127.47, 144.31, 152.78, 167.38.

3,4,5-Tridodecyloxyphenyl Isocyanate (5a): Sodium azide (2.5 g, 38 mmol) and benzyltriethylammonium chloride (1.2 g, 5 mmol) were dissolved in water (15 mL), and the solution was cooled in an ice bath. To this solution, **4a** (5 g, 7.2 mmol) in the mixture of acetone (15 mL) and toluene (10 mL) was added dropwise. By controlling the addition rate of the solution of **4a**, the temperature of the reaction mixture was kept between 10 and 15 °C. After finishing the addition, the mixture was stirred over night, and it was extracted with toluene. The organic layers were combined and dried over anhydrous magnesium sulfate. The filtrate was heated at 80 °C, and solvent of the solution was removed to give 4.06 g (84%) of **5a**: IR (KBr): 2954, 2850, 2279, 1643, 1467, 1438, 1385,

1225, 1122, 721 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.88 (9H, t, J = 6.9 Hz), 1.20–1.52 (54H, m), 1.72 (2H, tt, J = 7.6, 6.6 Hz), 1.79 (4H, tt, J = 7.6, 6.6 Hz), 3.90 (2H, t, J = 6.6 Hz), 3.92 (4H, t, J = 6.6 Hz), 6.27 (2H, s); ¹³C NMR (100 MHz, CDCl₃): δ 14.11, 22.69, 26.03, 26.10, 29.24, 29.37, 29.63, 29.65, 29.69, 29.73, 30.26, 31.92, 69.16, 73.54, 103.41, 124.33, 128.38, 136.22, 153.48.

3.4.5-Trimethoxyphenyl Isocvanate (5b): Sodium azide (2.9 g, 45 mmol) and benzyltriethylammonium chloride (500 mg, 2.2 mmol) were dissolved in water (15 mL), and the solution was cooled in an ice bath. To this solution, 4b (5.5 g, 24 mmol) in the mixture of toluene (30 mL) was added dropwise. By controlling the addition rate of the solution of 4b, the temperature of the reaction mixture was kept between 10 and 15 °C. After finishing the addition, the mixture was stirred over night, and it was extracted with toluene. The organic layers were combined and dried over anhydrous magnesium sulfate. The filtrate was heated at 80 °C, and solvent of the solution was removed to give 4.9 g (98%) of **5b**: IR (KBr): 2927, 2854, 2271, 1645, 1593, 1232, 1132 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 3.82 (3H, s), 3.84 (6H, s), 6.32 (2H, s); ¹³C NMR (100 MHz, CDCl₃): δ 56.07, 60.85, 102.11, 124.37, 128.92, 136.02, 153.54.

4,6-Decadiyn-1,10-diol (8): To the mixture of acetone (60 mL), copper(I) chloride (0.269 g, 2.7 mmol), and $N_N N'_N$ tetramethylethylenediamine (TMEDA) (0.362 g, 3.1 mmol), 4pentyn-1-ol (6) (2.0 g, 23.8 mmol) was added, and it was heated at 80 °C with oxygen bubbling for 20 h. Diluted hydrochloric acid was added to the reaction mixture and it was extracted with chloroform. The organic layers were collected and dried over anhydrous magnesium sulfate. After filtration, solvent of the filtrate was evaporated under reduced pressure. The residue was purified by the column chromatography (silica gel, hexane-ethyl acetate (3:7)) to give 1.62 g (82%) of 8 as colorless solid: ¹H NMR (400 MHz, CDCl₃): δ 1.54 (2H, broad s), 1.78 (4H, tt, J = 7.0, 6.1 Hz), 2.39 (4H, t, J = 7.0 Hz), 3.75 (4H, t, J = 6.1 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 15.70, 30.90, 61.40, 65.61, 76.77.

5,7-Decadiyn-1,12-diol (9): To the mixture of acetone (60 mL), copper(I) chloride (0.208 g, 2.0 mmol), and TMEDA (0.317 g, 2.7 mmol), 4-hexyn-1-ol (7) (2.0 g, 20 mmol) was added, and it was heated at 80 °C with oxygen bubbling for 20 h. Diluted hydrochloric acid was added to the reaction mixture and it was extracted with chloroform. The organic layers were collected and dried over anhydrous magnesium sulfate. After filtration, solvent of the filtrate was evaporated under reduced pressure. The residue was purified by the column chromatography (silica gel, chloroform–ethyl acetate (3:2)) to give 1.63 g (82%) of **9** as colorless solid: ¹H NMR (400 MHz, CDCl₃): δ 1.45–1.73 (10H, m), 2.31 (4H, t, J = 6.6 Hz), 3.68 (4H, t, J = 6.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 18.94, 24.54, 31.66, 62.24, 65.54, 77.16.

4,6-Decadiyn-1,10-diylBis[N-(3,4,5-tridodecyloxy-phenyl)carbamate] (10a):To toluene (30 mL), 5a (1.38 g,2.1 mmol), 8 (0.16 g, 0.96 mmol), and three drops of dibutyltindidodecanoate were added and the mixture was stirred at100 °C for 5 h. After removing the solvent under reducedpressure, the residue was purified by the column chromatog-raphy (silica gel, hexane-ethyl acetate (9:1)) to give 1.29 g

(89%) of **10a** as pale yellow solid: Mp 109 °C; IR (KBr): 3298, 2954, 2922, 2850, 1697, 1603, 1541, 1468, 1433, 1232, 1122 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.88 (18H, t, J = 6.7 Hz), 1.20–1.52 (108H, m), 1.67–1.83 (12H, m), 1.88 (4H, tt, J = 7.0, 6.2 Hz), 2.37 (4H, t, J = 7.0 Hz), 3.89 (4H, t, J = 6.7 Hz), 3.94 (8H, t, J = 6.5 Hz), 4.22 (4H, t, J = 6.2 Hz), 6.51 (2H, broad s), 6.63 (4H, s); ¹³C NMR (100 MHz, CDCl₃): δ 14.07, 16.03, 22.66, 26.07, 26.12, 27.70, 29.35, 29.40, 29.63, 29.68, 29.73, 30.27, 31.90, 63.57, 65.91, 69.04, 73.48, 76.19, 97.74, 133.40, 134.16, 153.23, 153.40. Found: C, 76.54; H, 11.19; N, 1.85%. Calcd for C₉₆H₁₆₈O₁₀N₂: C, 76.34; H, 11.21; N, 1.85%.

4,6-Decadiyn-1,10-diyl Bis[N-(3,4,5-trimethoxyphenyl)-To toluene (30 mL), **5b** (0.98 g, 4.68 carbamate] (10b): mmol), 8 (0.32 g, 1.93 mmol), and three drops of dibutyltin didodecanoate were added and the mixture was stirred at 100 °C for 12 h. After removing the solvent under reduced pressure, the residue was purified by the column chromatography (silica gel, hexane-ethyl acetate (9:1)) to give 0.98 g (87%) of 10b as pale yellow solid: Mp 189 °C; IR (KBr): 3444, 3291, 2963, 2944, 2843, 1722, 1614, 1512, 1454, 1417, 1227, 1126 cm⁻¹; ¹HNMR (400 MHz, CDCl₃): δ 1.88 (4H, tt, J = 6.9, 6.2 Hz, 2.37 (4H, t, J = 6.9 Hz), 3.81 (6H, s), 3.85 (12H, s), 4.24 (4H, t, J = 6.2 Hz), 6.63 (2H, broad s), 6.69 (4H, s); 13 C NMR (100 MHz, CDCl₃): δ 16.03, 27.63, 56.02, 60.95, 63.66, 65.87, 76.21, 96.28, 133.93, 134.03, 153.37. Found: C, 61.45; H, 6.19; N, 4.73%. Calcd for C₃₀H₃₆O₁₀N₂: C, 61.63; H, 6.21; N, 4.79%.

Bis[N-(3,4,5-tridodecvloxv-5.7-Dodecadivn-1.12-divl phenyl)carbamate] (11a): To toluene (30 mL), 5a (1.24 g, 1.85 mmol), 9 (0.16 g, 0.82 mmol), and three drops of dibutyltin didodecanoate were added and the mixture was stirred at 100 °C for 5 h. After removing the solvent under reduced pressure, the residue was purified by the column chromatography (silica gel, hexane-ethyl acetate (9:1)) to give 1.12 g (88%) of **11a** as pale yellow solid: Mp 74 °C; IR (KBr): 3298, 2955, 2922, 2852, 1699, 1602, 1532, 1468, 1431, 1232, 1120 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.88 (18H, t, J =6.4 Hz), 1.20-1.52 (108H, m), 1.56-1.83 (20H, m), 2.31 (4H, t, J = 6.6 Hz), 3.89 (4H, t, J = 6.5 Hz), 3.94 (8H, t, J = 6.3 Hz), 4.16 (4H, t, J = 6.1 Hz), 6.45 (2H, broad s), 6.54 (4H, s); ¹³C NMR (100 MHz, CDCl₃): δ 14.09, 18.84, 22.67, 24.72, 26.06, 26.12, 28.02, 29.35, 29.39, 29.63, 29.68, 29.73, 30.26, 31.90, 64.43, 65.73, 69.01, 73.46, 76.84, 97.58, 133.40, 134.11, 153.23, 153.55. Found: C, 76.68; H, 10.98; N, 1.87%. Calcd for C₉₈H₁₇₂O₁₀N₂: C, 76.51; H, 11.27; N, 1.82%.

5,7-Dodecadiyn-1,12-diyl Bis[*N*-(3,4,5-trimethoxyphenyl)carbamate] (11b): To toluene (30 mL), 5b (0.91 g, 4.3 mmol), 9 (0.32 g, 1.6 mmol), and three drops of dibutyltin didodecanoate were added and the mixture was stirred at 100 °C for 5 h. After removing the solvent under reduced pressure, the residue was purified by the column chromatography (silica gel, chloroform–ethyl acetate (9:1)) to give 0.88 g (87%) of 11b as pale yellow solid: Mp 161 °C; IR (KBr): 3415, 3306, 2947, 2841, 1728, 1605, 1511, 1455, 1417, 1230, 1132 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.63 (4H, tt, J = 7.6, 6.9 Hz), 1.79 (4H, tt, J = 7.6, 6.4 Hz), 2.32 (4H, t, J = 6.9 Hz), 3.81 (6H, s), 3.85 (12H, s), 4.18 (4H, t, J =6.4 Hz), 6.56 (2H, broad s), 6.68 (4H, s); ¹³C NMR (100 MHz, CDCl₃): δ 18.84, 24.72, 28.00, 55.99, 60.93, 64.53, 65.71, 76.87, 96.22, 133.87, 134.23, 153.36, 153.59. Found: C, 62.60; H, 6.62; N, 4.50%. Calcd for C₃₂H₄₀O₁₀N₂: C, 62.73; H, 6.58; N, 4.57%.

Gel Formation. Gels of monomers 10a and 11a were prepared as follows. At first, uniform solutions of a weighed monomer and a solvent were prepared in test tubes by heating. Then, the solutions were cooled in an ice bath. Gel formation was confirmed by their solidification. When the test tubes were turned upside down and the mixture inside did not come down, the mixture was decided to be gel.

Solid-State Polymerization. For UV-induced polymerization, UV at 254 nm from a 4-W lamp (UVP, UVG-11) was irradiated from a 1.5-cm distance. For γ -ray-induced polymerization, γ -ray from ⁶⁰Co was irradiated with a dose rate of 3.6 kGy h⁻¹ to degassed samples sealed in glass tubes. Conversions from a monomer to the corresponding polymer were obtained gravimetrically. Since the monomers can be dissolved in hexane, the polymerized samples were washed with hexane and the conversion was calculated from the mass ratio between the polymerized samples before and after washing with hexane.

We thank to Prof. Nobuyuki Tamaoki for his useful information on organic gels. We also thank to Prof. Atsuhiro Fujimori for his cooperation on the powder X-ray diffraction measurement. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 17067001) from the Ministry of Education, Culture, Sports, Science and Technology and a Grant-in-Aid for Challenging Exploratory Research (No. 21655048) from Japan Society for the Promotion of Science.

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