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Synthesis and Solid-State Polymerization of Triyne and Enediyne Derivatives with Similar π-Conjugated Structures

Kana Mizukoshi,[1] Shuji Okada,*[1] Tatsumi Kimura,[2] Satoru Shimada,[2] and Hiro Matsuda[2]

[1]Department of Polymer Science and Engineering, Graduate School of Science and Engineering,
Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510

[2]Photonics Research Institute, National Institute of Advanced Industrial Science and Technology,
Central 5-1, 1-1-1 Higashi, Tsukuba 305-8565

Received February 15, 2008; E-mail: okadas@yz.yamagata-u.ac.jp

Three diacetylene monomer model compounds with similar π-conjugation systems, 10-phenyl-5,7,9-decatriynyl *N*-phenylcarbamate (**1**), (*E*)-10-phenyldec-9-en-5,7-diynyl *N*-phenylcarbamate (**2**), and (*E*)-10-phenyldec-5-en-7,9-diynyl *N*-phenylcarbamate (**3**), were synthesized and their properties and solid-state polymerization were investigated. Based on the absorption spectra of the monomers, it was found that the conjugation effect of a double bond was different from that of a triple bond in solution. Monomers **1**, **2**, and **3** gave one, two, and five crystal forms, respectively, of which **1** and one of the crystal forms of **2** (**2a**) could be polymerized in the solid state. The conversions after γ-ray irradiation (1 MGy dose) were 53% and 20%, respectively. The longest-wavelength absorption maxima of the polymers prepared from **1** and **2a** were 645 and 655 nm, respectively. The polymerizable crystals **1** and **2a** were found to have layered monomer structures with spacing of 3.1–3.6 nm. Based on solid-state ^{13}C NMR spectra, the polymerization sites of **1** were determined to be the 1,4- and 3,6-positions with respect to the phenyl ring, and that of **2a** was determined to be the 3,6-position with respect to the phenyl ring.

Solid-state polymerization is a unique synthetic process for polymers, with the advantages of stereoregularity in topochemical synthesis, and environmental benignity, as no solvents are used in the reaction. When this polymerization process is applied to certain butadiyne derivatives, polydiacetylenes (PDAs) are obtained as single-crystalline polymers.[1,2] These have been considered for a variety of applications due to their π-conjugated polymer backbone structures. Color change in PDAs originates from an order–disorder transformation of the conjugated backbone structure in solution, the molecular aggregate and crystalline states,[3–7] and it has recently been applied in bio- and chemo-sensing.[8,9] Topochemical PDA synthesis has been used to obtain molecular wires.[10] Uniquely among conjugated polymers, significant third-order nonlinear optical (NLO) properties have been reported for PDAs;[11] thus, ultrafast NLO response[12] and device applications[13] have been the subject of extensive investigation.

In our studies on PDAs, we have investigated π-conjugation between the polymer backbone and the substituents,[14–20] because these effects are thought to result in an extension of effective π-conjugation, causing enhanced NLO properties.[21] When oligoyne derivatives with more than three conjugated acetylene groups were used, we obtained PDAs with acetylenic substituents.[19,20] However, 1,4-addition polymerization occurred at the butadiyne section at the end of the conjugated acetylenes in the presence of alkyl-type substituents, and regioselective polymerization was reported only for an asymmetrically substituted phenyloctatetrayne derivative.[22]

Compounds **1–3**, shown in Figure 1, have similar π-conjugation systems consisting of a benzene ring and three C–C multiple bonds. Solid-state polymerization in these compounds was expected to proceed in the diyne moieties, because solid-state polymerization of butenyne derivatives has not yet been reported. Thus, by controlling the polymerization site, we may prepare polymers with several π-conjugated systems from monomers with similar conjugation systems, as shown in Figure 1. In order to investigate this, we synthesized model compounds **1–3**. A phenylurethane group was introduced as a common substituent, as this group has often been found to give solid-state polymerizable butadiyne and oligoyne derivatives.[23–25] The properties of these monomers, including solid-state polymerizability, were then investigated.

Results and Discussion

Monomer Synthesis. Monomers **1**, **2**, and **3** were synthesized according to the procedures shown in Figures 2, 3, and 4, respectively. Compound **6** was synthesized by a coupling reaction between ethynylbenzene (**4**) and 4-bromo-2-methyl-3-butyn-2-ol (**5**) in 83% yield (Figure 2). This compound was also prepared by a coupling reaction between 2-methyl-3-butyn-2-ol (**10**) and 1-bromo-2-phenylethyne (**19**), but in this case the yield of **6** was 58%, which was 25% lower than that obtained from the reaction between **4** and **5**, and a considerable amount of diphenylbutadiyne (**21**) was obtained as a by-product from the self-coupling reaction of **19**. In order to synthesize **1**, phenylbutadiyne (**7**) and 6-bromo-5-hexyn-1-ol (**8**) were coupled to form 10-phenyl-5,7,9-decatriyn-1-ol (**9**) (Figure 2). We also attempted to prepare **9** by a coupling reaction between 5,7-octadiyn-1-ol (**22**) and **19**, but in this case the polarity of starting material **22** was quite similar to that of the product **9**, so that

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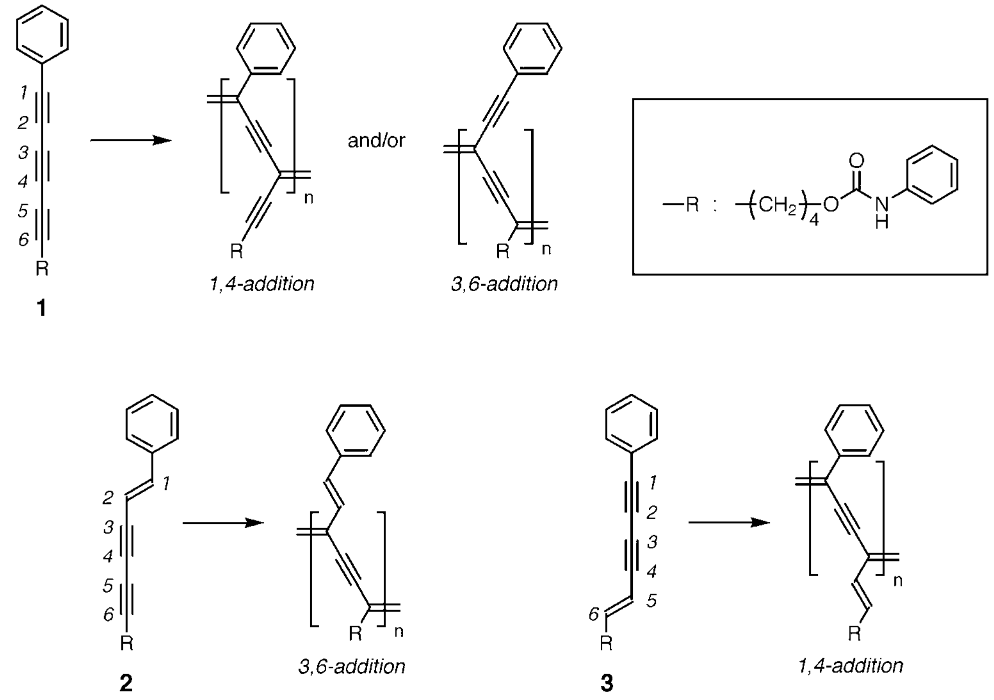

Figure 1. Chemical structures of model compounds **1**–**3** and possible schemes for polymerization in the solid state. In this study, the polymerization positions are counted from the phenyl-substituted end for all compounds, as indicated above.

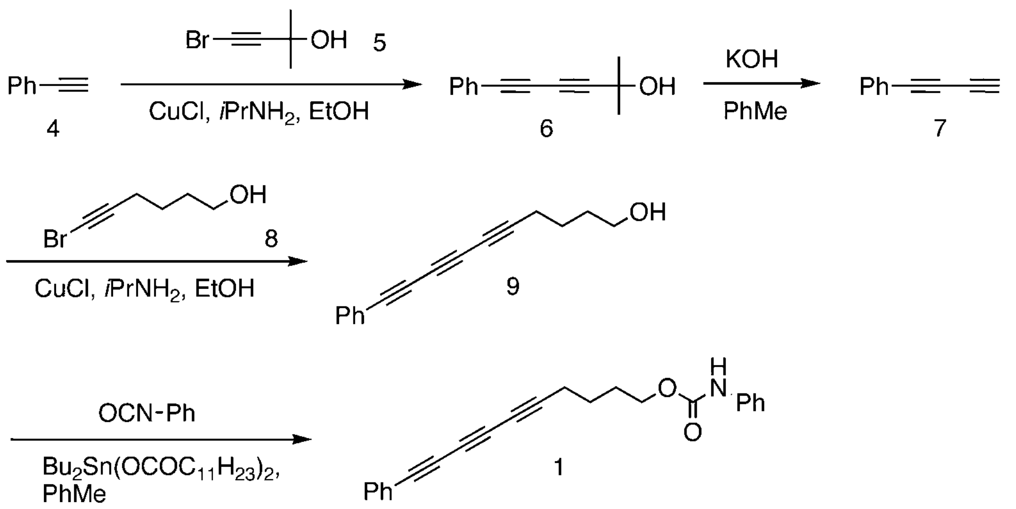

Figure 2. Synthesis scheme of **1**.

separation using conventional column chromatography was difficult. In addition, the yield of **9** was low because the self-coupling reaction of **19** occurred predominantly to give diphenylbutadiyne (**21**) in 62% yield. For these reasons, we selected the synthesis scheme shown in Figure 2.

Because compound **11** was commercially available only as an E/Z mixture, all products prepared in the following reactions (Figure 3) were also E/Z mixtures. In addition to this, 5-hexyn-1-ol (**23**) was produced after the reaction of **13** and **8** to synthesize **14**, although the mechanism by which **23** was produced from **8** was unclear. Separation of the E isomer of **14** from the corresponding Z isomer and **23** by conventional column chromatography was quite difficult. To overcome this difficulty, the mixture was successively reacted with phenyl isocyanate and, at the final stage, the E isomer of **2** was isolated by repeated recrystallization from ether.

The problem of the E/Z mixture also occurred in the synthesis of **3** (Figure 4). When ring-opening reaction of **17** was carried out using a strong base, an E/Z mixture of **18** was obtained. In this reaction, the use of potassium amide rather than sodium amide resulted in a better yield of **18**.[26] Although subsequent reactions were carried out using the E/Z mixture, the E isomer of **3** was finally isolated by repeated recrystallization from ether, as in the case of **2**.

Characterization of Monomers in Solution. All of the monomer structures were confirmed by ^1H and ^{13}C NMR spectroscopy and elemental analysis (see the Experimental section and Table 1, respectively). UV spectra were used to

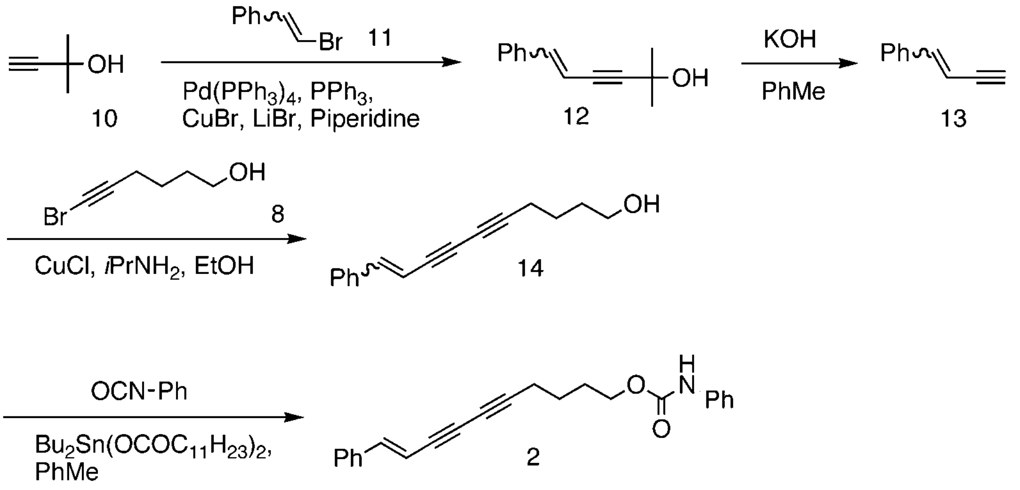

Figure 3. Synthesis scheme of **2**.

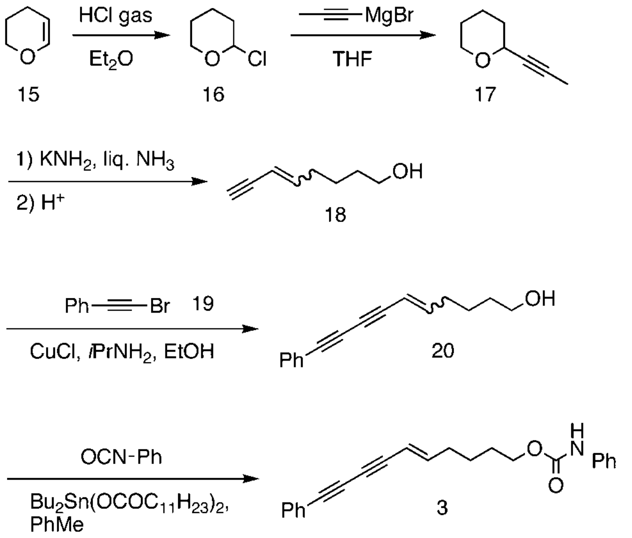

Figure 4. Synthesis scheme of **3**.

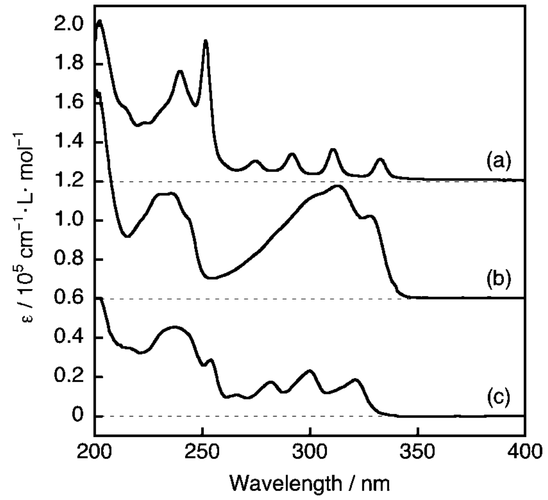

Figure 5. UV absorption spectra of (a) **1**, (b) **2**, and (c) **3** in ether. The base lines of **1** and **2** are shifted by 0.6×10^{-5} and $1.2 \times 10^{-5}\,\mathrm{cm^{-1}\,L\,mol^{-1}}$, respectively.

Table 1. Elemental Analysis, Melting Points, Characteristic IR Peaks, and UV-Induced Color Changes of Monomers **1**, **2**, and **3**

Compound	Polymorph	Elemental analysis[a]/%			Melting point/°C	Wavenumber/cm^{-1}		Color change[b]
		C	H	N		$\nu_{C\equiv C}$	$\nu_{C=O}$	
1		80.68	5.31	4.08	100	2213, 2190	1697	Blue
2	**2a**	80.54	6.12	4.03	115	—[c]	1697	Blue
	2b	80.19	6.03	4.02	115	—[c]	1705	Yellow
3	**3a**	80.58	6.05	4.10	106	2214	1701	Yellow
	3b	80.37	6.10	4.06	106	—[c]	1701	Yellow
	3c	80.69	6.05	4.10	80–90[d]	2214	1697	Red

a) Calculated values for **1**: C, 80.92; H, 5.61; N, 4.10%. Calculated values for **2** and **3**: C, 80.44; H, 6.16; N, 4.08%. b) After UV irradiation. c) Not detected. d) In this range, there is an endothermic peak followed by an exothermic peak, corresponding to the transition from **3c** to **3d**.

obtain information on monomer π-conjugation systems, as shown in Figure 5. The monomer spectra showed different features. The order of the longest-wavelength peaks was **1** (333 nm) > **2** (328 nm) > **3** (321 nm). When we compare the absorption peaks at wavelengths longer than 260 nm, fine structure was observed for **1**, although the ε values were small. On the other hand, **2** shows relatively broad peaks, but the largest peak was observed for **2** ($\varepsilon = 5.79 \times 10^4\,\mathrm{cm^{-1}\,L\,mol^{-1}}$ at 313 nm). The spectral shape of **3** seems to be intermediate between these two. It was concluded that double and triple bonds showed different conjugation effects in solution. It is known that conjugated polyyne compounds show absorption

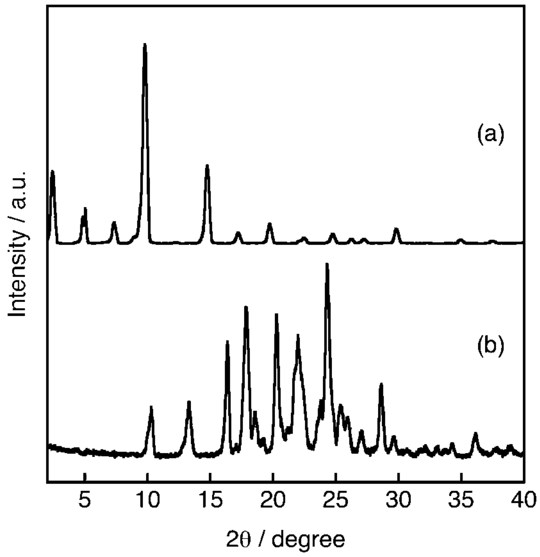

Figure 6. Powder X-ray diffractograms of (a) **2a** and (b) **2b**.

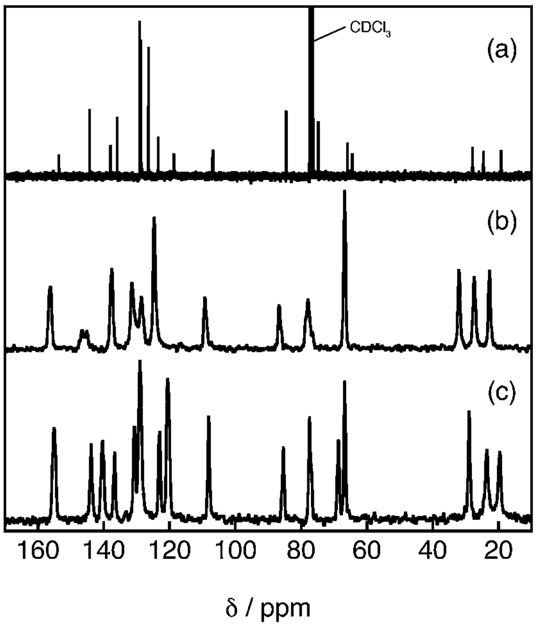

Figure 7. ^{13}C NMR spectra of (a) **2** in CDCl$_3$ and (b) **2a** and (c) **2b** in the solid state using the TOSS pulse sequence.

Table 2. ^{13}C Peaks of Monomer **2** Observed in the Upfield Region[a)]

δ/ppm			Assignment[b),c)]
2 in CDCl$_3$	**2a**	**2b**	
19.14	22.8	19.6	a
24.58	27.4	24.3	b
27.92	32.0	28.9	c

a) The full spectra are shown in Figure 7. b) Referring the ^{13}C NMR spectrum of 5-hexyn-1-ol (SDBS Web: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology)). c) $\equiv\mathrm{C{-}\underset{a}{C}H_2{-}\underset{b}{C}H_2{-}\underset{c}{C}H_2{-}}$.

spectra with fine structures[27] and ε values of conjugated polyene compounds are larger than the corresponding polyyne compounds in the long-wavelength region.[28] Similar tendency was also observed in the present case. We recently found that there was a large difference in the solution absorption spectra of diyne and diene compounds substituted by two aromatic rings.[29] This was explained as being due to the ease of rotation of the aromatic ring in the diyne compound, which results in less conjugation between the aromatic rings at each end. However, in the present case, the compounds have only one aromatic ring and the effect of aromatic ring rotation in the triyne compound seemed to be ignored.

Characterization of Monomer Crystals. Monomer **1** was obtained as colorless needle-shaped crystals from chloroform solution by cooling. Monomer **2** exhibited polymorphism, which was confirmed by powder X-ray diffraction patterns (Figure 6). Colorless needle-shaped crystals of **2a** were obtained from methanol solution by the cooling method, while **2b** was obtained as a white powder from ether solution by slow evaporation. Figure 7 compares the ^{13}C NMR spectra of **2** in deuterated chloroform solution with those of the two polymorphs in the solid state, and the methylene carbon chemical shifts in the upfield region are tabulated in Table 2. The chemical shifts of **2b** in Table 2 are found upfield of those of **2a**. However, the peak positions of **2b** and **2** in solution are similar, which indicates that the molecules are more loosely packed in **2b** than in **2a**.

Polymorphism was also observed for monomer **3**, although it was much more complicated. From methanol solution, two types of colorless needle-shaped crystals **3a** and **3b** and plate crystals **3c** were grown by the cooling method. Type **3c** transformed irreversibly to **3d** in the temperature range from 80 to 90 °C. When **3d** was melted at 105 °C and cooled to ambient temperature, **3e** was obtained. Powder X-ray diffraction patterns of the five crystalline forms of **3** are shown in Figure 8. The different diffraction patterns obtained clearly indicated five polymorphs. Some phenylurethane-substituted butadiyne derivatives are know to show polymorphism,[30,31] and bis(3-quinolyl)butadiyne has been found to show three types.[32] Thus, polymorphism in butadiyne derivatives is not unusual. However, five modifications in one compound are rare.

Solid-State Polymerization. The monomer crystals were subjected to UV irradiation to investigate polymerization. Upon irradiation, **1** and **2a** turned blue due to production of polydiacetylene structures via regular 1,4-addition polymerization. However, the other crystals became yellow. Figure 9 shows diffuse reflectance spectra of **1** in the visible region after various periods of UV irradiation. After 2 min irradiation, peaks appeared at 645 and 600 nm. These peaks became more intense as irradiation continued up to about 20 min. Finally, the spectral edge reached ≈800 nm.

Diffuse reflectance spectra of **2a** and **2b** after UV irradiation are shown in Figure 10. Although **2a** shows peaks at 655 and 590 nm, **2b** shows only an increase in the visible region less than ≈600 nm. The changes in the spectra of the five polymorphs of **3** were similar to those observed for **2b**. Since conventional polydiacetylenes generally show an absorption peak at wavelengths shorter than 640 nm, it was thought that the π-conjugated systems had been extended in **1** and **2a** due to π-

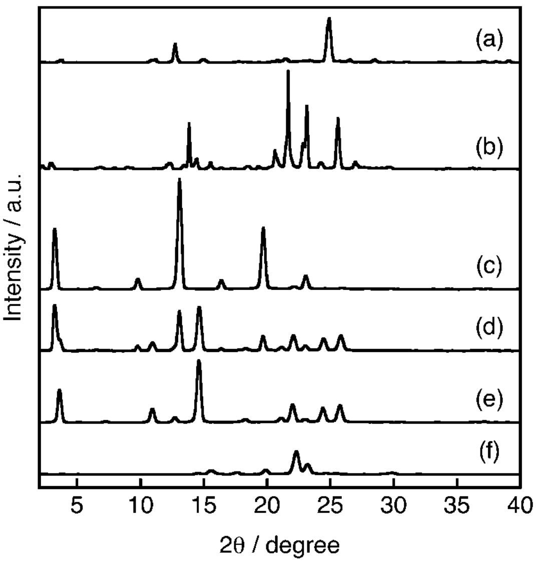

Figure 8. Powder X-ray diffractograms of (a) **3a**, (b) **3b**, (c) **3c**, (d) **3c** heated at 77 °C accompanied by newly formed **3d**, (e) **3d** obtained by heating **3c** at 90 °C and (f) **3e** obtained by cooling after melting.

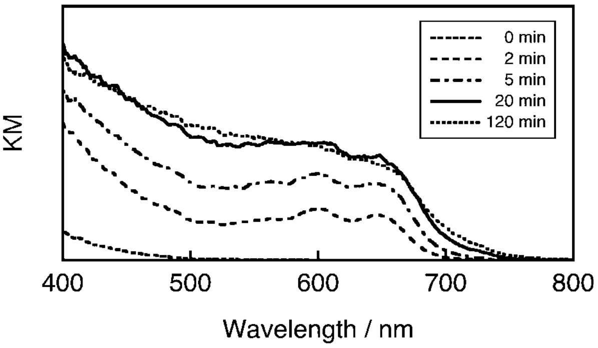

Figure 9. Variation in diffuse reflectance spectra of **1** with UV irradiation time.

conjugation between the polymer backbone and the substituents. Although polymerization of styryl-substituted butadiyne has been reported for 1,6-diphenylocta-1,7-dien-3,5-diyne derivatives in the liquid-crystalline state,[33] this is the first example, to our knowledge, of polymerization of styryl-substituted butadiyne in the crystalline state to give polydiacetylene. Changes in absorption similar to those observed for **2b** and **3a**–**3e** have often been observed for compounds with irregular polymerization or oligomerization, irrespective of conversion.[34,35]

In the polymerization of monomer **1** by UV irradiation, the conversion was determined to be about 40% based on the decrease in the absorbance of the $\nu_{C\equiv C}$ band in the IR spectra. Since UV cannot usually penetrate samples completely due to absorption and scattering, the samples were then subjected to γ-ray irradiation (1 MGy). In this case, the conversions obtained by gravimetric analysis were 53%, 20%, and 0% for **1**, **2a**, and **2b**, respectively. Similarly to **2b**, not all of the polymorphs of **3** yielded polymers, which were defined as solid portions insoluble in monomer-soluble ethyl acetate.

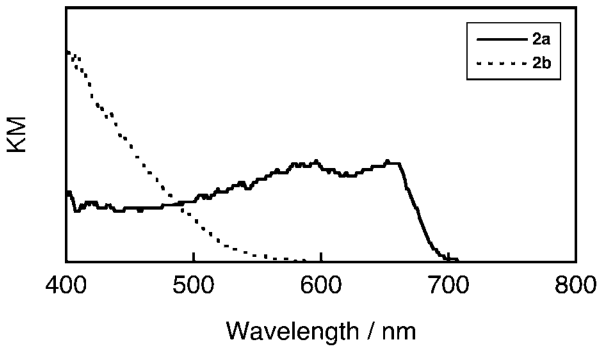

Figure 10. Diffuse reflectance spectra of **2a** and **2b** after UV irradiation.

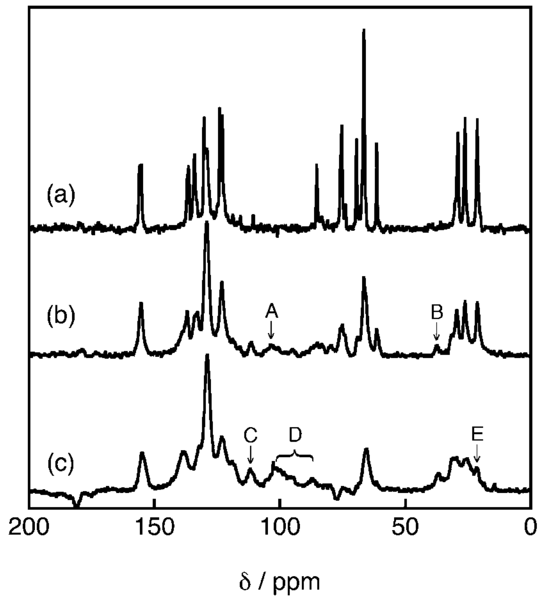

Figure 11. Solid-state ^{13}C NMR spectra (TOSS) of (a) **1**, (b) **1** after γ-ray irradiation (1 MGy), and (c) the isolated polymer, obtained as the part of the γ-irradiated sample insoluble in ethyl acetate. Peaks A and B in spectrum (b) are assigned as the sp-carbon in the polydiacetylene backbone and the methylene carbon attached to the polymer backbone, respectively. Peaks C, D, and E in spectrum (c) correspond to the sp^2-carbon in the polydiacetylene backbone, sp-carbons in the side chains and the sp^3-carbon attached to the acetylenic moiety, respectively.

In order to confirm the polymer structures, solid-state ^{13}C NMR spectra were measured for the polymers obtained from **1** and **2a** (Figures 11 and 12, respectively). In both figures, the upper spectra (a) are of the monomers, and the spectra in the middle (b) are of the samples after 1 MGy γ-ray irradiation. The γ-irradiated samples were then washed with ethyl acetate to remove the remaining monomer, and the spectra of the resulting polymers are shown in (c). Despite the polymerization reaction, the signals assigned to the phenyl groups and methylenes away from the polymerization site did not show significant changes. However, a prominent difference between spectra (a) and (b) in both cases is the appearance of new peaks at around 103 ppm (indicated as peak A) and around 37 ppm (peak B) in spectra (b). Peaks A and B appear

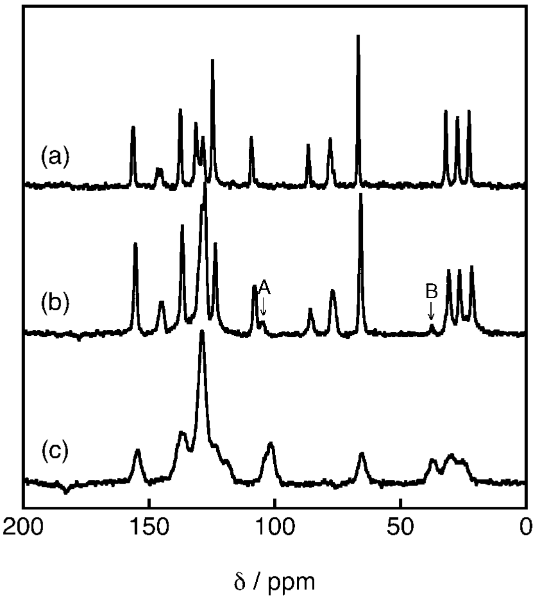

Figure 12. Solid-state ^{13}C NMR spectra (TOSS) of (a) **2a**, (b) **2a** after γ-ray irradiation (1 MGy) and (3) the isolated polymer, obtained as the part of the γ-irradiated sample insoluble in ethyl acetate. Peaks A and B in spectrum (b) are assigned as the sp-carbon in the polydiacetylene backbone and the methylene carbon attached to the polymer backbone, respectively.

even in spectra (c), indicating that they are due to the polymers. As it has been confirmed that the sp-carbon in the polydiacetylene backbone generally appears in the range from 100 to 110 ppm,[19,20,36–39] peak A can be assigned as the acetylenic carbon in the polymer backbone. In addition, peak B, in the aliphatic carbon region, corresponds to a newly formed sp^3-carbon next to the polymer backbone.[19,20,40,41] Based on this information, it was concluded that polymerization proceeds at the 3,6-position with respect to the phenyl ring in both **1** and **2a**, as shown in Figure 1. In contrast, in the spectrum of the polymer obtained from **1** after extraction of the monomers, there is a peak around 22 ppm (indicated by E in Figure 11c). Monomers **1** and **2a** also show a peak at around 22 ppm and these peaks are assigned as sp^3-carbons directly attached to the acetylenic moiety. Thus, polymer **1** contains the same type of carbon. As this means that polymerization took place without loss of the aliphatic carbons next to the acetylene moieties, it was concluded that **1** also undergoes polymerization at the 1,4-position with respect to the phenyl ring. 1,4-Addition polymerization of **2a** was concluded not to have taken place because no peak around 22 ppm was observed in the spectrum after removal of the monomer (Figure 12c). Referring to the data of a polymer from triyne,[19] peak C at 112 ppm and peaks D in the range from 80 to 105 ppm of polymer **1** (Figure 11c) can be assigned as the olefinic carbon in the polymer backbone and the acetylenic carbons in the side chain, respectively.

Among the eight crystal forms investigated in this study, only **1** and **2a** showed solid-state polymerizability. Criteria for polymerizability in butadiyne derivatives have been crystallographically established: the distance between adjacent monomers along the translation direction must be about 0.5 nm, and the angle (ϕ) between the butadiyne moiety and the translation direction is about 45°.[2] To create polymerizable stacks in the crystalline form for molecules like **1**–**3**, layered structures are often essential. Typical examples are amphiphilic butadiyne derivatives in Langmuir–Blodgett films[42,43] and other crystalline butadiyne derivatives with methylene chains.[44] Table 3 summarizes 2θ of the X-ray diffraction peaks, which correspond to the progression related to the interlayer spacing d. The polymerizable crystal **2a** shows an X-ray diffraction pattern with progression, corresponding to a layered structure (Figure 6a) with interlayer spacing (d) of 3.61 nm. The polymerizable crystal **1** showed a similar diffraction pattern to **2a**, with a d value of 3.14 nm. In contrast, **2b** did not show a clear diffraction pattern corresponding to a layered structure (Figure 6b). Similarly, **3a**, **3b**, and **3e** do not have layered structures (Figures 8a, 8b, and 8f, respectively), and they do not undergo polymerization. Layered crystal structures were observed for **3c** and **3d** (Figures 8c and 8e, respectively); however, the d values are 2.71 and 2.42 nm, respectively, which are smaller than those of **1** and **2a**. Figure 13 shows molecular orientation models for **1** in the layered structure, and similar molecular arrangements were also considered for **2** and **3**. In this figure, d is the interlayer spacing, L is the length of the molecular long axis, ψ is the molecular tilting angle, which is defined as the angle between the layered plane and the long axis of the molecule, and ϕ is one of the packing parameters for solid-state polymerization of butadiyne moieties mentioned above. Since compounds **1**–**3** have a kink in the molecular structures, ϕ can be varied as shown in Figure 13, in which model A is for the smallest ϕ and model B is for the largest ϕ. From the optimized molecular structures obtained by a semiempirical calculation, ψ and ϕ were roughly estimated (Table 4). Angle ψ becomes large in the following order: **2a** < **1** < **3c** < **3d**. If the molecular arrangement like model B were realized for **3c** and **3d** to give ϕ of about 45°, they could be polymerized. Actually, however, **3c** and **3d** do not polymerize, and their monomer alignments in crystals deviate from polymerizable conditions.

Table 3. 2θ of the X-ray Diffraction Peaks Assigned to the Progression Related to the Interlayer Spacing d

Order of diffraction	**1**	**2a**[a)]	**3c**[b)]	**3d**[c)]
1	2.78	2.38	3.22	3.60
2	5.56	4.88	6.46	7.28
3	8.40	7.34	9.80	10.94
4	11.28	9.78	13.08	14.06
5	—[d)]	12.24	16.36	18.30
6	16.96	14.74	19.70	22.00
7	19.88	17.20[e)]	23.04	25.74

a) The diffractogram is shown in Figure 6a. b) The diffractogram is shown in Figure 8c. c) The diffractogram is shown in Figure 8e. d) The peak was too weak. e) Peaks were observed up to the fifteenth diffraction.

Conclusion

We prepared phenyl-substituted triyne **1** and two types of enediynes **2** and **3** as model compounds with similar π-conjugated systems. The shapes of the absorption spectra of the monomers were quite different, and the conjugation effects of double and triple bonds were found to be different in the so-

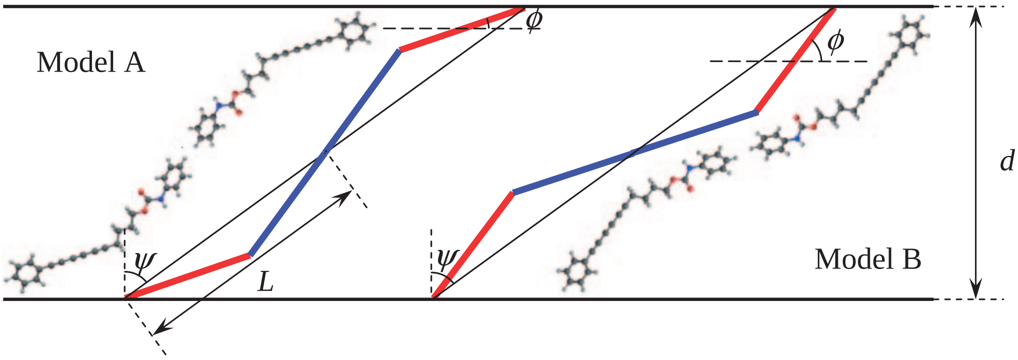

Figure 13. Molecular orientation models for **1** in the layered structure. Red and blue thick lines indicate phenylhexatriynyl group and methylene chain with phenylurethane group, respectively, and the corresponding molecular models are displayed beside these lines.

Table 4. Interlayer Spacing d, Molecular Length L, and Estimated Angles ψ and ϕ

Crystal	$d^{a)}$/nm	$L^{b)}$/nm	$\psi^{c)}$/°	$\phi^{d)}$/°
1	3.14	2.66	54	19–53
2a	3.61	2.64	47	28–58
3c	2.71	2.64	59	16–46
3d	2.42	2.64	63	12–42

a) Obtained from X-ray diffraction experiments (see Table 3). b) Calculated using PM3 in MOPAC 2002 (ver. 2.5.0). c) $\psi = \cos^{-1}(d/2L)$. d) Left and right numbers correspond to the angles for models A and B in Figure 13, respectively.

lution state. Although monomer **1** gave polymerizable crystals, monomer **2** gave two types of crystal, one polymerizable (**2a**) and the other not polymerizable (**2b**). Monomer **3** was found to give five polymorphs **3a**–**3e** that could not be polymerized. X-ray powder diffraction measurements showed that the crystals of the polymerizable monomers **1** and **2a** had layered structures with spacings in the range 3.1–3.6 nm. The polymer absorption maxima of **1** and **2a** were observed at around 650 nm. The conversions of **1** and **2a** after 1-MGy γ-ray irradiation were 53% and 20%, respectively. It was found that polymerization of **1** occurred at both the 1,4- and 3,6-positions with respect to the phenyl ring, while that of **2a** proceeded only at the 3,6-position. This result indicates that the solid-state polymerization site within conjugated multiple bonds can be controlled by the introduction of a double bond next to the polymerizable butadiyne moieties when appropriate monomer arrangements for solid-state polymerization are obtained in crystals.

Experimental

Apparatus. Melting points were measured using a Yanaco MP-500P micro-melting-point apparatus and are uncorrected. Differential thermal analysis was performed using an SII TG/DTA 220 analyzer. UV–visible spectra were measured using a Jasco V-570 spectrophotometer, which was equipped with an integration sphere (Jasco ILN-472) for diffuse reflectance spectrum measurement. IR spectra were recorded on a Horiba FT-210 spectrometer. NMR spectra were obtained using Jeol EX-270 and ECX-400 spectrometers for solution-state spectra and an ECX-400 spectrometer for solid-state spectra. For solution-state measurements, tetramethylsilane was used as an internal standard. In solid-state ^{13}C NMR measurements, CP/MAS, dipolar dephasing and TOSS (total suppression of spinning sidebands) pulse sequences were used to assign peaks. The methylene carbon of adamantane at 29.5 ppm was used as an external standard. Powder X-ray diffraction patterns were recorded on a Rigaku RINT-Ultima III diffractometer using a Cu Kα source. Elemental analysis was performed using a Perkin-Elmer 2400II analyzer.

Preparation of Compounds. **2-Methyl-6-phenyl-3,5-hexadiyn-2-ol (6):** To a mixture of copper(I) chloride (0.30 mg, 3 mmol), isopropylamine (150 mL), and ethanol (90 mL), ethynylbenzene (**4**) (10.2 g, 100 mmol) was added under a nitrogen atmosphere, and 25.0 g (80 mmol) of 4-bromo-2-methyl-3-butyn-2-ol[45] (**5**) was then added dropwise for 6 h. When the color of the reaction mixture became deep green, hydroxylamine hydrochloride was added until the color changed to yellow. After addition of **5** was completed, the reaction mixture was further stirred for 18 h. The solvent was removed under reduced pressure and water was added to the residue for extraction with ether. The ether layer was collected and dried over anhydrous magnesium sulfate. After filtration to remove the solid portion, the solvent in the filtrate was evaporated and the residue was purified by column chromatography (silica gel, chloroform) to give 12.2 g (83%) of **6** as yellow solid: δ_H (400 MHz, CDCl$_3$): 1.58 (6H, s), 1.99 (1H, br s), 7.28–7.39 (3H, m), 7.48 (2H, d, $J = 7.7$ Hz); δ_C (100 MHz, CDCl$_3$): 31.07, 65.70, 67.01, 73.11, 78.75, 86.66, 121.49, 128.38, 129.20, 132.47.

Phenylbutadiyne (7): Alcohol **6** (6.00 g, 33 mmol) was dissolved in benzene (60 mL) and 1.45 g of powdered potassium hydroxide was added. The mixture was refluxed for 1 h and filtered. The solvent of the filtrate was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, chloroform) to give 2.90 g (71%) of **7** as a brown viscous oil: δ_H (400 MHz, CDCl$_3$): 2.47 (1H, s), 7.29–7.41 (3H, m), 7.51 (2H, d, $J = 7.5$ Hz); δ_C (100 MHz, CDCl$_3$): 68.08, 71.27, 73.46, 75.32, 121.05, 128.52, 129.60, 132.84.

10-Phenyl-5,7,9-decatriynyl *N*-Phenylcarbamate (1): To a mixture of copper(I) chloride (100 mg), isopropylamine (36 mL), and ethanol (20 mL), **7** (2.90 g, 23 mmol) was added under a nitrogen atmosphere. 6-Bromo-5-hexyn-1-ol (**8**) (3.54 g, 20 mmol) was then added dropwise for 90 min. When the color of the reaction mixture became deep green, hydroxylamine hydrochloride was added until the color turned to yellow. After addition of **8** was completed, the reaction mixture was further stirred for 17 h, and the solvent was removed under reduced pressure. Water was added to the residue for extraction with ether. The ether layer was collected and dried over anhydrous magnesium sulfate. After filtration, the solvent in the filtrate was evaporated to give 4.44 g of brown viscous oil. This residue was found to contain **8** and 10-phenyl-5,7,9-decatriyn-1-ol (**9**), which were difficult to separate by column chromatography because of their similar polarities. Thus, the mixture was used in the subsequent reaction.

The mixture of **8** and **9** (4.40 g) and phenyl isocyanate (3.00 g, 26 mmol) were dissolved in 100 mL of toluene under a nitrogen atmosphere. To this solution, two drops of dibutyltin dilaurate were added, and the mixture was stirred for 1 h at ambient temperature. The solvent was then evaporated and the residue was purified by column chromatography (silica gel, chloroform). After recrystallization from hexane–chloroform mixed solvent, 2.40 g (36% from **7**) of **1** was obtained as colorless solid: $\delta_{\rm H}$ (400 MHz, $CDCl_3$): 1.69 (2H, tt, $J = 7.7$, 7.1 Hz), 1.81 (2H, tt, $J = 7.7$, 6.2 Hz), 2.42 (2H, t, $J = 7.1$ Hz), 4.20 (2H, t, $J = 6.2$ Hz), 6.60 (1H, br s), 7.07 (1H, tt, $J = 7.2$, 1.4 Hz), 7.28–7.41 (7H, m), 7.50 (2H, dtt, $J = 7.0$, 2.3, 1.3 Hz); $\delta_{\rm C}$ (100 MHz, $CDCl_3$): 19.23, 24.51, 28.02, 59.83, 64.42, 66.16, 67.09, 74.49, 75.59, 81.69, 118.63, 120.99, 123.41, 128.41, 129.01, 129.50, 132.91, 137.78, 153.50.

2-Methyl-6-phenylhex-5-en-3-yn-2-ol (12): 1-Bromo-2-phenylethene (**11**) (E:Z = 1:0.16, 26.8 g, 146 mmol), tetrakis(triphenylphosphine)palladium(0) (441 mg), and triphenylphosphine (220 mg) were mixed and stirred for a few minutes at ambient temperature under a nitrogen atmosphere.[45] To this mixture, piperidine (100 mL), 2-methyl-3-butyn-1-ol (**10**) (14.8 g, 176 mmol), and copper(I) bromide (220 mg) were added, and the mixture was stirred for 30 min. Finally, lithium bromide (700 mg) was added, and the mixture was further stirred for 90 min. After removal of the volatile portion of the reaction mixture under reduced pressure, water was added to the residue and the mixture was extracted with ether. The collected ether layer was washed twice with 2 mol L^{-1} hydrochloric acid solution and dried over anhydrous magnesium sulfate. The solid portion was removed by filtration, and the solvent in the filtrate was removed under reduced pressure. The residue was then purified by column chromatography (silica gel, chloroform) to give 18.7 g (68%) of **12** (containing less than 10% Z isomer) as brown viscous oil. NMR spectral data for the E isomer are as follows: $\delta_{\rm H}$ (270 MHz, $CDCl_3$): 1.58 (6H, s), 2.06 (1H, br s), 6.16 (1H, d, $J = 16.3$ Hz), 6.93 (1H, d, $J = 16.3$ Hz), 7.24–7.41 (5H, m); $\delta_{\rm C}$ (100 MHz, $CDCl_3$): 31.36, 65.64, 81.32, 96.03, 107.66, 126.30, 128.68, 128.78, 136.26, 141.49.

1-Phenylbut-1-en-3-yne (13): To a solution of **12** (7.3 g, 38 mmol) in toluene (100 mL), powdered potassium hydroxide (2.0 g) was added, and the mixture was heated at 80 °C for 1 h. The reaction mixture was filtered and solvent in the filtrate was removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane–ethyl acetate (4:1)) to give 4.5 g (90%) of **13** as pale orange liquid: $\delta_{\rm H}$ (270 MHz, $CDCl_3$): 3.05 (1H, d, $J = 2.4$ Hz), 6.13 (1H, dd, $J = 16.3$, 2.4 Hz), 7.05 (1H, d, $J = 16.3$ Hz), 7.27–7.45 (5H, m); $\delta_{\rm C}$ (67.5 MHz, $CDCl_3$): 79.23, 84.12, 107.05, 126.43, 128.37, 128.84, 135.95, 143.25.

(*E*)-10-Phenyldec-9-en-5,7-diynyl *N*-Phenylcarbamate (2): To a mixture of copper(I) chloride (300 mg), isopropylamine (94 mL), and ethanol (100 mL), **13** (4.5 g, 35 mmol) was added under a nitrogen atmosphere, followed by **8** (7.4 g, 42 mmol), which was added dropwise for 1 h. When the color of the reaction mixture changed to deep green, hydroxylamine hydrochloride was added until the color turned to yellow. After addition of **8** was completed, the reaction mixture was further stirred for 17 h, and the solvent was evaporated. Water was added to the residue and the mixture was extracted with ether. The ether layer was collected, washed twice with dilute hydrochloric acid, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to give brown viscous oil. This residue contained the E and Z isomers of 10-phenyldec-9-en-5,7-diyn-1-ol (**14**), with 5-hexyn-1-ol as a by-product. These three compounds were difficult to separate by column chromatography, and thus the mixture was used for subsequent reactions.

The above mixture (5.0 g) and phenyl isocyanate (2.7 g, 23 mmol) were placed in 50 mL of toluene under a nitrogen atmosphere. To this, two drops of dibutyltin dilaurate were added, and the mixture was stirred for 3.5 h at ambient temperature. The solvent was then evaporated. At this stage, separation of the compounds by column chromatography was still difficult. After repeated recrystallization from ether, only the E isomer of **2** (2.5 g, 21% from **13**) was obtained: $\delta_{\rm H}$ (270 MHz, $CDCl_3$): 1.68 (2H, tt, $J = 6.8$, 6.8 Hz), 1.82 (2H, tt, $J = 6.8$, 6.8 Hz), 2.43 (2H, t, $J = 6.8$ Hz), 4.21 (2H, t, $J = 6.8$ Hz), 6.16 (1H, d, $J = 16.4$ Hz), 6.58 (1H, br s), 7.06 (1H, d, $J = 16.4$ Hz), 7.07 (1H, tt, $J = 6.2$, 1.4 Hz), 7.27–7.43 (9H, m); $\delta_{\rm C}$ (67.5 MHz, $CDCl_3$): 19.14, 24.58, 27.92, 64.49, 65.84, 74.73, 76.41, 84.53, 106.83, 118.70, 123.44, 126.39, 128.80, 129.09, 129.14, 135.88, 137.94, 144.22, 153.67.

2-(1-Propynyl)tetrahydropyran (17):[26,45] To a 0.5 mol L^{-1} tetrahydrofuran (THF) solution of 1-propynylmagnesium bromide (240 mL), 2-chlorotetrahydropyran (**16**)[45,46] (11.2 g, 93 mmol) was added dropwise over a few minutes at −15 °C. After addition was completed, the cooling bath was removed and the reaction mixture was stirred for 14 h. To this, saturated ammonium chloride solution was added, and the mixture was extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and filtered, following which the solvent was evaporated to give 9.2 g (80%) of **17** as a pale yellow oil: $\delta_{\rm H}$ (400 MHz, $CDCl_3$): 1.45–2.00 (6H, m), 1.86 (3H, d, $J = 2.3$ Hz), 3.50 (1H, m), 3.98 (1H, m), 4.19 (1H, ddd, $J = 8.3$, 2.4, 2.4 Hz).

Oct-5-en-7-yn-1-ol (18):[26,45] Dried ammonia gas was introduced to a four-necked flask cooled to −78 °C, and about 400 mL of liquid ammonia was collected. A piece of iron(III) nitrate was added, and 19.6 g (500 mmol) of potassium in small pieces was added over 6 h. After addition of potassium was completed, the cooling bath was removed to allow completion of the reaction of potassium with ammonia under reflux conditions. The cooling bath was then reattached, and **17** (13.0 g, 105 mmol) was added dropwise for 30 min. The reaction mixture was stirred for 20 min, and then for a further 10 h after removal of the cooling bath. During this period, most of the ammonia was vaporized. Water was added to the residue and the mixture was extracted with ether. The collected ether layer was dried over anhydrous magnesium sulfate, the drying agent was removed by filtration, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform) to give 11.0 g (84%) of **18** (E:Z = 1:0.57) as pale yellow oil. NMR spectral data for the E isomer are as follows: $\delta_{\rm H}$ (400 MHz, $CDCl_3$): 1.43–1.66 (4H, m), 1.77 (1H, br s), 2.16 (2H, ddt, $J = 7.0$, 1.3, 7.2 Hz), 2.79 (1H, d, $J = 2.3$ Hz), 3.64 (2H, t, $J = 7.0$ Hz), 5.47 (1H, ddt, $J = 15.9$, 2.3, 1.3 Hz), 6.24 (1H, dt, $J = 15.9$, 7.0 Hz); $\delta_{\rm C}$ (100 MHz, $CDCl_3$): 24.58, 31.81, 32.53, 62.17, 75.73, 81.34, 108.71, 146.20.

10-Phenyldec-5-en-7,9-diyn-1-ol (20): To a mixture of copper(I) chloride (440 mg), isopropylamine (137 mL), and ethanol (100 mL), **18** (11.0 g, 89 mmol) was added under a nitrogen atmosphere; then, 1-bromo-2-phenylethyne (**19**) (16.1 g, 89 mmol) was added dropwise for 4.5 h. When the color of the reaction mixture changed to deep green, hydroxylamine hydrochloride was added until the color turned to yellow. After addition of **19** was completed, the reaction mixture was further stirred for 17 h, and the solvent was removed under reduced pressure. Water was added to the residue and the mixture was extracted with ether. The ether layer was collected and dried over anhydrous magnesium sulfate. The solvent was then evaporated and the residue was purified by column chromatography (silica gel, chloroform) to give 12.5 g (63%) of **20** (E:Z = 1:0.54) as yellow viscous oil. NMR spectral data for the E isomer are as follows: δ_H (400 MHz, $CDCl_3$): 1.33–1.80 (5H, m), 2.20 (2H, ddt, $J = 7.3, 1.6, 7.2$ Hz), 3.65 (2H, t, $J = 6.1$ Hz), 5.60 (1H, dt, $J = 16.0, 1.6$ Hz), 6.35 (1H, dt, $J = 16.0, 7.3$ Hz), 7.28–7.38 (3H, m), 7.45–7.50 (2H, m); δ_C (100 MHz, $CDCl_3$): 24.62, 31.94, 32.93, 62.38, 72.50, 74.02, 80.52, 80.71, 108.83, 121.84, 128.33, 128.94, 132.32, 148.43.

(*E*)-10-Phenyldec-5-en-7,9-diynyl *N*-Phenylcarbamate (3): The E/Z mixture of **20** (6.1 g, 27 mmol) and phenyl isocyanate (4.6 g, 41 mmol) were placed in 100 mL of toluene under a nitrogen atmosphere. Two drops of dibutyltin dilaurate were added and the mixture was stirred for 3 h at ambient temperature. The solvent was then removed under reduced pressure. The E/Z mixture of the resulting phenylurethane was separated by column chromatography (silica gel, chloroform) to give a yellow solid in quantitative yield. Recrystallization from methanol gave 2.8 g (30%) of E isomer **3** as colorless solid: δ_H (400 MHz, $CDCl_3$): 1.53 (2H, tt, $J = 7.6, 7.2$ Hz), 1.69 (2H, tt, $J = 7.6, 6.6$ Hz), 2.21 (2H, dt, $J = 7.3, 7.2$ Hz), 4.17 (2H, t, $J = 6.6$ Hz), 5.61 (1H, d, $J = 16.0$ Hz), 6.34 (1H, dt, $J = 16.0, 7.3$ Hz), 6.61 (1H, br s), 7.06 (1H, t, $J = 7.5$ Hz), 7.27–7.41 (7H, m), 7.48 (2H, dd, $J = 7.7, 1.8$ Hz); δ_C (100 MHz, $CDCl_3$): 24.77, 28.27, 32.73, 64.77, 72.67, 74.03, 80.62 (two peaks overlapped), 109.10, 118.62, 121.83, 123.33, 128.32, 128.95 (two peaks overlapped), 132.34, 137.83, 147.98, 153.56.

Crystal Preparation. In the cooling method, saturated solution at the boiling point of the solvent was prepared and it was spontaneously cooled from the boiling point to ambient temperature. In the slow evaporation method, saturated solution at ambient temperature was prepared in a flask and the flask was covered with aluminum foil with pinholes. It was kept at ambient temperature until the solvent was completely evaporated.

Solid-State Polymerization. Solid-state polymerization of the monomers was performed using UV or γ-ray irradiation. The UV source was a 4 W lamp at 254 nm (UVG-11, UVP). Spectral measurements during the course of UV irradiation were obtained as follows. For IR measurement, the monomer crystals were mixed with potassium bromide, and the mixture was ground and pressed into pellet samples. For UV–visible diffuse reflectance measurements, the monomer crystals were mixed with potassium bromide, ground and placed into a quartz window cell. The γ-ray source was ^{60}Co, and the dose rate was about 4.8 kGy h^{-1}. For γ-ray irradiation, crystalline samples were put into glass tubes that were then evacuated and sealed. Conversions were obtained by the weight ratio of the solid portions insoluble in ethyl acetate, in which all monomers were soluble.

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