Polydiacetylenes from Asymmetrically Substituted Diacetylenes Containing Heteroaryl Side Groups for Third-Order Nonlinear Optical Properties

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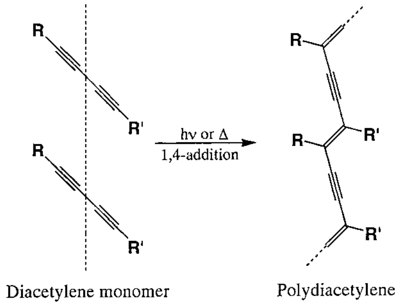
ABSTRACT: Synthesis of a series of asymmetrically substituted diacetylenes containing a thienyl moiety or a quinolyl moiety as one of the side groups directly bound to diacetylene and a urethane group as the other one was carried out. Though some of the prepared diacetylenes could be polymerized in solid state by using UV and γ-radiation, all of them were stable when heat was used as the stimulus. The monomer to polymer conversion for the polymerizable ones was found to be in the range 35−60%. Various spectroscopic techniques, such as FTIR, solid state ^{13}C NMR and visible absorption spectroscopies, and powder X-ray diffraction were used to elucidate the structures of the polydiacetylenes. One of the polymers containing quinolyl moiety as directly bound side group showed unusually long and sharp absorption maximum indicating long and uniform conjugated chains. Third-order nonlinear optical susceptibility, $\chi^{(3)}$, of two of the polymers were measured using Maker's fringe technique. The largest value for $\chi^{(3)}$ in the resonant region for polymer backbone direction in single crystalline form was estimated to be on the order of 10^{-11} esu.

Introduction

Diacetylenes (DAs) have generated a lot of interest during the last 2 decades due to its peculiar solid state polymerization behavior.[1,2] DA can be polymerized topochemically via 1,4-addition reaction to give polydiacetylene (PDA) (Scheme 1). The PDA, being a quasi one-dimensional π-conjugated system, shows nonlinear optical (NLO) properties as well as chromic properties arising due to conjugated systems.[3−5] However, third-order nonlinear properties of PDAs have emerged as the most promising and therefore, research in this direction has been vigorously pursued.[1,6,7] In principle, third-order NLO susceptibility, $\chi^{(3)}$ should increase as the conjugation length of the one-dimensional polymer elongates. It has earlier been reported that PDAs with aromatic substituents directly attached to the main backbone might be employed to do this job.[8] The number of π-electrons per repeating unit and the nature of π-delocalization may be increased through π-conjugation between the main backbone and the side groups. However, there had been few investigations related to such kind of DAs and PDAs. Moreover, most of these DAs are not polymerizable by 1,4-addition, and the few which polymerize generally give polymers in low percentage conversion.[9,10]

We have been dealing with preparation of diacetylenes with an aim to get good third-order nonlinear optical materials.[11−21] One class of diacetylenes, which we have been investigating, consists of aryl and heteroaryl moieties directly bound to the diacetylene backbone.[22] The design of such diacetylenes have been based on the premise that the aromatic side group will, in suitable cases, help the backbone conjugation to extend further to provide longer effective conjugation length. The heteroaryl moiety, by virtue of its aromatic interactions in adjacent molecules, enhances the probability for the monomer to stack appropriately in the crystal for topochemical polymerization. The other side group consists of a long alkyl chain with urethane group. This has been incorporated into the design of the diacetylene to make it solid-state reactive. The methylene spacers attached to diacetylene unit allow for certain flexibility to accommodate structural changes that occur during the solid state polymerization reaction. Here, we report the syntheses and solid state polymerization of a series of diacetylenes each of which are unsymmetrically substituted with a heteroaryl moiety, namely thienyl or quinolyl, and a urethane as the two side groups. The charaterisation of the resulting polymers as well as NLO properties of some of them are also discussed.

Scheme 1. Topochemical Polymerization of Diacetylene



Experimental Section

The monomers were prepared according to the routes shown in Scheme 2. **7a** and **7b** were prepared using slightly different

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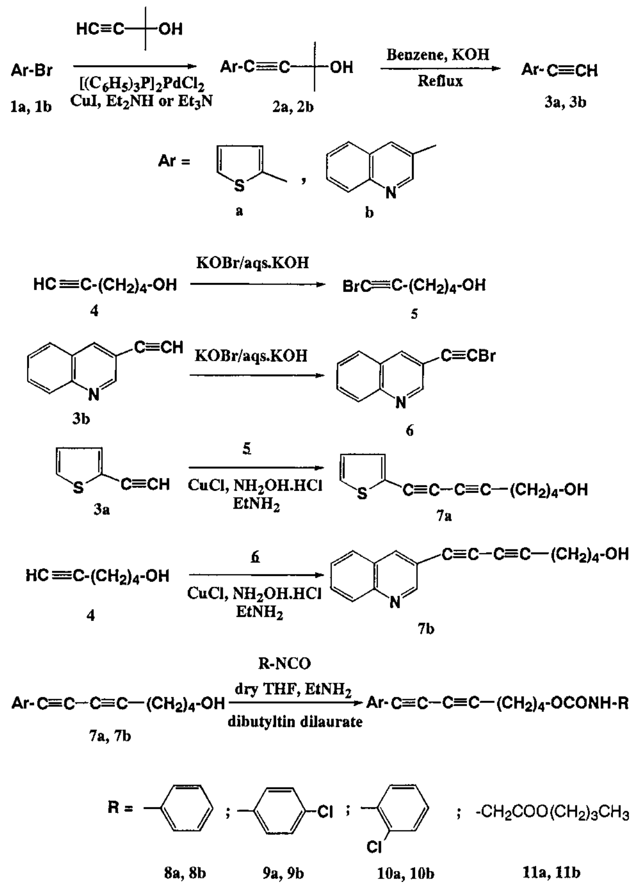
Scheme 2. Synthetic Route to Diacetylene Monomers



routes. Unlike **7b**, **7a** could not be obtained when **3b** and **4** were used as starting materials. So, the alternative approach, using **3a** and **5** as the starting materials, was used to prepare this comound. Synthesis of **2a**,[23] **2b**,[24] **3a**,[23] **3b**,[24] and **5**[25] were carried out as reported in the literature. The detailed procedure for the preparation of other compounds are as follows.

Preparation of 1-Bromo-2-(3′-quinolyl)ethyne, 6. Bromine (320 mg, 0.004 mol) was added to KOH/H_2O (0.01 mol/10 mL) while stirring at 0−5 °C. 3-Quinolylacetylene, **3d**, in dioxane (153 mg, 0.001 mol)/20 mL) was added dropwise to the above mixture over a period of 15 min. The reaction mixture was stirred for another 15 min without further cooling. Then the reaction mixture was poured into 50 mL of ice-cold water when a white solid precipitated out. The precipitate was filtered, dried, and recrystallized from methanol. Yield: 82%. Mp: 118−119 °C. IR (KBr), cm^{-1}: 2200 (−C≡C−). ^1H NMR (60 MHz, $CDCl_3$): δ 7.50−9.00 (m, 6H). Anal. Calcd for $C_{11}H_6NBr$: C, 56.92; H, 2.60; N, 6.03. Found: C, 57.48; H, 2.63; N, 5.90.

Preparation of 8-(2-Thienyl)octa-5,7-diyn-1-ol, 7a. Ethynyl thiophene (**3a**) (3.024 g, 0.028 mol) was taken in a three-neck round-bottom flask equipped with an N_2 gas inlet and outlet. Dry methanol (15 mL) was added to it. Nitrogen gas was passed through the solution for 5 min. CuCl (100 mg), $NH_2OH.HCl$ (150 mg), and 10% aqueous ethylamine solution (10 mL) were added to the above reaction mixture. The color of the reaction mixture turned bright yellow as soon as ethylamine was added. N_2 gas purging was continued during and after the addition. In another three-neck round-bottom flask, **5** (2.058 g, 0.021 mol) was dissolved in 100 mL of methanol and nitrogen gas was purged through it. This solution was transferred dropwise to the yellow solution of the previous flask through a cannula while N_2 gas was passed through the reaction mixture throughout the process. The addition of the reaction mixture was controlled so that the temperature of the flask does not go beyond 35 °C. The addition was completed in 30 min. It was stirred overnight under nitrogen atmosphere. The progress of the reaction was monitored by TLC. Upon completion of the reaction, aqueous NH_4Cl was added to the reaction mixture and stirred vigorously for an hour. The reaction mixture was extracted with ether. The ether layer was dried over $MgSO_4$ and then concentrated by evaporation at reduced pressure. The crude pruduct was obtained as a brownish slurry. The required product was purified by column chromatography using silica gel as column material and hexane/ethyl acetate (80:20) as eluent. Pure **7a** was obtained as colorless oil. Yield: 70%. IR (neat), cm^{-1}: 3400 (−OH), 2925, 2850 (aliph. C−H), 2200, 2150 (−C≡C−), 1810, 1750, 1660 (arom. C−H). ^1H NMR (400 MHz, $CDCl_3$): δ 1.5−1.8 (m, 4H), 2.1 (broad s, 1H), 2.42 (t, 2H), 3.68 (t, 2H), 6.95 (dd, 1H), 7.24 (d, 1H), 7.27 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.43, 24.62, 31.62, 62.10, 65.23, 67.80, 78.38, 86.41, 122.21, 126.98, 128.09, 133.82. Anal. Calcd for $C_{12}H_{12}SO$: C, 70.59; H, 5.86; S, 15.68. Found: C, 70.29; H, 6.07; S, 15.16.

Preparation of 8-(3-Quinolyl)octa-5,7-diyn-1-ol, 7b. The procedure for preparing **7b** was similar to that for **7a**. In this case bromoethynylquinoline (**6**) and 5-hexyn-1-ol (**4**) were used as the starting materials. After workup of the reaction mixture, the required product was purified by column chromatography using silica gel as column material and hexane/ethyl acetate (80:20) as eluent. Pure **7a** was obtained as a colorless solid. Yield: 74%. Mp: 74−76 °C. IR (KBr), cm^{-1}: 3380 (−OH), 2925, 2850 (aliph. C−H), 2220, 2150 (−C≡C−), 1740, 1660 (arom. C−H). ^1H NMR (400 MHz, $CDCl_3$): δ 1.6−2.0 (m, 4H), 2.1 (broad s, 1H), 2.46 (t, 2H), 3.72 (t, 2H), 7.57 (dd, 1H), 7.73 (dd, 1H), 7.78 (d, 1H), 8.09 (d, 1H), 8.27 (s, 1H), 8.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.40, 24.52, 31.72, 62.10, 64.53, 72.51, 77.10, 87.28, 116.38, 127.00, 127.41, 127.55, 129.48, 130.49, 139.71, 146.57, 152.32. Anal. Calcd for $C_{17}H_{15}NO$: C, 79.53; H, 6.02; N, 5.62. Found: C, 79.83; H, 6.11; N, 5.47.

Preparation of 8-(2-Thienyl)-5,7-octadiynyl *N*-Phenylcarbamate, 8a. In a round-bottom flask, **7a** (1.02 g, 0.005 mol) was taken in 7 mL of dry THF. Phenyl isocyanate (0.714 g, 0.006 mol) was added to it. Triethylamine (3−4 drops) and dibutyltin dilaurate (3−4 drops) were also added to the reaction mixture. The resulting solution was stirred overnight at room temperature. The reaction mixture was then concentrated by evaporation under reduced pressure. Crude product was obtained as colorless solid. It was then column chromatographed using silica gel as the column material and hexane/ethyl acetate (75:25) as eluent, to obtain pure **8a** as colorless crystals. Yield: 74%. Mp: 75 °C. IR (KBr), cm^{-1}, 3350 (−OH), 2925, 2850 (aliph. C−H), 2220, 2150 (−C≡C−), 1710 (−C=O), 1650, 1595, 1525 (arom. C−H). ^1H NMR (400 MHz, $CDCl_3$): δ 1.65−1.69 (m, 2H), 1.78−1.82 (m, 2H), 2.43 (t, 2H), 4.20 (t, 2H), 6.69 (s, 1H), 6.95 (dd, 1H), 7.05 (t, 1H), 7.24−7.39 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.36, 24.82, 28.02, 64.50, 65.53, 68.00, 78.28, 86.01, 118.63, 122.21, 123.39, 126.98, 128.09, 129.00, 133.92, 137.81, 154.00. Anal. Calcd for $C_{19}H_{17}NO_2S$: C, 70.59; H, 5.26; N, 4.33; S, 9.91. Found: C, 70.37; H, 5.32; N, 4.23; S, 9.52.

Preparation of 8-(3-Quinolyl)-5,7-octadiynyl *N*-Phenylcarbamate, 8b. **8b** was prepared from **7b** in a similar way as **8a**. The pure product was obtained as colorless needle-shaped crystals. Yield: 70%. Mp: 100 °C. IR (KBr), cm^{-1}: 3250 (−OH), 2925, 2850 (aliph. C−H), 2230, 2160 (−C≡C−), 1750 (−C=O), 1600 (arom. C−H). ^1H NMR (400 MHz, $CDCl_3$): δ 1.65−1.77 (m, 2H), 1.85−1.90 (m, 2H), 2.47 (t, 2H), 4.24 (t, 2H), 6.75 (s, 1H), 7.06 (t, 1H), 7.28−7.41 (m, 4H), 7.51 (t, 1H), 7.73−7.76 (m, 2H), 8.07 (d, 1H), 8.29 (s, 1H), 8.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.20, 24.62, 28.07, 64.00, 65.00, 72.01, 77.10, 85.21, 116.00, 119.03, 123.44, 126.90, 127.45, 127.56, 129.04, 129.33, 130.49, 137.00, 139.76, 146.00, 152.31, 154.00. Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.61. Found: C, 77.98; H, 5.65; N, 7.45.

Preparation of 8-(2-Thienyl)-5,7-octadiynyl *N*-(4-Chlorophenyl)carbamate, 9a. The procedure followed was similar to the above preparation. **7a** and 4-chlorophenyl isocyanate were used as the starting materials. The product was purified by column chromatography so as to obtain **9a** as colorless crystalline solid. Yield: 74%. The compound does not have a clear melting point. Instead, it goes to liquid crystalline phase at 75 °C and remains so until 90 °C. IR (KBr), cm^{-1}: 3350 (−OH), 2925, 2850 (aliph. C−H), 2220, 2150 (−C≡C−), 1750 (−C═O), 1700, 1580, 1525 (arom. C−H). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.65−1.69 (m, 2H), 1.79−1.86 (m, 2H), 2.44 (t, 2H), 4.18 (t, 2H), 6.61 (s, 1H), 6.96 (dd, 1H), 7.25−7.34 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.36, 24.65, 27.99, 64.72, 65.59, 68.06, 78.25, 85.53, 119.53, 122.23, 127.09, 128.14, 128.29, 129.02, 133.90, 136.43, 154.00. Anal. Calcd for $C_{19}H_{16}NO_2SCl$: C, 63.78; H, 4.48; N, 3.92; S, 8.95. Found: C, 63.59; H, 4.56; N, 4.07; S, 9.04.

Preparation of 8-(3-Quinolyl)-5,7-octadiynyl *N*-(4-Chlorophenyl)carbamate, 9b. The procedure followed was similar to the preparation of **8b**. In this case, **7b** and 4-chlorophenyl isocyanate were used as the starting materials. The product was purified by column chromatography so as to obtain **9b** as a colorless crystalline solid. Yield: 74%. Mp: 146−147 °C; IR (KBr), cm^{-1}: 3350 (−OH), 2925, 2850 (aliph. C−H), 2225, 2150 (−C≡C−), 1750 (−C═O), 1650, 1590, 1525 (arom. C−H). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.68−1.75 (m, 2H), 1.82−1.89 (m, 2H), 2.44 (t, 2H), 4.22 (t, 2H), 6.64 (s, 1H), 7.25−7.35 (m, 4H), 7.55 (dd, 1H), 7.71 (dd, 1H), 7.76 (d, 1H), 8.07 (d, 1H), 8.26 (s, 1H), 8.91 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.33, 24.63, 27.92, 64.49, 65.45, 72.21, 78.29, 86.02, 118.65, 122.20, 126.97, 127.46, 127.56, 128.97, 128.99, 129.27, 130.49, 137.82, 139.74, 146.76, 152.22, 154.00. Anal. Calcd for $C_{24}H_{19}N_2O_2Cl$: C, 71.55; H, 4.72; N, 6.96. Found: C, 71.45; H, 4.78; N, 7.02.

Preparation of 8-(2-Thienyl)-5,7-octadiynyl *N*-(2-Chlorophenyl)carbamate, 10a. The procedure followed was similar to the above preparation. **7a** and 2-chlorophenyl isocyanate were used as the starting materials. The product was purified by column chromatography so as to obtain **10a** as colorless crystalline solid. Yield: 69%. Mp: 70 °C. IR (KBr), cm^{-1}: 3340 (−OH), 2925, 2850 (aliph. C−H), 2225, 2150 (−C≡C−), 1750 (−C═O), 1680, 1575, 1525 (arom. C−H). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.67−1.72 (m, 2H), 1.80−1.86 (m, 2H), 2.50 (t, 2H), 4.24 (t, 2H), 6.74 (d, 1H), 6.96 (dd, 1H), 7.25−7.34 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.18, 24.72, 28.11, 64.81, 65.78, 68.09, 78.32, 85.55, 119.88, 122.23, 123.11, 127.00, 127.81, 128.15, 129.04, 133.96, 134.68, 136.31, 154.04. Anal. Calcd for $C_{19}H_{16}NO_2SCl$: C, 63.78; H, 4.48; N, 3.92; S, 8.95. Found: C, 63.66; H, 4.51; N, 4.02; S, 9.05.

Preparation of 8-(3-Quinolyl)-5,7-octadiynyl *N*-(2-Chlorophenyl)carbamate, 10b. The procedure followed was similar to the preparation of **8b**. In this case, **7b** and 2-chlorophenyl isocyanate were used as the starting materials. The product was purified by column chromatography so as to obtain **10b** as colorless crystalline solid. Yield: 72%. Mp: 86 °C. IR (KBr), cm^{-1}: 3200 (−NH), 2220, 2180 (−C≡C−), 1725 (−C═O), 1600 (arom. C−H). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.65−1.77 (m, 2H), 1.85−1.92 (m, 2H), 2.49 (t, 2H), 4.25 (t, 2H), 6.97 (dd. 1H), 7.15 (s, 1H), 7.28 (dd, 4H), 7.33 (d, 1H), 7.58 (d, 1H), 7.72 (dd, 1H), 8.07 (d, 1H), 8.15 (d, 1H), 8.23 (s, 1H), 8.91 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.31, 24.59, 28.01, 64.82, 65.47, 72.25, 77.44, 85.24, 116.30, 119.87, 123.69, 126.97, 127.41, 127.55, 127.75, 129.04, 129.42, 130.44, 134.67, 136.21, 139.68, 146.88, 152.34, 153.15. Anal. Calcd for $C_{24}H_{19}N_2O_2Cl$: C, 71.55; H, 4.72; N, 6.96. Found: C, 71.24; H, 4.92; N, 6.64.

Preparation of 8-(2-Thienyl)-5,7-octadiynyl *N*-(2-Chlorophenyl)carbamate, 11a. The procedure followed was similar to the above preparation. **7a** and isocyanatoacetic acid *n*-butyl ester were used as the starting materials. The product was purified by column chromatography so as to obtain **11a** as colorless slurry. Yield: 65%. IR (neat), cm^{-1}: 3260 (−NH), 2920, 2900 (aliph. C−H), 2225, 2185 (−C≡C−), 1750 (−C═O), 1600 (arom. C−H). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.01 (t, 3H), 1.31−1.40 (m, 4H), 1.55−1.78 (m, 4H), 2.51 (t, 2H), 3.92 (t, 2H), 4.14 (s, 2H), 4.18 (t. 2H), 5.25 (s, 1H), 6.94−6.96 (dd, 1H), 7.24−7.26 (d, 1H), 7.28−7.30 (d, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.54, 19.01, 19.17, 24.22, 27.99, 30.51, 64.98, 65.16, 65.22, 65.58, 67.45, 78.11, 86.57, 122.32, 126.75, 127.91, 133.67, 154.11, 169.88. Anal. Calcd for $C_{19}H_{16}NO_2SCl$: C, 63.13; H, 6.41; N, 3.88; S, 8.87. Found: C, 63.95; H, 6.36; N, 3.81; S, 8.66.

Table 1. Solid State Reactivity of Diacetylenes

monomer[a]	solid state reactivity[b] UV	γ	Δ	% conversion[c]
7a[d]				
7b	X	X	X	
8a	O	O	X	35
8b	O	O	X	50
9a	X	X	X	
9b	O	O	X	60
10a	X	X	X	
10b	O	O	X	60
11a[d]				
11b	X	X	X	

[a] Monomers except for **10b** were crystallized from solution. Crystals of **10b** were obtained by cooling from molten state. [b] Key: X, unreactive; O, reactive. [c] When polymerized by γ-irradiation. [d] Oil at room temperature.

Preparation of 8-(3-Quinolyl)-5,7-octadiynyl *N*-(2-Chlorophenyl)carbamate, 11b. The procedure followed was similar to the preparation of **8b**. In this case, **7b** and isocyanatoacetic acid *n*-butyl ester was used as the starting material. The product was purified by column chromatography so as to obtain **11b** as a colorless crystalline solid. Yield: 72%. Mp: 75 °C; IR (KBr), cm^{-1}: 3250 (−NH), 2925, 2900 (aliph. C−H), 2220, 2180 (−C≡C−), 1750 (−C═O), 1700, 1600 (arom. C−H). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.95 (t, 3H), 1.32−1.40 (m, 4H), 1.58−1.80 (m, 4H), 2.48 (t, 2H), 3.96 (t, 2H), 4.14 (s, 2H), 4.16 (t, 2H), 5.27 (s, 1H), 7.56 (dd, 1H), 7.72 (dd, 1H), 7.78 (d, 1H), 8.07 (d, 1H), 8.27 (s, 1H), 8.91 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.59, 18.97, 19.25, 24.54, 28.06, 30.47, 64.54, 65.17, 65.31, 65.33, 72.12, 77.49, 85.38, 116.32, 126.96, 127.39, 127.52, 129.35, 130.41, 139.67, 146.80, 152.29, 154.00, 170.16. Anal. Calcd for $C_{24}H_{26}N_2O_4$: C, 73.47; H, 6.63; N, 7.14. Found: C, 73.17; H, 6.30; N, 7.02.

Solid State Polymerization. Solid state polymerization of the monomers was done by UV or γ-radiation. ^{60}Co γ-radiation dosage was used to convert bulk monomers taken in evacuated and sealed glass tubes to their respective polymers. To calculate the rate of polymerization, various dosages were used for a given monomer and the conversion to polymer was determined by extracting the reaction with hot chloroform and weighing the undissolved polymer portions. The percentage polymer conversion was calculated by comparing the weight of the sample before and after extraction.

THG Measurement. Third-harmonic generation (THG) measurement for two of the polymers were carried out by means of the Maker fringe method.[26] The fundamental beam used was 1.83−2.10 μm pulsed (ca. 5 ns of pulse width) laser light. The power of laser light used was about 2 mJ/pulse. A fused quartz plate, whose $\chi^{(3)}$ is 1.0×10^{-14} esu, was used as a reference sample.[27] The thin film samples for THG measurement were prepared as follows. The monomer (20 mg) was dissolved in chloroform (10 mL). A quartz glass slide (3 × 1 cm) was placed on the spin coating apparatus platform. It was heated to 40 °C and then the monomer solution (200 mL) was pipetted out on the quartz plate. After 10 s, the plate was spun at a speed of 1000 rpm for 30 s. The spin coated monomers were polymerized by γ-irradiation. According to the above procedure, thin film samples of **8a** and **9b** could be obtained.

Results and Discussion

Solid State Reactivity. Table 1 summarizes the solid-state reactivity of the synthesized diacetylenes. The monomers **8a**, **8b**, **9b**, and **10b** were reactive in the solid state when irradiated with UV or γ-radiation. However, none of them showed solid-state reactivity when heat was used as stimulus. This behavior is not without precedent. For example, the diacetylene 3BCMU [R = $-(CH_2)-OCONH-CH_2-COO(CH_2)_3CH_3$] can be polymerized by γ-radiation, but it is unreactive when heat is used.[28] Similar is the case for R−C≡C−C≡C−R

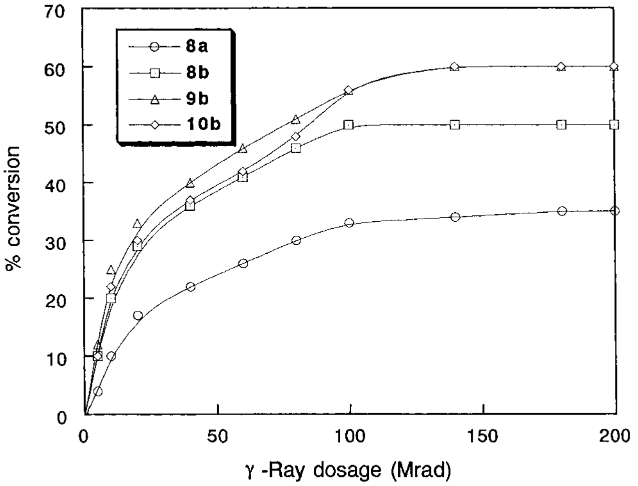


Figure 1. Plot of γ-irradiation dosage vs polymer conversion of reactive DAs.

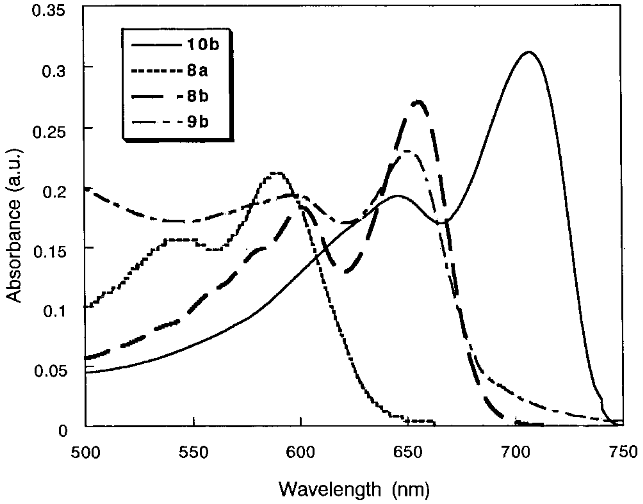


Figure 2. Absorption spectra of PDAs.

[R = $-CH_2-CH_2-OH$].[29] For 3BCMU, an explanation that has been proposed is that, in the crystal, the molecules are held together by strong H-bonds and thermal activation is not enough to overcome these strong interactions and hence is thermally inactive. On the other hand, in photopolymerization and radiation polymerization enough energy is available to initiate the reaction, the crystal packing being quite suitable for reaction.

The monomer **10b**, in fact, exists in two crystallographic forms. When the crystals were obtained by slow evaporation of the solvent, such as methanol, ethyl acetate, etc., they were shiny colorless needles. This crystal form is totally unreactive toward topochemical solid state polymerization. On the contrary, however, when the compound **10b** was melted and quickly cooled, colorless crystals are obtained which are reactive toward topochemical polymerization when irradiated with UV or γ-radiation. Crystallographic difference in **10b** crystals will be shown in the latter section.

The polymers obtained from **8b**, **9b** are blue while **8a** yielded a violet-colored polymer. The polymer from **10b** was blue-green. All the polymers were, however, insoluble in common organic solvents.

From the solid state polymerization behavior for the synthesized monomers, it is observed that all the quinolyl diacetylenes having phenyl-capped urethane side groups are reactive in solid state. Thus by introducing a quinolyl moiety as well as a phenyl-capped urethane side group, one can achieve a favorable packing of the monomer molecules in crystal to react topochemically. On the other hand, only one thienyl containing DA, **8a**, shows solid-state reactivity. Incidentally, **8a** is the first DA containing a directly bound thiophene side group which shows solid-state reactivity.[20]

The monomers **8a**, **8b**, **9b**, and **10b**, although quite reactive, do not reach 100% conversion upon solid state 1,4-addtion polymerization. The percentage conversion achieved for **8a**, **8b**, **9b**, and **10b** are 35, 50, 60, and 60% respectively. Figure 1 shows the polymer conversion kinetics for the reactive monomers. The fact that quantitative conversion was not obtained is similar to other diacetylenes with directly bound heteroaryl side group, for example 1,4-diquinolylbutadiyne(DQ).[9] The reason is not very clear at the moment, but the crystal phase transition while going from monomer to polymer seems to play a role in it. Investigations are now continuing in order to explain the nonquantitative conversion of the DAs to PDAs.

Among the other DAs, **7a** and **11a** are oils at room temperature and therefore were not considered for the solid-state reaction. The lack of reactivity of alcohol derivative **7b** suggests that the terminal phenyl group at the urethane end of the diacetylene is responsible for the appropriate crystal packing to make the monomers reactive. Similarly, **11b** is unreactive although it has a flexible urethane chain at one end of the diacetylene backbone. Thus, it implies that, in the reactive DAs, the phenyl groups of adjacent molecules, due to intermolecular $\pi-\pi$ interaction and hydrogen bonding between urethane groups in adjacent molecules may be helping the monomers to pack in appropriate manner for solid state polymerization to occur. However, this seems to be only one of the factors deciding the overall reactivity of the monomer. **9a** and **10a**, which are thienyl DAs with chlorophenyl-capped urethane moieties as the other side groups, do not polymerize topochemically. Thus it becomes apparent that, in order to obtain reactive diacetylenes, one needs to address multiple factors at the same time. The outcome of all the factors is in the form of crystal geometry and molecular arrangements inside it.

The monomer to polymer conversion has been greatly improved in case of **8b** (50%), **9b** (60%) and **10b** (60%) against that of DQ (25%). This result also indicates that our molecular design for polymerizable diacetylene by introducing a phenyl urethane group is efficient.

Visible Absorption Spectra. The visible absorption spectra for the polymers are shown in Figure 2. It can be observed that between **8a** and **8b**, the latter, which is a quinolyl DA, gives a polymer with significantly longer absorption maximum wavelength at 655 nm than thiophene containing PDA (590 nm). The visible absorption spectra of the polymers can be assigned for excitonic bands, which are characteristic for PDAs. It only appears for polymers, and not for oligomers. Further, the polymers after extraction, devoid of short repeat units, also showed the same absorption maxima as before extraction. Since these excitonic bands are known to be observed along the polymer backbone direction, the difference in absorption is due to the extension of excitons, namely the effective conjugation length along the PDA backbone direction, which is naturally affected

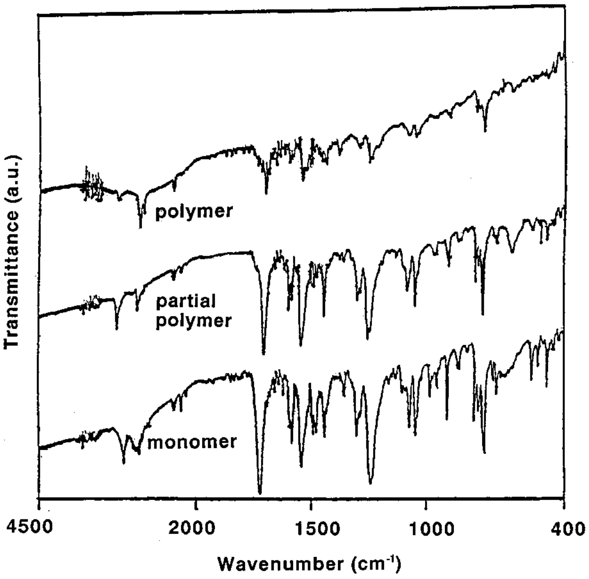


Figure 3. FTIR spectra of **10b**.

by π-conjugated side groups. Since other structural features are similar, the λ_{max} of **8b** is boosted obviously due to greater contribution of directly bound quinolyl side group to the backbone, the thienyl group in **8a** being less contributing. The quinolyl moiety increases the effective conjugation length of the polymer backbone which may be due to larger numbers of π-electrons in the side chain, which can conjugate with the polymer backbone.

Monomer **10b** is of particular interest since it gives PDA with λ_{max} of 715 nm which is among the longest in this category of PDAs. Also, the absorption band for this polymer is quite sharp indicating improved ordering of the polymer chains. It may be noted that DQ, a symmetric diacetylene with quinolyl moiety at both ends of the backbone, gives PDA with almost the same λ_{max}.[9] Therefore, it follows that only one directly bound quinolyl group is sufficient to boost the conjugation length of the polymer backbone while the other end of monomer could be used to introduce a side group to engineer the crystal for greater reactivity.

FTIR Spectra. It was observed that the peaks due to the $-C{\equiv}C-$ stretching frequency at 2220 and 2150 cm^{-1} for **8a**, 2225 and 2150 cm^{-1} for **8b** and 2220 and 2180 cm^{-1} for **10b**, in the monomer samples decrease gradually as the samples are polymerized. For the monomer-free samples, the FTIR spectra show no $-C{\equiv}C-$ peak. As a typical example, FTIR spectra of **10b** and its polymer are shown in Figure 3. In the spectra, the small peak at 2300 cm^{-1} is due to the carbon dioxide in air, which should be ignored. According to 1,4-addition reaction, the acetylenic bonds of monomer backbone react to form polymer whose backbone too contains a new acetylenic bond (see Scheme 1). Consequently, a new $-C{\equiv}C-$ peak is expected in the FTIR spectrum of the polymer. In the present cases, the absence of the $-C{\equiv}C-$ stretching frequency peak in the polymer samples may be due to the molecules being IR-inactive. The decrease in the intensity of the two $-C{\equiv}C-$ peaks in the monomers with the progress in polymerization clearly indicates that both the acetylenic bonds of the monomers are involved in the polymerization. This is consistent with the mechanism for 1,4-addition reaction.

Solid-State ^{13}C NMR Spectra. To further confirm the above results, we recorded ^{13}C CP$-$MAS NMR spectra for the monomers and their partial polymers. As a typical example, Figure 4 shows the ^{13}C CP$-$MAS NMR for **10b**. For **10b**, the monomer shows peaks at 65, 72, 76, and 85 ppm for the four acetylenic carbon atoms of the diacetylenic group. As the polymerization proceeds, there appears a pair of new peaks. This can be seen in the spectra of the partial polymer of **10b** at 104 and 106 ppm. These are assigned to the acetylenic carbon atoms for the polymeric backbone of polydiacetylene. The other new peak for the alkene carbon of the polymeric backbone is expected around 120 ppm. This position is already having peaks for the thiophene moiety and hence the new peak must be overlapped. The CP$-$MAS NMR spectra of the pure polymer of **10b**, obtained after extraction, was too noisy, due to small amount of the sample, to find the acetylenic peaks and it is difficult to say that there is total absence of peaks of monomer acetylenic carbons from the spectrum. In case of **8b** and **9b**, similar results are observed in the solid state NMR spectra. All the peaks for the monomers' acetylenic carbon atoms along with those of the corresponding polymers are tabulated in Table 2. Thus from the results of solid state NMR, we can clearly see the formation of polydiacetylene. From this, together with FTIR spectral data, the 1,4-addition mechanism along with the polymer structure is clearly confirmed.

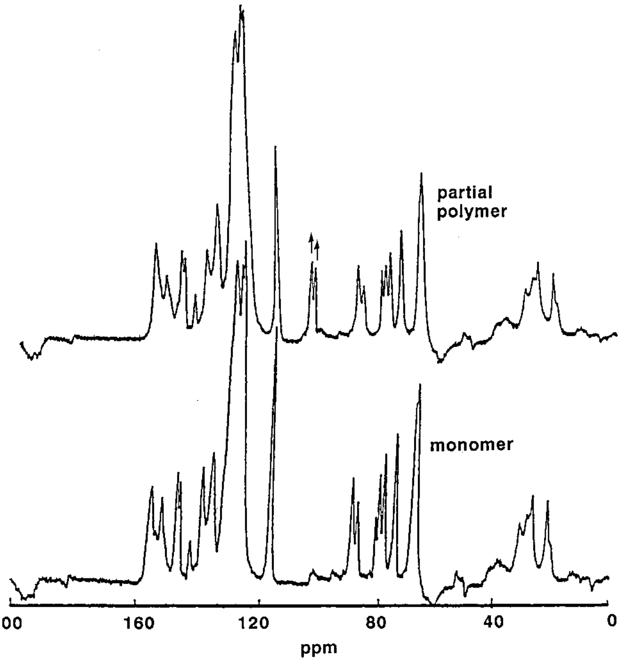


Figure 4. Solid state ^{13}C NMR spectra of **10b**. The spectra for monomer and partial polymer were obtained using a TOSS pulse sequence to suppress the spinning sidebands.

Table 2. Solid State ^{13}C NMR Peaks for the Acetylenic Carbon Atoms in Monomers and Polymers

	monomer (ppm)	polymer (ppm)
8a	65.5, 68.0, 76.2, 87.7	101.2, 103.7
8b	65.4, 72.8, 77.3, 87.2	103.1, 105.2
9b	65.6, 73.8, 87.4	103.4, 106.1
10b	65.5, 72.8, 76.1, 85.7	104.0, 106.3

Powder X-ray Diffraction. Powder XRD for the monomers and the polymers shows that the crystallinity is maintained while going from monomer to polymer in all the reactive DAs studied in this report. Figure 5 shows the powder XRD pattern for monomer **10b** in two crystalline forms and that of the partial polymer obtained from the reactive form of monomer. The powder

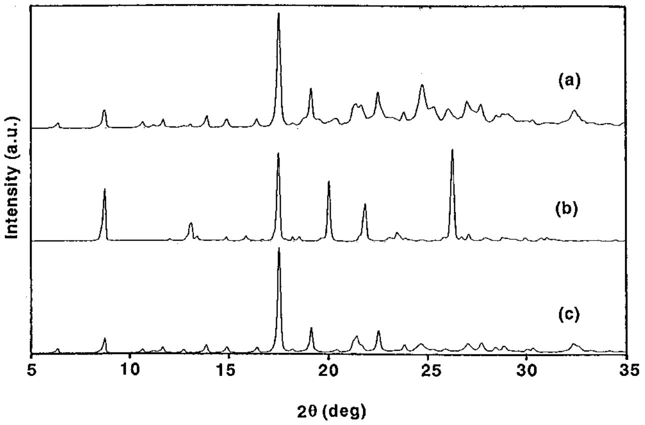


Figure 5. Powder XRD of **10b**. (a) reactive monomer crystals obtained by melt–crystallization; (b) unreactive monomer crystals obtained by slow evaporation from methanol solution; (c) partial polymer from the melt-crystallized monomer form.

XRD of pure PDA from **10b** showed broad bands instead of sharp peaks. However, this XRD pattern was the result of extraction process, wherein the crystal geometries of the polymer are disturbed considerably, and did not reveal the actual XRD of fully polymerized sample. Therefore, the powder XRD of pure polymer has not been used for analysis. The two crystalline forms of the monomer have quite different XRD patterns as seen from the spectra whereas the reactive form of the monomer gives partial polymer which maintains its crystallinity. **8a**, **8b**, and **9b** also show similar results. It is an improvement over DAs having long alkyl groups with urethane type moieties as both side groups tend to give polymers with low crystallinity even though they show high reactivity.

Third-Order Nonlinear Optical Susceptibility. For the third harmonic generation measurement, spin-coated monomers **8a** and **9b** were polymerized to PDAs. 10% polymer conversion was determined by dissolving the unreacted monomers and weighing the residual polymers on the quartz plates. Since the PDAs absorb at THG wavelengths for used fundamental beams, the $\chi^{(3)}$ values obtained are for resonant region.

For PDA from **8a**, the $\chi^{(3)}$ value at 1.74 mm is 3.0×10^{-13} esu which is higher by 1 order of magnitude than the $\chi^{(3)}$ of quartz. This $\chi^{(3)}$ value is for a 10% polymerized film and if we calculate for a 100% polymerized film, the $\chi^{(3)}$ value will be on the order of 10^{-12} esu. Further, it was found from the powder XRD analysis that the polymer crystals are deposited on the quartz plate at random; i.e., the conjugated backbone of the polymer is randomly oriented in the spin-cast film. The $\chi^{(3)}$ value for single crystal of polymer of **8a** in the main chain direction is estimated to be 5 times the experimental value for the film[30] which turns out to be about 1.5×10^{-11} esu for a fully polymerized single crystal. Figure 6 shows the relationship between the absorption spectrum of PDA from **8a** and the fundamental wavelengths.

In case of **9b**, the $\chi^{(3)}$ value at 1.98 mm is 3.2×10^{-13} esu for 10% polymerized sample which is higher by 1 order of magnitude than the $\chi^{(3)}$ of quartz. As discussed in the previous case and using the same arguements, the $\chi^{(3)}$ value of a single crystal of **9b**, in the direction of the backbone should be about 1.6×10^{-11} esu for a fully polymerized single crystal. Figure 7 shows the relationship between the absorption spectrum of PDA from **9b** and the fundamental wavelengths. The values of polymerized **10b** could not be obtained as we were unable to prepare a thin film of this sample.

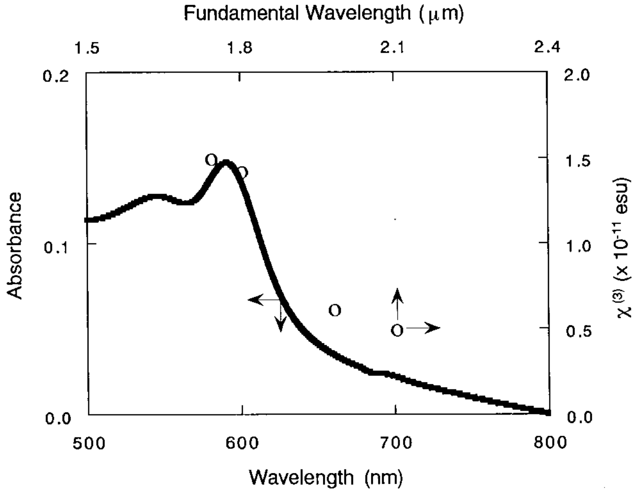


Figure 6. Absorption spectrum of polymerized film of **8a** with a thickness of 0.9 mm. The arrows indicate the fundamental wavelength. When the wavelength of arrows is read using the lower abscissa, it corresponds to the third-harmonic wavelength.

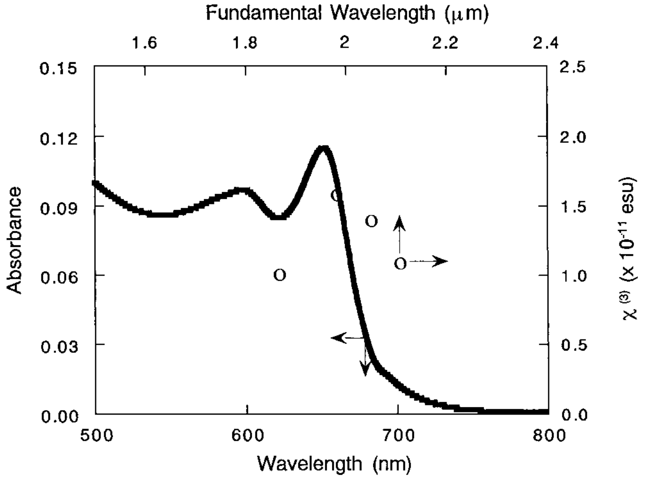


Figure 7. Absorption spectrum of polymerized film of **9b** with a thickness of 0.6 mm. The arrows indicate the fundamental wavelength. When the wavelength of arrows is read using lower abscissa, it corresponds to the third-harmonic wavelength.

Although the $\chi^{(3)}$ values for the present PDAs are not among the highest in the PDA family, these particular PDAs containing thiophene and quinolene have significantly large $\chi^{(3)}$ values. Moreover, the thiophene-containing PDA is a first case, and the $\chi^{(3)}$ value of this is quite encouraging to begin with. These results are very significant in view of the future optimization of the structure for better third-order NLO materials.

Conclusions

In conclusion, we have succeeded in the preparation of a series of diacetylenes having directly bound heteroaryl moieties. The monomers react in the solid state to give PDAs which have enhanced π-conjugation as evidenced from their absorption spectra. The presence of aromatic moieties as directly bound side groups to the acetylenic backbone has resulted in polymers with longer effective conjugation lengths according to our postulations before beginning this work. The structure of the polymers have been elucidated using various spectroscopic methods. The $\chi^{(3)}$ values for the polymers are reasonably high, prompting further explorations. This work demonstrates that polydiacetylenes containing directly linked heteroaryl side groups are accessible. The future lies in the optimization of the structure via subtle changes in the side groups so that high quality third-order NLO materials are obtained.

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