Octatetraynes with Directly Linked Aromatic Sidegroups: Preparation and Polymerization

Abhijit Sarkar, Shuji Okada, Kyoji Komatsu, and Hachiro Nakanishi*

Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Sendai 980-8577, Japan

Hiro Matsuda

National Insititute of Materials and Chemical Research, 1−1 Higashi, Tsukuba 305-8565, Japan

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ABSTRACT: Preparation of two symmetrically substituted tetrayne monomers has been described which have directly linked heteroaryl moieties (2-thienyl and 3-quinolyl) as the side groups. These two monomers undergo solid state polymerization when heated. The polymerization rate is directly related to the heating rate. The polymers are insoluble in organic solvents. The polymerization seems to proceed in two steps to yield polymers with irregular structure but with aromatic character. The polymers have been characterized by spectroscopic techniques, such as FTIR and solid state ^{13}C NMR spectroscopy, and by powder XRD. One of the monomers could be obtained in single-crystal form, whose X-ray structure revealed the arrangement of the molecules in the crystal lattice in context with the topochemical reaction.

Introduction

Solid state polymerization of diacetylenes (DAs) has been an important area of research, for chemists, physicists, and material scientists alike.[1] This interest was initiated about two and a half decades ago due to Wegner's work wherein he identified the polymerization of a DA containing $CH_2-OSO_2C_6H_4CH_3$ (PTS) as a topochemically controlled 1,4-addition reaction.[2] The reaction, as shown in Figure 1, was unique in the sense that monomer single crystal was transformed into polymer single crystal in its entirety. The implications of this observation were immense as far as potential for practical applications are concerned, and further knowledge of this polymerization reaction and of the polymers themselves was deemed worth investigating. Investigations covering various aspects of polydiacetylene(PDA), such as electrical properties,[3] solution properties,[4] optical and nonlinear optical properties,[5] and mechanical properties[6] have been pursued. However, nonlinear optical (NLO) properties have emerged as the most potential and important aspect of investigation in PDA research. The reason for enhanced NLO properties in PDAs can be identified in the basic structure of the polymer. PDAs are one-dimensional systems of highly polarizable conjugated π-electrons. The polarization depends strongly on delocalization length.[7] Moreover, the electronic origin of NLO susceptibility implies short response time.[8] Indeed, the third-order NLO suceptibility, $\chi^{(3)}$ value for degenerate four-wave mixing is on the order of 10^{-6} esu in the resonant region[9] and n_2 value of 2.2×10^{-12} cm^2/W at 1600 nm in the nonresonant region[10] were reported for conventional PDAs. Their ultrafast response times have also been confirmed.[11] The above factors, in combination with the ability to form single crystals or thin films in the case of some polydiacetylenes, make them promising materials from the viewpoint of fabrication and application,

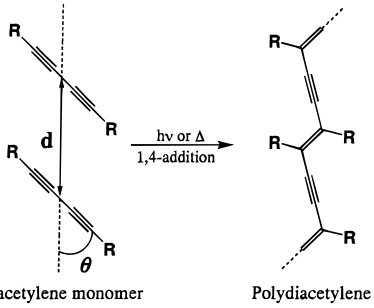

Figure 1. Topochemical solid-state polymerization of diacetylene by 1,4-addition. When the monomer in crystal has appropriate geometry, where the distance d and the angle θ are about 5 Å and 45°, respectively, it can be polymerized via topochemical 1,4-addition.

thus giving them an edge over conventional inorganic NLO materials.

Nevertheless, PDAs need further improvements before they can become viable candidates for NLO applications. Proper substituents for diacetylene monomers have to be found which first will help the monomers to polymerize topochemically to give regular polymers and then will help to produce PDAs with optimal qualities, such as large susceptibilities and short response times. The realization of these qualities depends on, aside from other factors, the physical form of the polymer. Hence the factor, whose improvement is aimed at, is the versatility of the polymer's physical form so that the material can exist as a single crystal or can form uniform thin films.

The other vital factor for NLO property enhancement is to increase the effective conjugation length of the PDA backbone. It can be realized via two ways. One option is to have aromatic substituents which are directly bound to the conjugated backbone. In this way, the electronic structure of the backbone is perturbed by electron donation or withdrawl due to the substituents. Another way to achieve absorption at longer wavelength is by increasing the number of acetylenic units in the backbone itself. Various substituted oligoynes such as

* To whom correspondence should be addressed. Telephone: +81-22-217 5643. Fax: +81-22-2175645. E-mail: hnakanis@icrs.tohoku.ac.jp.

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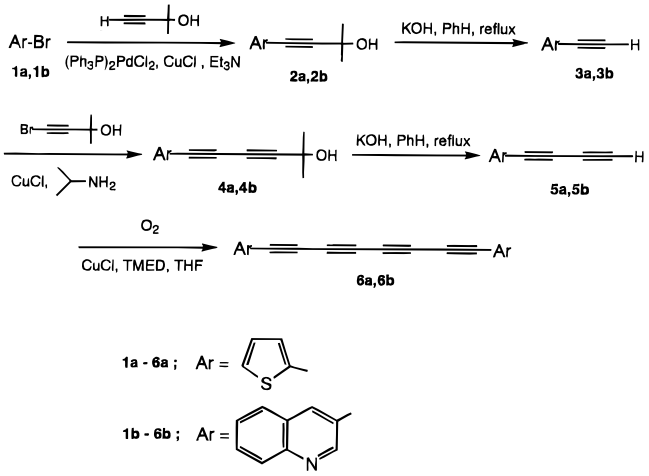
Scheme 1. Synthetic Procedure for the Preparation of 6a and 6b



triynes, tetraynes, and hexaynes are the examples for this type.[12] Once these oligoynes are polymerized, the resulting polydiacetylenes will have acetylenic side groups which are in direct conjugation with the backbone. In both of the above cases, an increased conjugation length is achieved by introduction of conjugated side groups, either aromatic or acetylenic moiety. Although few diacetylenes having directly bound aromatic side groups undergo solid-state polymerization, there are still a few which react to give PDAs and many of them show enhanced π-conjugation.[13−15] On the other hand, previous investigations in our laboratory have established that an increase in the number of acetylenic units in the monomer backbone contributes toward the enhancement of the conjugation length of the resulting polymer.[16]

We report here oligoyne compounds, namely tetraynes which have heteroaryl side groups (thiophene and quinoline) directly bound to the acetylenic backbone. We have selected the quinolyl moiety since, in previous studies, its incorporation as a side-group has produced reactive diacetylenes with promising results.[14] On the other hand, thiophene has been one of the most promising structural moieties in many promising NLO materials and constantly attracts attention.[17] The preparation of such compounds was carried out with an attempt to take advantage of both of the factors as mentioned above, to favor longer π-conjugation by using increased acetylenic units in the backbone as well as by introducing directly bound aromatic side groups. Synthesis of these novel oligoynes and their solid state polymerization behavior are described.

Experimental Section

Synthesis of the monomers **6a** and **6b** were carried out according to Scheme 1. Preparations of **3a** and **3b** have been reported previously.[18] Details of the synthetic procedures from **4** onward are as follows.

Preparation of 2-Methyl-6-(2-thienyl)-3,5-hexadiyn-2-ol, 4a. CuCl (300 mg), 2-aminopropane (25 mL), and hydroxylamine hydrochloride (250 mg) were taken in a three-neck round-bottom flask. Nitrogen atmosphere was maintained inside the flask by bubbling nitrogen gas through the reaction mixture. Into the reaction mixture was syringed dry methanol (10 mL). 2-Ethynylthiophene (10.8 g, 100 mmol) was added dropwise to the reaction mixture. Nitrogen gas was bubbled through the reaction mixture for another 15 min.

In another three-neck flask equipped with septa, 4-bromo-2-methyl-3-butyn-2-ol[19] (19.62 g, 120 mmol) was taken with 2-aminopropane (25 mL). Nitrogen gas was bubbled through the solution for 15 min. This solution was added dropwise for 30 min to the reaction mixture in the previous flask through a cannula. The reaction was monitored by TLC using hexane/ethyl acetate (90:10) solvent system as eluent. The reaction was found to be complete after 2 h.

The reaction mixture was concentrated in a rotary evaporator. It was then washed with water and extracted with ether. The ether layer was dried over anhydrous Na_2SO_4. The dried solution was then concentrated on rotavac to get the crude product as brown solid. The crude was purified using a silica gel column and hexane/ethyl acetate (80:20) solvent system as eluent. The pure **4a** was obtained as yellowish crystals. Yield: 75%. Mp: 65−66 °C. IR (KBr), cm^{-1}: 3300 (OH), 3030 (arom C−H), 2965 (aliph C−H), 2200 (C≡C), 1370 and 1380 (*gem*-dimethyl). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (s, 6H), 2.00 (s, 1H), 6.99−7.01 (dd, 1H), 7.32 (d, 1H), 7.33−7.35 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.61, 67.20, 68.42, 70.34, 71.70, 82.58, 121.64, 127.10, 128.83, 134.57. Anal. Calcd for $C_{11}H_{10}OS$: C, 69.47; H, 5.26; S, 17.78. Found: C, 69.27; H, 5.47; S, 17.25.

Preparation of 2-Methyl-6-(3-quinolyl)-3,5-hexadiyn-2-ol, 4b. The preparation method was similar to that of **4a**. Yield: 76%. Mp: 169−171 °C. IR (KBr), cm^{-1}: 3300 (OH), 3030 (arom C−H), 2970 (aliph C−H), 2210 (C≡C), 1370 and 1380 (*gem*-dimethyl). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (s, 6H), 2.17 (s, 1H), 7.52−7.63 (dd, 1H), 7.76−7.78 (dd, 1H), 7.81 (d, 1H), 8.10 (d, 1H), 8.29 (s, 1H), 8.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.52, 65.30, 66.48, 75.66, 76.50, 89.01, 116.02, 127.02, 127.63, 127.66, 129.04, 130.81, 140.03, 144.64, 152.22. Anal. Calcd for $C_{16}H_{13}NO$: C, 81.70; H, 5.53; N, 5.96. Found: C, 81.64; H, 5.63; N, 5.88.

Preparation of 2-(1,3-Butadiynyl)thiophene, 5a. In a 300 mL round-bottom flask, **4a** (6 g, 33 mmol) alongwith 100 mL of benzene and 5 g of KOH was taken. The mixture was stirred and heated to 50 °C. The reaction was followed by TLC and was found to be complete after $3^1/_2$ h.

The reaction product was concentrated, washed with water, and extracted with chloroform. Organic layer was dried over anhydrous Na_2SO_4. The pure **5a** was obtained by subjecting the crude to a silica gel column using hexane/ethyl acetate (80:20) as eluent. The product was obtained as a brown syrupy liquid. Yield: 70%. IR (KBr), cm^{-1}: 3300 (C≡C−H), 3030 (arom C−H), 2965 (aliph C−H), 2180 and 2120 (C≡C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 1H), 6.97−6.99 (dd, 1H), 7.20−7.21 (d, 1H), 7.24−7.25 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 79.11, 80.92, 81.83, 82.31, 121.23, 127.02, 128.40, 133.81. Anal. Calcd for C_8H_4S: C, 72.71; H, 3.03; S, 24.26. Found: C, 72.77; H, 3.03; S, 24.21.

Preparation of 2-(1,3-Butadiynyl)quinoline, 5b. The procedure for preparation of **5b** was similar to that for **5a**. In this case, the reaction was carried out at 75 °C. The reaction was complete in 30 min. After extraction with chloroform and silica gel column chromatography, the pure **5b** was obtained as yellowish crystals. The compound was stored as acetone solution as it was sensitive to light in solid state. Yield: 75%. Mp: 70 °C. IR (KBr), cm^{-1}: 3300 (C≡C−H), 3030 (arom C−H), 2965 (aliph C−H), 2200 and 2120 (C≡C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.20 (s, 6H), 7.55−7.60 (dd, 1H), 7.74−7.77 (dd, 1H), 7.78 (d, 1H), 8.10 (d, 1H), 8.31 (s, 1H), 8.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 79.23, 80.22, 81.03, 87.21, 116.22, 127.00, 127.41, 127.50, 129.47, 130.44, 139.75, 146.52, 152.38. Anal. Calcd for $C_{13}H_7N$: C, 88.14; H, 3.95; N, 7.90. Found: C, 88.18; H, 3.93; N, 7.88.

Preparation of 1,8-Bis(2-thienyl)-1,3,5,7-octatetrayne, 6a. In a 500 mL three-neck round-bottom flask fitted with O_2 inlet and outlet, **5a** (1.2 g, mmol) was taken in 200 mL of acetone. *N,N,N′,N′*-Tetramethyl ethylenediamine (5 mL) was added to it, followed by 500 mg of CuCl. The reaction solution was stirred throughout at room temperature, and oxygen was bubbled through the solution. The reaction was monitored by TLC (hexane/ethyl acetate, 80:20) and was found to be complete after 30 min. The compound was passed through a silica gel column using hexane/ethyl acetate (80:20) as eluent when **6a** was obtained in pure form as greenish yellow powder.

Yield: 80%. No melting point; polymerized at 150 °C. IR (KBr), cm^{-1}: 3030 (arom C−H), 2200, 2120 (C≡C). ^1H NMR (400 MHz, $CDCl_3$): δ 6.99−7.02 (dd, 2H), 7.35−7.36 (d, 2H), 7.41−7.42 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.41, 70.22, 72.00, 79.41, 120.99, 127.32, 130.18, 136.47. Anal. Calcd for $C_{16}H_6S_2$: C, 73.28; H, 2.29; S, 24.43. Found: C, 73.36; H, 2.28; S, 24.72.

Preparation of 1,8-Bis(3-quinolyl)-1,3,5,7-octatetrayne, 6b. This tetrayne was prepared in a similar way as **6a**. Column chromatography of the crude product using a silica gel column and hexane/ethyl acetate (80:20) as eluent yielded pure **6b** as yellowish powder. Yield: 80%. No melting point; polymerized at 198 °C. IR (KBr), cm^{-1}: 3030 (arom C−H), 2200, 2120 (C≡C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51−7.61 (dd, 2H), 7.76−7.78 (dd, 2H), 7.82 (d, 2H), 8.12 (d, 2H), 8.30 (s, 2H), 8.95 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.86, 68.17, 75.40, 77.44, 114.76, 126.77, 127.76, 128.02, 129.56, 131.22, 141.08, 147.22, 152.21. Anal. Calcd for $C_{26}H_{12}N_2$: C, 88.64; H, 3.41; N, 7.95. Found: C, 88.62; H, 3.42; N, 7.93.

Solid State Polymerization. Investigations of the solid state polymerization of the monomers were carried out using UV- and γ-irradiation and annealing.

For UV-irradiation, the powdered sample was sprinkled in a beaker containing water, and it was irradiated with UV sources of different wavelengths (254, 366, and 420 nm) for various amounts of time. The sample was then filtered and dried and its solution in methanol was used to record the absorption spectrum of the remaining monomer. This was used to monitor the polymerization. For γ-irradiation, the sample was taken in a glass tube which was then evacuated and sealed. This tube was irradiated with a ^{60}Co γ source. Different radiation dosages up to 200 Mrad were given to the samples. The polymer conversion was monitored by absorption spectroscopy just like for the UV-irradiated samples mentioned above. For annealing, the sample was made into a pellet and heated at a fixed temperature in an oven. Different samples were used to heat at different fixed temperature. The samples were taken out after certain time intervals and their FTIR spectra were recorded. This was used to monitor the polymer conversion.

Results

Both the monomers **6a** and **6b** are bright yellow colored crystalline solids. At room temperature, they are stable. Although **6a** and **6b** do not undergo solid state polymerization at room temperature when irradiated with UV- or γ-radiation, both of them undergo polymerization at higher temperatures. **6a** and **6b** react in the solid state at 150 and 198 °C, respectively to give polymers within a few minutes. At temperatures less than 150 and 198 °C for **6a** and **6b**, respectively, the monomers react at relatively slower rates to yield the same polymers as obtained in the above cases. The polymers are reddish brown and are insoluble in common organic solvents as well as in mineral acids.

Thermal Studies. To confirm that the monomers are indeed undergoing polymerization reactions at higher temperatures, differential scanning calorimetry (DSC) and differential thermal analysis/thermogravimetric analysis (DTA/TGA) were recorded for **6a** and **6b**. The DSC scan at heating rate at 10 °C/min shows an exotherm with peak at 150 °C for **6a** while **6b** shows an exotherm with peak at 198 °C. Interestingly, there was no endotherm observed in either of the cases, indicating that the monomers do not melt upon heating. Instead, they undergo chemical reaction as manifested by the exotherms. DTA/TGA experiments done for **6a** and for **6b** (Figure 2) further clarify the exothermic reaction. There was negligible weight loss (0.4% for **6a** and **6b**) at the temperatures corresponding to the exotherms of DSC, suggesting that the exotherms

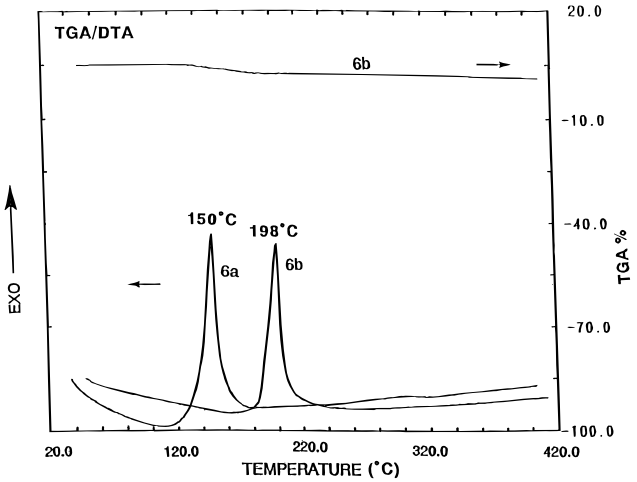


Figure 2. DSC and TGA of **6a** and **6b**.

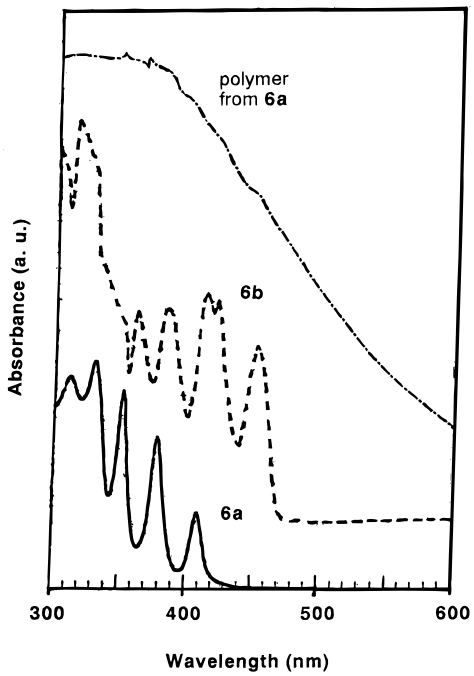


Figure 3. Absorption spectra of **6a**, **6b**, and the polymer from **6a**. Conditions: **6a** and **6b**, MeOH solution; polymer from **6a**, thin film.

observed in the DSC scans are due to the polymerization of the respective monomers in the solid state. The heat of reaction (ΔH) calculated from the area of the exotherm for **6a** and **6b** are 52.6 and 52.2 kcal/mol respectively. These values are larger than the usual range of 30−40 kcal/mol required for solid state 1,4-addition polymerization.[20] The larger value of ΔH can be explained if we consider that the polymerization reaction is not the simple 1,4-addition.

Absorption Spectra. The monomer solutions of **6a** and **6b** have sharp absorption bands with the longest absorption maxima at 420 and 450 nm respectively (Figure 3). Upon polymerization, these bands become broad. The band edges move to longer wavelengths, indicating greater π-conjugation in the polymers. The broadening of the peaks can be attributed to the inhomogenity of the π-conjugation length in the polymer network formed. However, the overall area under the absorption band remained almost unchanged for monomer to polymer transition. This indicates that there is

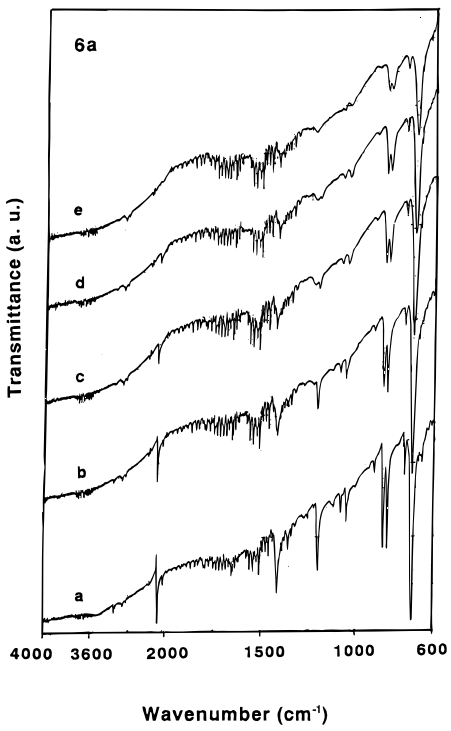


Figure 4. FTIR spectra of the **6a** after the following duration of heating at constant temperature at 120 °C: (a) 0 min; (b) 90 min; (c) 2 h; (d) 3 h; (e) 8 h. Peaks and valleys around 235 cm^{-1} are due to CO_2 in air.

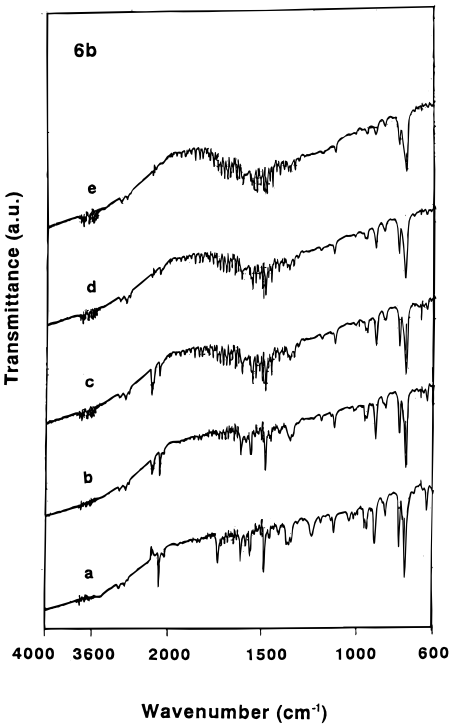


Figure 5. FTIR spectra of the **6b** after the following duration of heating at constant temperature at 150 °C: (a) 0 min; (b) 45 min; (c) 2 h; (d) 4 h; (e) 24 h. Peaks and valleys around 235 cm^{-1} are due to CO_2 in air.

almost no change in the conjugated unit density of polymer from that of the monomer.

FTIR Spectra. The IR spectra for monomers **6a** (Figure 4) and **6b** (Figure 5) show prominent peaks for acetylenic bonds as well as for aromatic side groups. IR spectral change during thermal annealing was recorded. Monomer **6a** was heated at a constant temperature of 120 °C while **6b** was heated at a constant temperature of 150 °C.

The FTIR spectrum for **6a** has two peaks at 2180 and 2080 cm^{-1} corresponding to the −C≡C− stretching frequencies and the 2180 cm^{-1} peak is stronger. Other characteristic peaks were observed at around 1520 cm^{-1} corresponding to the thiophene moiety and at 705 and 740 cm^{-1} for β-substituted thiophene. As the polymerization proceeded due to heating of the sample, the −C≡C− peaks were observed to be diminishing in intensity. After about 5 h at 120 °C, the 2180 cm^{-1} peak vanishes completely while the peak at 2080 cm^{-1} became very weak in intensity. Overnight heating at 120 °C of the sample did not change the above condition. At the same time, the peaks for thiophene units did not show any significant change during the entire process except that the peaks became slightly broadened. The disappearance of −C≡C− peaks indicates that the polymerization involves the acetylenic bonds. The peak at 705 cm^{-1} appears at the same frequency all along the polymerization process. It is known that the position of this peak is very sensitive to the substitutents on thiophene ring. Therefore the above observation implies that the thiophene ring is not disturbed during the polymerization process.

In case of **6b**, the monomer exhibits peaks for −C≡C− stretching at 2180 and 2080 cm^{-1} and multiple peaks in the 1600 cm^{-1} region for quinoline moieties. When the sample was heated above 150 °C, the intensity of −C≡C− peaks gradually diminished with time. After about 24 h of heating, both the peaks became negligible, implying polymerization of the sample via the acetylenic bonds.

Solid State ^{13}C NMR spectra. ^{13}C CP−MAS NMR spectra of monomers **6a** and **6b** were recorded. The monomers were then polymerized by heating at 150 and 198 °C respectively for 24 h. Solid-state NMR spectra of the resulting polymers were then recorded in order to have an insight into the structure of polymers. Figure 6 shows the solid state ^{13}C NMR spectrum of **6b** and that of its polymer. The monomer shows peaks for acetylenic carbons with chemical shifts (δ) from 65 to 85 ppm and quinoline carbons with δ from 115 to 145 ppm. After polymerization, all the acetylenic peaks for the monomer disappear while a single broad peak appears in the aromatic region. In the case of 1,4-addition reaction, the new peaks for the acetylenic carbons in the resulting PDA backbone should appear normally at around 105−110 nm.[16] In the present case, there is apparently no peak in this region. To further confirm this, we recorded a ^{13}C CP−MAS NMR spectrum using a dipolar dephasing pulse sequence, which emphasizes quaternary carbons together with mobile carbons such as terminal methyl carbon. Again, no peak could be seen in the 105−110 nm region. The absence of monomeric acetylenic peaks in the polymer confirms that the reaction has involved these bonds while the absence of any peak for polymeric acetylenic carbons indicates that the final polymer product has a structure other than that of a PDA.

^{13}C CP−MAS NMR of **6a** and its polymer also show similar structural changes. In this case, the peaks for the thiophene moiety at 120−140 ppm are completely overlapped by the resulting polymer's peak in the aromatic region.

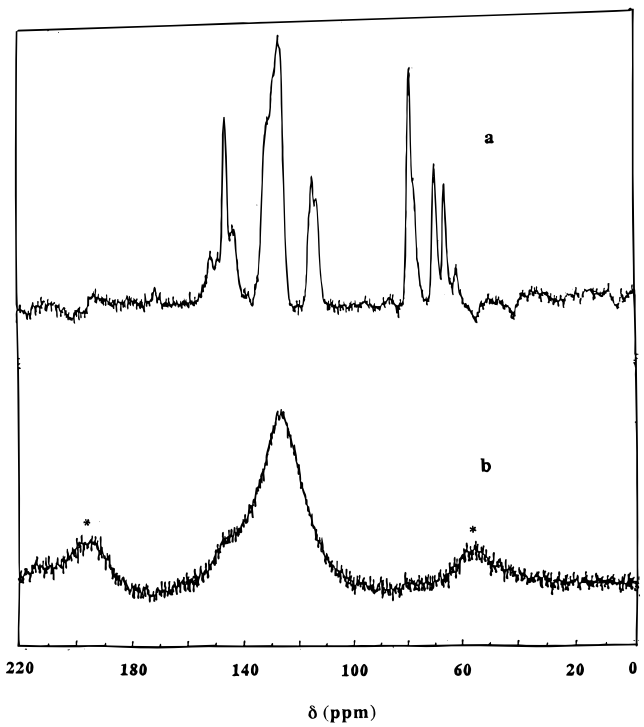


Figure 6. ^{13}C CP/MAS spectra of **6b**: (a) monomer, where the spinning sidebands have been suppressed using TOSS pulse sequence to avoid complexity in the spectrum; (b) polymer, where the asterisk marks indicate spinning sidebands.

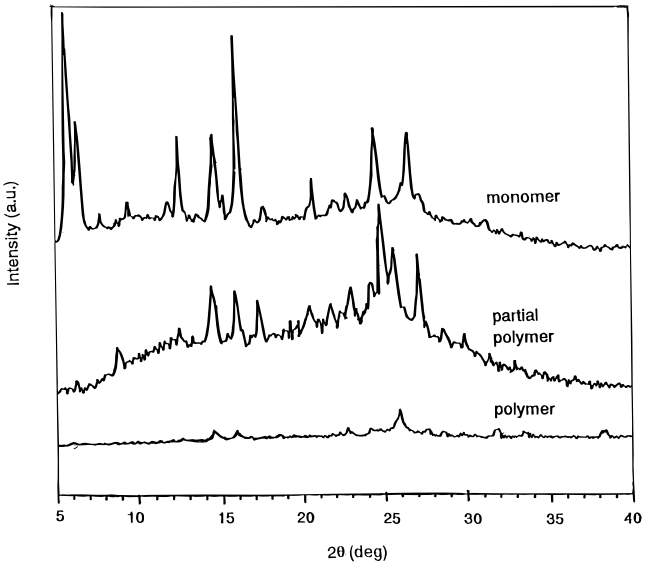


Figure 7. Powder XRD of **6b** (upper), its partial polymer by heating for 4 h (middle), and its polymer by heating for 24 h (lower).

X-ray Diffraction Studies. Powder X-ray diffraction (XRD) was recorded for the monomers **6a** and **6b** as well as for the polymers obtained from them after heating. Figure 7 shows the powder XRD pattern of monomer **6b** and that of its polymers obtained by heating the monomer at constant temperature (150 °C) for 4 and 24 h, respectively. The XRD patterns of the monomers showed sharp peaks, indicating that they are crystalline in nature. After 4 h, monomer and polymers were both present in the product. The polymer gave a few extra peaks apart from the original peaks of the monomers. When the compound was heated for a further time at the same temperature, monomer peaks kept on diminishing until, after 24 h of heating, there were almost no peaks corresponding to the monomer. The XRD showed a mostly broad pattern with a few sharp peaks. Similar results were obtained for **6a** also. In a separate experiment, the monomers **6a** and **6b** were heated at the DSC exotherm temperatures (150 and 198 °C, respectively), and the powder XRD patterns of these were recorded. These polymers showed similar XRD patterns as those obtained for the polymers after 24 h of heating at lower temperatures, as described above. Thus these studies indicates that the polymers obtained by both methods (slow heating and fast heating) were similar in nature and they are largely amorphous. Nevertheless, they contained some cystallinity after total conversion from monomers, as evident from the peaks in the XRD spectra.

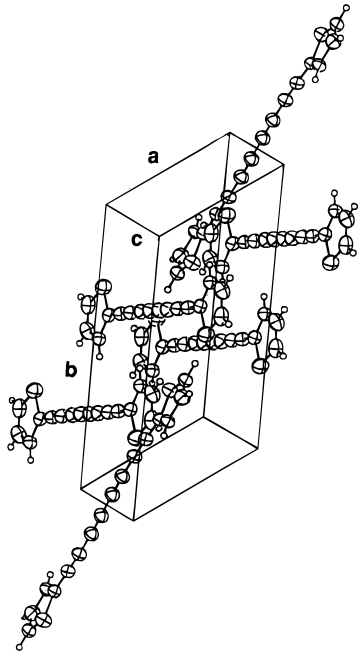


Figure 8. Crystal structure of **6a** in a crystal lattice unit.

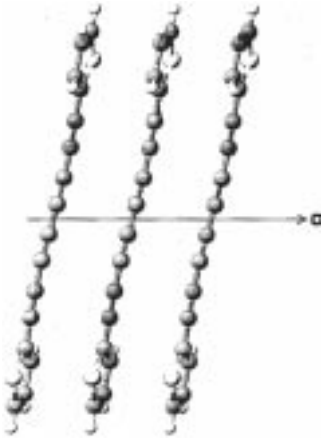
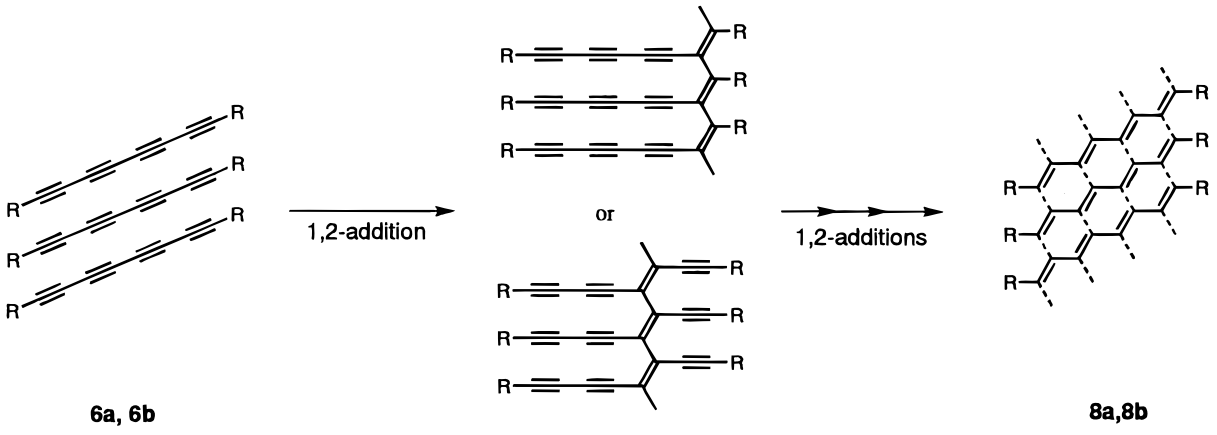


Figure 9. Stacking of **6a** molecules along the *c*-axis.

A single crystal of the monomer **6a** was obtained and its structure was analyzed using single-crystal X-ray diffraction.[21] Figure 8 shows the arrangement of **6a** molecules in the crystal lattice while Figure 9 shows the stacking of **6a** molecules along the *c*-axis. It was observed that the monomer molecules are packed in parallel stacks along the *c*-axis with a perpendicular distance of 3.9 Å. The angle which a molecule makes

Scheme 2. Polymerization Scheme of Octatetrayne Derivatives 6a and 6b



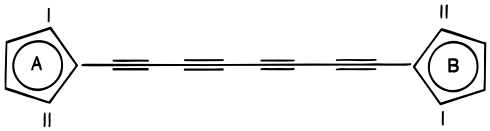


Figure 10. Structure of **6a** showing thiophene rings at A and B. I and II can have the C-atom and the S-atom in different probabilities.

with the axis, θ in Figure 1, is 71°, which is not suitable for a 1,4-addition reaction. Moreover, the thiophene rings in **6a** seems to have disordered structures. Figure 10 represents the schematic structure of the disordered **6a** molecule. The position of S-atoms in ring A and ring B are interchanged with the corresponding C-atom positions although the percentage of disorder is not very high. The S-atom resides the majority of its time at position I and a residual percentage at position II. In turn, the C-atom also occupies position I mostly, and the rest of the time, it is in the II position. Indeed, **6a** is stable at room temperature and only when it is pumped with energy in the form of heating does it react. It may be possible that by heating the monomers, we could have created a situation where the conditions for topochemical reaction were not so rigid and the reaction could proceed.

Discussion

The diacetylene analogues of **6a** and **6b**, namely 1,4-di(2-thienyl)-1,3-butadiyne (**7a**) and 1,4-di(3-quinolyl)-1,3-butadiyne(**7b**) have been previously investigated[14,22] out of which, **7b** is a very reactive DA in the solid state. The tetrayne **6a** and **6b** can be viewed as DAs having extended conjugation of the backbone through two more acetylenic groups and further capped by two aromatic units. Consequently, 1,4-addition reactions of these monomers in the solid state is expected. In reality, however, we have a complex scenario. Although **6a** and **6b** react in the solid state, the reaction takes place only at elevated temperatures, and the final polymers obtained did not conform to the 1,4-addition type.

In an attempt to confirm whether the reaction which occurs for **6a** and **6b** at elevated temperature, in fact produces polymers and if so then what is the mechanism, we carried out a series of investigations which have been described in the previous section. The DTA/TGA data confirmed beyond doubt that **6a** and **6b** react at 150 °C and 198 °C to produce polymers. The data further pointed out that the higher value of ΔH may have to do with a multistep reaction rather than simple 1,4-addition reaction only.

The single-crystal X-ray crystallographic analysis of **6a** reveals that the monomer is not suitable for topochemical polymerization, at least under normal conditions. The polymerization process corroborates this fact. At higher temperature, the polymerization was possible, most probably due to flexibility induced in the crystal geometry. We treated the monomers at different temperatures. It was observed that as the temperature is increased the rate of polymerization also increased. Clearly, heating the monomers helps them to react topochemically. There are four ways that the acetylenic bonds can react topochemically: a 1,2-, 1,4-, 1,6-, or 1,8-addition reaction. The corresponding distance between C-atoms of adjacent tetrayne backbones for 1,2-addition, 1,4-addition, 1,6-addition and 1,8-addition are 3.42, 4.40, 6.25, and 8.48 Å, respectively. Out of these, 1,6- and 1,8-addition reactions are out of the question as the huge distance between the reacting C-atoms will not allow them to occur. The 1,4-addition reaction may be ruled out on the basis of the fact that no corresponding peaks for the new acetylenic bonds of the polymer appear in the FTIR. Moreover, the stacking angle of 71° is far above the optimum value of 45° for the 1,4-addition reaction (see Figure 1). The topochemical principle says that a reaction in the solid state occurs with a minimum amount of atomic or molecular movement.[23] In view of this, the acetylenic C-atoms of adjacent molecules which are nearest to each other will prefer to react. On the basis of topochemical priciples, 1,2-addition seems most probable. The C−C distance for 1,2-addition reaction is the smallest among all the above cases, and hence the reaction takes places via 1,2-addition pathway. In our opinion, the initial reaction is 1,2-addition owing to shorter distance between the C-atoms of adjacent molecules.

The crystal structure of **6b** could not be analyzed and hence we do not know the exact distances and angles between the adjacent molecules in lattice. However, all the spectral data for **6b** suggests that the reaction takes place in a similar manner as that for **6a**, i.e., via a 1,2-addition reaction.

However, the final products are not just 1,2-addition product, since we cannot observe the presence of any acetylenic C-atoms or bonds for the final products. The broad bands observed in the absorption spectra of the polymers alongwith the broad peak obtained in the solid-state NMR spectra suggest that the final polymer in most probability is a cyclic polymer with aromatic rings. This indicates that the 1,2-addition reaction must have been followed by cyclization reaction to form an

irregular structure having aromatic character. This will also satisfy the thermal data.

In our laboratory, we have previously studied polymerization of tetraynes with long alkyl side groups. It has been observed that these monomers react in a two-step reaction as suggested above. For example, the polymerization scheme of 15,17,19,21-hexatriacontatetrayne (HTY), an octatetrayne monomer, to the polydiacetylene with butadiynyl substitutents has been studied.[12,16] It was found that solid-state polymerization for these monomers always proceeds by 1,4-addition. Further, the PDA formed could be thermally reacted. For the structure of the final polymer, a ladder polymer was proposed where the repeating unit is 1,6-didehydro[10]annulene, i.e., two conjugated PDAs. However, annulene is expected to be unstable. Thus the final structure of the polymers from octatetrayne derivatives after the thermal reaction may be either a planar cycloaromatized polymer and/or a three-dimensional polymer, which would be obtained if the polymerization proceeded in a direction different from that of the same column of the polymer side chain. However, in the present case, the reaction scheme does not follow the pathway via 1,4-addition. Instead, the reaction is initiated via 1,2-addition. If the reaction is allowed to proceed in regular manner, we should expect totally aromatized products (**8a** and **8b**) which may be seen as a ladder polymer with aromatic rings as the bridging groups (Scheme 2). We believe that in reality, the reaction does not proceed so regularly, and therefore instead of a very regular aromatic structure, we end up with a product which is an irregular cycloaromatized product.

Conclusions

In conclusion, we have reported the preparation of two novel monomers which have conjugated tetrayne units as the backbone and aromatic moieties as the side groups. These two monomers, although they do not give the usual polydiacetylene, react at high temperature and in the solid state to yield novel polymers. We have investigated the reaction to elucidate the polymerization mechanism and have proposed a mechanism consistent with the observations. The polymerization seems to be initiated via 1,2-addition reaction which is then followed by cyclization reaction to form irregular cycloaromatized products. These polymers, due to the conjugated system, are expected to have interesting optical properties which are being investigated.

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