First Example of Polydiacetylene from Diacetylene Monomer with Directly Linked Thienyl Sidegroup for Third-order Nonlinear Optics

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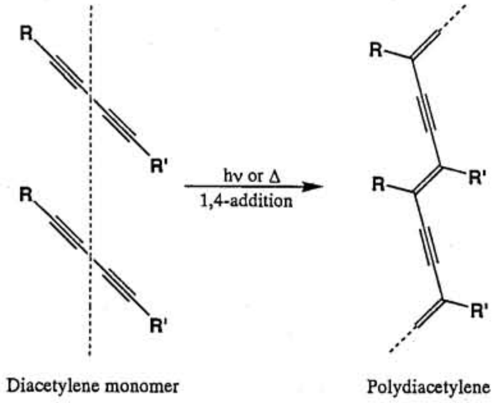
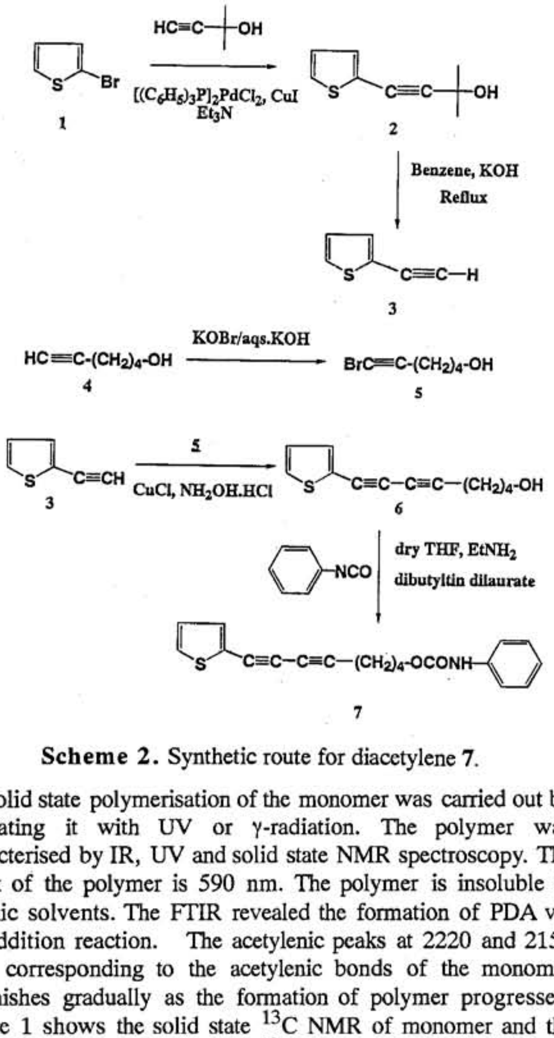
This work reports the first example of polydiacetylene(PDA) which has one of the side groups as a thienyl moiety directly linked to the π-conjugated backbone. The monomer, 8-(2-thienyl)-5,7-octadiynyl *N*-phenylcarbamate, undergoes solid state polymerisation via 1,4-addition reaction to yield the corresponding polydiacetylene.The third order nonlinear optical susceptibility of the polymer has also been evaluated.

The topochemical polymerisation of diacetylene(DA) to PDA in solid state(scheme 1) has generated enormous interest due to the unique single-crystal-monomer to single-crystal-polymer transformation and due to the unique optical and electronic properties of the conjugated PDA.[1-3] The choice of sidegroup in a DA is of vital importance because it solely controls the reactivity of the monomer as well as it controls all the properties of the resulting PDA. In an effort to enhance the sidegroup contribution in the conjugated backbone of PDA, our group as well as some other groups have been trying to use directly linked aromatic moieties as the sidegroups in DA.[4-6] Some success have been achieved to this end. However, the sidegroup which we have been most interested in, is the thienyl moeity. The thiophene, due to its S-atom, is of great interest as can be gauged by its use in conducting and superconducting materials. Thus, a directly bound thienyl moiety to the main chain backbone is expected to improve the electronic properties of the PDA. Our efforts till date have produced few such monomers, namely, 1,4-bis(2-thienyl)butadiyne[6], 1,4-bis(3-thienyl)butadiyne[6] and 1,8-bis(2-thienyl)-1,3,5,7-octatetrayne[7] but none of them could react to produce PDA as their crystal packing geometries do not conform to the ideal conditions for topochemical reaction. Therefore, we very carefully replaced one of the sidegroups with an alkyl chain having a terminal phenyl urethane unit. As a result, we obtained the first DA with formally linked thienyl moiety which can undergo topochemical polymerisation. In this letter, we report the synthesis and solid state polymerisation of a diacetylene which is unsymmetrically substituted with a 2-thienyl moiety and a urethane as the two sidegroups. The monomer, to our great satisfaction, undergoes 1,4-addition polymerisation in solid state to provide violet coloured PDA.



Scheme 1. Topochemical polymerisation of diacetylene.

The monomer, 8-(2-thienyl)-5,7-octadiynyl *N*-phenylcarbamate, **7** was prepared following scheme 2. Syntheses of **2**, **3** and **5** were carried out as reported in the literature.[7,8] The precursor diacetylene **6** was prepared in 50% yield by cross coupling **3** with the alcohol **5**. **6** is an oil at room temperature. The monomer **7** was prepared by reacting **6** with phenyl isocyanate in presence of dibutyltin dilaurate.[9]



Scheme 2. Synthetic route for diacetylene **7**.

Solid state polymerisation of the monomer was carried out by irradiating it with UV or γ-radiation. The polymer was characterised by IR, UV and solid state NMR spectroscopy. The λmax of the polymer is 590 nm. The polymer is insoluble in organic solvents. The FTIR revealed the formation of PDA via 1,4-addition reaction. The acetylenic peaks at 2220 and 2150 cm^{-1} corresponding to the acetylenic bonds of the monomer diminishes gradually as the formation of polymer progresses. Figure 1 shows the solid state ^{13}C NMR of monomer and the partial polymer. The CP MAS ^{13}C NMR of monomer showed peaks corresponding to the acetylenic C-atoms at 65, 66, 78 and 87 ppm. The methylene C-atom adjacent to the urethane moiety bonds as like consisting of a bipyridyl and a pyridyl moieties (see in Figure 1). The terpy ligand in complex **IV** shown in Figure 2 binds to Yb^{3+} ion also in the similar manner as that observed in **II**. The unsymmetrical coordination of terpy indicates that the ionic radius of Yb^{3+} is smaller than the bite of terpy ligand. The dihedral angles between two adjacent chelate rings of the terpy ligand in **II** and **IV** are 14.0 and 4.2 °, respectively. The larger distortion of terpy ligand in **II** than that in **IV** suggests that **II** has more steric hindrance (probably between the protons on the positions C5 and C15 of terpy and O atoms of dike ligand in same pentagonal plane).

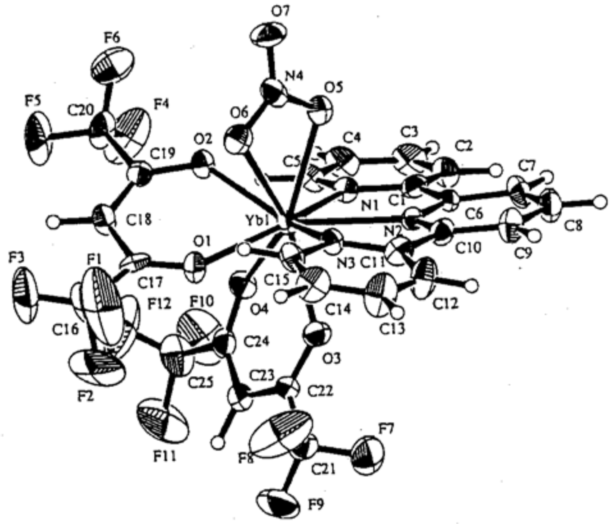


Figure 2. ORTEP drawing of $[Yb(hfac)_2(NO_3)(terpy)]$ (**IV**) with 30% probability ellipsoids giving atomic numbering. Selected bond lengths (Å) and angles (°) are as follows: Yb(1)-O(1), 2.261(7); Yb(1)-O(2), 2.312(7); Yb(1)-O(3), 2.309(7); Yb(1)-O(4), 2.339(8); Yb(1)-O(5), 2.381(8); Yb(1)-O(6), 2.537(8); Yb(1)-N(1), 2.476(8); Yb(1)-N(2), 2.477(8); Yb(1)-N(3), 2.509(8); O(1)-Yb(1)-O(2), 76.7(3) ; O(3)-Yb(1)-O(4), 70.7(3) ; N(1)-Yb(1)-N(2), 65.3(3) ; N(2)-Yb(1)-N(3), 65.9(3).

The bond distances of Yb-O(acac) placed at the trans position of terpy in **II**, 2.221(5) and 2.204(5) Å, is a little bit shorter than those in $[Yb(acac)_3(H_2O)]$ (the average value is 2.23 Å)[12] and are rather shorter than those of corresponding Yb-O(hfac) ones in **IV**, 2.261(7) and 2.312(7) Å, which means that the hfac ligand in **IV** is bound to the Yb^{3+} ion with weaker interaction. In other words, the combination of terpy-acac system is more convenient to form a π-base and a π-acid interaction than that of terpy-hfac system. These bond differences between Yb-acac and Yb-hfac reflects to the difference of dihedral angles of the terpy ligand described above. Consequently, these factors (shorter bond lengths of Yb-acac and therefore larger steric repulsion) prevent exchanging of NO_3^- ligand by another acac ligand to yield the bis-acac complex; $[Ln(acac)_2(NO_3)(terpy)]$.

For IR spectra of these complexes, we could obtain characteristic bands as C=C and C=O of β-diketonate at 1575 and 1520 cm^{-1} (for **I**), 1599 and 1521 cm^{-1} (for **II**), 1652 and 1602 cm^{-1} (very strong bands, for **III**), and 1664 and 1603 cm^{-1} (very strong bands, for **IV**). It is also interesting to note the nitrate coordination mode[13,14] by the IR bands in the region 1700-1800 cm^{-1}. For the acac series, there are two weak bands at 1778 and 1737 cm^{-1} (fot **I**) or 1782 and 1739 cm^{-1} (for **II**), which means the nitrate in the chelate acts as a bidentate ligand.[15] In case of the hfac series, unfortunately, there are rather strong absorption bands due to the hfac ligand in this region which obscure weak bands of the coordinated nitrate.

Finally, from the points of view concerned stereochemistries of ligands used and their coordination abilities (nitrate, hfac, acac and terpy), the behaviors of ligand exchange reactions for the lanthanide complexes are summarized as follows: (i) We could not obtain any ternary complexes, $[Ln(acac)_3(terpy)]$, when we tried to synthesize the chelates by using $Ln(acac)_3H_2O$ and terpy as starting materials. (ii) It is quite reasonable that the exchange reaction of NO_3^- ligand in the complex $Ln(terpy)(NO_3)_3 \cdot H_2O$ by β-diketonate one (hfac or acac) occurs to form the quaternary system. (iii) In the present study of quaternary systems (Yb-terpy-NO_3-acac or hfac), they contain two hfac (for **III** and **IV**) or one acac ligand (for **I** and **II**) by exchanging two or one nitrate, respectively. These behaviors are rather strange because the coordination ability of hfac is weaker than that of acac. We consider that the hardness of Ln^{3+} (Er^{3+} or Yb^{3+}) and hfac ligands are the cause that two nitrate ions may be displaced by two hfac ligands to give **III** or **IV**.

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10 Crystal Structure data for **II**: $YbN_5C_{20}O_8H_{18}$ (*FW* = 629.43), monoclinic, space group $P2_1/n$ (#14), $a = 10.917(4)$ Å, $b = 14.263(4)$ Å, $c = 14.915(5)$ Å, $\beta = 102.38(3)$ °, $V = 2268(1)$ Å^3, $Z = 4$, D(calcd) = 1.843 g/cm^3, μ(MoKα) = 41.78 cm^{-1}, $R = 0.034$ ($R_w = 0.022$) on 2376 reflections ($I > 3\sigma(I)$).

11 Crystal Structure data for **IV**: $YbN_4C_{25}O_7F_{12}H_{13}$ (*FW* = 882.42), triclinic, space group *P*-1 (#2), $a = 12.012(3)$ Å, $b = 15.695(2)$ Å, $c = 8.280(1)$ Å, $\alpha = 95.08(1)$ °, $\beta = 107.70(2)$ °, $\gamma = 88.39(2)$ °, $V = 1481.2(5)$ Å^3, $Z = 2$, D(calcd) = 1.978 g/cm^3, μ(MoKα) = 32.83 cm^{-1}, $R = 0.053$ ($R_w = 0.039$) on 3123 reflections ($I > 3\sigma(I)$).

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15 For **III** and **IV**, we could not assign the nitrate bands due to the existence of very strong diketonate bands in the same region.