The International Journal Of Engineering And Science (IJES)
||Volume||3 ||Issue|| 3||Pages|| 38-42||2014||
ISSN(e): 2319 – 1813 ISSN(p): 2319 – 1805

Effect of Spacers on 3, 4-Disubstituted Polythiophene Derivatives

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----------ABSTRACT----------

To control the steric interactions induced by disubstitution in the polythiophene and its derivatives a series of 3,4-disubstituted polythiophene derivatives have been described. In the present study the effect of various spacers (bithiophene, ethynylene and vinylene) on the effective conjugation length has been explored. The polymers with vinylene spacers showed the significant red shift in absorption maxima among the 3,4-disubstituted polymers.

KEYWORDS : *3-alkylthiophene), disubstitution, spacers, vinylene, ethynylene*.

Date of Submission: 07 January 2014 Date of Acceptance: 10 March 2014

I. INTRODUCTION

Semiconducting organic polymers have been extensively studied over the past few decades due to their promising applications in the field of electronics like field effect transistors and organic solar cells etc [1-5]. Among these conducting polymers, poly(3-alkylthiophene) (P3AT) and its derivatives have received great attention because of ease of their synthesis, functionalization and interesting optical and electronic properties [6-8]. The optical and electronic properties of the polymers strongly depend on its structure and P3HT has well organized lamellar structure whereby stacks of planar thiophene main chains are uniformly spaced by the alkyl side chains [9-10]. This perfect lamellar structure in the polymeric backbone is due to Head to tail (HT-HT) coupling of adjacent thienyl units.

The other modes of coupling like Head to Head (HH-HH) and Tail to Tail (TT-TT) gives the regio irregular counterparts. The polymers with high HH-HH and TT-TT dyads are blue shifted because of shorter effective conjugation length [5]. In the HH-HH configuration there is an increase in repulsive interaction between the substituents and the sp^2 lone pair on sulphur, which forces the backbone out of planarity [11]. It is not easy to maintain regioregularity throughout the backbone of the polymer because the polymer has some extent of regiorandom counterpart [12-16]. These polymerization defects affect the performance of the polymer in the devices significantly. Although there are several methods reported in the literature to control the regioregularity in the polymerization but all those processes are quite sensitive with respect to polymerization conditions like temperature, solvents and catalyst etc. [16-24]. Among the various polymerization methods for the 3-alkylthiophene the oxidative polymerization using $FeCl_3$ is the most simple and straightforward approach for the generation of polythiophene but it suffers from the polymerization defects by a great extent [1, 25]. Greater the structural defects lesser will be the effective conjugation length and hence wider will be the band gap of the polymer. By doing the structural modification in the main and/or side chain the regioregularity can be controlled. One of the effective ways to control the regioregularity and to get the polythiophene free from such defects is to symmetrically substitute the thiophene ring at both the β positions. This approach has not been much explored in the literature. This is because by the introduction of one more alkyl side chains as solubilising group disturbs the lamellar structure and therefore there is increase in the repulsive interactions caused by the incorporation of an additional alkyl side chain to the polymer backbone. The steric strain induced by disubstitution has a negative impact on conjugation because of decreased backbone planarity. Fig 1 showed some of the disubstituted polythiophenes with same or different substitutents at 3 and 4 positions [11, 26-27].
The present paper gives a method to control the steric strain in the 3, 4-disubstituted polythiophene and its derivatives by introduction of a spacer molecule in the polymer backbone. The steric strain introduced by disubstitution could be effectively reduced by placing a spacer in the polymer backbone. The effect of spacers on the optical properties (conjugation in the polymer backbone) of 3, 4-diaryl substituted polythiophene derivatives has been discussed.

In the following, the text is organized to follow the different types of spacers like bithienyl, ethynylene, and vinylene. Along with this a comparison of these polymers with similarly substituted polythiophene derivatives with and without spacers has also been presented. Fig 2 showed the structures of the various polythiophene derivatives discussed in the present study. Here the alkyl side chain has been replaced by alkylthienyl and alkylphenyl side chain.

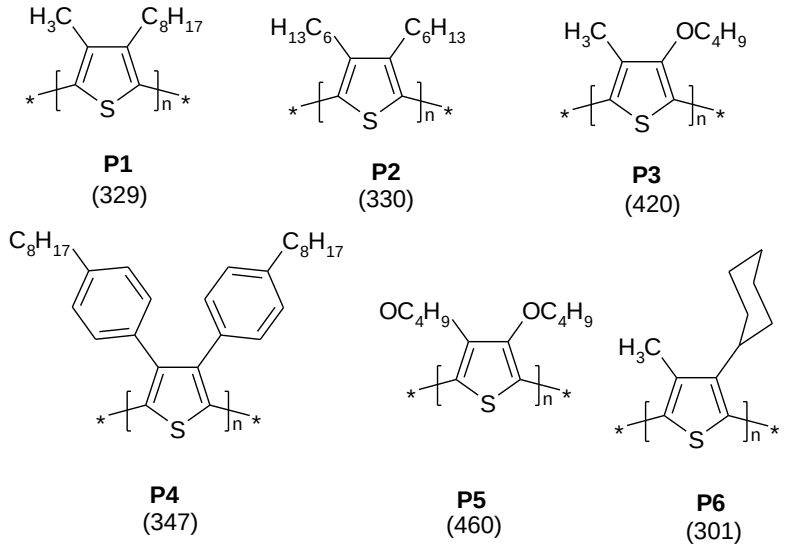


Figure1 Structures of 3,4-disubstituted polythiophenes (number in bracket indicates absorption maxima)

II. MATERIALS AND METHODS

The polymer **3T1** and **3T2** were prepared by Yamamoto method by polymerizing their dibromo monomers using Ni catalyst. All other polymers were prepared by Stille coupling from their respective dibromo monomers with either bis(tributyl stannyl)acetylene (for 3TE1, 3TE2, TE1 and TE2) or bis(tributylstannyl)ethene (for 3TV1, 3TV2, TV1and 3V2) via Pd catalyst. The detailed synthesis and characterization of these polymers has been reported elsewhere [28-29]. The number molecular weight (M_n) was determined using GPC with THF as eluent based on PS standards. Table 1 summarizes the number average molecular weight of these polymers.

III. RESULTS AND DISCUSSION

The polymers **3T1** and **3T2** are terthiophene based polymers and contains a centro-symmetric repeat unit with an unsubstituted terminal thiophene unit which allows regular spacing of the bulky substitutents. The absorption maxima of **3T1** and **3T2** polymer were measured in THF solution and were found to be at 484 nm and 478 nm respectively. These values are significantly blue shifted than the 3, 4-dialkylsubstituted polymers (**P1-P6**) shown above. The observed values of absorption maxima indicate stronger π-π transitions which are due to reduction of the steric strain induced by introduction of bithienyl as spacer. The two thiophenes per repeat unit act as spacer and therefore provide space for the accommodation of side chain.In the symmetrically β-disubstituted polyterthiophenes the oxidative coupling is forced to afford completely regio regular polymers, due to the chemical and geometrical equivalence of the coupling position [30]. **P7** and **P8** (see fig 3) are the terthiophene based polymers with the alkyl side chain and are regioisomer of each other. Their absorption maxima is slightly blue shifted than **3T1** and **3T2** which may be attributed due to enhanced conjugation in the polymer backbone induced by aryl alkyl side chains. **3T1** and **3T2** are polymerized by Yamamoto method while **P7** and **P8** by Stille coupling and oxidative polymerization using $FeCl_3$ respectively. Zhenan Bao et.al reported that polymer **P7** showed high charge carrier mobility of $0.17 cm^2V^{-1}s^{-1}$ in field effect transistors and power conversion efficiency of 4.2% in polymer:fullerene bulk heterojunction solar cells [31].

Fig 2 and 4 showed the structures of (**3TV1**, **3TV2**, **TV1** and **TV2**) 3, 4-diarylalkyl substituted polythiophene derivatives with vinylene group as spacer. The **TV1** and **TV2** have two side chains and a vinylene spacer per thienyl unit while **3TV1** and **3TV2** have two side chains per three thienyl units and a vinylene spacer. The absorption maxima of **3TV1** and **3TV2** are 520 and 511 nm respectively which is significantly red shifted than **3T1** and **3T2**.

This enhanced value of absorption maxima is attributed by the fact that by the incorporation of vinylene unit symmetrically along the polymer backbone there is increased conjugation and backbone planarity [32-33]. The absorption maxima for **TV1** and **TV2** occur at much higher value than **3TV1** and **3TV2** because in **TV1** and **TV2** the ratio of number of thiophene to vinylene decreases and therefore the planarity along the polymer backbone increases and there is enhancement in absorption maxima [34-36]. Roncali has described the synthesis of well defined soluble mono and disubstitued oligo thienylene vinylene and it was reported that incorporation of double bond at the regular interval make the oligomeric and polymeric backbone more planar, rigid and aromatic [33, 35].

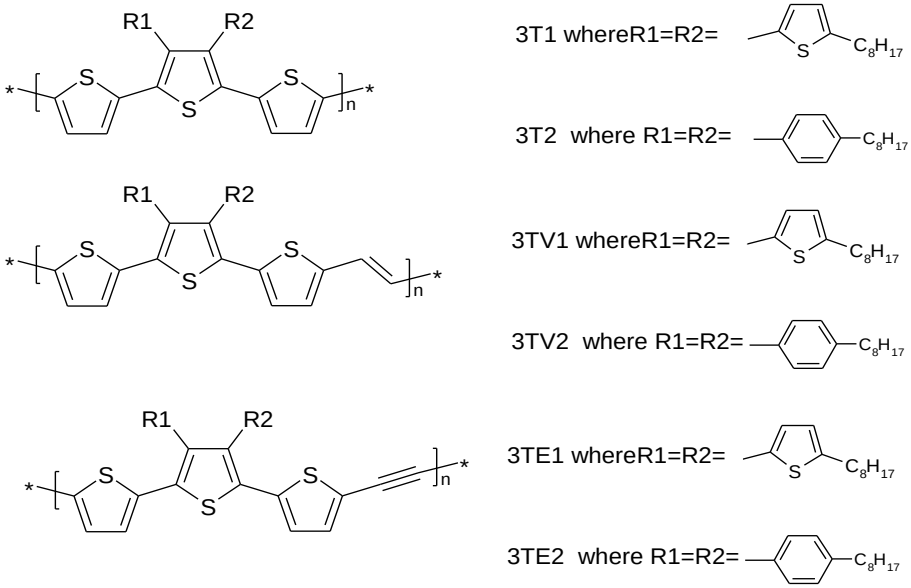
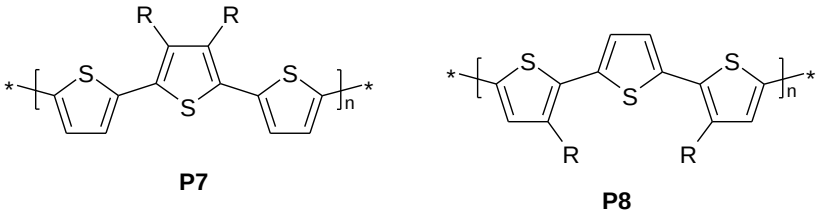


Figure 2 Structures of various terthiophene based polymers with spacers



R = -C_8H_{17}

Figure 3 Structure of terthiophene based polymers

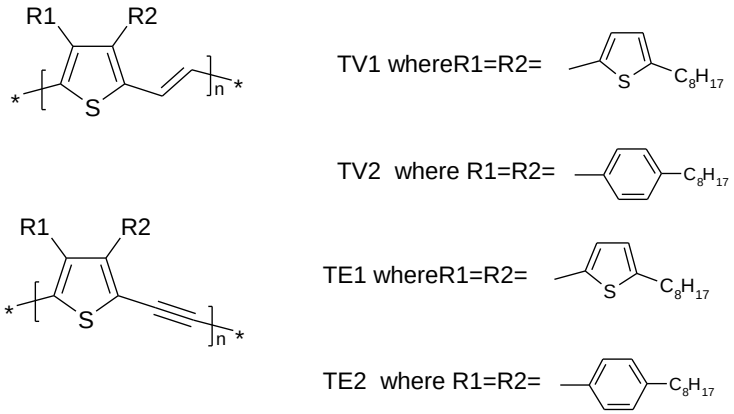


Figure 4. Structure of disubstituted polythiophenes

Fig 2 and 4 showed the structures of (**3TV1**, **3TV2**, **TV1** and **TV2**) 3, 4-diarylalkyl substituted polythiophene derivatives with vinylene group as spacer. The **TV1** and **TV2** have two side chains and a vinylene spacer per thienyl unit while **3TV1** and **3TV2** have two side chains per three thienyl units and a vinylene spacer. The absorption maxima of **3TV1** and **3TV2** are 520 and 511 nm respectively which is significantly red shifted than **3T1** and **3T2**. This enhanced value of absorption maxima is attributed by the fact that by the incorporation of vinylene unit symmetrically along the polymer backbone there is increased conjugation and backbone planarity [32-33]. The absorption maxima for **TV1** and **TV2** occur at much higher value than **3TV1** and **3TV2** because in **TV1** and **TV2** the ratio of number of thiophene to vinylene decreases and therefore the planarity along the polymer backbone increases and there is enhancement in absorption maxima [34-36]. Roncali has described the synthesis of well defined soluble mono and disubstitued oligo thienylene vinylene and it was reported that incorporation of double bond at the regular interval make the oligomeric and polymeric backbone more planar, rigid and aromatic [33, 35].

Table 1 Absorption maxima[a] and molecular weight of various polymers

Polymer	λmax (nm)	M_n (10^3) $gmol^{-1}$	Polymer	λmax (nm)	M_n (10^3) $gmol^{-1}$
3T1	484	6.86	**3TV1**	520	8.77
3T2	478	5.46	**3TV2**	511	6.59
3TE1	462	19.3	**3TE2**	452	29.9
TV1	595	6.93	**TV2**	588	8.93
TE1	464	11.4	**TE2**	436	11.3

[a] The absorption maxima were measured in solution

The third classes of polymers (**3TE1**, **3TE2**, **TE1** and **TE2**) described here are based on ethynylene spacers. These polymers were synthesized by Stille coupling and table 1 summarizes their absorption maxima which are found in the range from 436 to 474. Although these values are significantly red shifted than 3,4 dialkyl substituted polythiophenes and are comparable to regioregular P3AT. These polymers exhibit lower absorption maxima than vinylene based polymers. This suggests that incorporation of ethynylene moiety in the polymer does not have much effect on the extent of conjugation. It is reported that triple bond has strong electron withdrawing effect which makes it difficult to polymerize. The conjugation in this class of polymer is disturbed by the formation of cumulene structures which is less stable [37]. Bauerle et al. have described the synthesis of polymer based on alternating unit of bithiophene and triple bond and the polymer showed that incorporation of triple bond lowers the HOMO level and therefore exhibit high open circuit voltage. Later on they have published the synthesis of well defined homologous series of ethynylene containing oligothiophenes as model compounds [38-39].

IV. CONCLUSION

In conclusions, different classes of 3, 4-diaryl substituted polymers were described and it was found that incorporation of spacers molecules is the effective method for the reduction of steric strain. The vinylene is very effective in increasing the planarity in the polymer backbone followed by bithienyl. There is not much effect on planarity by incorporation of ethynylene as spacer. From the observed values of absorption maxima for the vinylene based polymers it could be anticipated that such polymers hold good promise as the future materials for photovoltaics.

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