

POLYMERS FOR SOLAR ENERGY APPLICATIONS

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Introduction

Availability of a variety low energy gap (E_g), stable, processible, and functionalizable acceptor type (n-type) of conjugated polymers is badly needed for developing various types of donor-acceptor (D/A or p/n) junction based polymer optoelectronic (OE) devices, such as solar cells made of all-polymer D/A bulk heterojunctions,¹⁻³ and the donor-acceptor block copolymers.²⁻⁵ For D/A block copolymer systems, the relatively less available acceptor type polymers must satisfy following: 1. Absorption spectrum covers a large portion of visible solar spectrum (with energy gaps E_g in the range of 1-2 eV), 2. LUMO level is sufficiently low to enable photo-induced electron transfer from donor polymers and to maintain air stability, 3. End-group functionalities allow covalent coupling with other donor block(s). In this study, a series of novel sulfone(SF)-containing polythiénylenetetra vinylene repeating unit [P(C6OTV-SFTV) shown in Scheme 1] has thus been developed. These new polymers can be considered as a PTV with the sulfur in every other thiophene ring being oxidized to sulfone (-SO₂-). By using co-monomers with different aromatic resonance energy and with/without electron donating side groups, a series of sulfone-containing conjugated polymers with a wide range of energy gaps were obtained. Furthermore, the terminal functional groups of these polymers would enable further block copolymer supramolecular structure developments.³⁻⁵

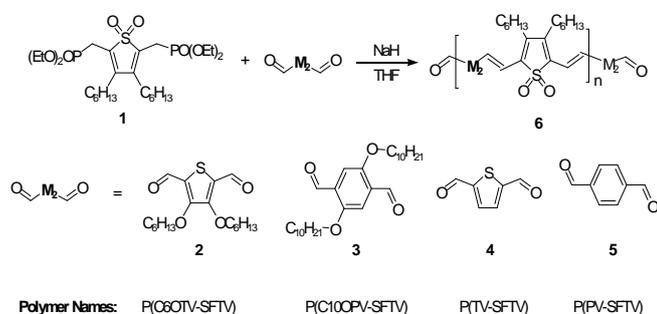
Experimental

All starting materials, reagents, and solvents were purchased from commercial sources (Sigma Aldrich and Fisher-Scientific) and used as received unless noted otherwise. NMR spectra were obtained from a Bruker Advance 300 MHz spectrometer with TMS as the internal reference. Elemental analysis was performed by Atlantic Microlab Inc. UV-vis data were collected on a Perkin Elmer Lambda 900 Spectrophotometer. Photoluminescence experiments were performed on an ISA Fluoromax-3 luminescence spectrofluorometer. Differential scanning calorimeter (DSC) and thermal gravimetric analyzer (TGA) data were collected by Perkin Elmer DSC-6 and TGA-6. Measurements of polymer molecular weights were done on a Viscotek GPC system with a UV-Vis absorption detector at ambient temperature using tetrahydrofuran as the solvent. Polystyrene standards were used for conventional calibration.

Results and Discussions

Materials synthesis As shown in Scheme 1, the polymers **6** were prepared from two types of co-monomers: the diphosphonate **1** and aromatic dialdehydes (**2**, **3**, **4** and **5**) via the Horner-Emmons reaction. Details of the synthesis were reported elsewhere.⁶

Optical and electrochemical properties Figure 1 shows the normalized absorption spectra of the solutions of the four SF-PTV polymers. The absorption λ_{max} and optical energy gaps (E_g^{opt} s, calculated from absorption cutoff wavelengths) are listed in Table 1. The energy gap decreases as the donor unit changes from simple phenylene all the way to 3,4-bis(hexyloxy)thiénylene, with a good correlation with aromatic resonance energy and electronic richness of the aromatic unit.



Scheme 1 Synthesis of PTV derivatives with sulfone embedded in polymer conjugated backbones.

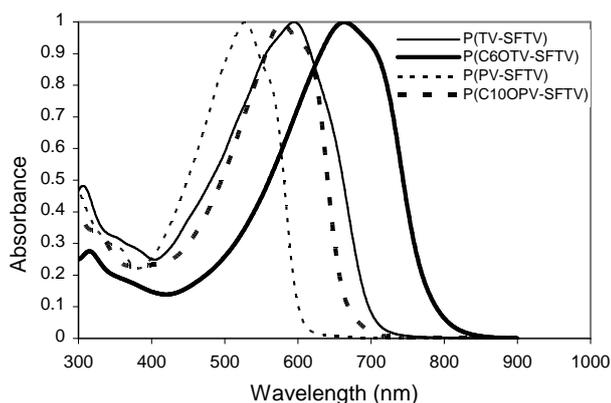


Fig. 1 Normalized UV-vis Absorption spectra of SF-PTVs chloroform solutions with nominal concentration of 0.1mM without filtration.

Table 1. Electronic properties of SF-PTVs

	$\lambda_{\text{cutoff}}/E_{\text{g}}^{\text{opt}}$ (nm/eV)	LUMO/ HOMO/ E_{g}^{EC} (eV)
P(PV-SFTV)	608/2.04	-3.48/-5.54/2.06
P(C10OPV-SFTV)	684/1.82	--/-5.23/--
P(TV-SFTV)	708/1.75	-3.56/-5.36/1.80
P(C6OTV-SFTV)	806/1.54	-3.54/-5.16/1.62

Electrochemical measurements were performed for SF-PPVs in thin films coated on Pt working electrode. LUMO/HOMO levels are estimated from the redox potentials, and corresponding electrochemical energy gaps (E_{g}^{EC} s) are also listed in Table 1 (Note the LUMO of P(C10OPV-SFTV was beyond CV measurement condition, so it should be estimated from the optical energy gap as -3.41eV). The LUMO levels of all SF-PTVs are very close (with differences < 0.1 eV). This is consistent with the fact that the acceptor unit is same for all SF-PTVs and that LUMO level is mostly affected by electron withdrawing sulfone group(s). The SF-PTVs are similar to the well known acceptor polymer CN-PPV⁷ in terms of LUMO level, and are likely to function as acceptors when paired with electron-rich π -conjugated polymers. Due to the fact that SF-PTVs have lower E_{g} s and are not luminescent, photoluminescence quenching may not be solely used to confirm the photo induced charge transfer in blend of SF-PTV with commonly used donor polymers. Other types of experiments (such as ESR, PIA, and photo conductivity) should be conducted to confirm the acceptor nature and

photovoltaic potentials of these polymers (especially the two soluble polymers).

Conclusion

A series of conjugated main chain terminal functionalized and evolving energy gap sulfone-containing thienylenevinylene-based co-polymers have been developed and studied. The HOMO/LUMO energy gaps of these polymers were in a range of 1.5-2.0 eV. The sulfone group greatly lowers both HOMO/LUMO levels, making these polymers potential electron acceptors (n-type) for polymeric electronic/optoelectronic applications. Lowering HOMO/LUMO levels also improve the air stability of the materials. The well-defined terminal functional groups (aldehyde or phosphonate) make these polymers potentially ideal acceptor polymer blocks for the development of D-A block copolymer supramolecular nanostructures.

References

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