

**P33T, P34T, P35T, P36T, P37T, P38T, P39T POLYMERS & FIBERS-
DETERMINATION OF ELECTROCHEMICAL BEHAVIOUR;
HOMO-LUMO and BANDGAP by CYCLIC VOLTAMMETRY and SPECTROSCOPY**

Purpose of the Visit

The main purpose of this project is to have the candidate getting experienced on the evaluation of conducting polymers as components of the active layer for solar cells applications. Characterization of semi-conducting materials will bring additional knowledge and experience on the use of laboratory instruments and evaluation of the results. This project might help the setting-up of an electro-active materials laboratory in Turkey. The candidate could then contribute to this laboratory in material characterization and device application.

Description of the Work

Electrochemical behavior of conjugated polymers is investigated by cyclic voltammetry to estimate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. For all calculations of HOMO and LUMO the method described by Bard et al. will be used. According to this method, ferrocene is chosen as a standard and all potentials are referenced using ferrocene/ferrocenium standard, 0.05 V versus Ag/Ag⁺. Well known literature value of the oxidation of ferrocene in acetonitrile versus SCE (saturated calomel electrode) of 0.31 V is used. By using literature value of SCE versus NHE (normal hydrogen electrode) of 0.24 and then using the generally accepted literature value of NHE versus vacuum of -4.43 eV, the energy level of reference electrode (SCE) is -4.67 eV below the zero vacuum energy level. Thus, the oxidation energy of ferrocene/ferrocenium ion couple relative to the vacuum level results as -4.98 eV. The reference electrode is calibrated with ferrocene ($E^0 = 0.05$ V versus Ag/AgNO₃). A value of 4.93 eV versus vacuum level for the reference electrode is obtained.

Polymers which are soluble in chlorobenzene or dichlorobenzene are used to prepare thin polymer films by dropcasting polymer solution (5 mg/mL) on ITO (indium tin oxide) covered glass substrates. The onset potential of oxidation and reduction values are used. The oxidation process corresponds to the removal of electron from the HOMO energy level whereas the reduction cycle corresponds to the electron addition to LUMO. The difference between two onset potentials can give the electrochemical bandgap of polymer.

Thin film electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 Potentiostat/Galvanostat using a conventional three-electrode cell under N₂ atmosphere (electrolyte: 0.1 mol/L TBAPF₆ in anhydrous CH₃CN). For the measurements, an Ag/AgNO₃ reference electrode (0.01 mol/L AgNO₃ and 0.1 mol/L TBAPF₆ in CH₃CN), a platinum counter electrode and an Indium-Tin Oxide (ITO) coated glass substrate as working electrode were used. For the measurements, the polymers and fibers were deposited by dropcasting directly onto the ITO substrates. Cyclic voltammograms were recorded at 50 mV/s. All potentials were referenced using a known standard, ferrocene/ferrocinium, which is estimated, in CH₃CN solution, to have an oxidation potential of -4.98 eV vs. vacuum.

Results

The cyclic voltammograms of thin films of polymers and their fibers display distinct characteristic quasi-reversible oxidation and reduction processes. Although the polymer oxidation peaks are broad and overlapping with the second oxidation peak, sharper and better defined oxidation and reduction peaks were obtained with the fibers. From the onset potentials of the oxidation and reduction the position of the energy levels can be estimated vs. Ag/AgNO₃. The corresponding energy levels of the highest occupied molecular orbitals (HOMO) and for the lowest unoccupied molecular orbitals (LUMO) are shown on the table. The corresponding energy levels for the highest occupied molecular orbitals (HOMO) have different values within the different derivatives and it is same for the lowest unoccupied molecular orbitals (LUMO). However the resulting electrochemical band gaps are close to each other. These bandgaps should be considered as almost same regarding the ±0.06 eV experimental error on the HOMO-LUMO values. Although electrochemical band gaps are comparable within each other, they are larger than the observed optical band gaps which must be considered also same within each other. This is an expected case because of the nonpolar side groups of those polymers and their fibers. The migration of electrolyte ions towards the polymer backbone is more difficult if the backbone has nonpolar side chains. This makes the oxidation occurs in higher positive potential and reduction in more negative potential which results in a wider bandgap.

Table 1. Onset potentials of oxidation and reduction, HOMO-LUMO values, electrochemical and optical bandgaps.

	$E_{\text{onset}}^{\text{OX}}$ (V)	$E_{\text{onset}}^{\text{RED}}$ (V)	HOMO (eV)	LUMO (eV)	E_{g}^{EC} (eV) (film)	E_{g}^{OP} (eV) (film)
P33T (Nonfiber)	0.288	-2.130	-5.22	-2.80	2.42	-
P33T (Fiber)	0.245	-2.095	-5.18	2.84	2.34	1.90
P34T (Nonfiber)	0.112	-2.240	-5.04	-2.69	2.35	1.91
P34T (Fiber)	0.158	-2.222	-5.09	-2.71	2.38	1.90
P35T (Nonfiber)	0.046	-2.220	-4.98	-2.71	2.27	1.90
P35T (Fiber)	0.085	-2.170	-5.02	-2.76	2.26	1.93
P36T (Nonfiber)	0.095	-2.205	-5.03	-2.73	2.30	1.91
P36T (Fiber)	0.130	-2.236	-5.06	-2.69	2.37	1.93
P37T (Nonfiber)	0.170	-2.210	-5.10	-2.72	2.38	1.91
P37T (Fiber)	0.176	-2.210	-5.11	-2.72	2.39	1.92
P38T (Nonfiber)	0.125	-2.212	-5.06	-2.72	2.34	1.91
P38T (Fiber)	0.158	-2.200	-5.09	-2.73	2.36	1.92
P39T (Nonfiber)	0.120	-2.245	-5.05	-2.69	2.36	1.90
P39T (Fiber)	0.173	-2.236	-5.10	-2.69	2.41	1.92

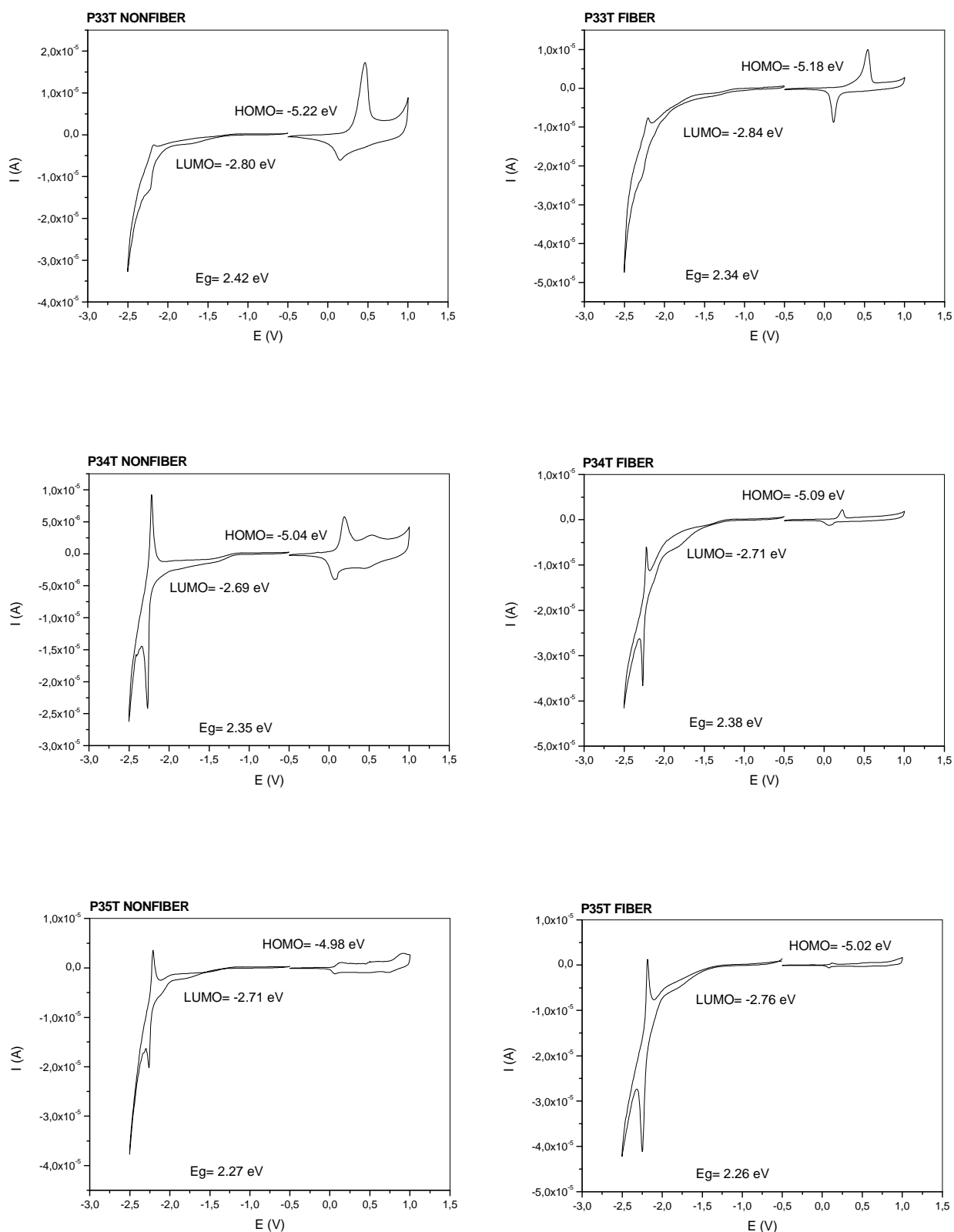


Figure 1. Cyclic voltammograms of polymers P33T, P34T, P35T and their fibers.

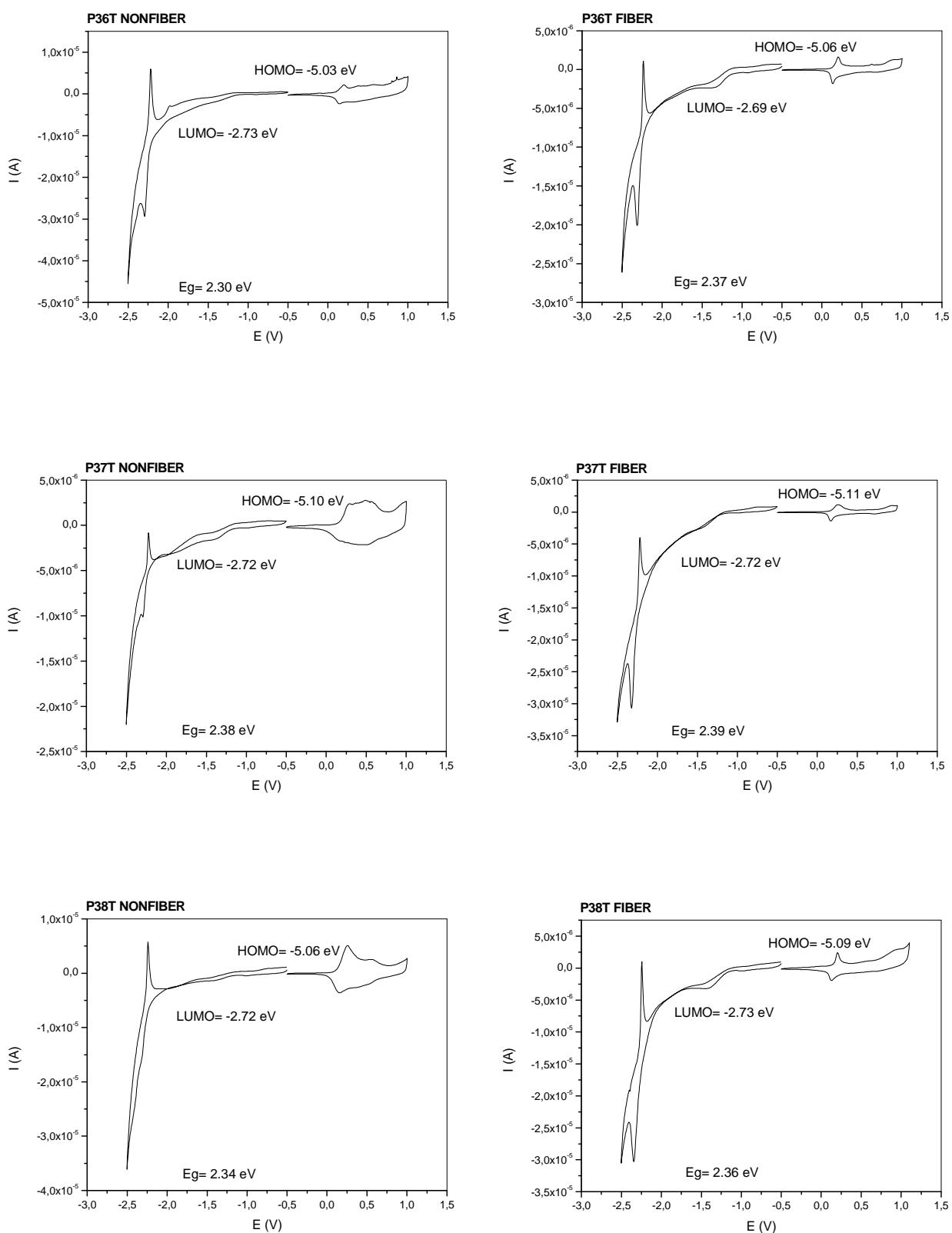


Figure 2. Cyclic voltammograms of polymers P36T, P37T, P38T and their fibers.

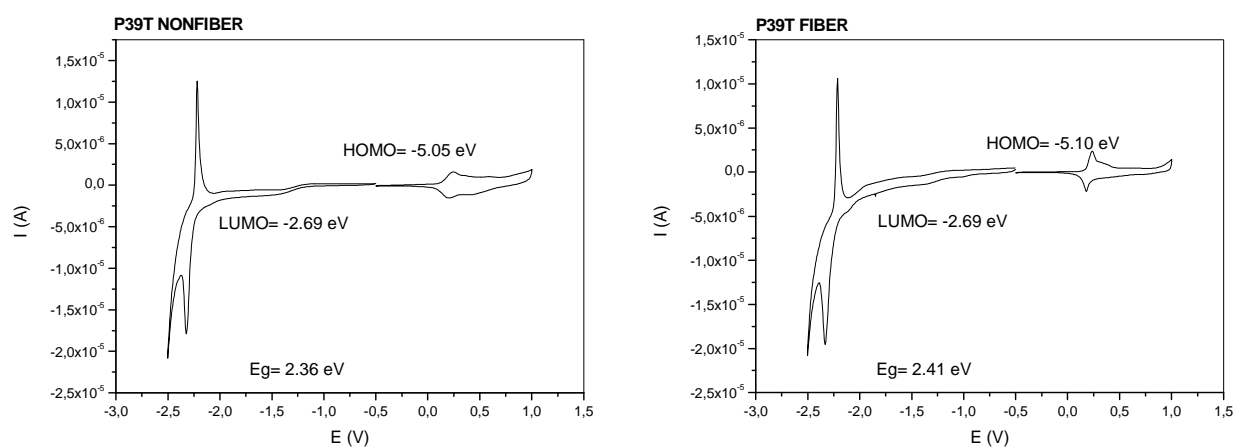


Figure 3 . Cyclic voltammograms of polymer P39T and its fibers.