



## **ELECTROLUMINESCENCE PROPERTIES OF PURE PVK AND DOPED TiO<sub>2</sub> POLYMER THIN FILMS**

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### **Abstract**

Polymeric thin films of poly (N-vinylcarbazole) (PVK) with nano-crystalline titanium oxide (TiO<sub>2</sub>) were fabricated by using bath deposition method. The X-ray diffraction (XRD) data revealed the amorphous nature of PVK polymer matrix and increased with increase of TiO<sub>2</sub> concentration. The complexation of the polymer was confirmed by Fourier transform infrared (FTIR) and UV-Visible studies. The Electroluminescence (EL) spectra of the thin films of polyvinylcarbazole (PVK) with titanium oxide (TiO<sub>2</sub>) showed an enhancement in the electroluminescence properties with various molar concentration of dopant. Moreover, the TiO<sub>2</sub> based Poly (N-vinylcarbazole) (PVK) exhibited a remarkable variation at higher molar concentration of the EL spectrum as compared to that of the pure polyvinylcarbazole film. The current-voltage characteristics of the various molar concentrations of TiO<sub>2</sub> shows the same trained in comparison with EL.

KEY WORDS: Electroluminescence (EL), Poly (N-vinylcarbazole) (PVK)

### **1. Introduction**

Poly (N-vinylcarbazole) (PVK) has well known for its photoconducting and Electroluminescence properties. PVK have widely use for electronic display, many electrical & electronic devices and home appliances [1-2]. In the present study PVK modified thin films have been prepared by using bath deposition method. In this synthesis the PVK is doped with Titanium oxide with various molecular concentrations with the help of chloroform. We investigate the Electroluminescence prosperities of PVK in with different molar concentration of TiO<sub>2</sub> the most typical inorganic thin-film EL (TFEL), for example, is TiO<sub>2</sub> with its yellow-orange emission. Examples of the range of EL material include [3]. Electrochemically



generated intermediates undergo a highly exergonic reaction to produce an electronically excited state that then emits light upon relaxation to a lower-level state. This wavelength of the emitted photon of light corresponds to the energy gap between these two states. ECL excitation can be caused by energetic electron transfer (redox) reactions of electro generated species. In the present work polyvinyl carbazole (PVK) was selected as a host polymer. PVK is one of the most important polymeric materials as it has many applications in industry and is relatively cheaper. Its unique chemical and physical properties led to its wider applicability. Due to its high tensile strength and good abrasion resistance, PVK is used in double-layer capacitors and electrochemical windows etc [3].

Polymer thin films are formed by incorporating a metal into highly polar polymer complexes. During the last few decades, the utilization of polymer light emitting diode in various applications has led to intensive interest in these materials [4-6]. Aiming to enhance its electroluminescence properties,  $\text{TiO}_2$  was doped into PVK host matrix in the present work.  $\text{TiO}_2$  was taken as a dopant for a variety of reasons like its low cost, thermal stability and good electrical properties. In this paper an effort has been made to study the effect of addition of Titanium oxide to PVK and study its structural and electroluminescence properties. The results obtained from these measurements are analyzed and reported.

## **2. Experimental**

### **2.1 Sample preparation**

Commercially available Poly (N-vinylcarbazole) (PVK) (Across manufacturing Belgium) material dissolved in chloroform in air ambient and modified with different molar concentration of  $\text{TiO}_2$ . The nanocomposite blends were used in a bath deposition onto the glass substrates and the samples are further dried in an air ambient for 1 h. The thickness of the polymer layer was controlled with help of different

deposition time and by the concentration of polymer in the solvent. The thicknesses of the films were measured to by Michelson interferometer which is found to be around 120 nm. The absorption spectra of the coated films were recorded using a Shimadzu UV-Visible spectrometer. Electroluminescence characteristics of various samples and photo physical measurements were performed at room temperature in air.

## 2.2 Analytical techniques

In the present study, X-ray diffraction spectra were recorded at room temperature in the range 10-70° Bragg angle by a SEIFERT X-ray diffractometry.  $\text{CuK}_\alpha$  radiation was used along with Zr filter for better monochromatic radiation. Infrared spectra of polymer complexes films were recorded using EO-SXB IR spectrometer with a resolution of  $4 \text{ cm}^{-1}$  in the range  $400\text{-}4000 \text{ cm}^{-1}$  and UV-Visible spectrometer were recorded. The I-V characterization and voltage-EL intensity measurements were carried by a computer controlled .

## 3 Results and discussion

**3.1 UV-Visible Analysis:** UV-Visible spectra of bulk films of PVK and  $\text{TiO}_2$  exhibits absorption in ultraviolet region with maximum absorption is as shown in figure-1 along with in table -1

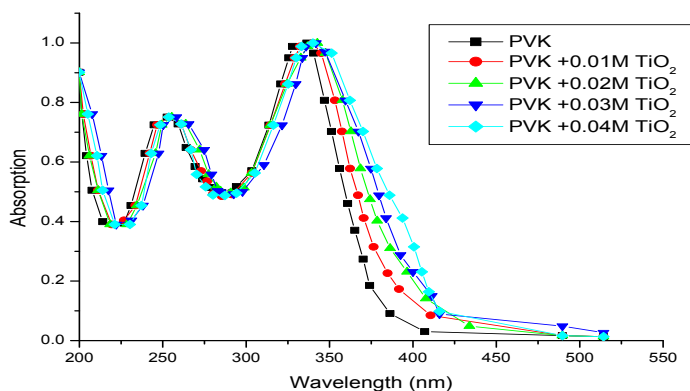


Figure-1, UV-Visible spectra of pure PVK and doped  $\text{TiO}_2$  polymer thin films.

Table -1, UV-Visible spectral data.

Materials	$\lambda_{\max}$ nm	Electronic Transition
PVK	250 333	$\Pi$ - $\Pi^*$ n- $\Pi^*$
PVK+0.01MTiO <sub>2</sub>	255 340	$\Pi$ - $\Pi^*$ n- $\Pi^*$
PVK+0.02MTiO <sub>2</sub>	259 344	$\Pi$ - $\Pi^*$ n- $\Pi^*$
PVK+0.03MTiO <sub>2</sub>	263 346	$\Pi$ - $\Pi^*$ n- $\Pi^*$
PVK+0.04MTiO <sub>2</sub>	266 348	$\Pi$ - $\Pi^*$ n- $\Pi^*$

Photoconductive polymers have a conjugate system of double bonds on their backbone. The photoconductive polymers have some of the conventional transfers in the UV-visible region, such as  $\sigma$ - $\sigma^*$ ,  $\Pi$ - $\Pi^*$ , n- $\Pi^*$  etc. The  $\sigma$ - $\sigma^*$  transition of conjugated double bonds are related to near UV regions around 200 nm, UV-visible spectra of Polyvinyl carbazole (PVK) show two absorption bands at 250 nm and 333nm associated with  $\Pi$ - $\Pi^*$  and n- $\Pi^*$  transition respectively [7-8]. These two bands are shifted towards the higher wavelength as the doping molar concentration of TiO<sub>2</sub> is increases, the values associated with these transitions are 255 nm, 259 nm, 263 nm and 266 nm for  $\Pi$ - $\Pi^*$  transition and 340 nm, 344 nm, 346 nm and 348 nm for n- $\Pi^*$  in 0.01M, 0.02 M , 0.03M and 0.04M TiO<sub>2</sub> dopants respectively. Since photoconductive polymer shows red shift in formal peaks.

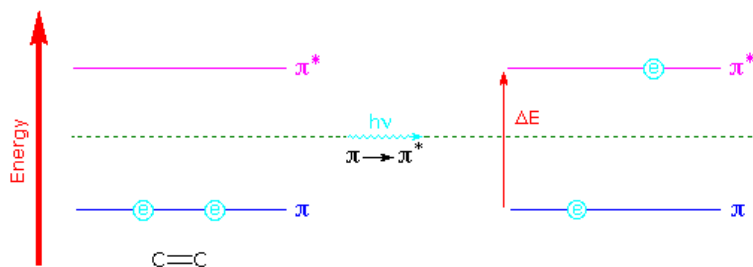


Fig.4. Electronic transition

Figure-2, UV-Visible spectra of pure PVK and doped TiO<sub>2</sub> polymer thin films.

### 3.2 FTIR

FTIR characterization of pure PVK and doped TiO<sub>2</sub> thin films has been observed by using spin coating deposition technique. FTIR spectroscopy is an important investigation of polymer structure that provides information about the complexation and interactions between the various constituents in the polymeric films. Each type of bond has a different natural frequency of vibration, so the identification of an absorption peak in the vibration portion of the infrared region will give a specific type of bonding [9]. The FTIR spectra for pure PVK and TiO<sub>2</sub> complexes are shown in Figure-3, Figure-3a and Figure-3b. The absorption band in the region 1610.11 cm<sup>-1</sup> is due to the Aromatic C=C stretching frequency of PVK which is shifted to the ranges 1609.25 cm<sup>-1</sup>, 1607.42 cm<sup>-1</sup>, 1602 cm<sup>-1</sup> and 1602.20 cm<sup>-1</sup>, the band at 1520 cm<sup>-1</sup> for pure PVK is attributed to aromatic C=N stretching vibration are shifted to 1518.41 cm<sup>-1</sup>, 1505.10 cm<sup>-1</sup>, 1495.55 cm<sup>-1</sup>, 1494.91 cm<sup>-1</sup>, the peak at 1300.31 cm<sup>-1</sup> for PVK is assigned for C-C stretching frequency are shifted to 1330.55 cm<sup>-1</sup>, 1305.73 cm<sup>-1</sup>, 1302.42 cm<sup>-1</sup>, 1303.02 cm<sup>-1</sup>, band at 1190.84 cm<sup>-1</sup> for PVK is assigned for C-N stretching vibration is shifted to 1188.84 cm<sup>-1</sup>, 1180.91 cm<sup>-1</sup>, 1160.88 cm<sup>-1</sup>, 1158.95 cm<sup>-1</sup>, the frequencies at 760.52 cm<sup>-1</sup> for stretching and 520.67 cm<sup>-1</sup> for bending vibration are observed for pure PVK were as it shifted to 750.44 cm<sup>-1</sup>, 765.42 cm<sup>-1</sup>, 770.81 cm<sup>-1</sup> and 769.05 cm<sup>-1</sup> for stretching and 520.67 cm<sup>-1</sup>, 510.42 cm<sup>-1</sup>, 525.55 cm<sup>-1</sup>, 540.12 cm<sup>-1</sup> and 530.83 cm<sup>-1</sup> for bending vibrations in 0.01 M, 0.02 M, 0.03 M and 0.04 M TiO<sub>2</sub> complexes PVK thin films respectively. Bands towards the lower wave numbers indicate that the positively charged Titanium ions are coordinated through ionic bonds with the negatively charged Pi electrons containing vinyl group belonging to different chains in PVK [10]. The broadening in the C-N band in all the complexes as compared to pure PVK, confirms that the increase in the concentration of

Titanium reduces the intermolecular interaction between chains and expands the space between them [11].

Materials	Frequencies in $\text{Cm}^{-1}$					
	Ar C=C	Ar C=N	C-C	C-N	Ti-O	
					Bending	Stretching
PVK	1610.11	1520.15	1300.31	1190.84	520.67	760.52
PVK + 0.01 M $\text{TiO}_2$	1609.25	1518.41	1330.55	1188.45	510.42	750.44
PVK + 0.02 M $\text{TiO}_2$	1607.42	1505.10	1305.55	1180.91	525.55	765.42
PVK + 0.03 M $\text{TiO}_2$	1602.55	1495.55	1302.42	1160.88	540.12	770.81
PVK + 0.04 M $\text{TiO}_2$	1602.20	1494.91	1303.02	1158.95	530.83	769.05

The observed vibrational frequencies are enclosed in Table-2,

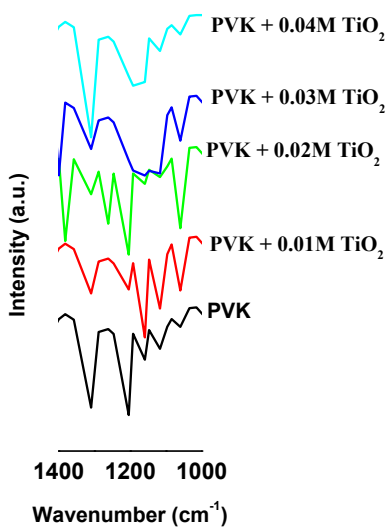


Figure-3(a)

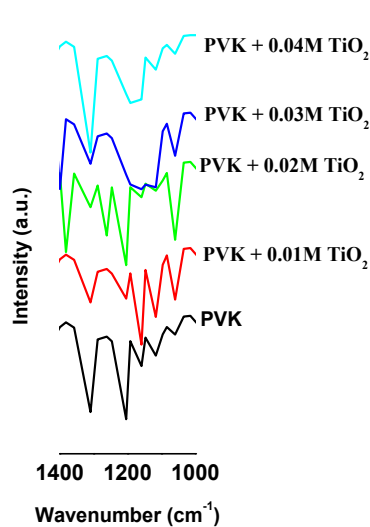


Figure-3(b)

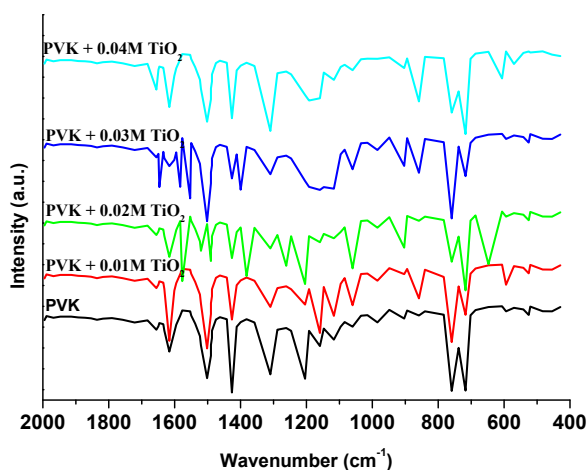


Figure-3, FTIR Spectra of pure PVK and doped  $\text{TiO}_2$  thin films.

### 3.3 XRD analysis

The XRD profiles of pure polyvinylcarbazole (PVK) and doped  $\text{TiO}_2$  with different molar concentration are shown in Figure-4, pure polyvinylcarbazole shows characteristic broad peak for an orthorhombic lattice centered at  $25^\circ$  including with semicrystalline nature [12] with addition of Titanium oxide, intensity of this peak decreases suggesting the decrease in degree of crystallinity of the complex [13]. This would be due to the disruption of the PVK crystalline structure by  $\text{TiO}_2$  as suggested by Hodge et al [14]. They are compared with JCPDS 88-1175, JCPDS 84-1286 and observed that the intensity of XRD pattern decreases as the amorphous nature increases with addition of dopant. This amorphous nature results in greater ion diffusivity with high ionic conductivity, which can be expressed as amorphous polymers having flexible back bone [15-18].

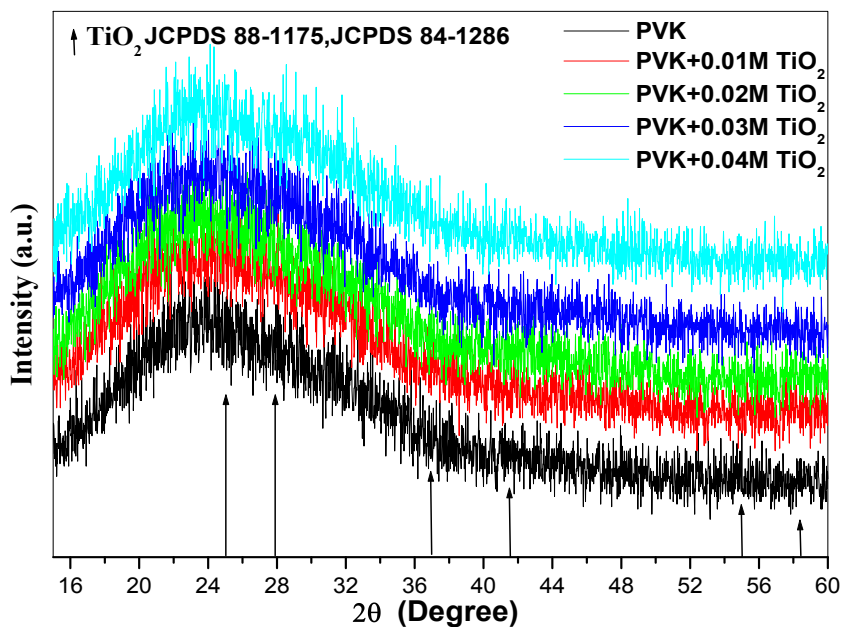


Figure-4, XRD patterns of pure PVK and  $\text{TiO}_2$  doped PVK polymer thin films.

## 4 Electroluminescence Properties

### 4.1 Current-Voltage (I-V)

The electrical and luminescent characteristics of the EL devices has analyzed by using a source meter 2400 (Keithley) and an optical power meter 1830S.

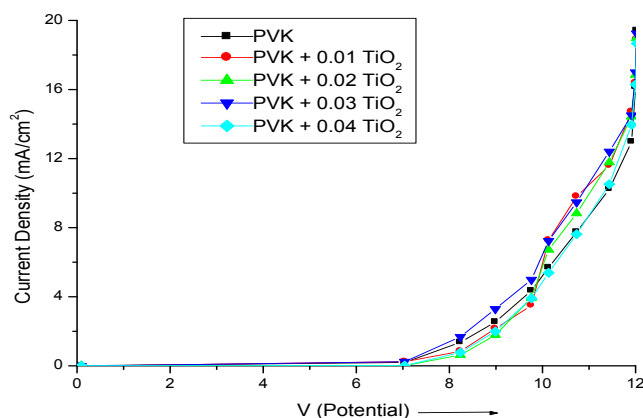


Figure-5, the I-V characteristic pure PVK and doped TiO<sub>2</sub> Polymer thin films.

Figure Shows the I-V characteristic of the single layer devices. According to figure.5 doping with molar concentration of titanium oxide, however, appears to stabilize the device to a significant extent the curve reveals threshold field around 9V and good stability. The result suggests that the optimal ratio of the molar concentration of TiO<sub>2</sub> in the complex of PVK is a promising material for a high efficiency electroluminescence curve as well as organic solar cell applications.

### 4.2 Voltage-EL intensity:

In bath deposition technique the relationship between voltage-EL intensity of pure PVK and doped TiO<sub>2</sub> thin films has observed as



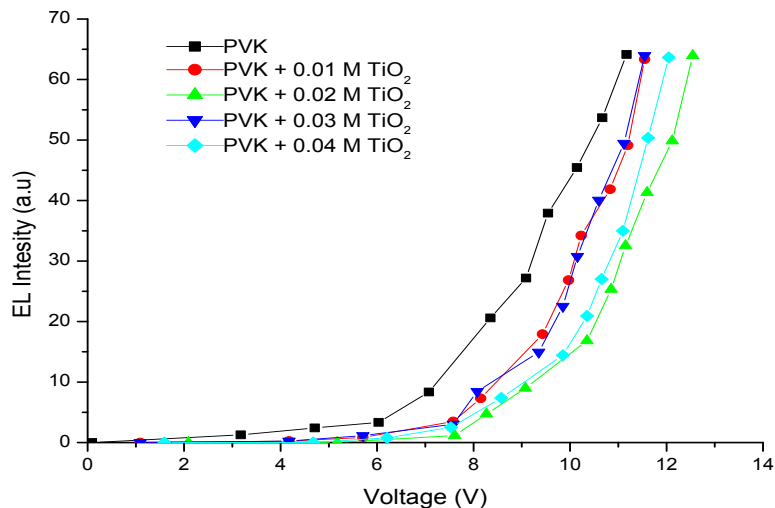


Figure-6, Voltage-EL Intensity characteristic of pure PVK and doped  $\text{TiO}_2$  polymer thin films.

Figure shows the relationship between voltage Vs. EL intensity. The turn on voltages are in the 5-9 volt range table-3 and the highest emission intensity was observed for the 0.04M  $\text{TiO}_2$  sample as found for the film electroluminescence, peak at 644 nm, with the brightness of  $66 \text{ cd m}^{-2}$  at 7.7 volt .

Table-3, show the  $\lambda_{\text{max}}$  (nm) and Turn-on (V).

Materials	$\lambda_{\text{max}}$ (nm)	Turn-on (V)
PVK	440	6
PVK+0.01M $\text{TiO}_2$	608	7.2
PVK+0.02M $\text{TiO}_2$	620	7.5
PVK+0.03M $\text{TiO}_2$	635	7.7
PVK+0.04M $\text{TiO}_2$	644	7.7

## 5 Conclusions

Formation of polymer thin films PVK with different molar concentration  $\text{TiO}_2$  is confirmed by XRD UV-Visible and FTIR studies. Result show that PVK polymer thin films materials emits strong red luminescence when excited by UV-Visible light. The Voltage-EL intensity is found to increase with increasing dopant concentration. The dopent



PVK materials has higher sensitizes luminescent efficiency and longer life time than pure PVK.

### References

- C. W. Tang, and S. A. VanSlyke; (1987). Appl. Phys. Lett. 51,913.
- J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holms , (1990). Nature, 347,539-541.
- C.S.Sunandana and P. Sentil Kumar, (2004) . “Theoretical approaches to superionic conductivity”, Bull Mater Sci., 27,1-17.
- M. Jaipal Reddy, T. Sreekanth, M. Chandrsekar and U.V. Subba Rao, (2000) . “Ion transport and electrochemical cell characteristic studies of a new (PVP+NaNO<sub>3</sub>) polymer electrolyte system”, J.Mater.Sci. 35, 2841-2845.
- G.L.J.A. Rikken, (1995). Phys. Rev., A 51, 4906.
- R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughs, R.N. Marks,C. Taliani, D.D.C. Bradley, D.A. Dossantos, J.L. Bredas, M.Logdlund, and W.R. Salaneck, (1999). Nature 397, 121.
- N.P.H.Nam, S.W.Cha, B.S.Kim, Choi S.H, Choi D.S., and Jin J.I.; (2002). Synth. Met. 130,271.
- Chung S.J., Jin J.I., and Kim K.K.; (1997). Adv. Mater 9,551.
- V. Madhu Mohan, V. Raja, A.K.Sharma and V.V.R. Narasimha Rao, (2005). “Ionic conductivity and Discharge characteristics of solid-state battery based on novel polymer electrolyte (PEO+NaBiF<sub>4</sub>)”, Mater. Chem. Phys., 94,177-181.
- D.A. Skoog, F.J. Holler and T.A. Nicman, (1998). “Principle of Instrumental Analysis 5<sup>th</sup> ed (Fluoride: Saunders College Publication and Harcourt Brace College Publication)”.



- F.H Abd El.-Kdar, G. Attia and S.S.Ibrahim, (1993). "Optical absorption and thermally stimulated DE polarization current studies of nickel chloride poly(vinyl alcohol) irradiated with low-level fast neutron doses", *J.Appl.Polym. Sci.*,50,1281-1286.
- A. Shehap, R.A. Abd Allah, A.F. Basha and F.H. Abd El-Kader, (1998). "Electrical properties of gamma- irradiated,pure,and nickel chloride poly(vinyl alcohol) films", *J.Appl.Polym.Sci.*, 68, 687-698.
- S. Ramesh and A.K. Arof, (2001). "Structural, thermal and electro chemical cell characteristics of poly (vinyl chloride)- based polymer electrolytes", *J.Power sources*, 99, 41- 47.
- R.Baskaran,S.Selvasekarapandian, N. Kuwata, J. Kawa mura, and T. Hattori, (2006). "Conductivity and thermal studies of blend polymer electrolytes based on PVKc-PMMA", *Solid State Ionics*,177, 2679-2682.
- M. Hema, M. Selvasekerapandian, G. Hirankumar, A Sakunthala, D. Arunkumar and H. Nithya, (2009). "Structural and thermal studies of PVK: NH<sub>4</sub>I", *J. Phys. Chem. Solids*, 70, 1098-1103.
- LI, B., X. Wang, M.Yan and L.Li. (2002). Preparation and characterization of nano TiO<sub>2</sub> Powder.; *Mater.Chem.Phys.*78, 184-188.
- Bilik, P. AND G. Plesch. (2007). Mechanochemical synthesis of anatase and rutile nanopowders from TiOSO<sub>4</sub>.; *Mater.Lett.*61, 1183-1186.
- Zhang, Q., L. Gao and J.Guo. (2000). Effect of hydrolysis conditions on morphology and crystallization of nanosized TiO<sub>2</sub> powder. *J.Eur.Ceram.Soc.*20, 2153-2158.