

# Electrochromism and electrochemical characterization of soluble poly[3-alkylhetero(arylene)s]

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Soluble conducting poly[3-alkylhetero(arylene)s] have been prepared electrochemically from 3-alkylheteroarylene monomers. Optical conditions for the electrochemical polymerization were in acetonitrile and tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) as the solvent and the electrolyte, respectively. Two oxidation potential values ( $E_{\text{ox}}$ ) were exhibited in the ranges 0.75–1.12 V and 1.86–2.02 V versus Ag/AgCl, respectively. On the other hand, the polymer oxidation potentials ( $E_{\text{pox}}$ ) in monomer-free solution were 1.34–1.42 V versus Ag/AgCl. The electrochemical data of these compounds are compared with those of poly(3-methylthiophene), polythiophene and their derivatives prepared under the same polymerization conditions. The conductivities of the electrochemically grown films were measured using the four-probe technique before and after exposure to doping agents. The values for the conductivities ( $\sigma$ ) of the “as-grown” films were in the order of  $\approx 10^{-2}$ – $10 \Omega^{-1} \text{ cm}^{-1}$ . The infrared (IR) and nuclear magnetic resonance (NMR) spectra of these polymers indicated that the bonding of the monomer units are mainly 2,5 linkages. Solubility tests of these polymers are also given. Thin films formed under constant current density of  $1 \text{ mA cm}^{-2}$  (galvanostatically) or cast by evaporation of the solvent on optically transparent electrodes (OTE) displayed electrochromic properties. The film colors are dark blue and brick red in the oxidized (doped) and in the neutral (undoped) states, respectively. The formal potentials ( $E^{0'}$ ) and  $n$  values of the polymer films are reported. The  $E^{0'}$  values of the films in the monomer-free solution were 0.73–0.96 V versus Ag/AgCl. These values were compared to the ( $E_{\text{pox}}$ ) values from the cyclic voltammetric technique for the same polymer films. The fluorescence spectra of the polymer solutions in different solvents showed an intense broad emission band at  $\approx 410$ – $660 \text{ nm}$ .

## 1. Introduction

Conjugated polymers containing the thiophene ring have received considerable attention due to their remarkable electrical conductivity [1]. These conducting

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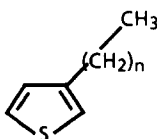
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materials proved to be suitable candidates for several technological applications [2], e.g., microelectronic and photovoltaic devices [3], solid state batteries and energy storage [4], electrochromic devices [3a,5], electrocatalytic systems and modified electrodes [6]. However, practical applications of these polymers so far are limited due to the unsatisfactory mechanical properties of the films. Recently, many approaches have been proposed in order to improve the processibility of such polymer. One approach was to blend the conducting polymer with a common polymer [7] or substitute "the base" monomeric thiophene at the 3-position with an alkyl group or other appropriate substituent [8]. Electrochemical methods proved to be suitable means for the synthesis of conducting polymers [9]. The polymerization proceeds via the oxidative coupling of the radical cation of the 3-alkylthiophene monomer as reported earlier for the parent thiophene [9a]. In this work we describe the electrosynthesis, electrochromic properties and characterization of a series of polymers derived of long chain 3-substituted thiophenes of the type shown below.



$n = 13, 14, 15, 16, 17, 19$

## 2. Experimental

The 3-alkylthiophene monomers were synthesized as reported previously [10]. The electrochemical preparation of the corresponding polymers was carried out at room temperature in a one compartment cell using platinum ( $0.3 \text{ cm}^2$ ) or indium-tin oxide (ITO) thin film coated glass ( $1.6 \text{ cm}^2$ ) anodes in carefully dried acetonitrile in the presence of tetrabutylammonium hexafluorophosphate as supporting electrolyte. The polymerization products which were obtained as films on the anode were isolated either by peeling off mechanically or by dissolution in a suitable solvent. The films were "undoped" electrochemically by immersing them in a monomer free solution and applying a negative potential of  $-0.2 \text{ V}$  versus  $\text{Ag}/\text{AgCl}$  for 45 min. Oxidation potential values were measured in monomer-free solution by square-wave voltammetry, using a platinum sheet ( $1 \times 1 \text{ cm}^2$ ) and  $\text{Ag}/\text{AgCl}$  (sat.) as the counter and reference electrodes, respectively. All the electrochemical and electrochromic experiments were performed in degassed and moisture-free solutions. All the polymer films were electrochemically synthesized under galvanostatic conditions where the applied current densities ranged between  $1$  and  $5 \text{ mA cm}^{-2}$ . Monomer and supporting electrolyte concentrations were  $0.05$  and  $0.1 \text{ M}$ , respectively. Electrochemical experiments were performed with PAR 175 potentiostat/galvanostat and BAS-100 electrochemical analyzer. UV-VIS absorption spectra were obtained on a Perkin-Elmer lambda 5 spectrophotometer. For this purpose, the films were prepared on the (ITO) electrodes with thicknesses

ranging from 500 to 1000 Å as estimated from the amount of charge passing through the cell during the deposition. Spectroelectrochemical experiments were performed in a  $1 \times 1 \text{ cm}^2$  quartz cuvette and the cell potential was monitored by a CV-1B instrument (BAS, West Lafayette, IN). Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. The IR spectra were measured from pressed pellets of the polymer in a KBr matrix. Fluorescence measurements were performed on a Perkin-Elmer LS-5 fluorescence spectrophotometer. Proton NMR spectroscopic characterization of the polymer were recorded using a Bruker AC 250 instrument in  $\text{CD}_3\text{Cl}$  and reported in parts per million as  $\delta$  relative to internal TMS. Conductivity measurements were made on pressed pellets mounted on an insulator substrate using the four-probe technique. The polymer was purified by Soxhlet extraction, successively with methanol and chloroform, and dried under vacuum prior to the above experiments.

### 3. Results and discussion

Table 1 lists the electrochemical and spectroelectrochemical data obtained by the square-wave technique for the monomers and the polymer films prepared using a charge of 100 and 50  $\text{mC/cm}^2$  on Pt and ITO electrodes, respectively. These data show the following observations:







(i) The oxidation potential values ( $E_{\text{ox}}$  mon.) showed no trend with respect to varying the number of carbon atoms in the 3-alkyl chain. However, the relatively close ( $E_{\text{ox}}$ ) values of the monomers is in good agreement with similar inductive effect studies of different alkyl substituents as was previously reported [11].

(ii) A primary ill-defined anodic peak appeared in the region 0.75–1.12 V (versus Ag/AgCl) which increased with the 3-alkyl chain length. This could be attributed to an initial thin polymer film formation. A typical square-wave voltammogram and the cyclic voltammogram (CV) of compound **5** are shown in figs. 1a and 1b respectively. The CV displays a well-defined peak at 1.92 V versus Ag/AgCl and the absence of a reversible cathodic peak which is an indication for the insulating character of the film formed. This is in agreement with previous observations for 3-alkylthiophenes [8c].

(iii) Fig. 2 shows a CV of (as estimated from coulometric experiments) a polymer film of about 1000 Å thickness of compound **6** in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{AcN}/\text{monomer-free}$  solution. The data listed in table 1 revealed no particular trend for the polymer oxidation peak potentials in dependency of the length of the 3-alkyl chain. The CV in fig. 2 shows a relatively well-defined anodic peak and a broad cathodic peak. Moreover, the charging current is less pronounced as compared to that of poly(3-methylthiophene) [12].

(iv) Following known experimental procedures [13] “ $E^0$ ” and  $n$  values” for polymer films of compounds **1** through **6** grown on ITO electrodes were obtained. They were cycled in monomer-free solutions containing 0.1 M  $\text{Bu}_4\text{NPF}_6$ , and are also listed in table 1. It was found for the as-grown films that as the length of the 3-alkyl substituent increased, the peak wavelength shifted to smaller wavelengths

Table 1  
Electrochemical spectral and spectroelectrochemical data for 3-alkyl substituted thiophenes monomers and polymers

3-Alkylthiophene compounds	No.	$E_{ox}$ (V/Ag/AgCl)		$\lambda_{max}$ (nm)/CHCl <sub>3</sub>		$E^0$ (V) (polymer)	$n$	Color <sup>a)</sup>		$\lambda_{max}$ (nm)/ITO as-grown film <sup>d)</sup>
		monomer	polymer	monomer	polymer			oxidized form <sup>b)</sup>	reduced form <sup>c)</sup>	
	<b>1</b>	0.75	1.34	244	443	0.73	0.21	blue	red	481
		1.86								
	<b>2</b>	0.85	1.39	244	440	0.82	0.24	blue	red	479
		2.02								
	<b>3</b>	0.90	1.40	245	440	0.86	0.23	dark blue	red	485
		1.86								
	<b>4</b>	0.96	1.40	244	428	0.91	0.25	blue	brick red	467
		1.90								
	<b>5</b>	1.09	1.40	244	426	0.94	0.27	greenish blue	red	455
		1.90								
	<b>6</b>	1.12	1.42	242	418	0.96	0.30	blue	dark red	450
		1.92								

a) Apparent transmitted colors to human eye. b) The electrode at 1.4 V versus Ag/AgCl. c) The electrode at -0.2 V versus Ag/AgCl. d) Films grown electrochemically on ITO.

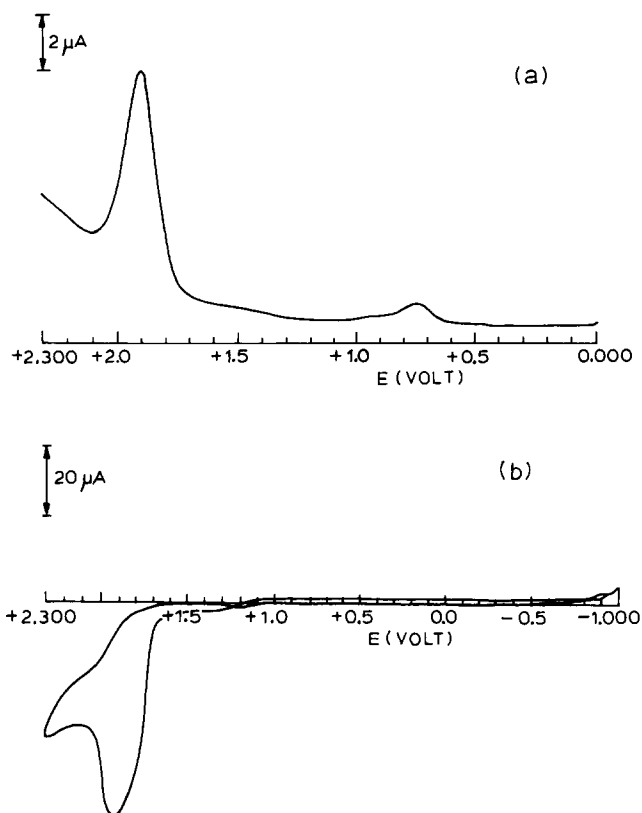


Fig. 1. (a) Square-wave voltammogram for compound 5 at Pt electrode. (b) Cyclic voltammogram of compound 5. Scan rate  $100 \text{ mV s}^{-1}$  at Pt electrode. Monomer concentration  $5 \text{ mM}$  in  $0.1 \text{ M Bu}_4\text{NPF}_6$ , deaerated solution/AcN.

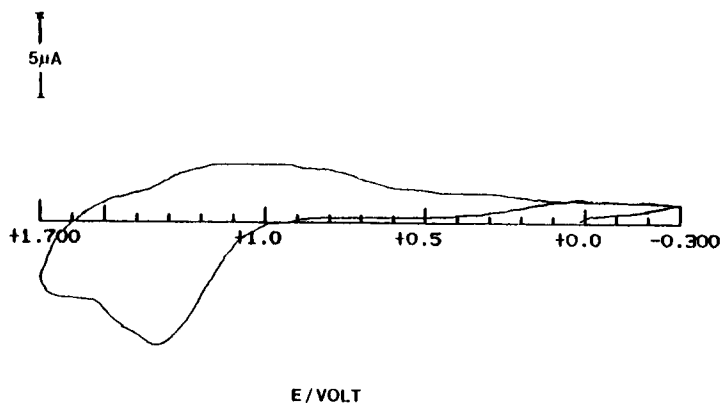


Fig. 2. Cyclic voltammogram of  $1000 \text{ \AA}$  polymer film of compound 6. Scan rate  $50 \text{ mV s}^{-1}$  in monomer-free solution containing  $0.1 \text{ M Bu}_4\text{NPF}_6$ /AcN.

Table 2  
Electrical conductivities of polymer films electrochemically grown

No. <sup>a)</sup>	$\sigma$ ( $\Omega^{-1} \text{ cm}^{-1}$ )		
	As-grown films <sup>b)</sup>	Neutral films <sup>c)</sup>	Redoped films <sup>d)</sup>
1	115	$2.3 \times 10^{-4}$	18
2	85	$2.1 \times 10^{-4}$	22
3	52	$2.2 \times 10^{-4}$	12
4	30	$2.5 \times 10^{-4}$	9
5	2	$1.6 \times 10^{-4}$	14
6	0.1	$1.1 \times 10^{-5}$	11

<sup>a)</sup> Same numbers as in table 1. <sup>b)</sup> Electrochemically oxidized (doped).

<sup>c)</sup> Undoped electrochemically. <sup>d)</sup> After exposure to  $\text{I}_2$ .

(except for compound 3). Further investigation of the  $E^{0'}$  values (table 1) in relation to the number of carbon atoms in the 3-alkyl substituent reveals an important trend. As the number of carbon atoms in the chain increases,  $E^{0'}$  values become more positive, with the exception of compound 4. This correlation was not observed in the  $E_{\text{pa}}$  values of the polymer obtained from the voltammetry experiments. However, previous data [13] from our group on substituted thiophene

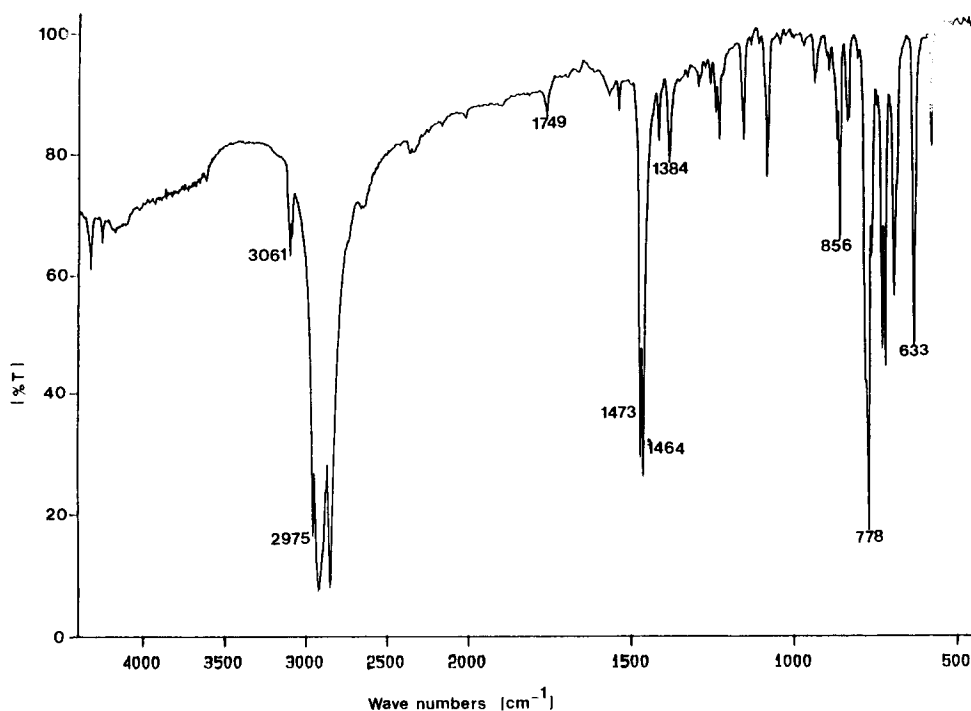


Fig. 3. FT-IR spectrum for a KBr pressed pellet of the polymer of compound 6.

dimers exhibited an opposing trend. As the degree of substitution increases, less orderly polymerization is expected owing to steric hindrance and concomitant lower coplanarity. This assumption is also confirmed by a significant blue-shift of the  $\lambda_{\max}$  of the films as well as with the calculated values for ( $E^{0'}$ ). It is noteworthy to mention that the  $\lambda_{\max}$  values of the films on ITO casted from chloroform are similar to the ones taken from dissolved films in chloroform. Moreover, the  $n$  values were found to increase with the strain imparted to the film by the substituent as reported earlier [13]. The film's absorption at 450–481 nm due to the  $\pi$ - $\pi^*$  transition disappears and broad absorptions appears at 620–900 nm. The latter absorptions are referred to the transitions of the two "localized" bipolarons [14].

The electrical conductivities of the electrochemically formed polymer films for compounds 1–6 are given in table 2. The conductivities of all samples were measured by the four-probe technique at 25°C under atmospheric pressure. The conductivity of the as-grown films was measured on pressed pellets. The conductivities of the polymers that had been dissolved and were reprecipitated were measured on films casted on insulating surfaces. The conductivity values are also listed in table 2. They show a good agreement with the UV-VIS data. The conductivity of the as-grown film decreases as the length of 3-substituted alkyl chain increases. Again, it is proposed that this is due to a decrease of the degree of coplanarity and lower conjugation of the rings in the polymer film [15]. The level of

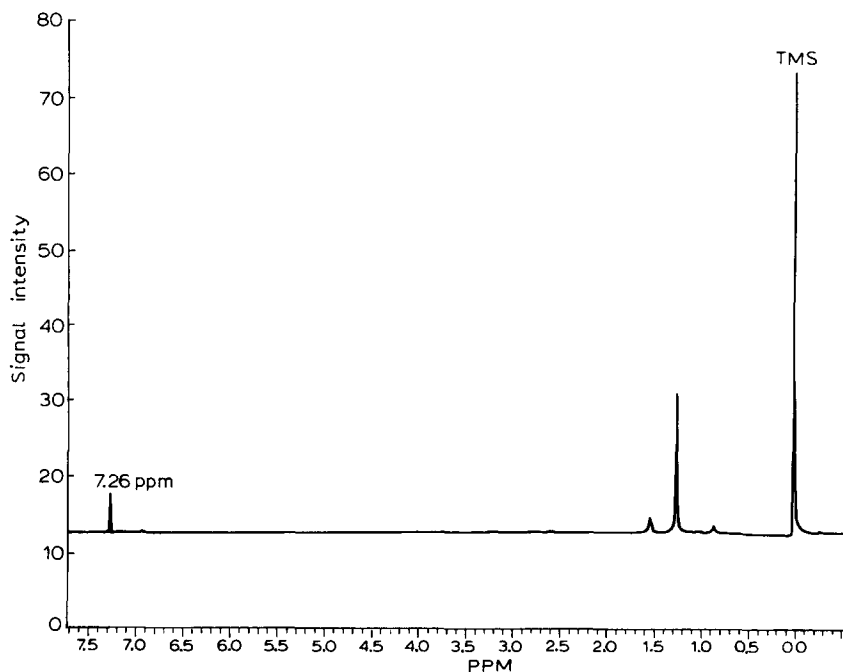


Fig. 4. 250 MHz  $^1\text{H}$  NMR spectrum of the polymer of compound 6 in  $\text{CDCl}_3$ .

doping of polymers is 10–24% as calculated from the coulometric data. Redoping of the neutral film by iodine has a lower effect on the enhancement of the conductivity when compared to the “self-doped” electrochemically grown films.

The structural regularity of the polymer chain and bonding sites were examined by infrared spectroscopy. The number of scans collected at a resolution of  $2\text{ cm}^{-1}$  and with an accuracy of  $0.004\text{ cm}^{-1}$  was 2000 scans for all samples. The FT-IR spectrum for a KBr pressed pellet of the polymer of compound **6** is given in fig. 3 as a representative example. The assignments of the principal absorption bands are as follows: the bands between  $856$  and  $633\text{ cm}^{-1}$  are characteristic of the C–H out-of-plane vibrations. The sharp absorption band at  $778\text{ cm}^{-1}$  is attributed to the ring C–H out-of-plane bending vibration which is specific for 2,5-disubstituted thiophene rings. The well-defined sharp peaks at  $1464$  and  $1473\text{ cm}^{-1}$  (actually one peak splitting into two) is attributed to the stretching vibrations of the 2,3,5-trisubstituted thiophene rings. The bands at  $2975$ – $1849\text{ cm}^{-1}$  are due to the stretching vibrations of the methyl group, while that at  $3061\text{ cm}^{-1}$  could be attributed to the C–H aromatic stretching mode.

The absorption band at  $1384\text{ cm}^{-1}$  can be attributed to the deformation vibration of the methyl group. These data are in good agreement with those published earlier [16]. Fig. 4 shows the 250 MHz  $^1\text{H}$  NMR spectrum of the same polymer (of compound **6**). The signal at 7.26 ppm is due to the hydrogen of the aromatic ring. The IR and NMR data imply a well-defined linear structure, predominantly of poly(3-alkyl-2,5-thienylene) type for all the polymers studied in this work.

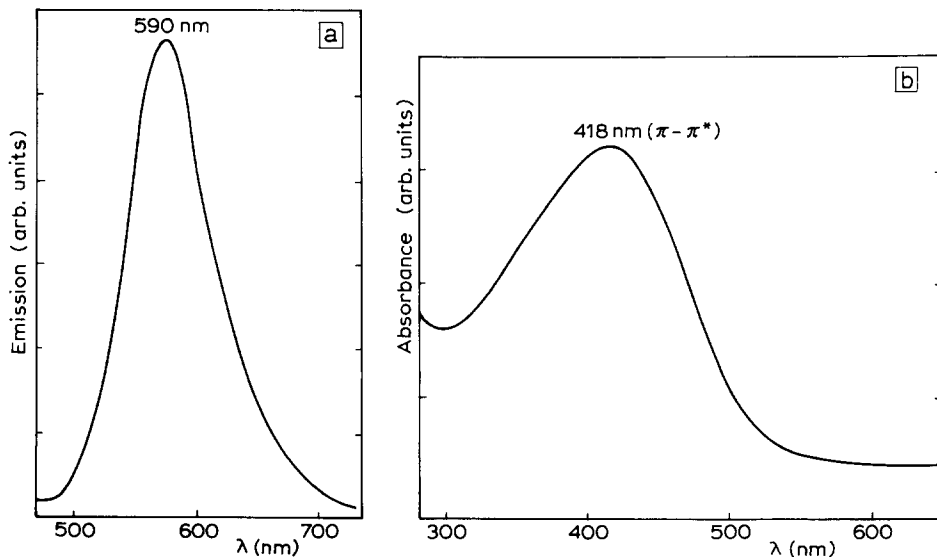


Fig. 5. (a) Photoluminescence spectrum of the polymer of compound **6** in chloroform,  $\lambda_{\text{ex}} = 420\text{ nm}$ . (b) UV-VIS absorption spectra of the polymer of compound **6** in chloroform.



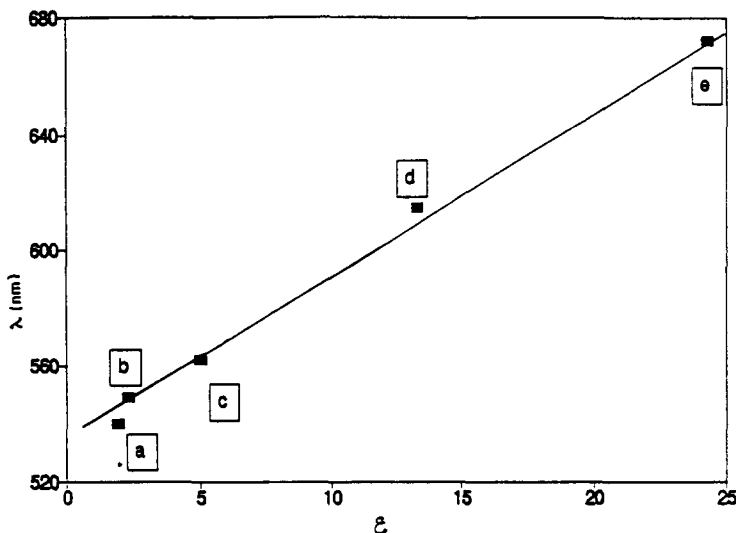


Fig. 6. Effect of solvent polarity on the emission band of the polymer of compound 6. (a) Hexane, (b) benzene, (c) ether, (d) hexanol, (e) ethanol.

The photoluminescence spectrum of the polymer of compound 6 in chloroform solution is given in fig. 5a. The broad band luminescence with peak at 590 nm ( $\lambda_{\text{ex}} = 415$  nm) has a peak width at half height of 90 nm. The UV-VIS absorption spectra of the same compound is shown in fig. 5b. The maximum extinction coefficient,  $\epsilon_{\text{max}}$ , at 418 nm is  $7969 \text{ M}^{-1} \text{ cm}^{-1}$ . The band at 418 nm can be assigned to a  $\pi-\pi^*$  transition which is also implied by the polymer color. The undoped film formed on ITO electrode does not show a change in its spectrum over four months, however, a major shift of the absorption band was noticed for the corresponding polymer in solution upon standing. The “mirror symmetry” analogy observed between the absorption and emission bands indicates that the luminescence in solution is due to the conjugated  $\pi$ -system. Fig. 6 shows the effect of solvent on the emission process of the polymer prepared from compound 6. It can be seen in fig. 6 that the emission band shows a red-shift with the increase in the dielectric constant of the solvent used. Similar behavior is also observed for polynuclear condensed aromatic systems [17].

In conclusion, the electrochemical data showed that the length of the 3-alkyl chain in the monomer exerts only a limited effect on the polymerization reaction, but the steric effect influences the yield and ease of polymerization. We report for the first time the spectroelectrochemical data for a series of long chain 3-substituted thiophenes. The IR and NMR features verify that these polymers have a well-defined linear structure. The analogy between the absorption and emission spectra in solution proves that the excitation is predominantly due to the  $\pi-\pi^*$  transition. Finally, the conductivities of the as grown films are relatively higher than those redoped upon exposure to iodine vapors.

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