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Electrochemical syntheses of photoluminescent polymers from thienylene-poly(phenylenevinylene) derivatives

Summary — Two compounds, 1,4-bis-(2(Z)-thienylenevinylene)-benzene (M1) and 1,4-bis-(2(Z)-thienylenevinylene)-2,5-dimethoxybenzene (M2) were synthesized and characterized using spectroscopic and electrochemical methods. Spectroscopic and photoluminescent properties of these compounds were found to be evidently dependent on their structure. Both M1 and M2 can be oxidized electrochemically producing forms of higher molecular weight. Intermediate products, which include stable oligomeric forms, were distinguished using spectroscopy during polymerization. In the final stage, oxidation of the oligomers at the electrode surface led to homogeneous, well adhering polymer films. The doping process of these polymers that also reflects their structure is discussed. Generally, polarons produced during oxidation do not undergo a process of recombination to bipolarons due to the block structure. Both polymers studied have photoluminescent properties. Effects of structure on the observed phenomena and parameters, like the wavelength position, the half width of the peak maximum are demonstrated and discussed.

Key words: conjugated polymers, electrochemistry, conducting polymers, thienylenevinylene-benzene.

ELEKTROCHEMICZNA SYNTEZA POLIMERÓW FOTOLUMINESCENCYJNYCH Z TIENYLENOWYCH POCHODNYCH POLIFENYLOWINYLENU

Streszczenie — Otrzymano dwa związki o właściwościach fotoluminescencyjnych, 1,4-bis-(2(Z)-tienylenwinylen)-benzen (M1) oraz 1,4-bis-(2(Z)-tienylenwinylen)-2,5-dimetoksybenzen (M2), które następnie poddano szczegółowym badaniom spektroskopowym (rys. 1—3, rys. 7) i elektrochemicznym (rys. 4—6). Stwierdzono, że właściwości spektroskopowe oraz fotoluminescencyjne obu substancji zależą od ich struktury. Zarówno M1 jak M2 ulegają elektrochemicznemu utlenianiu dając produkty o większym ciężarze cząsteczkowym. Proces polimeryzacji przebiega przez etapy pośrednie polegające na tworzeniu trwałych oligomerów, obserwowanych w roztworze reakcyjnym za pomocą metod spektroskopowych (rys. 10 i 11). W wyniku utleniania, oprócz oligomerów otrzymuje się również homogeniczne, dobrze przylegające do elektrody, błonki polimerowe. Proces domieszkowania polimerów zależy również od struktury użytego monomeru i generalnie polega na powstaniu polaronów, które ze względu na blokową strukturę polimeru, nie rekombinują do bipolaronów. Oba polimery mają właściwości fotoluminescencyjne, przy czym zarówno długość emitowanego światła jak i szerokość połówkowa piku emisji zależy od budowy polimeru.

Słowa kluczowe: polimery sprzężone, elektrochemia, polimery przewodzące, tienylwinylen-benzen.

There is a continuously growing interest in new synthetic materials that have designated properties. In this field, the linear, π-conjugated polymers and oligomers are the subjects of great interest due to their attractive optical properties, particularly these displaying electroluminescence [1—7].

During the last 20 years a substantial progress has been observed, in both recognizing of physical properties of these type of materials [8], and in methods of syntheses of new monomers and polymers. Many new materials basing on conjugated polymers were introduced [9, 10], in which the required above physical and chemical properties had been obtained as results of structural manipulations at the stage of monomer or oligomer syntheses [11—13]. It is worth of mention here that the first polymer displaying electroluminescence, poly(*p*-phenylene vinylene) (PPV) has established a good base for the developing of the whole family of this type of polymers [1]. There are numerous examples of chemical syntheses of PPV derivatives that, depending on the structure may emit light of different wavelength, besides they are "processable", due to a good solubility in solvents. This, in turn, allows forming thin films of those materials using a method of spin coating.

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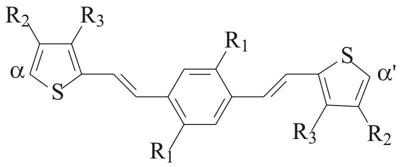
Recently, a new approach has been reported in which PPV was synthesized electrochemically in the process of catalytic reduction of α,α,α′,α′-tetrabromo-*p*-xylene [14, 15].

Polythiophenes create an other group of π-conjugated polymers that is of great interest recently. These compounds offer unique combination of stability, simplicity in modifications of the structure, and selection between chemical and electrochemical methods of syntheses, and, as a matter of great importance, simple modification of their band gap [16—18]. Using this group of polymers or oligomers it is relatively easy to form ordered, regular and 3D structures [19—22]. All these are requirements for a large charge-carrier mobility that is of fundamental importance for optoelectronics [22].

We have recently demonstrated effectiveness of electrochemical methods in studies of regioregular oligo(thiophene)s [24—28]. For that reason we are expecting the usefulness of that approach, together with spectroelectrochemistry, in studies of new oligomers and polymers, which combine features of PPV and polythiophenes.

The aim of the present work was the study on thienylene-PPV derivatives having a general structure given below:



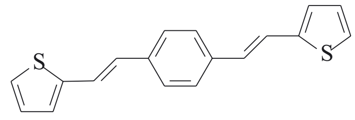
(I)

R_1, R_2, R_3 = H, or alkoxy

It is known that molecules of this structure have electroluminescent properties [29], besides, their polymerization under electrochemical conditions should be possible. Indeed, α,α′ positions are unsubstituted, free to form new bonding and the conjugated molecule is sufficiently short to convert to unstable radical cation when oxidized. It is assumed that the proposed route would be a simple and convenient method of formation of photoluminescent polymers. Use of electrochemical methods of polymerization is beneficial in that case for many reasons. The electric charge recorded during electropolymerization allows determining of the film thickness, solubility of the polymer is not a problem, and the film formed this way is homogeneous, uniformly thick even at more complicated surface morphology of the supporting substrate.

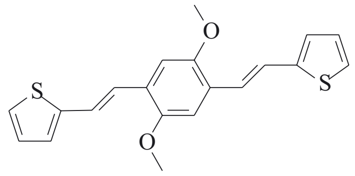
Oligomers of thienylene-PPV derivatives and polymers obtained from such monomers were in fact subjects of interest recently [30—34], however not much attention was focused on detailed electrochemical and spectroelectrochemical properties. Our introductory results of studies on electrochemical properties of dicyano substituted thienylene-PPV and poly(3,4-ethylenedioxythiophene)-PPV have demonstrated usefulness of electrochemical methods in case of these compounds [35].

The electrochemical and optical properties of our compounds of interest depend to a large extent on the type of substituent denoted as R1—R3. A presence of that groups in the molecule allows to modify simply the energetic levels HOMO and LUMO, and consequently to produce oligomers of required electronic properties. Electrochemical and spectroelectrochemical methods are useful not only for these oligomers, the same is valid for the electrosynthesized polymers. In this work we report electrochemical polymerization and optical properties of two monomers: 1,4-bis-(2(Z)-thienylenevinylene)-benzene [M1, formula (II)] and 1,4-bis-(2(Z)-thienylenevinylene)-2,5-dimethoxybenzene [M2. formula (III)] and their polymers.



(II)

M1



(III)

M2

EXPERIMENTAL

Materials

The following substances were used:

— thiophene-2-carboxyaldehyde (98 % pure, Aldrich),

— 1,4-bischloromethylbenzene (98 % pure, Aldrich),

— 1,4-bischloromethyl-2,5-dimethoxybenzene (97 % pure, Aldrich),

— tetrabutylammonium hexafluorophosphate [$(Bu)_4NPF_6$, 98 % pure, Aldrich],

— dichloromethane (CH_2Cl_2, 99.9 % HPLC grade, PROLABO),

— acetonitrile (CH_3CN, HPLC grade, Aldrich).

Monomer synthesis

The monomers were synthesized by Knoevenagel condensation, described in [35], of commercial thiophene-2-carboxaldehyde with 1,4-bischloromethylbenzene (for M1 synthesis) or 1,4-bischloromethyl-2,5-dimethoxybenzene (for M2 synthesis).

The yields of the reaction were moderate (about 20 %) in each case [35]. The characterization of monomers M1 and M2 was performed using 1H NMR, mass spectrometry (electron ionization) analysis, and FT-IR spectroscopy. The results [36] were satisfactory and consistent with *cis*-vinylene structures.

Electrochemical set-up

The electrochemical cyclic voltammetry (CV) experiments were performed using an EG & G Princeton Applied Research potentiostat-galvanostat model 273A controlled by a PC class computer, which also has collected the results. The working electrode was a platinum disc of geometric area about 0.071 cm^2 sealed in a glass tube. The surface of the electrode was cleaned by polishing it with 2 μm and 1/10 μm diamond pastes from MECAPREX and rinsed with acetone. Ag/(0.01 M) Ag$^+$ reference electrode was used and its exact potential was measured versus ferrocene in the electrolyte solution used. Platinum plate connected to platinum wire was used as a counter electrode. No IR compensation was applied. To observe the electrochemical process macroscopically, the SONY DCR TRV30E digital camera with a resolution of 1.6 megapixels was applied. In these measurements a conventional 1 cm cuvette served as electrochemical cell, in which 1 mm in diameter Pt wire was used as the working as well the counter electrode.

For CV method, and for UV-Vis spectroelectrochemical measurements the solution $(Bu)_4NPF_6$, in CH_2Cl_2 or in CH_3CN, with concentration 0.2 M, was used. All measurements were carried out at room temperature under ambient atmosphere.

UV-Vis spectroelectrochemical studies were carried out using ITO/quartz optically transparent working electrode. Again, a Pt counter electrode and an Ag/Ag+ reference electrode were used. The spectra were recorded using a Cintra 5 spectrophotometer. Photoluminescence spectra were recorded using Perkin Elmer Luminescence spectrometer LS 50B.

RESULTS AND DISCUSSION

Spectroscopy of the monomers

Both monomers, M1 and M2 are well soluble in CH_3CN and even slightly better in CH_2Cl_2. Figure 1 shows UV-Vis absorption spectra in CH_2Cl_2 recorded for these two compounds. The apparent absorption maxima that correspond to π-π* transition are found respectively at λ_{maxM1} = 376 nm, and at λ_{maxM2} = 404 nm, however both spectra display a complex character. In the spectrum of M1 there are additional vibrational bands at 362 nm and 397 nm, whereas for the M2 additional band at 347 nm is observed. In each case the molecules have delocalized bonding system, therefore it is difficult clearly to attribute them the corresponding absorption bands. Nevertheless, the spectra demonstrate evidently an effect of the substituent on the optical properties. The structures of M1 an M2 molecules imply that there are three possible main conformational forms of both of them: *trans-trans*, *trans-cis* and *cis-cis*. Among them, the most stable isomer should be *trans-trans*. As found from molecular calculations for conformers of oligo(thiophene) derivatives and oligo(phenylene-fluorene)s [37] each conformational form should absorb energy at different wavelength. However, taking into account the

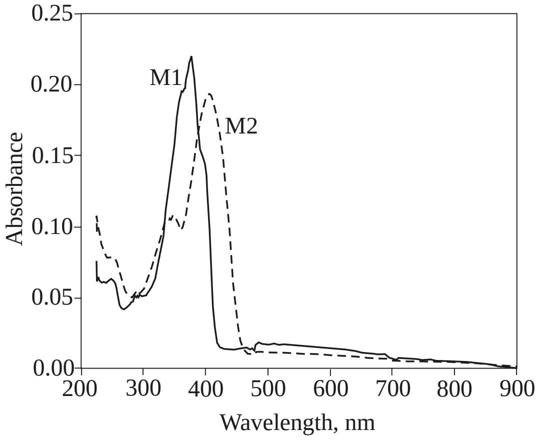
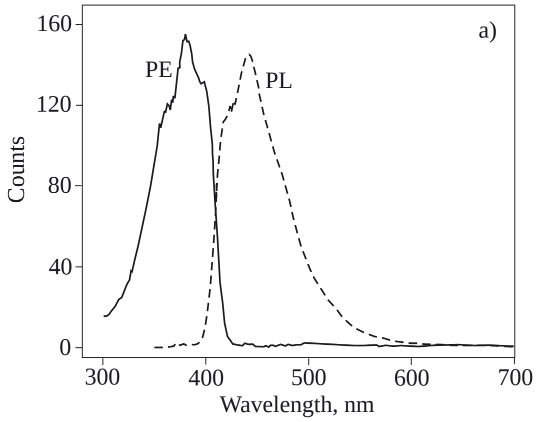


Fig. 1. UV-Vis absorption spectra of ~ 0.5 mM solutions in CH_2CL_2 of: M1 — solid line, M2 — dashed line



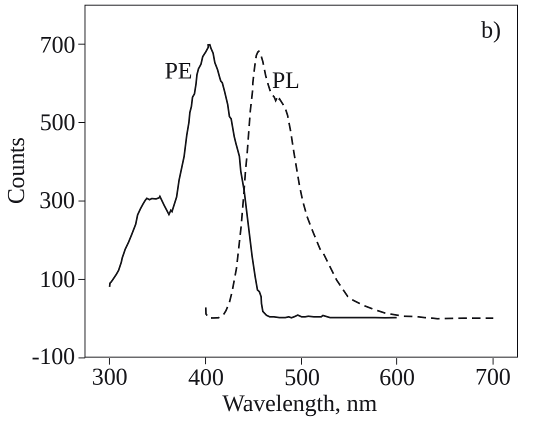


Fig. 2. Photoluminescence (PL) and photoexcitation (PE) spectra of ~ 0.5 mM solutions in CH_2CL_2 of: a) M1, b) M2

lack of any vibrational fine structures in the absorption band, the M2 molecules remain fairly flexible in their ground electronic state. This indicates that upon relaxation of the excited singlet state, the M2 molecules adopt more planar structure. The last was reported earlier for similar compounds [38].

The photoluminescence (PL) and photoexcitation (PE) spectra for these two monomers dissolved in CH_2Cl_2 are shown in Figure 2. All the emission spectra given here were obtained under excitation at the wavelength of the main absorption band. In case of M1, the PL spectrum exhibits a main emission peak at λ_{em} = 441 nm, accompanied by two shoulders, at 420 nm and 472 nm, whereas M2 exhibits a peak at λ_{em} = 455 nm with two shoulders at longer wavelengths, at 470 nm and at 523 nm. The PE spectra shown here reflect in fact truly the absorption spectra shown in Fig. 1. Generally, all the features observed in spectra recorded for PL and PE of these molecules in solution are similar to those well known in the literature.

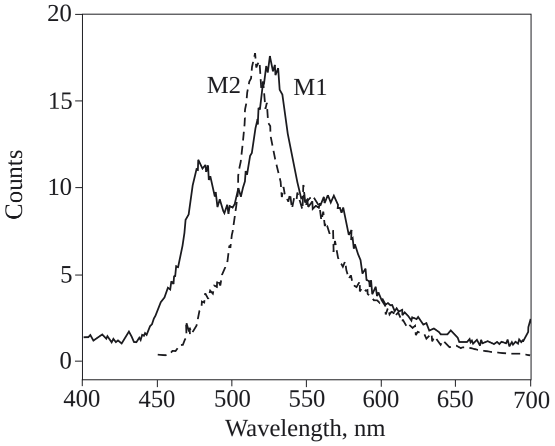


Fig. 3. Solid state PE spectra of M1 and M2, taken in an air; thin films were cast on microscopic glass slides from CH_2CL_2 solutions

Two molecules studied, M1 and M2, are also able to produce photoluminescence, when they are prepared in form of solid state films. It is demonstrated in Figure 3 for the films that were cast on microscopic slides from CH_2Cl_2 solution at the concentration of 2 mg/ml. In the PL spectrum of the thin solid film of M1 there are three emission peaks, the main at λ_{em} = 526 nm and two well formed satellites, at 480 nm and at 566 nm. In case of M2, the PL spectrum exhibits the main emission peak at λ_{em} = 516 nm with two shoulders at longer wavelengths, one at 552 nm and the other at 600 nm.

To a large extent similar, fine structures of the spectra have also been observed for other thiophene polymers [39] and oligo(thiophene-*m*-phenyleneethenylene) molecules [40]. These features in spectra were attributed to a larger rigidity of the molecules in their relaxed excited state rather than that in a ground state. It is noteworthy that the films produced on glass substrates are not fully uniform since after casting they crystallize quickly, forming a fine crystalline structures. Therefore it is difficult to obtain the good quality transmission spectra for them.

There are some evident differences in the PL spectra of both M1 and M2 recorded for the solution and for the solid phase. In case of M1 the emission maximum is redshifted for solid film as compared to the solution spectrum. It proves the strong molecular interactions in a solid state. This behavior is also confirmed by the measurements of the emission efficiency. The measured value of quantum efficiency for solid film of M1 is below 0.1 %. A shift of photoluminescence maximum towards lower energies occurs also for the films of M2 but the effect is not as large, thus the molecular interactions are probably weaker. The measured quantum efficiency is still low, 0.3 %, but larger than that for M1.

Electrochemistry of monomers

Cyclic voltammetry (CV) of both monomers indicates the multiple oxidation steps taking place within the range of potentials 0—2 V. Besides, significant differences have been found between the voltammograms of the first and the second scan, as shown in Figure 4 for M2 molecule. Three main peaks are recorded: at E_1 = 0.87 V, at E_2 = 1,38 V, and at E_3 = 1.83 V during the first scan. Also, two shoulders between E_1 and E_2 and one between E_2 and E_3 might be distinguished in this part of the CV curve. The second scan reveals quite different features in the voltammogram. A new peak appears at E_4 = 0.7 V, whereas the peak at E_3 disappears and that at E_2 moves to the slightly lower value of 1.29 V. Thus, the oxidation of M2 monomer within the range of 0—2 V appears to be very complex. However, some evident conclusions might be drown, based on the CV curves shown in Fig. 4. The formation of cation radical takes place at E_1,

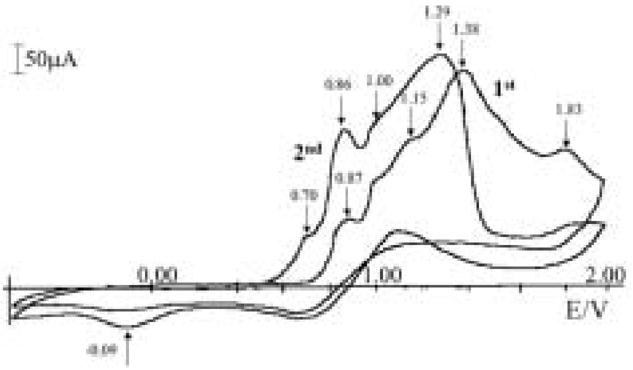


Fig. 4. Cyclic voltammetry curves on Pt electrode for ~ 1 mM solution of M2 in 0.2 M $(Bu)_4NPF_6/CH_3CN$; 1 — first scan, 2 — second scan, both scans at 0.1 V/s

whereas the further oxidation of that product to dication occurs at E_2. The cation radical may also undergo dimerization or/and further oligomerization processes. The two shoulders between E_1 and E_2 are results of the oxidation to dication and trication. The peak disappearing at E_3 might be a proof of a degradation of the oxidation products at the applied potential that is for that sufficiently high. The new peak appearing at E_4 = 0.7 V is responsible for oxidation of the dimer and some other high-molecular oligomers to cation radicals. A shift of the potential at E_2 is a result of two processes overlapping: one is the oligomer oxidation, and the other process is oxidation of M2 cation radical to its dication. Generally the same behavior was found in case of M1 voltammetry measurements, however all the potentials reported for the M2 are in case of M1 moved towards positive direction.

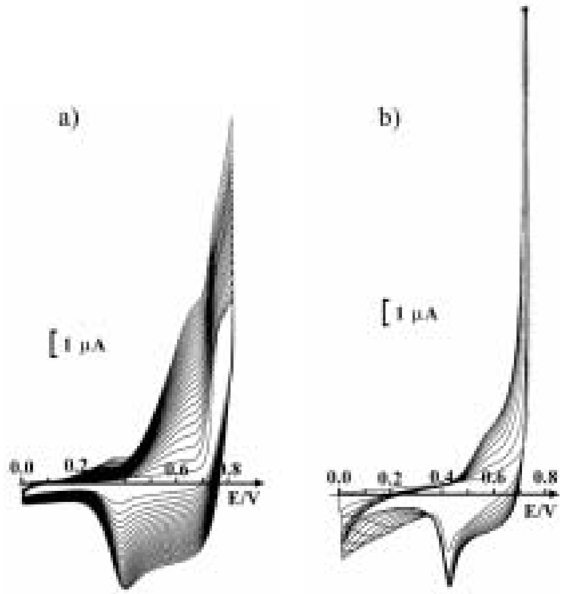


Fig. 5. Cyclic voltammetry curves recorded during electropolymerization of 5 mM solution of M1 in: a) 0.2 M $(Bu)_4NPF_6/CH_3CN$, b) 0.2 M $(Bu)_4NPF_6/CH_2Cl_2$; scan rate 0.02 V/s

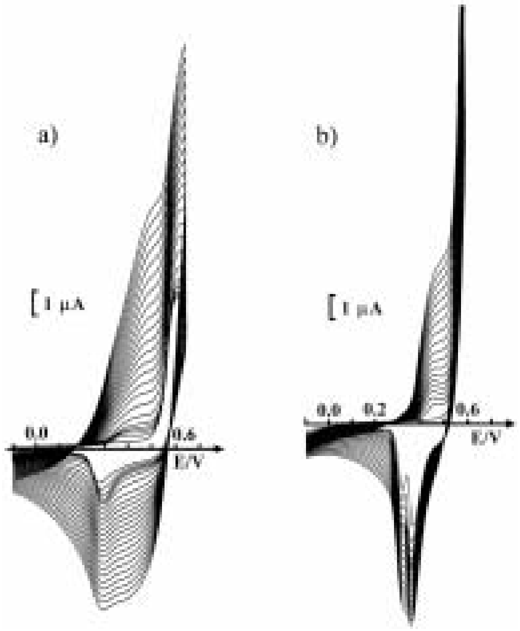


Fig. 6. Cyclic voltammetry curves recorded during electropolymerization of 5 mM solution of M2 in: a) 0.2 M $(Bu)_4NPF_6/CH_3CN$, b) 0.2 M $(Bu)_4NPF_6/CH_2Cl_2$; scan rate 0.02 V/s

All the results shown above demonstrate that under electrochemical conditions, when the electrode potential is high enough, both the monomers can polymerize. The last statement is more clearly demonstrated in the experiment shown in Fig. 5. The CV curves were obtained during continuous scanning to the potential that was limited to the value of the first step of M1 oxidation in 5 mM CH_3CN solution (Fig. 5a) and in CH_2Cl_2 solution (Fig. 5b). As can be seen, the electroactive products of the consecutive reactions are produced, which after reduction are in the second scan oxidized at potentials lower than those in the initial scan. This proves that the monomer is oxidized to cation radical, in which the charge is localized in the thiophene ring. Free α,α'- positions in the 1,4-bischloromethylbenzene molecule make possible the formation of higher molecular weight products. These are likely oligomers or polymers being deposited on the electrode surface. An indication for that are wide current peaks for both, oxidation and reduction processes, which are continuously growing when the potential is cycled within the limits of 0.2 and 0.7 V. At the same time, a growing layer of well adhering polymer is observed on the electrode surface.

The same processes of M2 electropolymerization from the 5 mM solutions in CH_3CN or CH_2Cl_2 are shown in Fig. 6. As earlier, the applied potential was not higher than that for the first oxidation stage. If one compares the voltammetric curves obtained for M1 (Fig. 5) with those reported here for M2, some differences are evidently seen. At least partially they are related to a higher solubility of the reaction products due to the presence of methoxy- substituents in the M2 molecule. First of all, the M2 monomer is oxidized at the potential about 200 mV lower than M1 one. In this case the formation of the electroactive products of oxidation is seen, which are reduced and oxidized at potentials lower than for initial scan. Observation of the electrochemical cell during the process shows clearly some orange-coloured products of the oxidation that are soluble in solvent, so they are diffusing to the bulk of the cell. Longer polymerization time leads to the formation of polymer film well adhering to the electrode surface. Similarly to the above, the process runs through a stage of well soluble oligomers to the final polymeric product.

If one compares the first four voltammetric cycles with the following cycles, which are recorded either for CH_3CN or in CH_2Cl_2 solutions, some differences can be noticed. During the initial scans for CH_3CN solution (see Fig. 5a) a well defined reduction peak is recorded at 0.28 V. This peak moves toward more positive potential during initial scan, then, it occurs at stable position. At the same time, a formation of the anodic peak is observed at 0.37—0.40 V; this in turn, starts to grow a little during scanning. After the fourth scan, clear changes are taking place for both, oxidation and reduction peaks. On the reduction site, a substantial increase in current occurs within the range of potentials — 0.1 V—0.28 V, whereas the current value at 0.28 V remains practically unchanged. And secondly, a similar behaviour is observed on the oxidation site, in the potential range 0.20 V—0.40 V.

M2 has higher solubility in CH_2Cl_2 than in CH_3CN. The CV curves shown in Fig. 6b were obtained for 1 mM M2 solution in CH_2Cl_2 containing 0.2 M $(Bu)_4NPF_6$. These curves are different than the corresponding, obtained in CH_3CN. In the cathodic range, two well-defined peaks occur at 0.32 V and at 0.38 V, whereas for the anodic scans, one peak is recorded at 0.45 V. As in case of the CH_3CN solution, after the fourth scan, the peaks on cathodic site start to grow in a wide range of potentials, between 0.10 V and -0.28 V.

The observed phenomena might be interpreted as follows: during oxidation at the potential close to 0.6 V, the M2 molecule is converted to cation radical, which in turn undergoes consecutive dimerization (or oligomerization) reactions. Formation of oligomers provides of well-defined reduction peaks during four initial scans. In CH_3CN solution this is the single peak at 0.28 V, whereas in CH_2Cl_2 one the formation of two peaks is caused by dimer (reduction at 0.38 V) and trimer (reduction at 0.32 V). Dimer and trimer, which are produced at the electrode, are weakly soluble in the solvent, as found from the visual observations of the cell during the whole process. Besides a yellow coloured solution, one may see some products changing colour from yellow to orange in the space adjacent to the working electrode and diffusing to the bulk of solution. From the spectrum of solution taken from the cell after electrolysis, shown in Fig. 7, a presence of two new absorption maxima at 482 nm and at 516 nm is evident, together with the features characteristic for the unreacted monomer. These peaks are assigned to the dimeric form and to the trimer, respectively.

The reaction course, described above, is a result of relatively slow chemical step due to stabilization of the cation radical, which is delocalized along the π-bonding system of 1,4-bischloromethyl-2,5-dimethoxybenzene. If the process runs longer (here at least four voltammetric cycles) then oxidation of oligomers, present at the electrode surface at a high enough concentration, leads to formation of a polymer. Since the polymer is insoluble under conditions of the electrolysis, it is deposited on the electrode surface as a homogeneous film.

It is noteworthy that the polymerization process of both compounds appears to be very sensitive on the electrochemical conditions and on the monomer concentration. If the anodic end-potential of voltammetric scan is larger than the potential of the first oxidation step of the monomer, then a black powder is produced instead of the well adhering film.

Electrochemistry and spectroelectrochemistry of polymers

Thin polymer films of both M1 and M2 are homogeneous, lightly orange in colour, well adhering to the indium tin oxide **(ITO)** electrodes, and they are insoluble in most of organic solvents. Typical voltammetric curves of these polymers in CH_3CN solution are shown in Figure 8. The main peak of poly(M1) oxidation occurs at E_{pM1} = 0.65 V. The peak position is stable when the scan

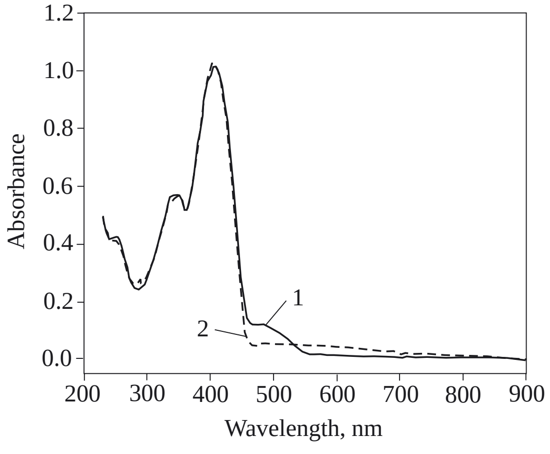


Fig. 7. UV-Vis absorption spectra of M2 solution in CH_2CL_2 measured before (curve 1) nad after electropolymerization (curve 2)

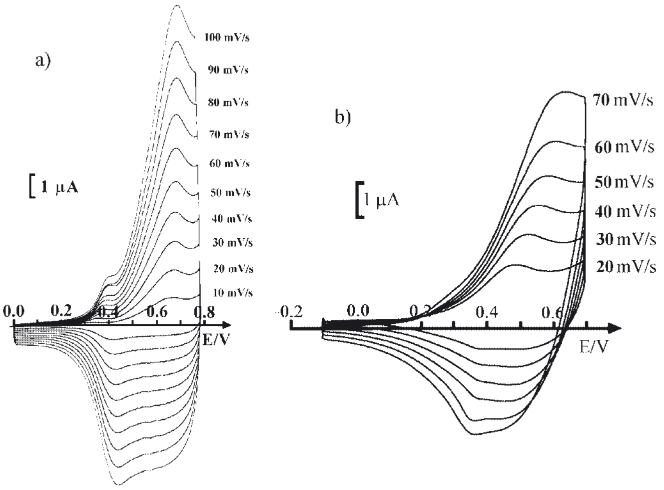


Fig. 8. Cyclic voltammetry curves recorded at variable scan rates in CH_3CN solution containing 0.2 M of $(Bu)_4NPF_6$ for solid films of: a) poly(M1), b) poly(M2); scan rate 0.05 V/s

rates are in a range of 0.01—0.10 V/s. The analogous peak position E_{pM2} of poly(M2) is shifting from 0.48 V at 0.02 V/s to 0.60 V at 0.07 V/s. This may suggest a better conductivity of poly(M1) as compared to poly(M2). The other possibility exists that a more compact film structure of the poly(M2) causes more difficult diffusion of doping anions. An argument for better conductivity of poly(M1) than poly(M2) arises from a fast decrease in the current that in fact is observed after the change of the scanning direction. During the cathodic scan for poly(M1), a wide peak is recorded with the maximum at 0.42 V. In case of poly(M2), both cathodic and anodic scans result in a potential shift due to a larger resistance; a shift of the peak maximum is observed towards more positive potential when the applied scan rate increases.

Similar voltammetry results to that described for CH_3CN solution are observed when the polymers were obtained in CH_2Cl_2 solutions. However, if polymerization takes place in CH_2Cl_2 and voltammetry is carried out in CH_3CN, then the solvent remaining in the polymer matrix causes effects shown in Fig. 9. Very sharp peaks for both oxidation and reduction processes are then recorded which overlap the 'normal' voltammograms of the polymer. These effects do not occur, if the polymer is carefully rinsed with CH_2Cl_2 before measurements. Oligomers have better solubility in CH_2Cl_2 than in CH_3CN, thus rinsing with CH_3CN allows removing monomer only from the film. This is in agreement with the earlier thesis that polymerization progresses through the phase of formation of stable oligomers that are soluble in CH_2Cl_2. The oligomers disappear during voltammetry measurement as a result of polymerization into solid state film or due to good solubility of oxidised oligomer in strongly polar CH_3CN. Since the peak current decreases during few initial scans and then it becomes stable, the second thesis is more likely.

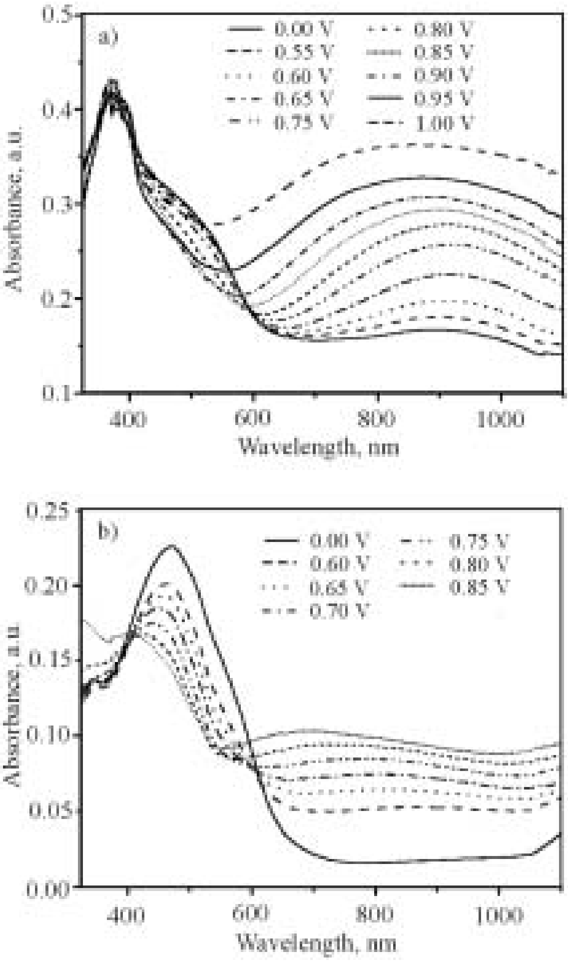


Fig. 10. UV-Vis is spectroelectrochemistry of polymer solid films on optically transparent ITO electrodes in CH_3CN solution containing 0.2 M $(Bu)_4NPF_6$: a) poly(M1), b) poly(M2); each spectrum recorded at potential indicated in the insert of the figure

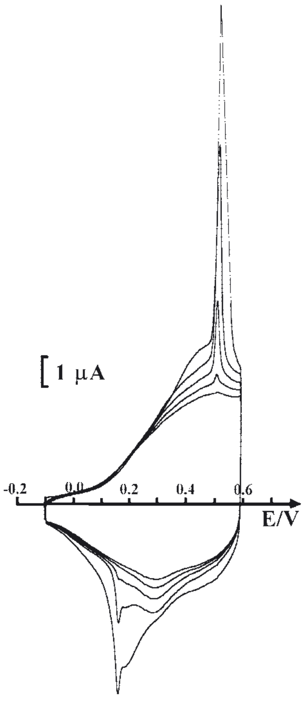
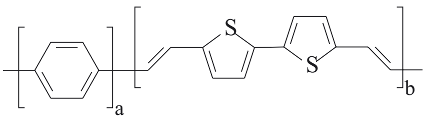


Fig. 9. Cyclic voltammetry curves recorded in CH_3CN solution containing 0.2 M of $(Bu)_4NPF_6$ for solid film of poly(M2) that was synthesized in CH_2CL_2 solution; scan rate 0.05 V/s

Each of two polymers has electrochromic properties. Typical UV-Vis spectra recorded during oxidation of poly(M1) in the potential range of 0.0 V to 1.0 V and poly(M2) in the range of 0.0 V to 0.85 V are shown in Fig. 10. Spectrum of poly(M1) in the reduced state consists of two overlapping bands with the maximum at 380 nm and shoulder at 550 nm. The band gap found from the spectroscopic data is at the level of 1.97 eV. During oxidation, only the band at 550 nm is decreasing, whereas the band at 380 nm remains practically unchanged up to 0.6 V. At the potentials above 0.6 V, a little change is observed in the region of 380 nm, a substantial decrease in absorbance occurs above 1.0 V. However, at the last potential region, the changes in spectra are irreversible due to decomposition of the film. The spectral behavior of the polymer is a result of the fact that the film is a mixture of oligomers and polymers in which oligomers absorb energy at shorter wavelength than polymers do. In the case described, it could be only a monomer that absorbs at 376 nm. However, monomer is well soluble and cannot be responsible for the large absorbance observed at this range, as shown in Fig. 10a. It is important to add that the electropolymerization was carried out in the solution of the monomer of the concentration far from saturation. An assignment of that absorption peak to a presence of the dimer should also be excluded, since dimer is expected to absorb at a wavelength shifted towards lower energies, approximately about 80 nm as compared to monomer. This is consistent with the results obtained for M2 (as shown in Figure 7). The observed behavior might be also explained taking into account that poly(M1) is a block–type polymer that consists of bithiophene-vinylene and *p*-phenylene segments, as it is shown below:



(IV)

It may be assumed that bithiophene-vinylene segments should be oxidized at lower potentials than *p*-phenylene segments. The π-π* electronic transitions in the bithiophene-vinylene segments could be responsible for the absorbance at 505 nm. It is well known that oligothienylenevinylenes exhibit the band gap smaller than oligothiophenes [41, 42], therefore the value of 505 nm found in those studies seems to be reasonable.

Oxidation of the polymer provides a wide absorption band in the region of 910 nm. That spectrum remains practically unchanged until the potential reaches the value of 0.50 V. In this range of potentials an isobestic point occurs at about 610 nm. Oxidation of the polymer at more positive potentials moves the absorption maximum from 910 nm to about 870 nm, besides, there is a broadening of the band, and the isobestic point disappears. The spectroelectrochemical data imply that a simple oxidation takes place up to 0.50 V when poly(M1) is converted to the cation radical poly(M1)$^{\bullet+}$ in which the charge is delocalized along the polymer chain. Above that potential, also phenylene part of the polymer chain undergoes the oxidation. As may be concluded from these results, within the applied potential region bipolarons are not produced, as has been concluded earlier from the results obtained for other complex polymeric forms [43].

Spectroelectrochemical behavior of poly(M2) is slightly different, as shown in Fig. 10b. The electron-donor character of the methoxygroup cause a shift of the absorption band of methoxyphenyl group towards lower energies, and in turn, overlapping of that band with the absorption band of bithiophene-vinylene. At 470 nm, there is a single band responsible for the π-π* transition of the whole molecule. The band gap of that polymer, as found from the spectroscopic measurements is equal 1.85 eV, thus it is slightly less than that found for poly(M1). It is in fact an expected result, taking into account a presence of the electron donating methoxy substituents. In the course of oxidation, this band is disappearing, whereas at the same time, a new broader band appears in the range of 800—900 nm. This broadening is likely a result of formation of the doping products. Also in that case, the isobestic point exists at lower doping levels. It diffuses at higher oxidation potentials; besides, the absorption band of polarons is being gradually shifted to the wavelength of 670 nm.

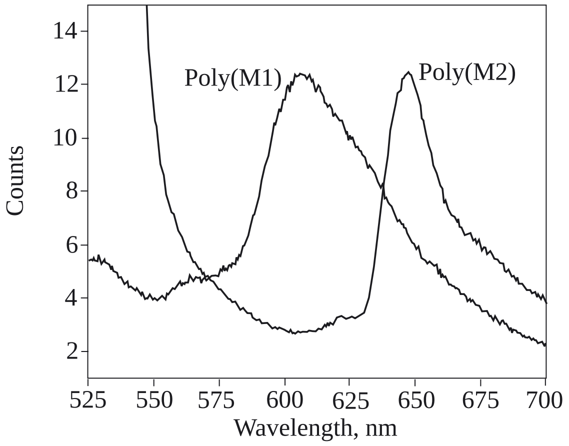


Fig. 11. Photoluminescence spectra of poly(M1) and poly(M2) solid in an air; films of about 50 nm thick were deposited electrochemically on optically transparent ITO

Both polymers, poly(M1) and poly(M2) have electroluminescent properties, the PL spectra of them are shown in Fig. 11. The polymer films for these measurements were electrochemically deposited on ITO electrodes to a thickness of about 50 nm. In contrast to photoluminescence of monomers, the PL spectra of poly(M1) and poly(M2) display only single maxima at 606 nm and at 642 nm, respectively. The luminescence band of poly(M2) is specific and very narrow, since its half width is only 25 nm, whereas for poly(M1) this value is doubly wide, equal to 50 nm. Besides, in comparison to the monomers, these polymers have the maximum of emission shifted of about 0.03 eV towards lower energies. The quantum efficiency is not high, however slightly higher than that for monomers. It is at the level of 0.3 % and 0.5 %, for poly(M1) and poly(M2), respectively. This proves the polymer structure is less crystalline than of M1 and M2 monomer films. Also, a presence of additional substituents in phenylene ring reduces interactions between the polymer chains. Therefore, to enhance a photoluminescence performance of such polymers it is reasonable to apply substituents that considerably increase an entropy of the polymeric system.

CONCLUSIONS

We have proved that an electrochemical route may be applied to synthesize the polymers that have photoluminescence properties. Some monomer structural effects were demonstrated to enhance the overall photoluminescence performance of resultant polymers. Electrochemical and spectroelectrochemical studies led us to the proposed mechanisms of polymerization and doping processes under electrochemical conditions. It was established that during oxidation of both, 1,4-bis-(2(Z)-thienylenevinylene)benzene and 1,4-bis-(2(Z)-thienylenevinylene)-2,5-dimethoxybenzene, the first step of the process results in soluble oligomers, which in the second step provide insoluble, well transparent films on the electrode surface.

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REFERENCES

1. Burroughes J. H. C., Bradley D. D., Brown A. R., Marks R. Mackay N. K., Friend R. H., Burn P. L., Holmes A. B.: *Nature* 1990, **347**, 539.
2. Gustafsson G., Cao Y., Treacy G. M., Klavetter F., Colaneri N., Heeger A. J.: *Nature* 1992, **357**, 477.
3. Schwartz B. J.: *Ann. Rev. Phys. Chem.* 2003, **54**, 141.
4. Hide F., Diaz-Garcia M. A., Schwartz B. J., Heeger A. J.: *Acc. Chem. Res.* 1997, **30**, 430.
5. Hong-Ku Shim, Jung-Il Jin: *Adv. Polym. Sci.* 2002, **158**, 193.
6. Roncali J.: *Ann. Rep. Prog. Chem., Sect.* 1999, **C95**, 47.
7. Iwan A., Sęk D.: *Polimery* 2005, **50**, 581.
8. Brédas J. L., Calbert J. P., da Silva Filho D.A., Cornil J.: *PNAS* 2002, **99**, 5804.
9. Łapkowski M.: *Polimery* 1986, **31,** 325.
10. Łapkowski M.: *Polimery* 1986, **31**, 451.
11. Pei J., Yu W.-L., Ni J., Lai Y.-H., Huang W., Heeger A. J.: *Macromolecules* 2001, **34,** 7241.
12. Xu J. M., Ng S. C., Chan H. S. O.: *Macromolecules* 2001, **43**, 4314.
13. Wang H., Ng M. K., Wang L., Yu L., Lin B., Meron M., Xiao Y.: *Chem. Eur. J.* 2002, **8**, 3246.
14. Peres L. O., Varela H., Garcia J. R., Fernandes M. R., Torresi R. M., Nart F. C., Gruber J.: *Synth. Met.* 2001, **118**, 65.
15. Damlin P., Kvarnstrom C., Neugebauer H., Ivaska A.: *Synth. Met.* 2001, **121**, 141.
16. Roncali J.: *Chem. Rev.* 1992, **92**, 711.
17. Higgins S. J.: *Chem. Soc. Rev.* 1997, **26**, 247.
18. Jiang X. M., Osterbacka R., Korovyanko O., An C. P., Horovitz B., Janssen R. A. J., Vardeny Z. V.: *Adv. Funct. Mater*. 2002, **12**, 587.
19. Horowitz G.: *Adv. Mater.* 1998, **10**, 365.
20. Maillou T., Le Moigne J., Dumarcher V., Rocha L., Geffroy B., Nunzi J. M.: *Adv. Mater*. 2002, **14**, 1297.
21. Videloi C., Ackermann J., Blanchard P., Raimundo J. M., Frere P., Allain M., De Bettignies R., Levillain E., Roncali J.: *Adv. Mater.* 2003, **15**, 306.
22. Bredas J. L., Cornil J., Beljonne D., Dos Santos D. A., Shuai Z.: *Acc. Chem. Res.* 1999, **32**, 267.
23. Katz H. E., Bao Z., Gilat S.: *Acc. Chem. Res.* 2001, **34**, 359.
24. Garnier F.: *Acc. Chem. Res.* 1999, **32**, 209.
25. Łapkowski M., Kolodziej-Sadlok M., Żak J., Guillerez S., Bidan G.: *Adv. Mater.* 2001, **13**, 803.
26. Łapkowski M., Żak J., Kołodziej-Sadlok M., Guillerez S., Bidan G.: *Electrochim. Acta* 2001, **46**, 4001.
27. Domagala W., Łapkowski M., Guillerez S., Bidan G.: *Electrochim. Acta* 2003, **48**, 2379.
28. Łapkowski M., Żak J., Kolodziej-Sadlok M., Guillerez S., Bidan G.: *Synth. Met.* 2003, **135-136**, 251.
29. Döttinger S. E., Hohloch M., Hohnholz D., Segura J. L., Steinhuber E., Hanack M.: *Synth. Met.* 1997, **84**, 267.
30. Lange F., Hohnholz D., Leuze M., Ryu H., Hohloch M., Freudenmann R., Hanack M.: *Synth. Met.* 1999, **101**, 652.
31. Leuze M., Hohloch M., Hanack M.: *Chem. Mater.* 2002, **14**, 3339.
32. Döttinger S. E., Hohloch M., Segura J. L., Steinhuber E., Hanack M., Tompert A., Oelkrug D.: *Adv. Mater.* 1997, **9**, 233.
33. Oelkrug D., Tompert A., Egelhaaf H. J., Hanack M., Steinhuber E., Hohloch M., Meier H., Stalmach U.: *Synth. Met.* 1996, **83**, 231.
34. Gierschner J., Egelhaaf H. J., Mack H. G., Oelkrug D., Martinez Alvarez R., Hanack M.: *Synth. Met.* 2003, **137**, 1449—1450.
35. Wagner P., Aubert P. H., Lutsen L., Vanderzande D.: *Electrochem. Commun.* 2002, **4**, 912.
36. *"Handbook of Organic Conductive Molecules and Polymers"*, (Ed. Nalwa H. S.) vols. 1—4, John Wiley & Sons, Chichester, 1997.
37. Balletête M., Morin J. F., Beaupré S., Leclerc M., Durocher G.: *Synth. Met.* 2002, **126**, 43.
38. Balletête M., Beaupré S., Leclerc M., Durocher G.: *Macromolecules* 2001, **34**, 2288.
39. Kang B. S., Seo M. L., Jun Y. S., Lee C. K., Shin S. C.: *Chem. Commun.* **1996**, 1167.
40. Kang B. S., Kim D. H., Lim S. M., Kim J., Seo M. L., Bark K. M., Shin S. C.: *Macromolecules* 1997, **30**, 7196.
41. Jestin I., Frere P., Levillain E., Miercier N., Stievenard D., Roncali J.: *J. Am. Chem. Soc.* 1998, **120**, 8150.
42. Jestin I., Frere P., Levillain E., Blanchard P., Roncali J.: *Angew. Chem., Int. Ed. Engl.* 1998, **37**, 942.
43. Lafolet F., Ph. D. Thesis, INP de Grenoble, 2003.

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