

Synthesis and properties of photoactive and electroactive polymers based on transition metal complexes

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Abstract

We report the photochemical and electrochemical activity of metallopolymers (organized molecular systems) based on transition metal complexes with 5-chloro-1,10-phenanthroline and Schiff bases. These polymers are redox conductive, optically transparent and electrochromic. Their calculated charge diffusion coefficients (D_{ct}) are in the range 10^{-11} – 10^{-10} cm² s⁻¹. The optimal conditions of polymer formation as a function of the potential, their time of growth and their spectral characteristics (absorption) were registered. In the solid polymer matrix, the activation barrier does not exceed 30 kJ mol⁻¹ for the bimolecular electron transfer reactions. The photopotential of the electrode, coated with a redox film, reached magnitudes of 70–450 mV depending on the polymer.

Keywords: Electroconductivity; Metallopolymers; Photoelectrochemical sensitivity; Reversible redox reactions in polymer matrix

1. Introduction

The progress and rapid development of supramolecular chemistry and photochemistry has opened up new perspectives for the treatment of topical problems of photosynthesis and catalysis [1–3].

Achievements in synthesis and investigations of photosensitive and electroconductive molecular assemblies have contributed to the development of modern electron and energy transfer theory and signal processing at the molecular level.

Recently, it has been shown [4–6] that molecular organized systems represent very convenient models for the investigation of long-range energy and electron transfer at redox sites.

In modern supramolecular chemistry, the methods of creation of molecular devices with given electron donor composition and spatial arrangement of redox equivalents are of importance. This approach makes it possible to achieve highly effective photoinduced and electroinduced energy and electron transfer processes.

Recently, it has been shown [7] that the rigid redox sites, structural anisotropy and properties of metal organic polymers corroborate the vector transfer of an electron along the polymeric chain.

In this paper, we study the photosensitivity of the polymeric systems poly-[M(5-Cl-phen)₃]^{3+/2+} (M ≡ Fe, Ru,

Os; 5-Cl-phen, 5-chloro-1,10-phenanthroline) and poly-[Msalen] and poly-[Msalphen] (M ≡ Pt(II), Pd(II), Cu(II), Mn(II, III); salen and salphen, bis-(salicylidene)-ethylenediamine and bis-(salicylidene)-*o*-phenylenediamine respectively).

2. Experimental details

2.1. Materials

The preparation and purification of [M(5-Cl-phen)₃](ClO₄)₂ (M ≡ Fe, Ru, Os), [Msalen] and [Msalphen] have been described previously [8–10]. Acetonitrile was distilled from CaH₂ and dried over 4 Å molecular sieves [11]. Tetra-*n*-butylammonium trifluoroacetate (TBA(CF₃COO)) was synthesized by mixing tetra-*n*-butylammonium hydroxide and trifluoroacetic acid in equimolar quantities. The crude product was collected, washed with water, recrystallized three times from 50% acetonitrile–50% water and dried in vacuum over P₂O₅ for 48 h.

2.2. Measurements

Cyclic voltammetry (CV) experiments were carried out using an impulse potentiostat (model PI-50-1) and a three-electrode cell with separate spaces for working, auxiliary and

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reference electrodes; 2 mM solutions of the 5-Cl-phen complexes were prepared in acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. A platinum wire (area, 0.23 cm²) was used as the working electrode, a platinum net served as the auxiliary electrode and Ag/AgCl was employed as the reference electrode. All voltammograms were recorded under an Ar atmosphere. Low-temperature CV experiments were carried out by cooling the background solution from +25 to –40 °C. Spectroelectrochemical experiments were performed using a two-electrode Pyrex cell. A high-pressure mercury lamp (DRSH-1000) with a water IR filter was used as irradiation source. Visible region spectral (absorption) measurements were made using LOMO spectrophotometers (models SF-20 and SF-26) employing platinum and indium-tin oxide optically transparent electrodes.

3. Results and discussion

3.1. Photochemical and electrochemical properties of polymers based on Fe(II), Ru(II) and Os(II) complexes with 5-Cl-phen

Electrochemical reduction of iron, ruthenium and osmium complexes containing 5-Cl-phen as ligand leads to the growth of metallopolymer on the electrode surface [8]. These polymers were very stable to repeated electrochemical cycling and were highly reproducible.

It is proposed that the central ion directly influences the process of polymer formation (via electrochemical reductive activation of the complexes) and their stability. For example, electrochemical polymerization of a Cr(III) complex with 5-Cl-phen leads to the formation of low-valent chemically unstable complexes capable of ligand loss [12].

It should be noted that a knowledge of the [ML_n]^{z+} lowest excited state (where L is a heterocyclic π-acceptor ligand with olefin fragments or halogen substituted in the aromatic ring) allows the relative distribution in energy and the filling of the energy levels to be predicted. This is crucial for the prediction of polymer stability. Complexes of Fe(II), Ru(II) and Os(II) with 5-Cl-phen possess a lowest energy d_π–π* excited configuration (nd⁶ structure of central ion), in contrast with the similar complex of Cr(III) which exhibits a lowest energy d–d* excited configuration [13]. Consequently, electrochemical reduction of the complex with a d_π–π* excited configuration leads to the filling of the π* orbitals of the coordinated ligands and the formation of radicals. Radical combination gives rise to the polymer as an electrode coating [8]. For [Cr(5-Cl-phen)₃]³⁺, electrochemical polymerization involves the reduction of the central ion (3d³ structure), labilization of the complex (which is verified by spectroelectrochemical measurements) and unstable polymer formation [12].

Polymer growth occurs not only by the repeated cycling of the potential between –0.7 and –1.7 V vs. Ag/AgCl [8],

but by potentiostatic polarization of the electrode in the potential range –1.7 to –1.4 V [14]. As long as the potentiostatic method made it possible to obtain thick films, this method was used for the investigations. Tests in the M(III)/M(II) potential region (metal centred potential region) of [M(5-Cl-phen)₃]²⁺-based films in background solution (0.1 M TBAP–CH₃CN) indicate the good reversibility of the redox processes in the polymer (Fig. 1). The kinetics of polymer formation as a function of the potential and time of growth were investigated (Fig. 2 and Fig. 3). The “laws of growth” for the osmium polymer were analogous with those for the ruthenium polymer. The coverage data of the polymers were calculated from the areas of the M(III)/M(II) CV peaks using a density for the polymers of 1 g cm^{–3} [15].

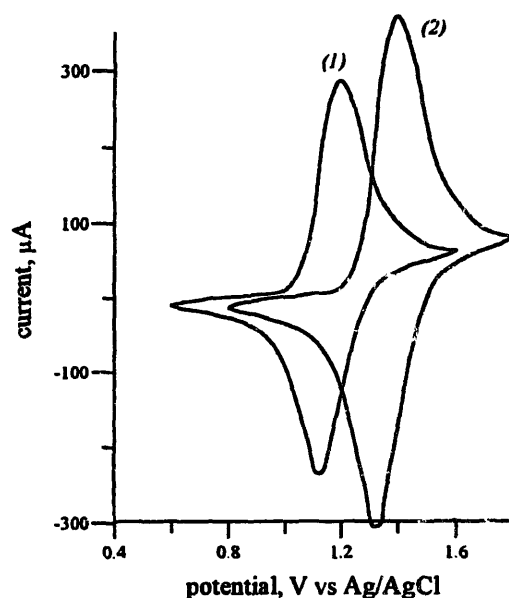


Fig. 1. Electrochemical response of the [Fe(5-Cl-phen)₃]²⁺-based (1) and [Ru(5-Cl-phen)₃]²⁺-based (2) polymers in CH₃CN–0.1 M TBAP. Scan rate, 50 mV s^{–1}.

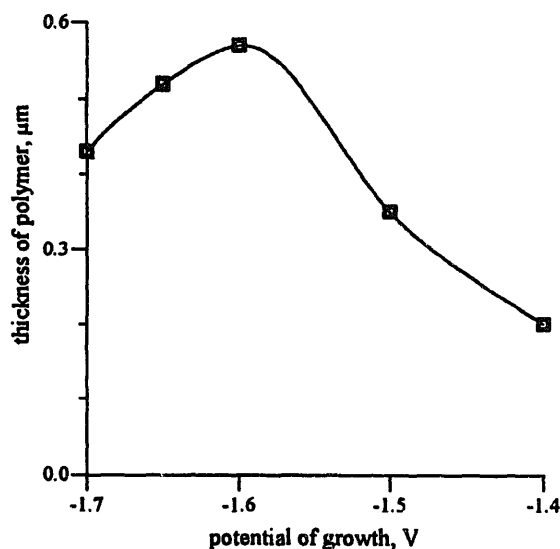


Fig. 2. [Ru(5-Cl-phen)₃]²⁺-based polymer thickness vs. the potential of growth (2 mM solution of complex; time of growth, 12 min).

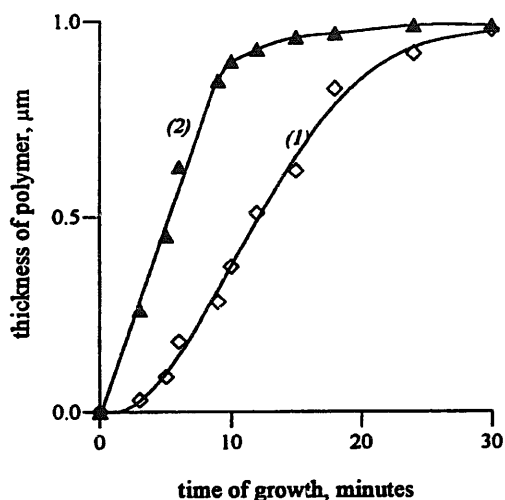


Fig. 3. $[\text{Ru}(5\text{-Cl-phen})_3]^{2+}$ -based (1) and $[\text{Fe}(5\text{-Cl-phen})_3]^{2+}$ -based (2) polymer thicknesses vs. the time of growth at the optimal potential of growth (-1.6 V).

The total reduction and oxidation of the film on the electrode surface (linear dependence of the anodic peak current on the scan rate) was observed at scan rates of less than 0.1 V s^{-1} for the Ru and Os polymers and less than 0.05 V s^{-1} for the $[\text{Fe}(5\text{-Cl-phen})_3]^{2+}$ -based films. At scan rates exceeding 0.1 V s^{-1} for the $[\text{Ru}(5\text{-Cl-phen})_3]^{2+}$ - and $[\text{Os}(5\text{-Cl-phen})_3]^{2+}$ -based polymers (linear dependence of the anodic peak current on $(\text{scan rate})^{1/2}$), the films were partially reduced and oxidized. Using the approach of diffusional kinetics [15], we calculated the magnitudes of the charge transfer diffusion coefficients (D_{ct} , $\pm 0.3\text{ cm}^2\text{ s}^{-1}$) for the M(III)/M(II) couples. These magnitudes were approximately 2×10^{-10} , 4×10^{-10} and $6 \times 10^{-10}\text{ cm}^2\text{ s}^{-1}$ for the iron, ruthenium and osmium polymers respectively.

The most important question in the behaviour of chemically modified electrodes coated with metallopolymeric films involves the search for the mechanism responsible for the charge propagation through the layer assembly. The estimation of charge transport has been the subject of numerous investigations [16–18]. The process of charge diffusion follows a multistep course:

1. heterogeneous electron transfer during film oxidation or reduction;
2. charge transport (diffusion of electrons) by electron self-exchange (electron hopping) between the neighbouring reduced and oxidized sites of the polymer;
3. movement of the charge compensation ions with their solvation spheres in the polymer matrix providing the necessary condition for the maintenance of the film electroneutrality during oxidation or reduction [17,19].

In the case of octahedral low-spin polypyridine complexes, stages (1) and (2) are expected to proceed rapidly because the M(III)/M(II) ($\text{M} \equiv \text{Fe, Ru, Os}$) reactions do not result in axial changes on transfer of a non-bonding d_{π} electron [16,20]. Consequently, the contribution of the intrinsic barrier (λ_{in}) to the total activation energy (E_a) will be small

compared with solvent molecule repolarization and counterion motion.

For stage (3), the rate of electron diffusion is not controlled by the charge compensation ion motion in the case of ultrathin films (e.g. poly- $[\text{Ru}(\text{v-bpy})_3]^{2+}$, 20–40 Å) or for redox polymers with bulky monomer sites and small counterions [19,21,22].

In order to investigate the influence of the counterions on the film conductivity, we used 0.1 M solutions of TBA(CF_3COO), TBABF₄ and TBAPF₆ in CH_3CN and low-temperature measurements. For a lack of dependence of D_{ct} on the counterion size, the limiting stage would involve electron hopping between the neighbouring sites. For the $[\text{Fe}(5\text{-Cl-phen})_3]^{2+}$ -based film, a change in supporting electrolyte (e.g. TBAClO₄ to TBABF₄) results in a decrease in D_{ct} from 1.9×10^{-10} to $8.4 \times 10^{-11}\text{ cm}^2\text{ s}^{-1}$.

We have investigated the temperature dependence of the charge diffusion coefficients. In general, the diffusion coefficients of ions depend on their size, charge and the solvent viscosity. During a temperature drop from $+20$ to $-30\text{ }^\circ\text{C}$, the values of D_{ct} varied proportionally with the increase in the solvent viscosity. For example, the diffusion coefficients of the ferrous polymer are reduced from 2×10^{-10} to $1.8 \times 10^{-11}\text{ cm}^2\text{ s}^{-1}$. Fig. 4 illustrates a plot of D_{ct} vs. the background solution temperature for the ruthenium polymer. The magnitudes of K_{ex} were calculated by the Dahms–Ruff equation [23]; the values of K_{ex} vary in the range 10^3 – $10^5\text{ M}^{-1}\text{ s}^{-1}$. The values of the activation barriers (E_a , $\pm 3\text{ kJ mol}^{-1}$) of electron exchange for the $[\text{M}(5\text{-Cl-phen})_3]^{3+/2+}$ couples approximate to 25 kJ mol^{-1} for the iron, ruthenium and osmium polymers.

The charge propagation in the polymers based on complexes of Fe(II), Ru(II) and Os(II) with 5-Cl-phen is controlled by counterion diffusion in the polymer matrix as indicated by the results obtained.

1. The magnitude of E_a does not depend on the central ion.
2. The use of charge compensating ions with a size exceeding that of the perchlorate ion (3.7 \AA) leads to an increase in

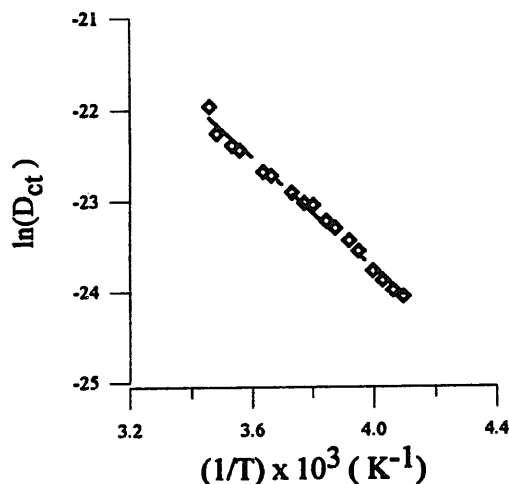


Fig. 4. Typical plot of the D_{ct} dependence on the reciprocal temperature for the $[\text{Ru}(5\text{-Cl-phen})_3]^{2+}$ -based film in CH_3CN -0.1 M TBAP.

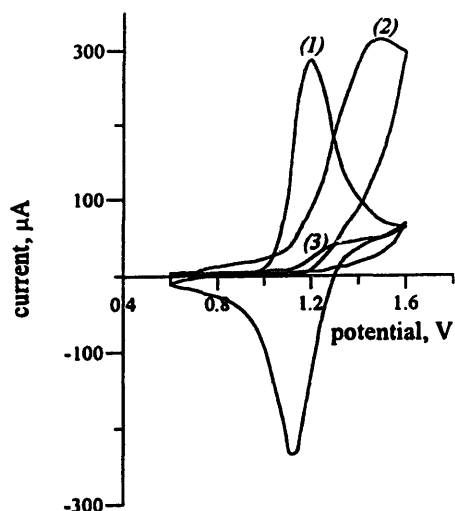


Fig. 5. Electrochemical response of an $[\text{Fe}(5\text{-Cl-phen})_3]^{2+}$ -based film in $\text{CH}_3\text{CN}-0.1 \text{ M TBAP}$ (1) and in $\text{CH}_3\text{CN}-0.1 \text{ M TBA}(\text{CF}_3\text{COO})$ (2 and 3, the first and subsequent cycles respectively).

the activation barrier to values of approximately 40 kJ mol^{-1} . This effect can be explained as follows. The increase in size of the counterions results in greater energetic losses accompanying the shift of the polymeric segments in order to produce the holes and cavities responsible for the motion of the charge compensating particles. Moreover, if a polymeric chain possesses a polyramified structure, the correlated motion of the polymeric segments responsible for the permeation of ions is violated.

3. Cycling of the $[\text{M}(5\text{-Cl-phen})_3]^{2+}$ -based films in acetonitrile solution containing TBA(CF_3COO) as the supporting electrolyte (trifluoroacetate ion possesses a radius twice as large as the perchlorate ion) produces the irreversible oxidation of the polymer and a loss of conductivity (Fig. 5).
4. The strong dependence of D_{ct} on the supporting electrolyte concentration.

We have registered the absorption spectra of the polymers. The absorption band maxima of the reduced forms of the polymers are at wavelengths of 525 nm (Fe), 480 nm (Ru) and 497 nm (Os) (Fig. 6). These bands are shifted to the red compared with the bands of the monomers.

In previous investigations, we introduced the photosensitive polymeric systems based on complexes of Fe(II) and Ru(II) with 5-Cl-phen [24]. As noted above, these complexes are polymerizable at a potential determined by the ligand. It is possible to apply different methods of photogalvanic system organization: a single-layer system in which a sensitizer ($\text{poly-}[\text{Ru}(5\text{-Cl-phen})_3]^{2+}$) is electropolymerized on the electrode surface and a quencher ($[\text{Fe}(5\text{-Cl-phen})_3]^{3+}$) remains in solution; a double-layer electrode with layers in series of the sensitizer and the quencher (and vice versa); copolymeric systems with a dimensional reaction zone. The distinction between the oxidation potentials of ferrous and ruthenium polymers (approximately 200 mV)

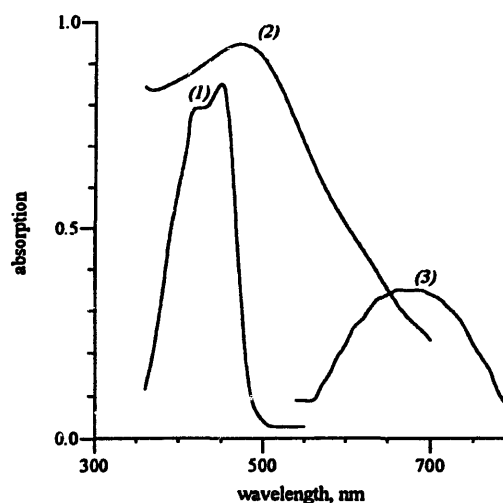


Fig. 6. Absorption spectra of the reduced form of the $[\text{Ru}(5\text{-Cl-phen})_3]^{2+}$ -based film at the indium-tin oxide optically transparent electrode (2) and $[\text{Ru}(5\text{-Cl-phen})_3]^{2+}$ (1) and $[\text{Ru}(5\text{-Cl-phen})_3]^{3+}$ (3) in acetonitrile solution.

offers a selective drive of $\text{poly-}[\text{Fe}(5\text{-Cl-phen})_3]^{2+}$ in the oxidized state, while the sensitizer remains in the reduced form. It was assumed that, on light irradiation ($\lambda^* = 436 \text{ nm}$), the electrode potential increases due to the increase in $[\text{Ru}(\text{III})]$ concentration in the polymer. This increase in concentration is associated with the bimolecular photostimulated electron transfer reaction between $^*\text{Ru}(\text{II})$ and Fe(III). The maximum values of the photogalvanic effect are close to 75–80 mV.

Recently, it has been established [25] that a change in the component ratio does not affect the magnitude of the photogalvanic effect. Further separate investigation of each component photosensitivity is required.

The electrode potential, modified by the mixed-valent $[\text{M}(\text{II})-\text{M}(\text{III})]$ polymer, increases to 50–100 mV on light irradiation, because it is partially determined by the ratio of M(III) with respect to M(II). The oxidized forms of the polymers do not exhibit photoactivity. For the reduced form of the ruthenium polymer, a value of 15–20 mV is observed in the vicinity of the partially oxidized form, i.e. a variation of 75–80 mV. The values of the photopotential for the reduced and partially oxidized forms of the ferrous polymer are 20 and 50–55 mV, and for the osmium complex the values are 15 and 60 mV. A drive of the polymers from the reduced state to the partially oxidized state was achieved by polarization of the chemically modified electrode (CME) at 1.2, 1.4 and 0.9 V for the iron, ruthenium and osmium polymers respectively. Under dark conditions, the potential of the modified electrode approaches that of pure platinum in background solution.

Whatever the form of polymer used, reduced or partially oxidized, the potential of CME does not correspond to the Nernst equation. One of the probable explanations is the insufficiently high redox conductivity of the polymers due to the low rates of electron exchange between the reduced and oxidized units of the polymeric chains. Therefore an increase

Table 1
Some physicochemical properties of the polymers

Polymer film	E^0 (V) vs. Ag/AgCl	$D_{ct} \times 10^{-10}$ ($\text{cm}^2 \text{s}^{-1}$)	E_a ($\pm 3 \text{ kJ mol}^{-1}$)	λ_{max} (nm)	$\Delta E(h\nu)$ (mV)	
					Reduced form	Partially oxidized form
Poly-[Fe(5-Cl-phen) ₃] ²⁺	1.12	2.0	24	525	25	35–40
Poly-[Ru(5-Cl-phen) ₃] ²⁺	1.36	4.0	24	480	10–15	50–55
Poly-[Os(5-Cl-phen) ₃] ²⁺	0.92	6.0	24	497	15	60–65
Poly-[Pdsalen]	0.85–0.9	5.0	30	800	450	
Poly-[Pdsalphen]	0.85–0.9	3.8	20	810	300	
Poly-[Cusalen]	0.85–0.9	2.6		680	350	
Poly-[Cusalphen]	0.85–0.9	5.0		780	280	
Poly-[Cosalen]	0.85–0.9	3.0		680	100	

in electron conductivity was secured by the photostimulation of electron transfer in the M(III)–M(II) system. On photoexcitation, M(II) becomes a powerful reductant, the rate of electron transfer increases and, consequently, the charge diffusion coefficient increases. The changes in the modified electrode potential on light irradiation are given in Table 1.

3.2. Photochemical and electrochemical properties of [Msalen]- and [Msalphen]-based polymers

This section deals with the original determination of the anode electrochemical synthesis principles. New photosensitive, electroconductive and electroactive polymers based on [Msalen] and [Msalphen] complexes with given properties were synthesized in acetonitrile solutions on solid carriers [9,10].

These carriers were planar and wire electrodes made of glassy carbon, Au, Pt and optically transparent materials. The following electrochemical and spectroscopic methods were applied: cyclic voltammetry, electronic absorption spectroscopy, electron spectroscopy for chemical analysis (ESCA), X-ray emission line chemical shift, photoelectrochemistry and X-ray scattering within wide angles.

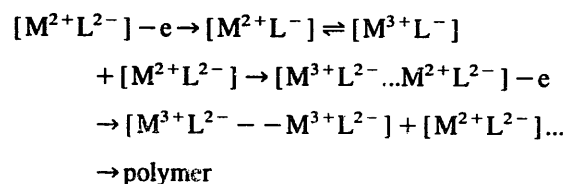
The polymers obtained exist in two electroinduced forms: oxidized and reduced. Both can be controlled by their spectral and electrochromic changes (Table 1).

The kinetic laws of polymer growth and the optimal conditions of electrochemical synthesis and behaviour, i.e. temperature, light energy and intensity, electrolyte properties, electrochemical window, etc., were determined.

The charge state 3+ of palladium and copper in [Msalen]-based polymers was determined by ESCA and X-ray emission line chemical shift using a 2M crystal curved X-ray spectrometer of Cauchois type.

We have proposed the mechanism of formation of metalopolymers [10]. Here, we give the principal stages applied during the process of formation of polymeric partially oxidized complexes. The first stage results in electron transfer from the ligand centred orbitals at +1.1 V. The second stage involves electron density redistribution between the d orbitals of the metal centre and the π orbitals of the ligands. The third stage comprises the coordination of the initial complex to the

oxidized complex via the π electrons of the phenyl rings. Electron transfer in the resulting dimer takes place due to the formation of a so-called ‘‘electron bridge’’, making possible the repetition of the processes mentioned above and polymeric chain growth. The scheme of electropolymerization is as follows



The crystalline structure of both oxidized and reduced forms of poly-[Msalen], where $M \equiv \text{Pd, Cu}$, was established using the method of X-ray scattering within wide angles. It was shown that the degree of order of the monomeric sites is much higher in the case of the oxidized polymeric form. The crystalline structure of the films based on [Pdsalen] comprises alternating regular monolayers parallel to the electrode surface with an identity period of 7.4 Å and a layer distance of 3.7 Å [7].

Using a microsounding installation, the pronounced anisotropy of the electrical properties of the polymeric films was determined. Electron transport occurs in the direction perpendicular to the plane of the aromatic rings. Thus the ohmic resistance (R) of an air-dried film, 1 μm thick (h), is 200 Ω . In contrast, $R = 20 \text{ M}\Omega$ for the direction parallel to the microelectrode surface of gold-coated $\alpha\text{-Al}_2\text{O}_3$ [7].

Electrochemical calculations, direct measurements of the film thickness by interferometry and electric conduction anisotropy data provided a basis for the refinement of the electrochemical notion of the physical thickness of multi-molecular layer films. These results support our hypothesis of the ‘‘molecular wire’’ formation mechanism.

The accumulation of oxidation products on the optically transparent electrode made it possible to record the absorption spectra. The absorption bands of the polymers in the reduced and oxidized forms are shifted to the red compared with those of the monomers in solution. The spectra of the reduced films are quite similar to those of the initial complexes in solution. Hence it is concluded that the reduced films are the polymeric

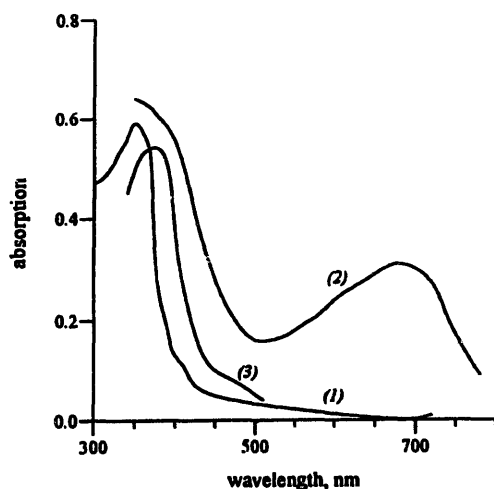


Fig. 7. Absorption spectra of [Cusalen]-based films at the indium–tin oxide optically transparent electrode: (1) monomers in CH_3CN ; (2, 3) oxidized and reduced forms of poly-[Cusalen] respectively.

forms of the initial complexes. In the spectra of the oxidized films, a new, broad, weak absorption band appears in the red region (Fig. 7). Literature data on the spectroscopy of mixed-valent complexes were used to attribute the discussed band to the intervalent transition between metal centres in different oxidation states [26].

High photoactivity of the organized molecular systems was observed [9,27]. The photopotential for the heterotriadic systems reaches a value of 450 mV depending on the polymer (Table 1). The film thickness, solvent, electrolyte and energy and intensity of light influence the effective value of the photopotential. The polymeric systems are photoactive only in the reduced and partially oxidized states. This means that the photoactive centres involve the metal ions in the reduced state. The shift of the redox potential under the action of light energy to the positive region reflects the process of photoinduced charge generation and separation. If the light is switched off, the heterotriadic system tends exponentially to its initial balanced state. The polymers undergo photoinduced multicyclic transformations (Fig. 8).

The quantitative data obtained for one-dimensional electroinduced charge transfer assume a similar vector character to photoinduced electron transport.

The conductivity and charge transfer under the action of UV and visible light seem to possess a general nature. It follows that the photoinduced and electroinduced conductivity mechanisms are identical. They are determined by the structure of the redox fragments and compounds. The electron transfer kinetics were investigated within Pd, Cu and Co films attached to the electrode surface. The electron mobility occurring via a hopping process [18] was expressed as an electron diffusion coefficient. The transfer of electrons through the polymer layers requires a low activation barrier (Table 1).

The oxidative polymerization of poly-[Msalen] and poly-[Msalphen] represents a new effective method of synthesis

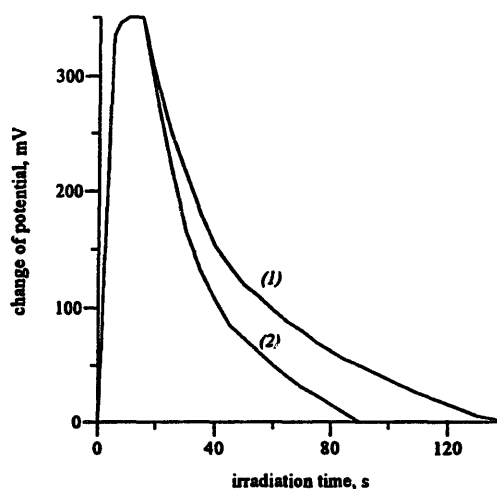


Fig. 8. Change in potential of the platinum electrode, coated with a reduced form of poly-[Cusalen] (1) and poly-[Pdsalen] (2), on light irradiation ($\lambda^* > 360 \text{ nm}$).

of highly oriented thin polymeric films. They function in a cyclic regime produced by electric and electromagnetic fields.

It should be noted that the creation of photosensitive CMEs presents a new trend in photochemical investigations. The problems raised suggest several interesting approaches to further research, e.g. the creation of highly conductive and photoactive systems for solar energy conversion.

Acknowledgements

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