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Processible conjugated polymers: from organic semiconductors to organic metals and superconductors

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Abstract

Since conjugated polymers, i.e. polymers with spatially extended π-bonding system offer unique physical properties, unobtainable for conventional polymers, significant research efforts directed to better understanding of their chemistry, physics and engineering have been undertaken in the past two and half decades. In this paper we critically discuss synthetic routes to principal conjugated polymers such as poly(acetylene), polyheterocyclic polymers, poly(*p*-phenylene vinylene)s, aromatic poly(azomethine)s and poly(aniline) with special emphasis on the preparation of solution (and in some cases thermally) processible polyconjugated systems. In their neutral (undoped) form conjugated polymers are semiconductors and can be used as active components of 'plastics electronics' such as polymer light-emitting diodes, polymer lasers, photovoltaic cells, field-effect transistors, etc. Due to its strongly non-linear $I = f(V)$ characteristics in high electric fields, undoped poly(aniline) can be used as stress grading material for high voltage cables. In the next part of the paper we describe redox and acid–base doping of conjugated polymers and its consequences on structural, spectroscopic and electrical transport properties of these materials. Special emphasis is put on dopant engineering, i.e. on the design of the dopants which not only increase electronic conductivity of the polymer but also induce desired properties of the doped polymer system such as improved processibility, special catalytic properties or special optical or spectroscopic properties. Selected examples of technological applications of doped conjugated polymers are presented such as their use as conductive plastics, optical pH sensors, heterogeneous catalysts, gas separation membranes, etc. The paper is completed by the description of the recent discovery of the first organic polymer superconductor.

Keywords: π-Conjugated polymers; Organic semiconductors; Intrinsically conductive polymers; Synthesis; Processibility; Redox and acid–base doping; Metallic-like conductivity; Superconductivity

Contents

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1. Introduction

Polymers with spatially extended π-bonding system, here abbreviated as 'conjugated polymers', although known for many years, did not draw significant research attention till the mid 1970s. This was caused by the fact that in their vast majority they were intractable and, in many respects, showed inferior properties as compared to already developed polymers. Before 1977, papers dealing with polyconjugated systems were rare and the research devoted to these materials was not systematic. Neither molecular nor electronic structures of conjugated polymers in their undoped state were elucidated. Moreover, the chemical nature of the doping reactions which render these polymers conductive was not known similarly as the mechanism of their conductivity, despite the fact that few papers describing unusually high conductivity of some conjugated polymers were published. In 1977 Heeger, MacDiarmid and Shirakawa showed that poly(acetylene), which is the simplest polyconjugated system, can be rendered conductive by the reaction with bromine or iodine vapors [1]. Spectroscopic studies that followed demonstrated without any ambiguity that this reaction is redox in nature and consists of the transformation of neutral polymer chains into polycarbocations with simultaneous insertion of the corresponding number of Br_3^- or I_3^- anions between the polymer chains in order to neutralize the positive charge imposed on the polymer chain in course of the doping reaction [2]. This important discovery initiated an extensive and systematic research devoted to various aspects of the chemistry and physics of conjugated polymers both in their neutral (undoped) and charged (doped) states. According to SCIFINDER almost 40,000 scientific papers were published in this field of research since 1977. This previously underestimated family of macromolecular compounds turned out to be extremely interesting both from the basic research and application points of view. As a result, in 2000, Heeger, MacDiarmid and Shirakawa — the founders of the 'conjugated polymer science' — were granted Nobel Prize in chemistry [3–5]. Another exciting event followed shortly after the attribution of the Noble Prize for conducting polymers. Schön et al. [6] demonstrated that regioregular poly(3-hexylthiophene) if used in a field-effect transistor (FET) configuration becomes superconducting at 2.35 K. This is the first case of superconductivity in an organic polymer, albeit not the first example of a superconducting polymer since superconductivity in an inorganic polymer-poly(sulfur nitride): $(SN)_x$– was discovered more than two decades ago [7].

In the past four years few review papers on various aspects of conjugated and conductive polymers were published in 'Progress in Polymer Science' [8–13]. For this reason, in our paper we will concentrate on problems, which either were not discussed in previous contributions or, despite their importance,

mentioned only briefly. Special emphasis will be put on the development in the conjugated polymer field observed in the last two years. The organization of this paper is as follows. In Section 2 we describe the synthesis of conjugated polymers in their undoped (semiconducting state), their basic chemical and physical properties and their applications, as semiconductors, in molecular electronics devices. In Section 3, we discuss the doping process which transforms 'polymeric semiconductors' into 'polymeric metals' with special emphasis on processes improving the processibility of these materials. Similarly as in Section 2 we describe basic chemical and physical properties of these polymeric metals and their application. In Section 4 we discuss electric field-induced superconductivity in poly(acene)s and poly(thiophene)s. In general, with the exception of poly(acene)s, in our paper we focus on truly polymeric systems. It should be however noted that equally intensive research is presently carried out for conjugated oligomers.

The selection of papers quoted is purely subjective and reflects our research interests. We are aware of the fact that the number of papers cited (321) constitute significantly less than 1% of all papers devoted to electroactive polyconjugated systems. Several important contributions had to be omitted due to space limits.

2. Conjugated polymers as semiconductors

2.1. Basic characteristics

It is convenient to start the discussion of the peculiarities of macromolecular polyconjugated systems by the description of the electronic structure of poly(acetylene) for two reasons. First, poly(acetylene) is the simplest conjugated polymer and for this reason can be considered as a prototype of other polyconjugated systems. Second, historically the discovery of poly(acetylene) doping triggered the explosion of the research devoted to electroactive polymers.

Poly(acetylene) $(-CH{=}CH-)_x$ can exist in two isomeric forms: *cis-transoid* and *trans-transoid*, commonly called *cis*- and *trans*-poly(acetylene), respectively (see Fig. 1). The latter form being thermodynamically stable since *cis–trans* isomerization is irreversible. In poly(acetylene) each carbon atom is sp^2 hybridized and for this reason this polymer can be formally treated as one-dimensional analogue of graphite. There exists however an important difference between the bonding system in the graphene plane of graphite and in the poly(acetylene) chain. Contrary to the case of graphite, the C–C bonds in poly(acelylene) are not equivalent, i.e. they are alternatively slightly longer and slightly shorter. This is due to so-called Peierls distortion. The described bond non-equivalence has an important effect on electronic properties of poly(acetylene) because it opens a gap between the HOMO level corresponding to fully occupied π-band (valence band) and the LUMO level corresponding to empty π^*-band (conducting band). Thus, in the simplest approach, poly(acetylene) can be treated as an intrinsic semiconductor with a band gap of 1.5 eV [14]. In the years which followed several polyene-type and aromatic conjugated polymers were synthesized and characterized, the most extensively studied are depicted in Fig. 1. All polymers shown schematically in Fig. 1 are colored which is associated with a strong absorption in the visible range of the spectrum usually attributed to a $\pi-\pi^*$ optical transition (Fig. 1).

In principle the value of the optical gap can be varied by appropriate functionalization of the conjugated backbone. In particular an appropriate combination of electron donating and electron withdrawing subsitutents may result in the preparation of semi-conducting conjugated polymers in which

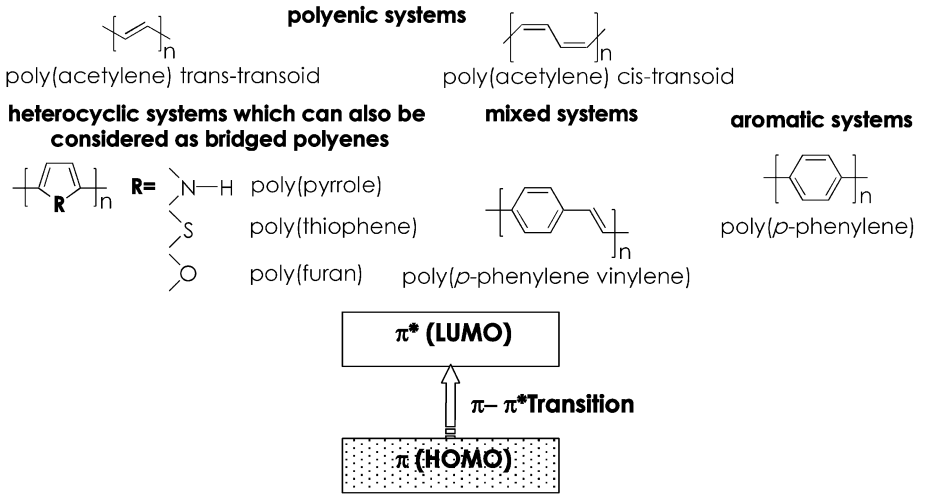
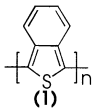


Fig. 1. Representative unsubstituted conjugated polymers and optical gap in π-conjugated systems.

bond alternation is lowered and by consequence they exhibit a narrow band gap. The first narrow gap semi-conducting polymer was poly(isothianaphtene) (**1**) prepared by Wudl et al. [15] whose band gap (1.1 eV) was about 1.0 eV lower than that of poly(thiophene). Since that time several dozens of narrow gap polymers were synthesized which were mainly derivatives of poly(isothianaphtene) but also polymers based on 3,4-ethylenedioxythiophene units and vinylene units [16,17]. This research direction has drawn significant interest of the scientific community over the past years, however conjugated polymer with vanishing band gap has not yet been synthesized.



(1)

The π-conjugated system in all polymers described above is formed by the overlap of carbon p_z orbitals. There exist however another family of conjugated polymers in which p_z orbitals of nitrogen also contribute to the conjugation. The principal representative of this type of macromolecular compounds is not only poly(-aniline) [18] and its derivatives but also aromatic poly(azomethine)s and others [19,20]. It is convenient to discuss poly(aniline) separately from other conjugated polymers because it shows distinctly different chemistry as compared to other polyconjugated systems. This is mainly associated with the presence of basic centers (amine and imine nitrogens) in its conjugated backbone.

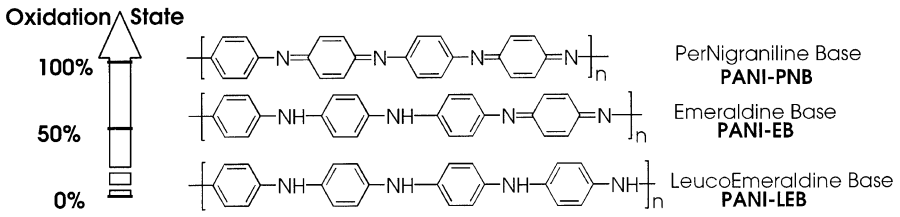


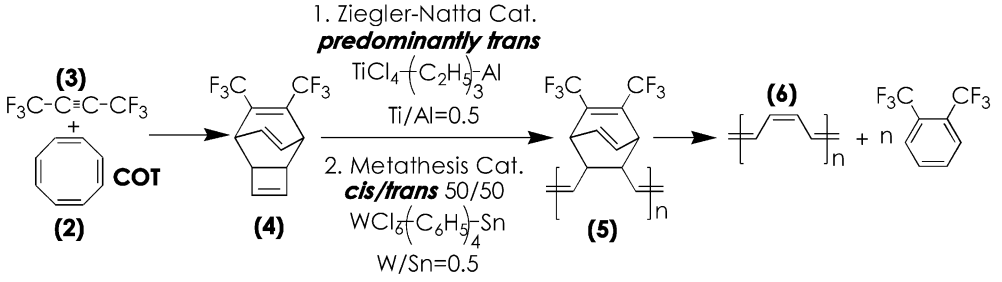
Fig. 2. Principal forms of poly(aniline) base (tetrameric repeat units are shown in each case for clarity).

Poly(aniline) can exist in a variety of forms which differ in their oxidation level. Principal neutral (base) forms of poly(aniline) are depicted in Fig. 2. The most reduced form, commonly called *leuco-emeraldine*, consists of phenylene rings joined together by amine type nitrogens. In fully oxidized poly(aniline), termed *pernigraniline*, phenylene rings with benzenoid type sequence of bonds and rings of quinoid type of bonds are present in the ratio 1:1 and are separated by imine nitrogens. In half oxidized polymer (*emeraldine*) imine and amine nitrogens are in equal numbers but the ratio of bezenoid type rings to the quinoid type ones is 3:1. For this reason the repeat unit of emeraldine must consist of four rings and four nitrogens.

2.2. Synthesis, processibility and environmental stability

Synthetic routes to conjugated polymers are extremely versatile and may involve classical polymer chemistry methods such as coordination polymerization as well as typical organic chemistry procedures or electrochemical techniques. For example poly(acetylene) can be conveniently prepared from acetylene using various modifications of Ziegler–Natta catalyst or Luttinger catalyst [21]. It can also be prepared from 1,3,5,7-cyclooctatraene (COT) (**2**) via ring opening metathesis polymerization in the presence of a metathesis catalyst [22]. The polymer is usually prepared in the form of a free-standing film whose morphology can be fibrillar or globular depending on the catalytic system used. The use of nematic liquid crystals as solvents in the process of acetylene polymerization enables the preparation of oriented poly(acetylene) films. It should be stressed that poly(acetylene) is neither solution nor melt processible. Thus the selection of an appropriate catalytic system is of crucial importance for the preparation of the polymer with the desired morphology. Some improvement in poly(acetylene) processibility was achieved by Edwards and Feast [23]. These authors prepared $(-CH{=}CH-)_x$ in a three step procedure (Scheme 1). In the first step the monomer (**4**) is synthesized by the reaction of cyclooctatraene (COT) (**2**) with hexafluoro-butyne (**3**). The polymerization of (**4**) with $WCl_6/Sn(C_6H_5)_4$ metathesis catalysts leads to the soluble precursor polymer (**5**). Thin films of this polymer can be cast from acetone or chloroform. Thermal decomposition of the precursor results in the formation of poly(acetylene) (**6**) with the *cis/trans* ratio depending on the temperature of the thermal transformation.

The major disadvantage of poly(acetylene) is its environmental instability [24]. In air, neutral poly-(acetylene) undergoes slow oxidation of irreversible type which is manifested in IR spectra by the appearance and growth of bands attributed to carbonyl groups. Of course the formation of carbonyl groups breaks the conjugation of the polymer backbone and the polymer looses all precious properties associated with polyconjugated π-bonding system.



Scheme 1.

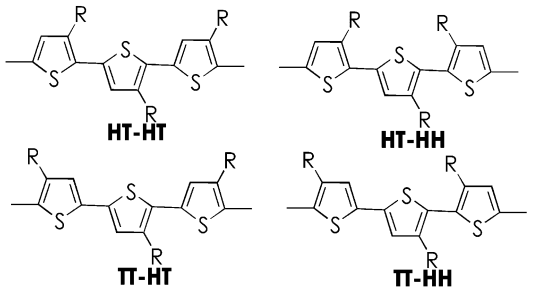
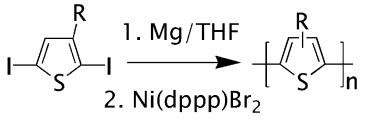


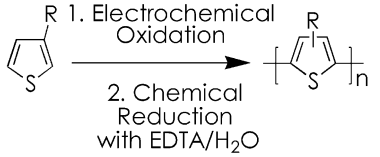
Fig. 3. Possible structurally non-equivalent triads in poly(3-alkylthiophene)s.

Heterocyclic conjugated polymers (poly(pyrrole), poly(furan), poly(thiophene)) can be conveniently prepared by electrochemical or chemical oxidation of pyrrole, furan and thiophene, respectively. If prepared electrochemically they form a coherent film, which can be easily removed from the electrode. It is generally accepted that the polymerization is initiated by the oxidation of the monomer to a radical cation. The mechanism of the propagation is the subject of some controversy. It is postulated that it may occur by coupling of two radical cations with simultaneous abstraction of two protons [25,26]. The dimer formed in such a manner has the oxidation potential lower than the monomer and the chain may propagate. Some authors however favor the mechanism of electrophilic addition of a neutral monomer molecule to the radical cation formed in the initiation process [27,28]. Anyhow, both types of mechanisms lead to the polymers in their doped (oxidized) state. To obtain neutral polymers one must reduce them, either electrochemically or chemically. It should be noted here that heterocyclic polyconjugated polymers differ significantly in their environmental stability. Poly(pyrrole) in its neutral state is extremely reactive and reacts even with minute amounts of oxygen whereas neutral poly(thiophene) is stable at ambient conditions.

First soluble, and for this reason solution processible, heterocyclic conjugated polymer was synthesized by Elsenbaumer and his co-workers [29,30]. It turned out that the substitution of hydrogen by an alkyl group longer than the propyl group in the 3 position of 2,5-tienylene ring (the repeat unit of poly(thiophene)) renders the polymer soluble without much perturbation of the conjugated system. This is manifested, among others, by a clear optical absorption with a maximum at ca. 440 nm ($\pi-\pi^*$ transition), only little dependent on the size of the alkyl substituent. Neutral poly(3-alkylthiophene)s here abbreviated as PATs exhibit two interesting optical features, namely solvatochromic [31] and thermochromic [32] effects. As a result of solvatochromism, the absorption ascribed to $\pi-\pi^*$ transition is red-shifted in the solid-state spectra as compared to the solution ones.



Scheme 2.



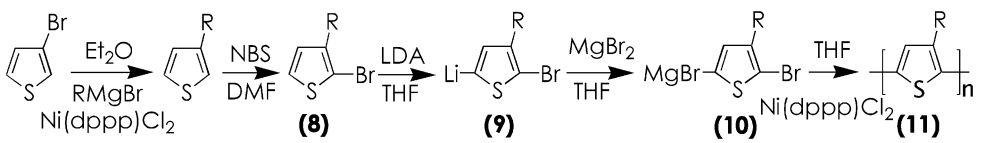
Scheme 3.

In the case of PATs, one must be aware of the problem of regioregularity. Since 3-alkylthiophenes (**7**), the monomers used for the polymerization of PATs, are not centrosymmetric, they can couple in three different manners: head-to-tail (HT), head-to-head (HH) and tail-to-tail (TT) which leads to four types of structurally non-equivalent triads (Fig. 3). Although HT coupling is favored, the two other types of couplings may occur during the preparation of PATs from (**7**) if the applied synthesis method is not regiospecific. Indeed, initially used synthetic routes for PATs such as Kumada cross-coupling (Scheme 2) [29,30], electrochemical oxidation [33–36] or oxidation with $FeCl_3$ [37] (Scheme 3) did not give regioregular PATs. Although they were predominantly HT coupled, in ^{1}H and ^{13}C NMR spectra, in addition to signals originating from HT–HT triads, lines attributable to three other structurally non-equivalent triads were detected (Fig. 3) which perturb the regioregularity of the polymer chain [38–40].

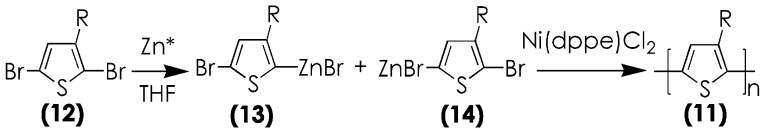
In the early 1990s two methods of the preparation of regioregular PATs (% of HT couplings ca. 99%) were proposed by McCullough and co-workers and Rieke and co-workers. The McCullough method [41–43] is shown in Scheme 4. In a four-step procedure first 3-alkylthiophene is obtained from 3-bromothiophene by Grignard coupling in the presence of Ni(dppp)Cl_2. 3-Alkylthiophene is then brominated in the 2 position using for example *N*-bromosuccinimide (NBS) [44] which gives better yields than the bromination with Br_2 in acetic acid originally used by McCullough et al. [41]. 2-Bromo-3-alkylthiophene (**8**) is then lithiated in the 5 position using lithium diisopropylamide (LDA). The lithiation with this reagent carried out at low temperature is very selective giving (**9**) [45]. (**9**) after transformation into the corresponding Grignard reagent (**10**) condenses regiospecifically to regioregular PATs (**11**). The purification of 2-bromo-3-alkylthiophene is of crucial importance. Gas chromatographic studies showed that the main contaminant of 2-bromo-3-alkylthiophene is 2-bromo-4-alkylthiophene which either causes chain termination or introduces regioregularity defects of TT–HH type [46].

Alternatively, regioregular PATs can be prepared from 2,5-dibromo-3-alkylthiophene (**12**) by the method of Rieke and co-workers [47,48] (Scheme 5). In the presence of active zinc this reagent gives a mixture of isomers (**13**) and (**14**) which in the presence of Ni(dppe)Cl_2 gives regioregular PATs (**11**).

Very recently, a very convenient route to highly regioregular PATs have been reported by McCullough group [49] which is based on magnesium halogen exchange (Grignard metathesis, abbreviated as GRIM). It turns out that the reaction of 2,5-dibromo-3-alkylthiophenes with an alkyl or vinyl Grignard



Scheme 4.



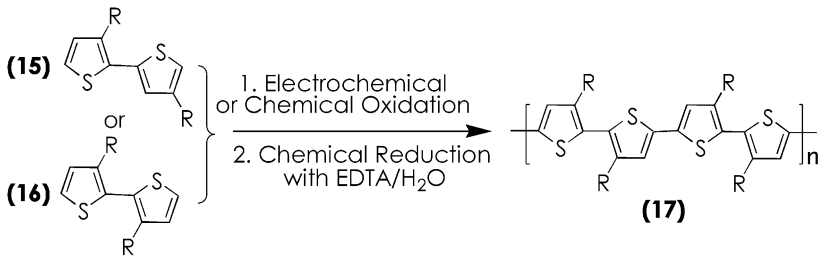
Scheme 5.

reagent gives two isomers namely bromo-3-alkyl-5-bromomagnesiothiophene and 2-bromomagnesio-3-alkyl-5-bromothiophene in a constant ratio independent of the reaction condition. The addition of catalytic amount of Ni(dppp)Cl_2 to the above isomeric mixture results in the formation of PATs with the percentage of HT coupling approaching 98%.

Regioregular PATs can be considered as much better defined materials as compared to PATs prepared by chemical or electrochemical oxidation. However, since they are prepared by Grignard type coupling they show much lower molecular weight. They can be fractionated using a sequence of extractions [46]. Such procedure leads to relatively sharp fractions, the highest giving M_n approaching 20×10^3 g. mol^{-1} (measured versus polystyrene standards) with polydispersity coefficient of 1.4.

Regioregular poly(alkylthiophene)s of different type of regioregularity (HH–TT) can be prepared from symmetrically disubstitued bithiophenes, namely 4,4′-dialkyl-2,2′-bithiophenes (**15**) or 3,3′-dialkyl-2,2′-bithiophenes (**16**) [50,51]. It should be noted that both reagents give the same polymer upon oxidative coupling (Scheme 6). The advantage of the use of dimers as reagents consists of the fact that the oxidation potential of the dimer is roughly twice lower than that the corresponding monomer, thus the polymerization can be initiated at milder conditions [52]. However the resulting polymers poly(4,4′-dialkyl-2,2′-bithiophene)s and poly(3,3′-dialkyl-2,2′-bithiophene)s (**17**), abbreviated as PDABTs show a hypsochromic shift of their band, associated with the $\pi-\pi^*$ transition, with respect to both regioregular and non-regioregular PATs [52]. This is indicative of lower conjugation as compared to PATs. Spectroscopic and structural studies unequivocally show in this case that, although the TT coupled dimer units PDABTs are planar, the adjacent HH coupled dimers are twisted (see Fig. 4), which lowers the conjugation in these polymers [53]. The effective conjugation is a result of a delicate equilibrium between the conjugation, which favors planar chain structures and steric factors that tend to give twisted chains. Evidently steric hindrance connected to HH coupled adjacent dimers results in an increased value of the twisting angle α. Contrary to PATs, PDABTs do not show the solvatochromic effect and their solid-state spectra are essentially the same as the solution ones.

The problem of steric hindrance is even more pronounced in 3,4-disubstituted poly(thiophene)s (**18**). To a first approximation, disubstituted thiophene monomers seem to be ideal candidates to give regioregular chain structures upon polymerization. However two alkyl subsitutents on each ring induce a steric hindrance



Scheme 6.

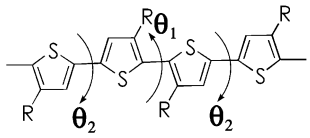
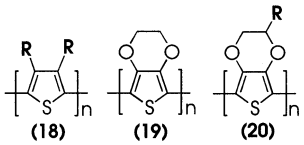


Fig. 4. Chain geometry in poly(4,4′-dialkyl-2,2′-bithiophene)s abbreviated as PDABTs. θ_1 and θ_2 indicate the torsion angle. θ_1 — the angle between HH coupled rings is 70° whereas θ_2 — the angle between TT coupled rings is 0°. (Reproduced with permission from J Chem Phys 1994;100(2):1731–41. Copyright 1994 American Institute of Physics.)

which results in a significant loss of the conjugation [54]. Much better results are obtained if alkoxy substitutents are used instead of the alkyl ones. First they cause less steric hindrance, second they can be polymerized at milder conditions as compared to alkylthiophenes [55]. Cyclization between the 3 and 4 position of the thiophene ring also helps to obtain better conjugated regioregular poly(thiophene)s [56,57]. One of such polymers, namely poly(3,4-ethylenedioxythiophene), abbreviated as PEDT (**19**), developed by Bayer, is commercially available.

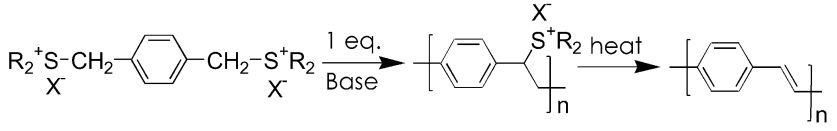
PEDT, similarly as other poly(alkoxythiophene)s shows a rather low oxidation potential. For this reason, in its neutral (undoped) state, this polymer is unstable at ambient conditions and must be handled in inert atmosphere, otherwise it undergoes rapid oxidation. Moreover it is insoluble. Alkyl derivatives of PEDT (**20**) are soluble [58,59]. Similarly as in the case of PATs, PEDT shows solvatochromism. In solution spectra the band associated with the $\pi-\pi^*$ transition is peaked at 575 nm whereas in solid-state spectra at 610 nm [57].



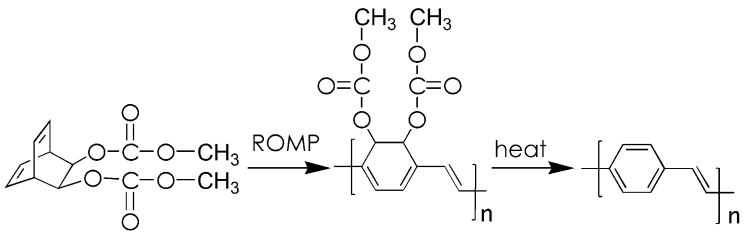
(18) (19) (20)

Poly(*p*-phenylene vinylene) (abbreviated as PPV) family of conjugated polymers (see Fig. 1) has been studied from the very beginning of the conducting polymer research, however, after the discovery of electroluminescence of these materials in early nineties of 20th century, these polymers became the subject of extensive research efforts allover the world.

Unsubstituted PPV — the principal representative of the above mentioned family of polymers — can be obtained by several direct routes [60]. These methods lead however to polymers of a rather low molecular weight because the reaction product is insoluble and readily precipitates from the reaction medium in a powdery form. Of course intractable powder is of very limited technological use, therefore it is better to prepare PPV by precursor routes. As it has already been mentioned in the case of the synthesis of poly(acetylene), the precursor route consists of a preparation of a soluble precursor polymer which can form solid films by casting. Solid films of the precursor are then transformed into PPV, preferably by thermal treatment.



Scheme 7.

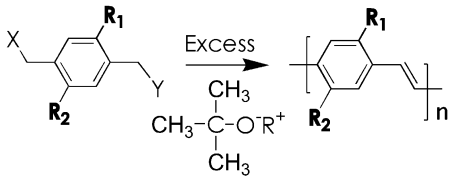


Scheme 8.

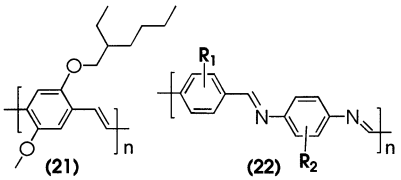
The first precursor route to PPV is relatively old and was developed by Wessling et al. [61–63]. It consists of the reaction of *p*-xylylene sulfonium salt with a base which produces polyelectrolyte polymer soluble in water (Scheme 7). The polyelectrolyte can be purified for example by dialysis. Films can easily be cast form aqueous solutions. Dried film can in turn be thermally decomposed to give PPV. More recent synthesis method leading to a soluble PPV precursor is based on ring opening methathesis polymerization (ROMP) of bicyclooctadiene derivative (Scheme 8) [64]. The resulting precursor polymer can be solution processed since it is soluble in organic solvents. Again as in the previous case thermal treatment of the precursor leads to PPV.

As in the case of poly(thiophene) the solubility of fully conjugated PPV can be induced by introducing alkyl or alkoxy groups into the phenylene ring. One of the first examples of solution processible PPV derivative was poly(1-methoxy-4-(2-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) (**21**). This polymer can be relatively prepared easily from dihalo-*p*-xylene in the reaction with a base such as potassium *tert*-butoxide using a modification of the method of Gilch (Scheme 9). It should be noted that the substitution on the phenylene ring does not only improve the solubility of PPV but also allows for a tuning of its optical band gap which is of crucial importance in view of electro-optical applications of this polymer. Several other phenylene ring substituted and/or vinylene group substituted PPV derivatives were synthesized in the past 10 years [60,65,66].

Aromatic poly(azomethine)s (**22**), which are isoelectronic with the corresponding poly(*p*-phenylenevinylene)s, were also extensively studied [19,20]. They are usually obtained by solution condensation of aromatic diamines with aromatic dialdehydes. Their optical gap is usually higher than that of the corresponding PPV derivatives (usually in the range 2.0–2.8 eV), which indicates that they are less conjugated as compared to the polymers belonging to the PPV family. The presence of basic centers in the polymer backbone (imine nitrogens) enables the complexation of poly(azomethine)s with such Lewis acids as $GaCl_3$ or others. Lewis acid complexation facilitates solution processing of these polymers. Similarly protonation with functionalized Brönsted acids for example aromatic diesters of phosphoric acid improves solution processibility of poly(azomethine)s.



Scheme 9.



(21) (22)

Aromatic poly(azomethine)s are intermediate between these conjugated polymers which show redox-type chemistry and those which in addition to the redox chemistry exhibit acid–base chemistry both in Brönsted as well as in Lewis sense. Poly(aniline) is the most extensively studied macromolecular compound from this category of conjugated polymers.

As it has already been mentioned, neutral poly(aniline) (here abbreviated as PANI) can exist in a variety of forms which differ in their oxidation states. The principal forms of PANI base, depicted in Fig. 2, differ in their reactivity in ambient atmosphere. The most reduced form — leucoemeraldine base (LEB) — is very reactive being oxidized even with minute amounts of oxygen. On the contrary, the semi-oxidized form — emeraldine base (EB) — is stable in air and can be stored in laboratory atmosphere without any chemical change. Thus the most practical approach to the synthesis of various forms of PANI at different oxidation states is to obtain this polymer in its semi-oxidized state (EB) and then to reduce it to LEB or oxidize it to pernigraniline base (PNB). LEB can be conveniently prepared from EB, in its powder form, by reduction with liquid phenylhydrazine at 120°C. The resulting polymer is then washed with dry methanol and pumped in vacuum for extended time. As it has already been mentioned all operations must be carried out in inert atmosphere or in vacuum since the reaction product is reactive [67]. PNB can in turn be prepared via oxidation of EB. In a typical procedure EB dissolved in *N*-methyl-2-pyrrolidinone (NMP) is treated with an appropriate oxidizing agent (for example *m*-chloroperbenzoic acid). The precipitated PNB powder is then washed first with acetone and then diethyl ether and dried in a dynamic vacuum [68].

EB can in principle be obtained via oxidative polymerization of aniline [69] or by polycondensation. The former method is so far the most extensively used.

In the simplest version oxidative polymerization of aniline is carried out in acidic aqueous solution using an appropriate oxidizing agent, usually ammonium persulfate $(NH_4)_2S_2O_8$ but also others such as KIO_3, $K_2Cr_2O_7$, $KClO_3$ and others [70]. In order to obtain poly(aniline) in the oxidation state of EB one must use strong deficit of the oxidizing agent with respect to aniline. This is associated with the mechanism of PANI polymerization. In the initial step of the reaction poly(aniline) in the oxidation state of pernigraniline (PN) is formed (the most oxidized form of PANI). This initially formed polymer is then reduced in the reaction with the excess of aniline to give the polymer in the emeraldine oxidation state. For better control of the reaction conditions, in the case where different oxidizing agents are used, it is convenient to introduce the normalized monomer to oxidant ratio, k, which is defined as follows:

$$k = 2.5 n_{ani}/n_{e^-} n_{ox}$$

where: n_{an} and n_{ox} is the number of moles of aniline and the oxidant, respectively, and n_{e^-} is the number of electrons necessary for the reduction of one molecule of the oxidant. It is assumed additionally that the oxidation of aniline to emeraldine requires the removal of 2.5 electrons per aniline molecule.

The preparation of good quality EB requires the use of $k \gg 1$. In some procedures external reducing

agents such as $FeCl_2$ are added at the end of the polymerization process with the goal to accelerate the reduction of pernigraniline to emeraldine. In this case lower value of k may be used, however still >1.

The polymerization reaction in the conditions described above always leads to emeraldine in the protonated form, so-called 'emeraldine salt' (ES). ES can be easily converted into the neutral base (EB) form by treatment with an aqueous solution of ammonia [71].

Molecular weight of oxidatively polymerized poly(aniline) depends on the temperature of the polymerization reaction. Viscosity measurements of the products synthesized at various temperatures show that the highest M_v is obtained if the reaction is carried out at low temperatures (down to $-40°C$) in the reaction medium of high ionic strength. For this reason LiCl is usually added to the reaction mixture [72–75]. The effect of LiCl on M_v of poly(aniline) was interpreted in terms of Donnan potentials [72]. The Donnan effect favors the inter-phase reaction of newly formed aniline radical cations with precipitated poly(aniline) rather than the initiation reaction resulting in the growth of a new chain. This leads of course to an increase in the molecular weight of PANI.

Classical oxidative polymerization of aniline in aqueous media requires harsh reaction conditions, as described above. For this reason in recent years significant modifications of the classical procedure have been developed. One of them is enzymatic polymerization. In this approach horseradish peroxidaze (HRP) is used as a catalysts together with hydrogen peroxide. The enzymatic reaction involves an oxidation of the initiator by hydrogen peroxide to give a reactive intermediate. This intermediate is then capable of oxidizing aniline and initiate its polymerization [76,77]. The addition of sulfonated polystyrene, polyvinyl phosphonic acid or other templates, to the reaction medium, promotes *para*-directed coupling and leads to poly(aniline) of better chain regularity and higher molecular weight as compared to that prepared without the template. The main advantage of this enzymatic, template-guided polymerization is the fact that the reaction is carried out in mild conditions, with pH close to 4.0, which is not the case in classical oxidative procedures. However enzymatically prepared PANI in its doped state shows 2–3 orders of magnitude lower conductivity with respect to doped PANI prepared by sub-zero temperature classical polymerization.

Poly(aniline) can also be prepared chemically by emulsion polymerization if functionalized sulfonic acids or phosphoric acid esters are used as protonating agents instead of simple inorganic acids such as HCl or H_2SO_4. In a typical procedure aqueous dispersed phase contains the oxidant and the continuous organic phase consists of xylene or other suitable solvent, aniline monomer and *n*-dodecylbenzenesulfonic acid (DBSA) as the protonating agent which in addition plays the role of the emulsifier. The reaction takes place at the interface. Since PANI protonated with DBSA is soluble in xylene it does not precipitate but dissolves in the organic phase [78,79].

Homogenous polymerization of PANI has been reported by Klavetter and Cao [80]. These authors oxidized aniline in chloroform, in the presence of DBSA, using tetrabutylammonium periodate as the oxidant. Since both the substrates and the product (PANI protonated with DBSA) are soluble in chloroform no precipitation of the polymer formed takes place.

Poly(aniline) can also be obtained by electrochemical oxidative polymerization. First electrochemical polymerization of aniline was reported in early sixties of the 20th century [81]. Electrochemical synthesis of poly(aniline) can be carried out either by constant current [82–84] or constant potential [85,86] or by potential scanning (cyclic-voltammetry polymerization). In order to avoid coupling defects which perturb chain regularity the potential of the electrosynthesis should not exceed 0.7 V vs. Cu/CuF_2 reference electrode. Thus even in the constant current method the potential of the working electrode should be continuously monitored [87–90]. The current densities used should not exceed 10 mA cm^{-2}.

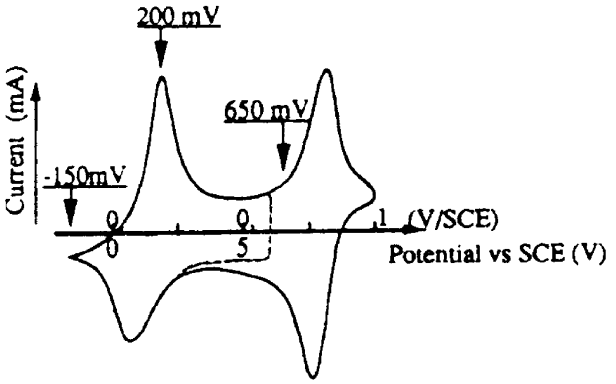


Fig. 5. Cyclic voltammetry of electrochemically deposited poly(aniline) in aqueous acidified solution (1 M HCl): scan rate 20 mV s^{-1}.

In the cyclic voltammetry method the film is deposited layer-by-layer by potential scanning between the potential characteristic of the most reduced state of PANI, i.e. leucoemeraldine and the potential of the onset of the peak of aniline polymerization. This method is recommended by several authors as leading to the most regular chain of PANI [89,90]. Electrochemical synthesis of PANI is usually performed in aqueous electrolytes, acidified with HCl or H_2SO_4, i.e. in the reaction medium similar to that used in chemical polymerization. There however exist reports on the synthesis in non-aqueous electrolytes such as sodium perchlorate/propylene carbonate/trifluoroacetic acid, lithium perchlorate/acetonotrile [91,92], to name a few. An interesting polymerization method has been proposed by Genies et al. [89,93] which consists of the use of a eutectic mixture of $NH_4 \cdot 2.3$ HF as the electrolyte. The polymer prepared in this medium shows good chain regularity with smaller content of coupling defects with respect to other types of electrochemically prepared poly(aniline)s.

The oxidation state of electrochemically prepared PANI depends on the potential of the working electrode. Typical cyclic voltammogram of PANI registered in acidified, aqueous solutions consists of two oxidation peaks. The first one with a maximum at $V = 0.2$ V vs. SCE corresponds to the oxidation of leucoemeraldine to emeraldine whereas the second one at higher potential is attributed to the oxidation of emeraldine to pernigraniline (Fig. 5). At the potentials of emeraldine stability the polymer is protonated [94]. Thus the preparation of EB requires the deprotonation of the polymer removed from the electrode with a base, similarly as in the case of chemically prepared PANI (vide supra).

Emeraldine base (EB) is difficult to dissolve. This is due to intermolecular hydrogen bonding which is formed between amine groups acting as donors and imine groups of the adjacent chain acting as acceptors [95–99]. Thus EB can be dissolved only in solvents which are capable of replacing chain–chain hydrogen bond interactions by chain-solvents hydrogen bonds. Typical solvents of EB such as *N*-methyl-2-pyrrolidinone (NMP) (**23**), tetramethylurea (TMU) (**24**), *N*,*N*-dimethylacetamide (DMAc) (**25**) or hexamethylphosphoramide (HMPA) (**26**) are hydrogen bond acceptors and interact with amine hydrogens. Solutions of EB in simple one component solvents have the tendency to undergo gelation, especially for higher EB concentrations. Solutions of higher concentration which do not gel can be prepared using mixed solvents consisting of both hydrogen bonding donors and acceptors [100–102]. For example the addition of simple aliphatic amines to HMPA efficiently blocks the gelation of EB solutions. Evidently in this case the interchain bondings are efficiently eliminated by mixed solvent

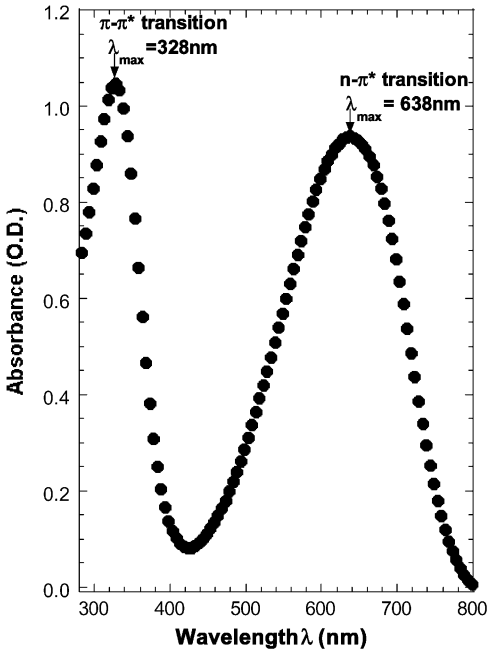
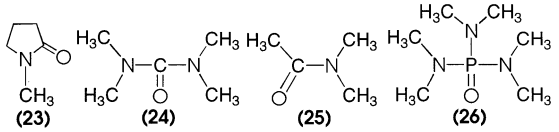


Fig. 6. UV–Vis spectrum of an emeraldine base solution in NMP.

interactions with both imine and amine sites. Highly concentrated solutions EB facilitate its processing in a form of fibers, films, etc.



EB differs spectroscopically from other conjugated polymers. As it has already been stated, polymers

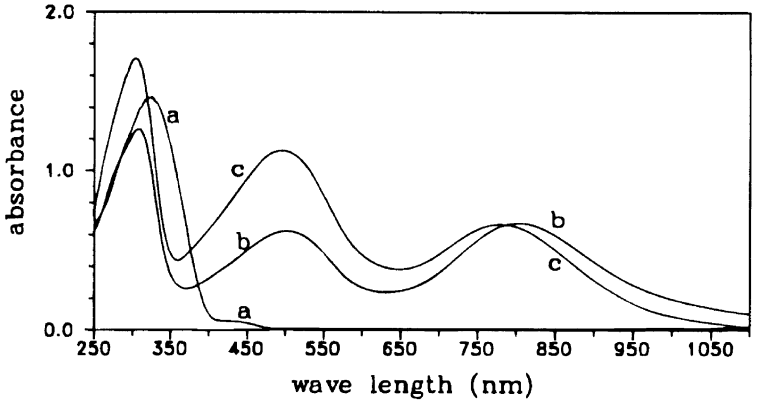
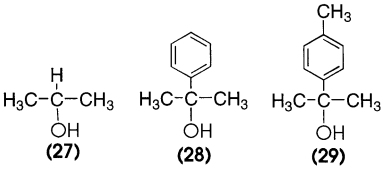


Fig. 7. UV–Vis–NIR spectra of poly(aniline): (a) LEB in 20 vol% NMP/ 80 vol% HFIP, (b) EB in HFIP, (c) PNB in HFIP. (Reproduced with permission from Macromolecules 1997;30(23):7091–5. Copyright 1997 Am Chem Soc.)

whose conjugation is assured by the overlap of p_z orbitals of sp^2 hybridized carbons exhibit one absorption band in the visible ascribed to $\pi-\pi^*$ electronic transition. In solution EB spectra (NMP solvent) two bands are present: the first one at 320 nm is usually ascribed to $\pi-\pi^*$ transition in benzene rings of the tetrameric repeat unit (see Fig. 2) whereas the second band at 630 nm is attributed to an excitonic-type transition between the HOMO orbital of the benzenoid ring and the LUMO orbital of the quinoid ring. Thus the latter one is inherently associated with the presence of quinoid rings in the oxidized units of EB (Fig. 6). Indeed the excitonic band disappears upon reduction of EB to LB and reappears on subsequent oxidation of LB to EB. Solutions of EB in solvents, which apart from the formation of hydrogen bonds do not exhibit other interactions with EB chains, are very similar. However, for low molecular weights the positions of the two observed bands depend slightly on the molecular weight, being red shifted with increasing M_v. The solid-state spectra resemble those registered for the solutions. The use of more active solvents of somehow acidic character leads to distinctly different spectra from those registered in NMP or HMPA. The case of hexafluoro-2-propanol (HFIP) (**27**) is very instructive and will be discussed here in greater details.

The spectra of LB, EB and PB in HFIP are presented in Fig. 7. Since LB is not soluble in pure HFIP, only spectra in mixed NMP/HFIP solvents can be recorded. If LB is first dissolved in NMP, it can be consecutively diluted up to 80 vol% with HFIP without the precipitation of the polymer. In pure NMP the $\pi-\pi^*$ transition peak in LB is located at 340 nm whereas in NMP/HFIP mixed solvents it is blue shifted with the extent of the shift being proportional to the content of HFIP in the mixed solvent. In 20 vol% NMP/80 vol% HFIP solvent the maximum of the peak is located at 314 nm. The extrapolation of the relationship between the content of NMP in the mixed NMP/HFIP solvent and the position of the maximum of the peak ascribed to the $\pi-\pi^*$ transition gives the value of 308 nm of a hypothetical LB solution in pure HFIP, close to the value of 305 nm observed in the cases of EB and PB.

For EB, two additional peaks are observed at 502 and ca. 800 nm [103–105]. The 502 nm peak can be ascribed to the benzoid to quinoid ring excitonic transition as described above. However, again as in the case of the $\pi-\pi^*$ transition the band due to the excitonic transition is blue-shifted as compared to EB spectra recorded in NMP solutions. The third peak at 800 nm can be unequivocally ascribed to the protonation of EB by HFIP solvent [105,106] because the addition of a small amount of a strong EB protonating agent such as for example phenylphosphonic acid (PPA) results in a strong increase of the 800 nm on the expense of the 502 nm peak. The spectra of EB in HFIP are time dependent. With increasing storing time the 800 nm peak increases whereas the 502 nm peak decreases in intensity clearly indicating that the solvent slowly protonates the dissolved polymer. Thus HFIP cannot be considered as an inert solvent. This is not unexpected. HFIP contrary to NMP is acidic in nature showing $pK_a = 9.3$. Due to strong solvent–polymer interactions it also changes the conformation of the macromolecules in the solution lowering the degree of the conjugation which is evidenced by the hypsochromic shift of the peaks ascribed to two principal transitions in EB. Other fluorinated alcohols such as hexafluoro-2-phenyl-2-propanol (HFPP) (**28**) or hexafluoro-2-*p*-tolyl-2-propanol (HFTP) (**29**) give similar results [106]. Other EB protonating solvents involve *m*-cresol and other phenols which exhibit similar pK_a as fluorinated alcohols.



To summarize this part of the paper, at the present state of art there exist several polyconjugated polymers which are solution processible in their undoped, i.e. semi-conducting state either directly or via a soluble precursor which in turn can be relatively easily transformed into the desired, conjugated polymer. In other words, progress in conjugated polymer chemistry resulted in the fabrication of polymeric *semiconductors in a bottle* which give semi-conducting films by casting, spin coating and other processing techniques. Of course, this type of processibility can in the future greatly facilitate the fabrication of different type of semi-conducting devices. For this reason, in the recent decade, the major research effort was directed towards the application of this new polymeric semiconductors in the fabrication of various electronic devices.

2.3. Application of undoped conjugated polymers

Undoped conjugated polymers are in fact intrinsic semiconductors whose band gap depends not only on the chemical constitution of the conjugated backbone but also on the nature of the substituents attached to the main chain. Thus optical and electronic properties of conjugated polymers can be varied to a very large extent by appropriate functionalization. As a result in many cases they can replace classical inorganic silicon, A(III)B(V) or A(II)B(VI) semiconductors offering among others much easier processing. One of the most extensively studied area of the application of undoped conjugated polymers is the fabrication of polymeric light-emitting diodes (PLEDs), i.e. electronic devices which exploit the phenomenon of electroluminescence. Quick search in SCIFINDER shows that more than 5500 papers devoted to this subject were published in the past 11 years. In the simplest manner electroluminescence can be defined as light generation caused by electrical excitation. This phenomenon, quite common in several inorganic semiconductors, has also been observed in conjugated organic system. For low-molecular weight organic matter it was first observed in the single crystals of anthracene [107,108]. Electroluminescence of conjugated polymers and more precisely poly(*p*-phenylene vinylene) was first reported by Burroughes et al. [109] in 1990. In the description of the recent progress in the fabrication of PLEDs we will limit ourselves to the discussion of the development of new electroluminescent polymeric materials with only minimum of the physical background. The readers interested in the physics of polymeric electroluminescent materials are referred to several excellent review papers [110–114].

In the simplest version PLED consists of a single layer of an electroluminescent polymer and two

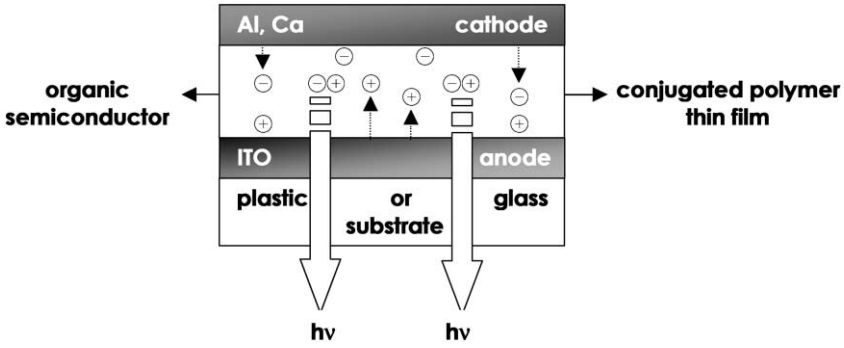


Fig. 8. Schematic structure of a single-layer polymer light-emitting diode (PLED).

electrodes (Fig. 8). One of the electrode must be transparent to transmit light created during the electroluminescence effect. This is usually the anode (hole injecting electrode) which may consists of a layer of indium-tin oxide (ITO) — a conductor which shows high transparency in thin layers. Other than ITO anodes were also tested, for example highly transparent blend of (±)-camphor-10-sulfonic acid-doped poly(aniline) with poly(methyl metacrylate) (PANI(CSA)$_{0.5}$–PMMA) or with a polyester resin (PANI(CSA)$_{0.5}$–PES) [115–117] but also other p-type doped conjugated polymers such as doped PEDT (**19**) [57] and mixtures of conjugated polymers with poly(ethylene oxide)-based polymeric solid electrolytes [118]. The anode must have a high work function, Φ, and the above mentioned systems are very well suited for this purpose. On the other hand, the cathode (electron injecting electrode) must be made of a metal with a low work function such as Ca but also Mg and Al which show higher Φ but still are suitable as cathodes [119].

Such a one layer-two electrodes device is called an electroluminescent diode because it shows non-linear I–V characteristics typical of diodes. This means that up to a given voltage no current flows and above this onset voltage the current increases quickly with increasing voltage. If quantum efficiency for electroluminescence is constant the luminance–voltage characteristics follows the I–V characteristics. In the simplest way the operation of the single-layer device can be described as follows. Opposite charge carriers, i.e. holes and electrons are injected into conjugated polymer layer from the anode and cathode, respectively. The holes are injected into the highest profile of the valence (π) band (HOMO level) whereas the electrons are introduced to the lowest profile of the conduction band (π^*) band (LUMO level). This is schematically depicted in Fig. 9. On both the electrodes there exist barriers for hole and electron injections (ΔE_h and ΔE_e). Usually the barrier for electron injection from the metal electrode is higher than that for hole injection from the ITO electrode. Injected opposite charge carriers may form either singlet or triplet excitons. The former ones decay radiatively to give out light. In the majority of conjugated polymers holes are dominant charge carriers due to the fact that $\Delta E_e > \Delta E_h$. The phenomenon of electroluminescence requires however both types of carriers, the quantum efficiency will therefore depend strongly on the electron injection barrier.

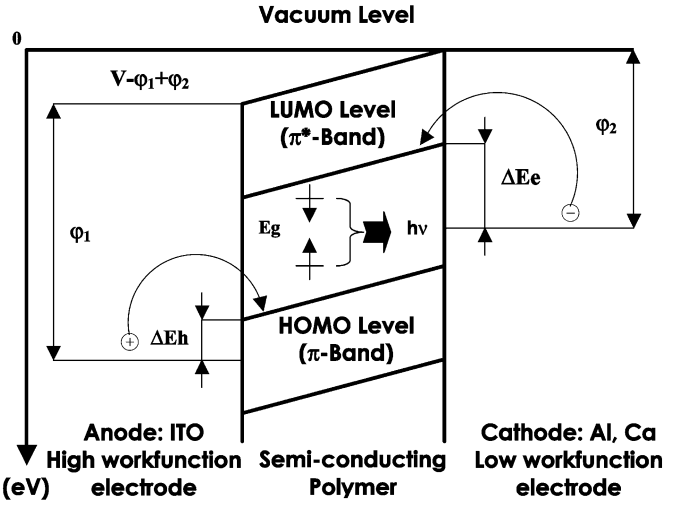
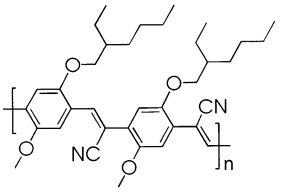


Fig. 9. Band diagram of a single-layer PLED.

In single-layer PLED devices the electroluminescence mainly occurs in the vicinity of the cathode because of better mobility of positive charges in conjugated polymers. This has a negative impact on the luminance efficiency because near the electrode the probability of a non-radiative recombination is very high. Thus it is favorable to move the area of excitons formation away from the cathode. One of the possible solutions is to fabricate a two-layer device in which the cathode and the electroluminescent polymer are separated by an electron transporting layer [120,121]. It is instructive to give one example of such approach. PPV derivative with solubilizing alkoxy groups on the ring and cyano group attached to the vinylic carbon (**30**) (MEH-CN-PPV) has significantly different properties as compared to unsubstituted PPV. First, it is solution processible. Second, the presence of electron withdrawing group increases the electron affinity of this polymer while maintaining the $\pi-\pi^*$ gap similar to that measured for MEH-PPV. Due to higher electron affinity MEH-CN-PPV is much better n-type conductor and can be used for the deposition of an electron transporting layer. In a two layer device (PPV/MEH-CN-PPV), the formation of the excitons followed by their radiative decay occurs at the interface between both polymers. As a result, quantum efficiency for the emitted light increases. Moreover, an easy electron injection from the metal electrode with higher work function, for example Al, is now possible. Of course the replacement of Ca by Al greatly facilitates the fabrication of PLEDs [119]. Similarly one can separate the anode from the light-emitting polymer by introducing a hole transporting layer which facilitates hole injection and in many cases improves the stability of the PLED and decreases its operating bias voltage. Several types of materials were used for this purpose, among other thin transparent layer of doped conjugated polymers exhibiting p-type conductivity such as doped PANI [122–125] or doped PEDT (**19**) [57]. In principle one can design three- or more-layer devices in order to improve the device parameters, one must be however aware of the fact that the cost of fabrication increases significantly for multilayer heterostructures.



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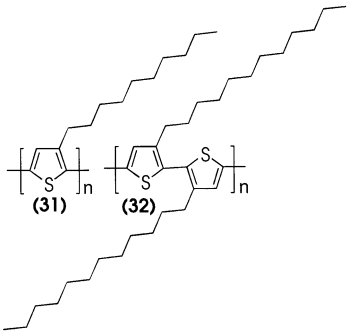
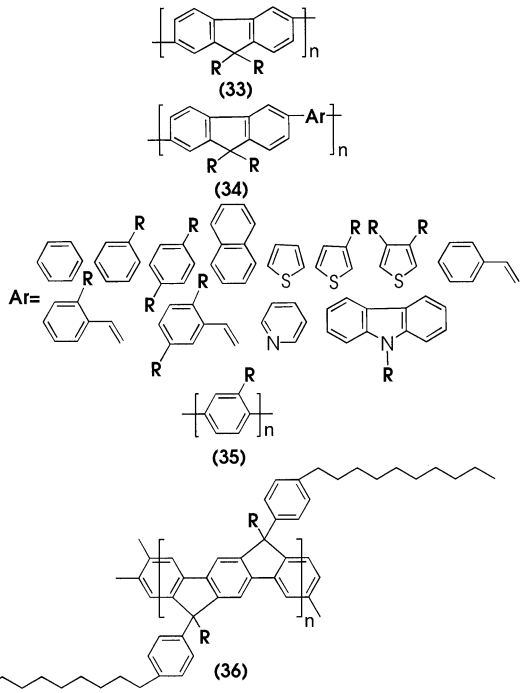
The design and fabrication of PLED based displays is a challenging task for chemists, materials scientists, physicists and electronic engineers. In view of the application of PLEDs in multicolor displays it is necessary to precisely tune the color with the goal to obtain red, green and blue PLEDs with a relatively narrow emission peak. This can be done by appropriate functionalization of the polymers and varying their $\pi-\pi^*$ optical gap. Electroluminescence of poly(alkylthiophene)s is an instructive example of such approach [126]. Regioregular, head-to-tail coupled poly(3-decylthiophene) (**PDT**) (**31**) is an electroluminescent polymer with a good color purity emitting in red. Its main disadvantage is a rather low quantum yield. Its isomer regioregular poly(4,4′-didecyl-2,2′-bithiophene) (PDDBT) (**32**) which shows head-to-head, tail-to-tail coupling sequence shows one order of magnitude higher quantum efficiency for photo and electroluminescence and emits in green. The observed blue-shift in the electroluminescence spectra is due to significantly larger optical gap in PDDBT as compared to PDT. Similar influence of regioregularity and substituent alteration on the color of light-emitting was reported for pyridine-based analogues of PPV [127]. As it has already been mentioned ring-disubstitued PPV derivatives with CN group attached to the vinylic carbon constitute

another family of electroluminescent polymers with tunable color of emitted light from near infrared to blue [112].



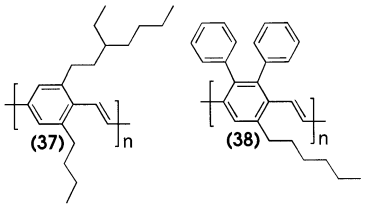
Blue emission is the most difficult to achieve not only in PLEDs but also in inorganic semiconductors-based LEDs. Polymers suitable for the fabrication of blue emitting PLEDs must show a high $\pi-\pi^*$ HOMO–LUMO) gap. Two groups of polymers can be used for this purpose, namely poly(fluorene) homopolymers/copolymers (**33**–**34**) [119] and substitued/ladder poly(*p*-phenylenes) (**35**–**36**) [111].

Due to solution processibility of new generations of electroluminescent polymers, ink-jet techniques can be applied in the fabrication PLED-based multicolor display. Commercial application of PLED-based devices requires materials with high purity, facile processibility, good thermal and oxidative stability. Enormous progress has been achieved in this respect in the last few years [119]. Industrially produced multicolor displays based on PLEDs have been demonstrated by CDT/SEIKO/Epson, Philips, Toshiba, UNIAX and other companies.



In principle, the same or very similar conjugated polymers can be used for the fabrication of optically pumped conjugated polymer based lasers. We will not discuss here the physics of lasing and the construction of polymeric lasers since many excellent reviews discuss these problems in great details [128–131]. Instead we will briefly describe polymers used as active laser materials and the specificity of their processing. In the simplest description lasers are devices emitting a spectrally narrow radiation, which is spatially coherent and strongly polarized. First lasing in conjugated polymers was reported by Moses [132] who used MEH-PPV (**21**) in a solution of xylene or chloroform. This was in fact a liquid dye-laser configuration in which the polymer replaced commonly used dyes. Further studies showed that stimulated emission, readily observed in solutions, is much more difficult to be achieved in the solid-state and in particular in solid films of neat polymers [133–137]. However if conjugated polymers are molecularly dispersed in a solid polymer matrix such as, for example, polystyrene matrix they may exhibit stimulated emission. This observation clearly shows that the removal of interchain interactions is crucial for the stimulated emission [138,139]. One may therefore expect that optical properties of conjugated polymers in the solid state will depend not only on their chemical constitution but also on the conformation of an individual chain as well as chain packing, i.e. supramolecular structure and morphology. It is known that for vast majority of conjugated polymers all the above-mentioned microstructural features are strongly dependent on processing conditions. Polymers used as materials for solid-state lasers, in their vast majority, consist of a conjugated backbone to which flexible, σ-bonded side groups are grafted. Therefore, they may differently interact with solvents. Casting from solvents interacting preferentially with non-conjugated side groups leads to tight coil-type conformation, which minimizes interchain interactions. To the contrary solvents containing aromatic rings interact preferentially with the conjugated backbone which leads to open type conformation with π-stacking. This conformation is preserved upon removal of the solvent and interchain interactions via π-stacking are enhanced. It is therefore evident that lasing or stimulated emission will be strongly dependent on the solution processing conditions [135,140–145].

In the poly(*p*-phenylene vinylene) family of conjugated polymers, the extent of interchain interactions may also be modified by the chemical nature of substituents in the 1,4-phenylene ring. In general more bulky alkyl side groups better prevent from π-stacking than alkoxy substituents. For this reason poly(2-butyl-5-(2′-ethylhexyl)-1,4-phenylene vinylene) (**37**) has less tendency to aggregate formation than MEH-PPV. Polymers with bulky substituents inducing significant steric hindrance like for example poly(2,3-diphenyl-5-hexyl-1,4-phenylene vinylene) (**38**) behave similarly.

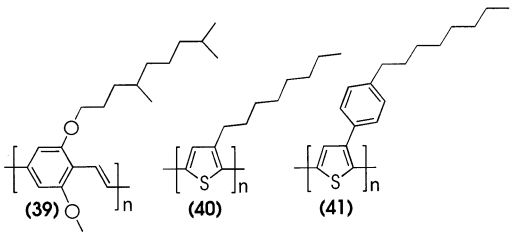


Why conjugated polymers are so good materials to serve as the gain medium in solid-state organic lasers? First, most conjugated polymers have a four-level electronic system, which causes that simulated

emission does not overlap with the ground state absorption spectrum. This shift between the absorption and emission spectrum minimizes self-absorption. Additional positive factors associated with conjugated polymers are high photoluminescence, high chromophore density and high stimulated emission cross section.

The construction of conjugated polymer-based photopumped lasers raised the question whether electrically-driven polymer diode lasers can be made? This is a more difficult task because of the fact that losses in diode structures are much higher than in photopumped waveguides. They are mainly associated with charge induced absorption and the absorption of the metal electrode. Electrically-driven organic laser has recently been constructed [146], however using a carefully grown single crystal of tetracene as the optically active layer instead of a conjugated polymer layer. In the field-effect electrode configuration higher charge (electron, hole) mobilities are observed in tetracene-based devices as compared to conjugated polymer-based ones, as well as much lower charge induced absorption.

Another spectacular application of undoped conjugated polymers involves the construction of plastic photovoltaic cells [147]. Photovoltaic cells are devices, which transform radiation energy into electricity and in this respect they can be considered as inverse to light-emitting diodes (LEDs). For this reason first polymer photovoltaic cells resembled single-layer PLEDs, i.e. they consisted of a conjugated polymer layer sandwiched between two electrodes of different work function (usually Al and ITO). Unfortunately in such a simple device the photo-induced charge generation, required for the operation of the cell, is extremely inefficient [148,149]. Undoped conjugated polymers are electron donors upon photoexcitation. If an electron accepting molecule is available in the close vicinity a charge separation takes place due to photoinduced electron transfer. In such case a stable charge storage configuration is formed in the conjugated backbone, so-called positive polaron which is highly delocalized and mobile. Fullerene molecules (C_{60}) are very suitable as electron acceptors. Thus one can imagine a bilayer photovoltaic cell structure in which a fullerene layer is introduced between the anode and the polymer layer. Both photocurrents and photovoltaic effects are in this case enhanced as compared to the single-layer device. However efficient photo-induced charge generation is in this case limited to the interface between the two (polymer and fullerene) layers [150]. Significant improvement of the power conversion efficiency of the conjugated polymer-based photovoltaic cells was achieved when a bilayer heterostrucure was replaced by a composite layer consisting of C_{60} dispersed in the conjugated polymer matrix [151]. In an ideal case such composite type 'bulk heterojunction' should consists of an interpenetrating network in which donor (polymer) and acceptor (fullerene) phases are bicontinuous. The real morphology as revealed by atomic force microscopy (AFM) is different and shows the coexistence of islands of both components. But even this imperfect morphology results in a significant improvement of the device performance. Several composite bulk heterojuctions have been tested. As polymeric components of the composite poly(*p*-phenylene vinylene) derivatives and poly(thiophene) derivatives were used, namely MEH-PPV (**21**), MDEMO-PPV (**39**), P3OT (**40**), POPT (**41**) [152–160].



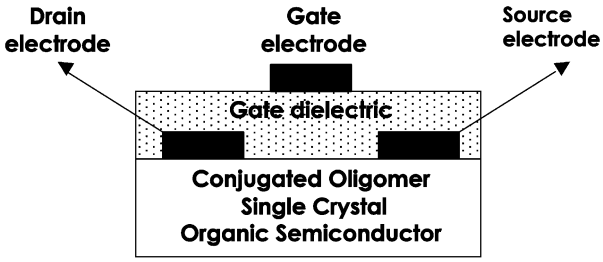


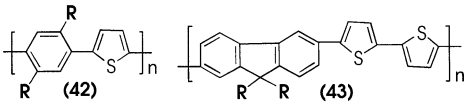
Fig. 10. Schematic structure of a conjugated oligomer single crystal organic FET.

'All-polymer bulk heterojunctions' can also be produced [161–165]. In this case instead of fullerenes, polymers with electron accepting abilities are used. Polymers used as electron transporting layers in PLEDs (vide supra), for example (MEH-CN-PPV) (**30**), are very well suited for this purpose.

All previously described applications of undoped conjugated polymers involve optoelectronic devices in which electrical energy is converted into radiation or vice versa. However conjugated polymers can be used in the fabrication of a large variety of other electronic devices. Polymer-based field-effect transistors (FETs) are among the most extensively studied. It should be noted here that polymer-based FETs constitute only a fraction of recently developed organic field-effect transistors (OFET). The main research effort is directed towards the devices based on oligomers or low molecular weight systems, i.e. n-OFET [166,167] and p-OFET [168–170]. This research is however outside the scope of this paper. The state-of-art of 'non-polymeric, organic electronics' is described in few excellent review papers [171–179]. FETs play a very important role in modern electronics since they constitute, for example, an inherent part of computer chips. In classical FETs inorganic crystals (Si, GaAs) are used as semiconductors. In its simplest representation (Fig. 10) FET consists of a semiconductor layer on which two metal electrodes, so-called 'source' and 'drain', are deposited. The source and the drain are separated from a third electrode (so-called 'gate') by a thin layer of a dielectric. With no voltage between the source and the gate electrodes the FET is in its insulating state. The device can be switched to the conducting state by application of a voltage between these electrodes, which results in the creation of charge carriers. These charge carriers can then flow between the source and the drain. Moreover, the injected charge carrier concentration can be precisely controlled by small variation of the gate voltage. The crucial parameter of the application of FETs in electronics is the ON/OFF ratio, i.e. the ratio of the conductivities with the gate voltage switched on and off, respectively. Usually ON/OFF ratios exceeding 10^6 are required. The level of conductivity in the OFF-state is strongly dependent on the amount of residual doping in the polymer. Incomplete purification of the polymer results sometimes in the presence of minute amounts of dopants, which create charge carriers in the polymeric semiconductors. These gate voltage independent carriers are undesirable since they increase the conductivity in the OFF-state and consecutively lower the ON/OFF ratio. Thus conjugated polymers used for FET application must be carefully purified and dedoped. To the simplest approximation the conductivity of the polymer in the ON state is proportional to the concentration of charge carriers created by gate voltage and their mobility. Thus high ON/OFF ratios require high charge mobilities. This is the weakest point of polymer-based FETs. Charge carriers mobilities in FETs based on Si single crystals exceed 1500 $cm^2 . V^{-1} . s^{-1}$ in the case of electron carriers and 400 $cm^2 . V^{-1} . s^{-1}$ in the case of hole carriers. Charge carriers mobilities in FETs fabricated from amorphous silicon are of the order of 0.1–1.0 $cm^2 . V^{-1} . s^{-1}$ which is sufficient for

many commercial applications. Charge carrier mobilities in properly grown, highly ordered layers of conjugated oligomers easily exceed 1.0 $cm^2 . V^{-1} . s^{-1}$ [176,177]. In best conjugated polymer based FET the carrier mobilities approach 0.1–0.2 $cm^2 . V^{-1} . s^{-1}$ [180,181].

The advantage of the use of polymeric materials as semiconductor layers is their easy solution processing as well as film forming properties. However one must be aware of the fact that polymers rarely give highly ordered structures. In general, layers of polymers are heterogeneous and consist of highly ordered areas of crystalline nature and less ordered amorphous zones. Of course charge mobility in ordered regions will be higher than in disordered ones. For this reason, polymers with regular chain structure are better candidates for FET applications since they more easily form ordered supramolecular structure. If the network of highly ordered zones percolates in the polymer layer then high charge carriers mobilities can be measured for macroscopic layers. The importance of the individual polymer chain regularity on the properties of the semi-conducting layer can be demonstrated by the comparison of the carrier mobilities in FETs produced from regiorandom and regioregular poly(3-alkylthiophene)s. In the latter charge carrier mobilities are much higher [182–188]. In general substituted regioregular poly(thiophene)s are very good candidates for FET applications provided that the solubility inducing pendant groups are not too bulky and appropriate processing conditions are established [189]. Other systems tested involve substituted poly(1,4-phenylene)s (see Fig. 1), disubstituted poly(1,4-phenylene-*co*-2,5-thienylene) (**42**), and copolymers of 2,2′-bithiophene and di-*n*-octylfluorene (**43**) [190,191]. However for all above mentioned polymers low mobilities were found [175]. Polymers from poly(*p*-phenylene vinylene) family as well as poly(pyrrole) give much higher carrier mobilities however suffer from low ON/OFF ratio [192]. Low values of the ON/OFF ratios is mostly associated with incomplete undoping of the polymer. The undoping is especially difficult in the case of poly(pyrrole) whose undoped form is very reactive and may be redoped even in the presence of minute amounts of contaminants with slightly oxidizing properties.



From the above brief discussion, it is clear that at the present state ‘plastic electronics’ cannot compete with Si or A(III)B(V) based electronics in highly sophisticated devices. However in modern technology there exist an increasing demand for low-cost and large-area flexible electronic components. For these applications polymer-based devices are frequently advantageous over the inorganic ones.

Although undoped poly(aniline) cannot compete with other families of conjugated polymers as a component of ‘plastic electronics’ devices it exhibits several interesting properties which make this polymer suitable for electrical engineering applications. One of these applications is its use as a stress grading material in high-voltage coaxial cables [193]. In the technology of high-voltage cables a so-called ‘semi-conducting layer’ is introduced between the metallic conductor and the insulating layer. The role of this intermediate layer is to suppress local increase of electric field which may occur in the areas of imperfections and defects of various types on the conductor–insulator interface and which are the major cause of electric breakdown. Usually this intermediate layer consists of a mixture of an insulating polymer with carbon black, the latter component being in quantity exceeding the percolation threshold. Carbon black can be replaced by undoped poly(aniline) which is advantageous mainly due to its strongly non-linear electrical transport properties. In fact undoped poly(aniline) is a ‘self-adapting’

material whose conductivity depends on the electric field. For low fields it behaves practically as an insulator whereas at applied field, E_a, exceeding 1 kV. mm^{-1} its $I = f(V)$ characteristics begin to strongly deviate from linearity leading to a significant increase in the polymer conductivity [194]. This property is extremely useful because in areas where electric field increases locally due to imperfections of the material, poly(aniline) becomes conductive and can easily dissipate the accumulated charge. Industrial tests show that the layer consisting of a blend of undoped poly(aniline) with poly(ethylvinyl acetate) better prevents cables from electric breakdown than commonly used carbon black-based layers [193].

3. Processible organic conductors from doped conjugated polymers

3.1. Principles of conjugated polymers doping

Before describing structural and electronic properties of doped conjugated polymers, it is instructive to discuss the chemical nature of the doping process. Two types of dopings are usually distinguished — the redox-type doping and the acid–base one.

Poly(acetylene), poly(*p*-phenylene), polyheterocyclic polymers (poly(thiophene), poly(pyrrole), poly(furan) and their derivatives) and other polyconjugated systems with no strong basic centers in their backbone usually undergo the redox-type doping. The doping process will be explained using poly(acetylene) and poly(thiophene) as examples but the presented reasoning can be extended to other polyconjugated macromolecular compounds.

p-Type oxidative doping of poly(acetylene) can be carried out chemically or electrochemically and involves either chemical or anodic oxidation of the polymer chains to polycarbonium cations with simultaneous insertion of an appropriate number of anions between the polymer chains which neutralize the charge of polycarbonium cations. Positive charges of polycarbonium cations are mobile and oxidized poly(acetylene) is a p-type (hole) conductor as shown from Hall effect and thermopower measurements [195–197]. The doping process is schematically depicted in Fig. 11. First the abstraction of an electron from the π-system of poly(acetylene) chain results in the formation of a radical cation (Fig. 11b). Removal of a second electron gives rise to a second

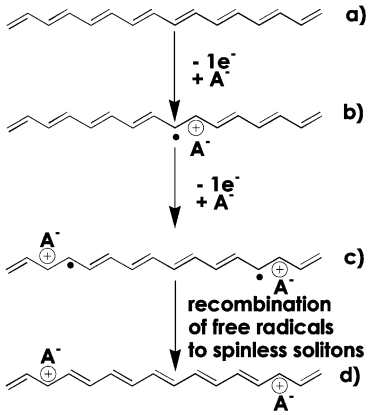


Fig. 11. p-Type doping of poly(acetylene).

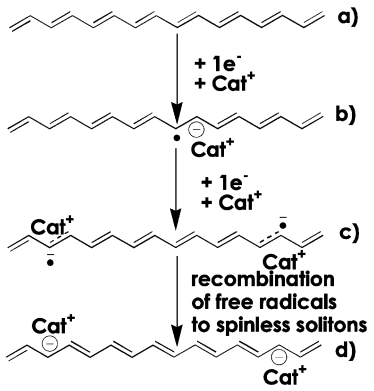


Fig. 12. n-Type doping of poly(acetylene).

radical cation (Fig. 11c). Then two radicals recombine to give a spinless dication (Fig. 11d). Further oxidation occurring in the same manner leads to spinless charge carriers called positive solitons [198]. Note that each soliton constitutes a boundary which separates domains differing in the phase of their π-bonds.

By hole–electron symmetry, one may postulate analogous picture for n-type doping of poly(acetylene). In this case neutral chains are either chemically or electrochemically reduced to polycarbonium anions and simultaneously charge compensated cations are inserted into the polymer matrix. Fig. 12 shows schematically the doping process. Negatively charged, spinless solitons are in this case charge carriers.

In heterocyclic conjugated polymers, different charge configurations are formed. The removal of one electron from the π-conjugated system of poly(thiophene) results in the formation of a radical cation (Fig. 13b). This radical cation, called polaron, is of a special nature because its presence induces the creation of a domain of quinone-type bond sequence within the poly(2,5-thienylene) chain exhibiting aromatic bond sequence. The removal of the next electron may lead to the creation of another polaron or to a spinless bipolaron which is a dication separating the domain of quinone bonds from the sequence of aromatic type bonds in the polymer chain (Fig. 13c). Electrochemical

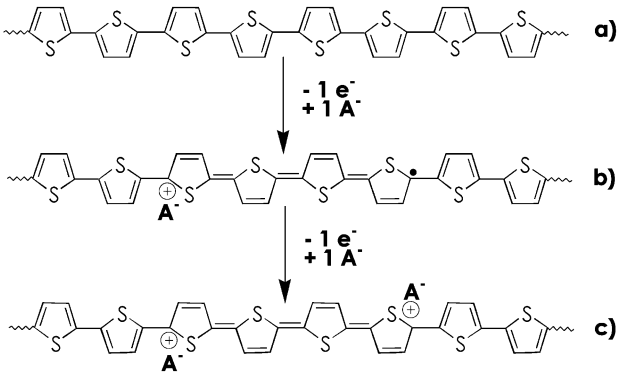


Fig. 13. p-Type doping of poly(thiophene).

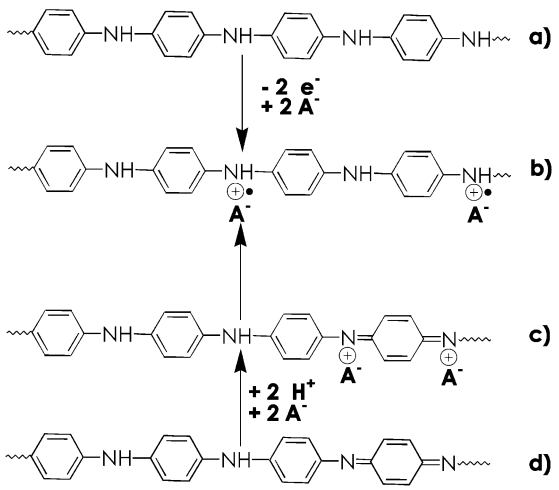


Fig. 14. Oxidative and acid–base doping of poly(aniline).

doping is specially suitable for the identification of the type of charge carriers. If the charge introduced during electrochemical doping is measured by coulometry and in the same time the number of spins created is monitored by EPR, the spin-charge correlation can be established. In the case of poly(thiophene) such correlation unequivocally shows that during doping initially polarons are formed which then recombine to bipolarons [199].

The most reduced form of poly(aniline)-leucoemeraldine-LB can also undergo oxidative type of doping (see Fig. 14a and b). In this case the oxidation of neutral LB chain leads to radical cations, i.e. polarons. However poly(aniline) and other conjugated polymers possessing strong basic centers in their backbone can be doped not only in a redox process but also in an acid–base one. This type of acid–base doping can be most clearly explained using the semi-oxidized form of polyaniline, i.e. emeraldine base (EB) as an example. EB can be protonated with a sufficiently strong protonic acid to give the corresponding salt form (ES). It is known from XPS and other spectroscopic studies that imine nitrogens are preferentially protonated. Thus protonation of EB gives first the product in which the charge is stored in a form of bipolarons (see Fig. 14c and d). Then a charge redistribution occurs which can be considered as an internal redox process which transforms these bipolarons into polarons (so-called polaron lattice) (Fig. 14b and c). The polymer chain adopts the structure of polysemiquinone radical (Fig. 14b). Note that the oxidative doping of LB leads to the same product as the acid–base doping of EB. However in the latter one the number of electrons in the polymer chain does not change upon doping and the charge is introduced by protonation. Fully doped EB is frequently denoted in the literature as $PANI(HA)_{0.5}$ where PANI corresponds to the repeat unit consisting of one ring and one nitrogen of the average formula $C_6H_{4.5}N$ and HA is the protonating acid molecule.

To summarize, since the doping process involves the transfer of the charge to or from π-bonding system of the conjugated polymer, leaving the σ-system essentially intact, the structural identity of an individual chain is preserved. However vibrational, electronic and other properties of the polymer are strongly altered upon the doping as well as its supramolecular structure. The most spectacular result of the doping is the increase of the polymer conductivity over several orders of magnitude. In some cases

conjugated polymers reach the conductivity of metals with a negative temperature coefficient which is characteristic of metallic behavior [106,200–203].

3.2. Methods of conjugated polymers doping

Historically, first doping agents used for converting conjugated polymers into polymeric conductors were halogens (Br_2 and I_2) and arsenic pentafluoride (AsF_5) [204]. They were used in the late 1970s for doping of poly(acetylene). The doping in its simplest version consists of the exposure of $(-C_2H_2-)_x$ films to the vapors of the above mentioned reagents. The chemical reaction describing the doping with halogens can be expressed as follows:

$$(-C_2H_2-)_x + 3/2yxX_2 = [(-C_2H_2-)^{y+}(X_3^-)_y]_x$$

Thus, upon oxidative doping (p-type) the doping agents are converted into linear polyhalogen anions (I_3^-, Br_3^-) which then are inserted into the poly(acetylene) matrix. The doping with Br_2 is more delicate. In this case the oxidation does not stop at the stage of polycarbonium cation but proceeds to the addition of bromine to the double bond. The oxidative addition reaction breaks of course the conjugation and transforms segments of poly(acetylene) chain into poly(dibromovinylidene) which is insulating. Therefore doping with Br_2 should be carried out in very mild conditions to avoid this undesirable side reaction.

The reaction of AsF_5 with $(-C_2H_2-)_x$ is of double nature — redox and acid–base:

$$(-C_2H_2-)_x - yxe = [(-C_2H_2-)^{y+}]_x, \qquad 3/2yxAsF_5 + yxe = 1/2yxAsF_3 + yxAsF_6^-,$$

$$[(-C_2H_2-)^{y+}]_x + yxAsF_6^- = [(-C_2H_2-)^{y+}(AsF_6^-)_y]_x$$

In the above reaction, 1/3 of doping agent molecules act as an oxidant whereas the remaining 2/3 as a Lewis acid ($AsF_5 + F^- = AsF_6^-$).

The use of nitronium salts of hexafluorophosphates, arsenates or antimonates ($NO_2^+XF_6^-$, where X = P, As, Sb) or nitrosonium salts ($NO^+XF_6^-$, where X = P, As, Sb) makes the doping purely redox in nature with the cations acting as the oxidants:

$$yxNO_2^+XF_6^- + (-C_2H_2-)_x = [(-C_2H_2-)^{y+}(XF_6^-)_y]_x + yxNO_2$$

In this case, the doping reaction is carried out in solution, preferably in nitromethane.

Transition metal halides with oxidizing properties can also serve as doping agents for poly(acetylene). Among them the most popular is $FeCl_3$ [205] which is incorporated into the polymer matrix in the form of $FeCl_4^-$ as shown by Mössbauer spectroscopy [206]. Other popular doping agents involve strongly or mildly oxidizing acids ($HClO_4$, H_2SO_4) [207].

All the above described doping systems can be used for the doping of all principal families of conjugated polymers depicted in Fig. 1.

Electrochemical doping of conjugated polymers is also widely used. Soluble conjugated polymers can be deposited from solution on platinum or other type of electrode by spin- or dip-coating. Insoluble polymers are either electropolymerized directly on the electrode or deposited by spin- or dip-coating from colloidal dispersions. It should be stressed here that the majority of conjugated polymers are electropolymerized in their doped states, thus they do not require additional doping [208]. However if an exchange of the dopant is required they must be electrochemically reduced to the neutral state prior

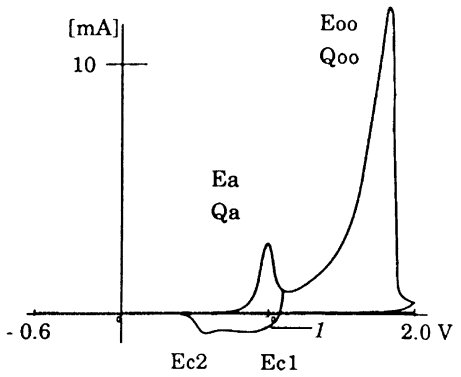


Fig. 15. Cyclic voltammetry curve of poly(bithiophene) obtained in 0.1 M NBu_4ClO_4/acetonitrile electrolyte: Scan rate: 20 mV s^{-1}. Curve 1 results if the sweep direction is reversed at 1.1 V (vs. Ag/AgCl reference electrode) in the first scan. (Reproduced with permission from Synth Met 1989;28(1–2):C257–262. Copyright 1989 Elsevier Science.)

to chemical or electrochemical doping with the desired anion. The main disadvantage of the electrochemical doping consists of the fact that it is difficult to dope large quantity of the polymer due to the limited surface area of the working electrode. On the other hand the principal advantage of the electrochemical doping is the possibility of precise control of the doping level via coulometric measurements provided that the current yield of the doping reaction is known.

Electrochemical doping is usually carried out in non-aqueous solutions (acetonitrile, propylene carbonate, etc.) containing quaternary amine salts of monovalent anions such as ClO_4^-, BF_4^-, PF_6^-, etc. as the electrolyte. During the doping the polymer is being oxidized at the anode and in the same time the dopant anions, originating from the electrolyte, are inserted to the polymer matrix. Electrochemical doping can be performed either at constant current or at constant potential. In the latter case three electrode, two compartment electrochemical cell is used.

It is very instructive to monitor electrochemical doping by cyclic voltammetry. The p-type doping of a neutral polymer gives rise to an anodic peak followed by a current plateau which is associated with an unusually high capacitance of doped conjugated polymers (see Fig. 15) [209,210]. On the reversed potential scan the corresponding cathodic peak is observed which is due to the dedoping process (reduction of the doped polymer to the neutral one). One must be aware of the fact that oxidative (p-type) doping produces the polymer in its semi-oxidized state. Further increase of the potential results in a second oxidation peak, which has no cathodic counterpart (Fig. 15). This second anodic peak is ascribed to irreversible oxidation of the conjugated backbone (overoxidation) which in turn renders the polymer insulating and electrochemically inactive [211]. Therefore during electrochemical doping the potential of the working electrode should be constantly monitored in order to avoid the overoxidation phenomena described above.

Spectroscopic changes which accompany electrochemical doping can be conveniently monitored using spectroelectrochemical methods. Joint UV–Vis–NIR/cyclic voltammerty (CV) experiments [212–214], FTIR/CV [215–218], Raman/CV [219,220] and EPR/CV experiments [221–224] have been carried out. Fig. 16 shows typical spectroelectrochemical behavior, in the UV–Vis–NIR region, of a conjugated polymer, in this case regioregular poly(3-decylthiophene) [225]. Increasing doping level which can be correlated with increasing electrode potential results in a bleaching of the π–π^* transition with simultaneous growth of two bands in the NIR part of the spectrum ascribed to two bipolaron

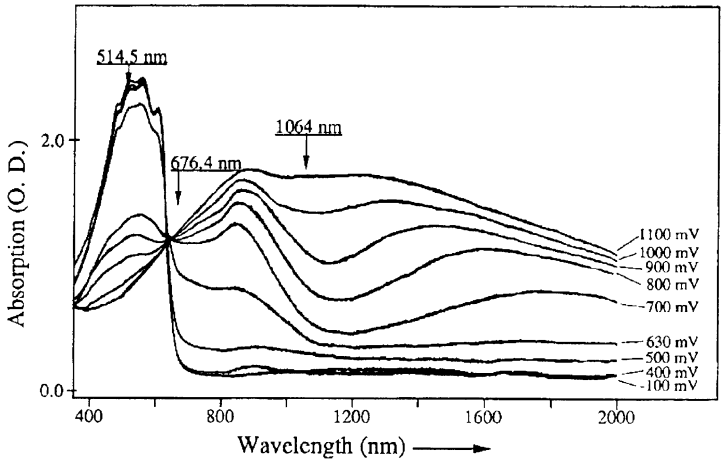


Fig. 16. Spectroelectrochemical behaviour of regioregular poly(3-decylthiophene) in 0.1 M Bu_4NBF_4/acetonitrile electrolyte vs Ag/AgCl. (Reproduced with permission from J Phys Chem 1996;100(30):12532–9. Copyright 1996 Am Chem Soc.)

transitions. Clear isosbestic point observed up to the potential of 1.0 V vs. Ag/AgCl unequivocally indicates that only two optically non-equivalent phases are present in the system (undoped polymer and the doped phase) which mutually reconvert. At higher potentials the spectra shift from the isosbestic point, which can be taken as an evidence of partial overoxidation. Note that the spectrum of the neutral polymer exhibits vibronic structure, which is indicative of high structural order.

At the end, one must state that conjugated polymers doped with simple or complex inorganic anions are neither soluble nor fusible and for this reason virtually impossible to process using conventional processing methods. Even if a given polymer is soluble in its neutral (undoped) state its doping with simple inorganic dopants results in a precipitation of an insoluble doped material. Thus the preparation of conjugated polymers processible in their doped state requires the development of special dopant engineering. This problem will be discussed later.

If solid films or powders of conjugated polymers are doped with large anions, frequently the doping reaction is limited to the surface of the polymer due to the fact that the diffusion of bulky dopants in the solid matrix is essentially blocked. However this diffusion hindered doping may be of use in the preparation of inorganic–organic hybrid materials with peculiar properties. The preparation of such materials has recently been reviewed by Gomez-Romero [226] therefore in this paper we will focus only on these aspects which were somehow omitted in this paper. This surface-limited doping is especially suitable for the preparation of new types of conjugated polymer-supported heterogeneous catalysts in which the dopant anions contain catalytically active centers. As a result of surface doping these anions are molecularly dispersed on the polymer surface. One should note that the doping with bulky anions renders the polymer surface conductive. Surface-doped samples exhibit macroscopic conductivity because in this case the percolation threshold for conductivity is extremely low. Thus the catalytic centers are ‘short-circuited’ by the conductive polymer support which facilitates the transport of electronic charge. This is of course of crucial importance for all catalytic processes in which electron transfer plays a dominant role. As it has already been mentioned poly(acetylene) (PA) can be synthesized in a form of entangled fibers of the diameter of few dozen Å. Such morphology facilitates surface doping by, for example poly(oxometalate)s, such as for example Keggin-type heteropolyanions

$[XM_{12}O_{40}]^{n-}$ (where X = P or Si, X = Mo or W) which are bulky anions of the size of several Å [227]. Poly(acetylene), surface-doped with anions of phosphomolybdic acid — $H_3PMo_{12}O_{40}$, is an extremely efficient and highly selective catalyst for alcohol conversion [228]. Other surface-doped conjugated polymers such as poly(aniline) [229] or aromatic poly(azomethine)s [230] were tested as catalysts for alcohol conversion [231] or olefin oxidation [232] showing high selectivity in each case.

Conjugated polymers can also be doped in the bulk with large size anions provided that the doping is carried out 'in situ' during the polymerization. For example polyheterocyclic polymers or poly(aniline) bulk-doped with polyheteroanions can be prepared by electropolymerization of the corresponding monomers in the electrolytic solutions containing heteropolyanions [233–236]. It should be stressed that catalytic and electrocatalytic properties of bulk-doped polymers are significantly different from those of surface doped polymers.

The n-type doping of conjugated can be performed chemically or electrochemically, similarly as p-type doping [237]. The first n-type doping of conjugated polymers was reported for poly(acetylene) which was doped using THF solution of sodium naphthalide ($Na^+Naph.^{-\cdot}$). The overall doping reaction can be expressed as follows:

$$yxNa^+Naph^{-\cdot} + (-C_2H_2-)_x + = [Na_y^+(-C_2H_2-)^{y-}]_x$$

with naphthalide radical anion serving as the reducing agent.

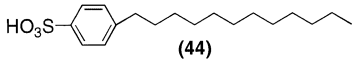
Poly(acetylene), poly(*p*-phenylene), and poly(*p*-phenylenevinylene) can also be n-doped in a direct reaction of alkali metal vapors with the neutral polymer [238–240]. Electrochemical n-doping with alkali metal cations or R_4N^+ quaternary salts was also reported for several conjugated polymers including poly(acetylene), poly(*p*-phenylene), and poly(thiophene) derivatives [241,242]. There exist only one report on poly(aniline) n-doping [243]. In this case emeraldine base is treated with strong reducing agents like KH or NaH to give n-doped polymer soluble in dimethylsulfoxide (DMSO).

It should be pointed out here that n-type doped conjugated polymers are much more reactive than the p-type doped ones. Usually their conductivity drops drastically even upon extremely short exposures to ambient atmosphere.

3.3. Doping induced processibility

As it has already been mentioned, unsubstituted conjugated polymers, in their vast majority, are insoluble. This is associated with the rigidity of their chains and strong interchain interactions. In polymer chemistry typical procedure of rendering rigid-chain polymers soluble is to attach flexible side groups to the stiff polymer backbone. Such approach resulted in the preparation of soluble derivatives of poly(thiophene) or poly(*p*-phenylene vinylene) for example. However poly(thiophene)s with solubility inducing side groups dissolve only in the neutral, i.e. undoped state. Upon doping they become insoluble and precipitate. This phenomenon is of course inconvenient from the technological point of view because it involves the necessity of post-processing doping of already cast films of the neutral polymers. Therefore, over the last 15 years, significant research effort has been directed towards the preparation of polyconjugated macromolecular systems soluble in their doped, i.e. conductive state. The idea of the preparation of conductive polymers processible in their doped state is very simple as schematically depicted in Fig. 17. The solubilizing or in general processing improving groups are introduced to the polymer matrix not as side groups attached to the polymer backbone by a covalent bond but rather as an inherent part of the doping anions. In such case the

polymer intractable in its neutral (undoped) state becomes processible after the doping. The use of anionic surfactants as poly(pyrrole) dopants can be considered as the first attempt to obtain dopant modified conducting polymers [244]. Although the resulting material was not solution processible it showed an interesting self-organized structure in which the chain–dopant–chain distance could be correlated with the length of the surfactant anion. In 1992 Cao et al. [245] used *n*-dodecylbenzene sulfonic acid (DBSA) (**44**) for the acid–base doping (protonation) of poly(aniline) in EB oxidation state. The use of this amphiphilic dopant induces the solubility of poly(aniline) in non-polar or weakly polar solvents which in turn facilitates its solution processibility. The supramolecular structure of solid films of fully-doped polymer of the formula PANI$(DBSA)_{0.5}$ prepared by casting from solution is very interesting. It is clear that ionic-type interaction between the protonated chain and the dopant counter-anion must prohibit phase separation between these two components of the doped polymer. Thus the system can be considered as comb-like polymeric structure capable of the formation of ordered, self-organized structures. PANI doped with surfactant anions usually shows layered and in some cases lamellar-type of structural organization in which stacks of polymer chains are separated by dopant anions. Such structure was postulated not only for PANI$(DBSA)_{0.5}$ [246] but also for other than PANI polymers containing basic sites in the chain backbone and protonated with acids containing alkyl-type surfactant groups [247,248].



(44)

Processing system consisting of PANI-(±)-camphor-10-sulfonic acid (CSA) (**45**)-*m*-cresol, first studied by Cao et al. [245] turned out to be extremely interesting. Films of PANI$(CSA)_{0.5}$ cast from *m*-cresol solutions showed metallic conductivity down to 220 K and a high degree of structural order [249–251]. According to Ikkala et al. [252–254] the above described processing system is unique in that sense that it involves the formation of a supramolecular complex between all three components of the processing system. The formation of such complex requires strong interactions via hydrogen-bonding between the solvent, the dopant counter-ion and the polymer chain, together with a steric matching

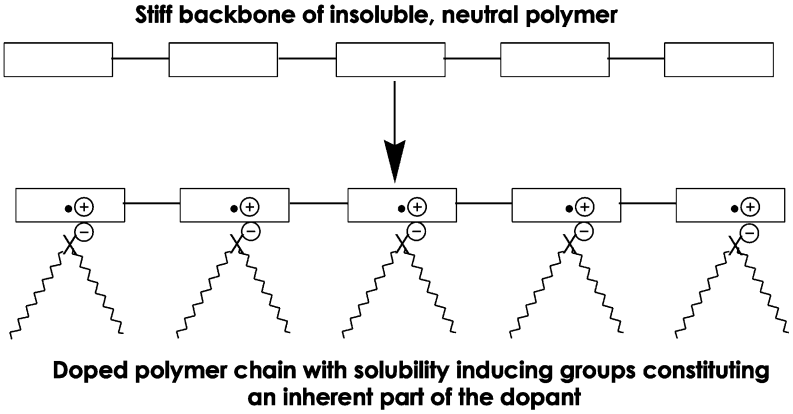
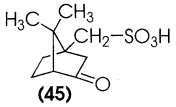


Fig. 17. Counter-ion induced processibility: the solubility of the polymer is induced by functional groups which are introduced to the polymer via doping reaction.

between the solvent and polymer repeat units in order to enhance van der Waals interactions. The formation of the complex favors extended chain conformation of PANI chains and facilitates supramolecular ordering in $PANI(CSA)_{0.5}$ cast from *m*-cresol.



(45)

Xia et al. [255], discussed the features of UV–Vis–NIR spectra of $PANI(CSA)_{0.5}$ films cast from different solvents. Spectra of films cast from *m*-cresol or other phenols solutions exhibit an absorption tail extending towards NIR (Fig. 18a). This tail is indicative of charge carriers delocalization favored by the extended chain conformation of PANI induced by the presence of the supramolecular complex described above. Such films show high electrical conductivity (300 S. cm^{-1} for non-oriented samples) of metallic character. On the other hand spectra of $PANI(CSA)_{0.5}$ films cast from non-interacting solvents (chloroform, chlorobenzene) show a strong localized band at ca. 800 nm which is ascribed to localized charge carriers. These films show low conductivity (10^{-1} S. cm^{-1}) of semi-conducting character. Thus in the case of doped PANI the shape of UV–Vis–NIR spectrum is predictive of the polymer conductivity.

For some years, PANI–CSA–*m*-cresol processing system was believed to be unique in yielding films or layers of PANI exhibiting metallic-type conductivity. Spectroscopic studies of other than phenols solvents for doped PANI processing showed that 1,1,1,3,3,3–hexafluoro-2-propanol (HFIP) is a promising solvent for casting PANI films of metallic conductivity [256]. Indeed $PANI(CSA)_{0.5}$ cast from HFIP shows metallic-type conductivity over a wider temperature range than $PANI(CSA)_{0.5}$ cast from *m*-cresol [106]. There are other advantages of the use of HFIP for casting of PANI films as compared to *m*-cresol. For example, it is extremely difficult to remove all *m*-cresol from the solution processed films. Casting from HFIP results in the fabrication of 'clean', residual solvent-free, films. Fluorinated alcohols, although good solvents for processing of PANI exhibiting metallic properties, are rather exotic and expensive solvents, and for this reason not likely to be used in a technological scale.

Another interesting solution processing system leading to metallic PANI has been developed by Adams et al. [257], in this case 2-acryloamido-2-methyl-1-propanesulfonic acid as the dopant and 2,2′-dichloroacetic acid (DCAA) as the solvent. In general functionalized sulfonic acids are excellent dopants inducing solution processibility of PANI [258]. However in many cases PANI doped with sulfonic acids and processed from solution exhibits rather poor mechanical properties. Therefore significant research effort was undertaken to develop new poly(aniline) processing systems which would lead to films combining metallic-type conductivity with good mechanical properties. One family of dopants improving mechanical properties of conductive PANI is especially worth mentioning, namely diesters of 4-sulfophthalic acid and of 5-sulfophthalic acid (**46**–**47**) [259,260]. Diesters of phthalic acid and especially its 2-ethylhexyl ester are the most popular industrial plasticizers, see for example: Ref. [261]. Esters of sulfophthalic acid should in principle combine PANI doping ability with plasticizing properties. This is indeed the case. Di-alkyl and di-alkoxy esters of sulfophthalic acids render PANI soluble in DCAA and other solvents. The films cast from this solvent are flexible, can be bent several times without damage and show elongation at break exceeding 45%. Supramolecular structure of PANI $(DESPA)_{0.5}$ (where DESPA denotes diesters of sulfophthalic acid) depends on processing conditions. Casting in inert atmosphere with slow evaporation

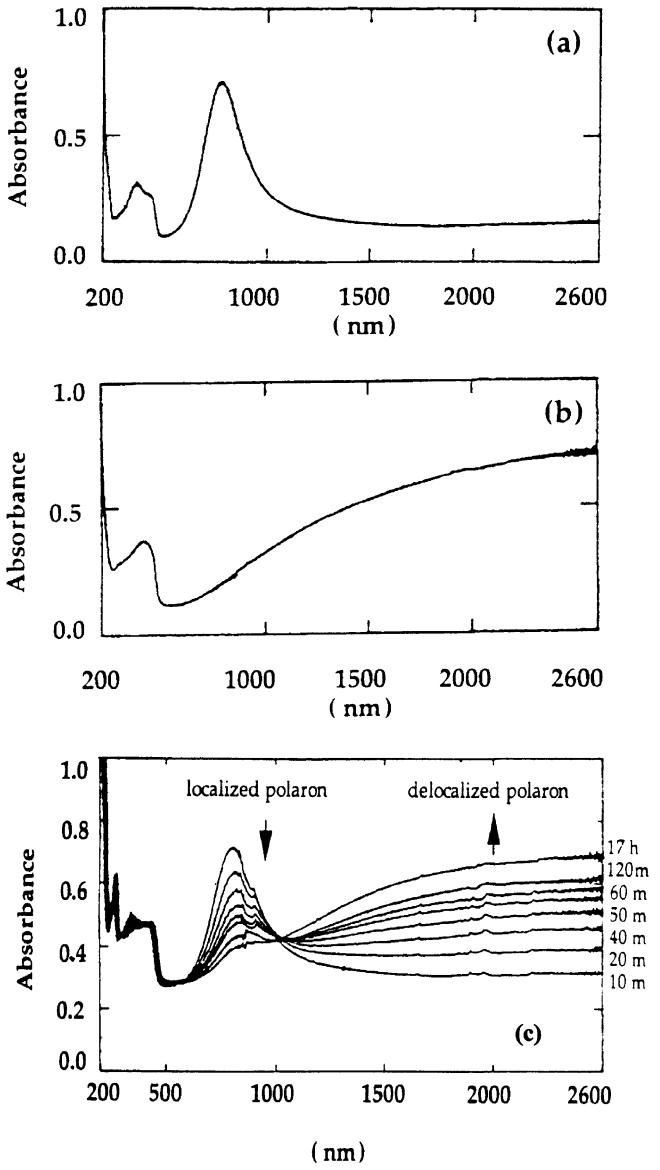
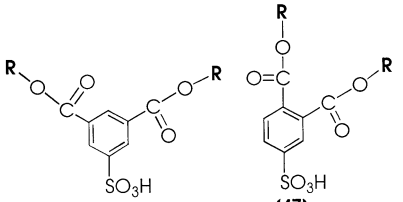


Fig. 18. UV–Vis–NIR spectra of PANI(CSA)$_{0.5}$ films cast from: (a) $CHCl_3$ (b) *m*-cresol, (c) $CHCl_3$ and exposed to *m*-cresol vapors for different times, respectively. (Reproduced with permission from Macromolecules 1994;27(24):7212–4. Copyright 1994 Am Chem Soc.)

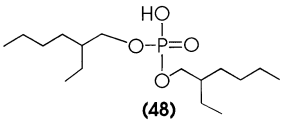
of the solvent leads to ordered supramolecular structure. As evidenced by WAXD and SAXS investigations PANI(DESPA)$_{0.5}$ exhibits layer-type structure in which stacks of polymer chains are separated by dopant anions. For a series of diesters with *n*-alkyl substituents the interlayer distance can be correlated with size of the counter-anion. Similarly as PANI(CSA)$_{0.5}$, poly(aniline) doped with dialkyl or dialkoxy ester of sulfophthalic acid exhibits metallic-type conductivity. One must also mention that the addition

of small amounts of external plasticizers, i.e. plasticizers which do not participate in the doping of the polymer, such as dioctyl phthalate, triphenylphosphate, or tritolyl phosphate improves supramolecular ordering of PANI(DESPA)$_{0.5}$ and extends the temperature range of metallic conductivity [262].



(46) (47)

Phosphoric acid diesters constitute another group of PANI dopants which combine plasticizing properties of phosphoric acid triesters with PANI doping ability of phosphoric acids. In fact diesters of phosphoric acid (abbreviated here as DPA) are extremely efficient plasticizers of PANI. If di-2-ethylhexyl hydrogen phosphate (DEHHP) (**48**) is used as the dopant, PANI becomes plasticized at the composition of PANI(DEHHP)$_{0.3}$, i.e. at strong deficit of the dopant [263]. If PANI is doped to saturation with respect to imine sites, which corresponds to the composition of PANI(DEHHP)$_{0.5}$, it behaves like a Bingham-type liquid [264]. In its simplest version plasticizing of poly(aniline) can be achieved without the use of a solvent by mechanical mixing of PANI base powder with a plasticizing dopant. Plasticized PANI can be thermally processed, however in this case the use of aromatic esters of phosphoric acid is recommended because they show better thermal stability than the aliphatic ones [265]. Other doping systems inducing solution or thermal processibility were also tested such as phosphonic acids and others.



(48)

Poly(aniline) is not only a Brönsted base but also a Lewis base. It can therefore be doped with Lewis acids. The Lewis acid–base chemistry of PANI has been somehow neglected and this type of doping has only recently been reported [266]. Complexation with a Lewis acid is a known method for the solubilization of stiff backbone polymers possesing Lewis base centers and was previously applied with success to aromatic poly(azomethine)s [19]. In Refs. [266,267] doping of PANI in the EB oxidation state with $SnCl_4$ and $FeCl_3$ is described. The selection of these Lewis acids as dopants was based on the fact that both molecules contain Mössbauer active nuclei and the doped polymer can be conveniently characterized by Mössbauer spectroscopy. The addition of a Lewis acid to a suspension of EB in nitromethane or acetonitrile results in a quick dissolution of the polymer. It should be noted here that neither PANI base nor protonated PANI dissolve in the above mentioned solvents. Solutions of Lewis acid-doped poly(aniline) have film forming properties and free-standing films of doped polymers can be obtained by slow evaporation of the solvent. The doping is purely acid–base in nature since upon doping no change in the oxidation state of Sn and Fe is observed in Mössbauer spectra. Moreover, the doping occurs not only on imine sites but also on amine ones. In the polymer matrix each dopant molecule is solvated with one solvent molecule, thus in the case of $SnCl_4$ doping in nitromethane the formula of the polymer doped to saturation can be expressed as follows: PANI$(SnCl_4)_{1.0}(CH_3NO_2)_{1.0}$. The observed Mössbauer parameters are characteristic of hexacoordinated Sn(IV) complexes consistent with the

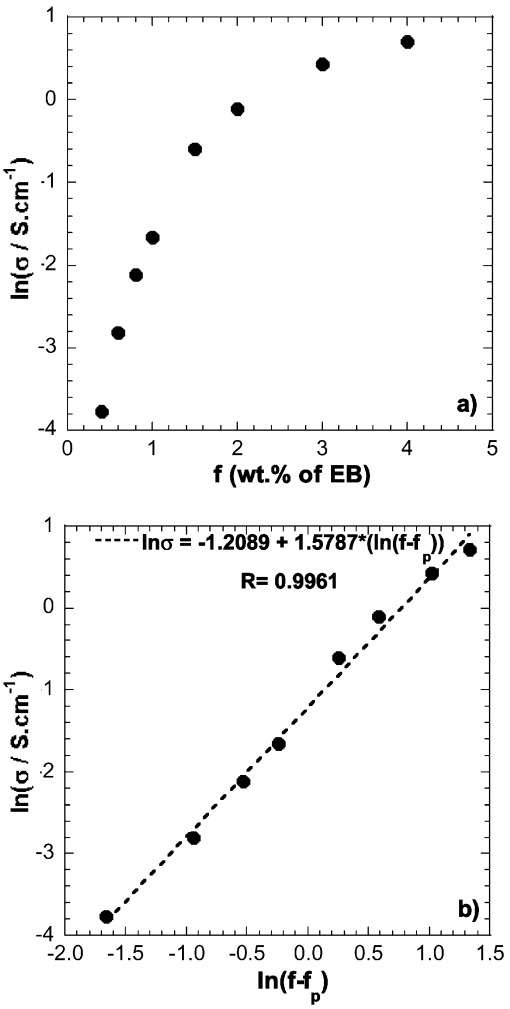


Fig. 19. (a) Conductivity vs. the content of conducting phase for PANI(DEHEPSA)$_{0.5}$-PMMA blend where DEHEPSA = 2-ethylhexyl ester of 4-sulfophthalic acid, (b) fit of data presented in (a) to the scaling law of percolation. (Reproduced with permission from Macromolecules 2000;33(6):2107–12. Copyright 2000 Am Chem Soc.)

above formulation. Thus Lewis acid doping broadens the range of solvents applicable for solution processing of PANI. Unfortunately Lewis acid doped poly(aniline) shows much lower conductivity as compared to protonated PANI, typically 10^{-2} S. cm^{-1}. This conductivity can be improved by an exchange of a Lewis acid dopant for a Brönsted acid one. This requires however a post-processing exchange reaction, which is technologically inconvenient.

Although as described above, doped poly(aniline) can be solution and thermally processed to give conductive plastics of excellent mechanical properties, its principal industrial application would involve its blending with conventional polymers with the main goal to combine specific properties of the conventional insulating polymer with high conductivity of poly(aniline) [268]. The conductivity in a blend of an insulating polymer with a conductive one can be described by so-called scaling law of

percolation [269]:

$$\sigma = c(f - f_p)^t \quad (1)$$

where c is a constant, t the so-called critical exponent, f is the volume fraction of the conductive polymer in the blend, and f_p is the volume fraction of the conductive polymer at the percolation threshold. Eq. (1) describes the conductivity in blends for which $f > f_p$. In the vicinity of the percolation threshold the conductivity increases very quickly over several orders of magnitude, then its increase is much slower. The conductivity of the blend below the percolation threshold is roughly the same as the conductivity of its insulating component. Typical percolation curve for a two component polymer blend, as well as its fit to the scaling law of percolation, are shown in Fig. 19a and b.

The value of the percolation threshold depends strongly on the morphology of the conductive phase. According to the percolation theory, for a conductive phase of globular shape, $f_p = 16$ vol%. However, if the conductive phase forms a continuous network in which the building blocks are strongly anisotropic, i.e. exhibit high aspect ratio (defined here as the ratio of the longest dimension of the objet to the dimension perpendicular to it) very low percolation thresholds can be obtained. For example in poly(aniline)-plasticized cellulose acetate blend the conductive phase consists of poly(aniline) rigid rods of ca. 10 nm diameter with the rigidity persistence of ca. 100 nm which, within the insulating polymer matrix, form a continuous network assuring macroscopic conductivity (see Fig. 20) [270]. As a result, an extremely low percolation threshold for electrical conductivity is obtained (0.07 wt%). It should be noted here that for conductive polymer blends percolation threshold is frequently expressed in wt% instead of vol%. This is formally incorrect because in Eq. (1) vol% should be used. This point is however of minimal importance in the majority of cases because the densities of conductive and insulating polymers are usually very close.

In general systems, with very low percolation threshold for electrical conductivity (below 1 wt%) are rare. Therefore it is rather surprising that in the case of blends in which doped conjugated polymers constitute the conductive phase several systems with extremely low percolation have been found [271–273].

There exist two principal methods for the preparation of such blends by solution processing. The first method involves classical intractable poly(aniline) prepared in a colloidal form. Armes and Aldissi [274] have demonstrated that colloidal particles of doped, i.e. conductive PANI can be prepared if a colloidal

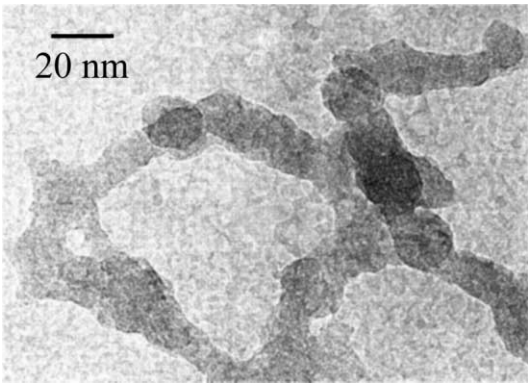


Fig. 20. Morphology of PANI(PPA)$_{0.5}$-plasticized CA blends. (Reproduced with permission from Appl Phys Lett 1999;75(10):1395–7. Copyright 1999 American Institute of Physics.)

stabilizer for example poly(vinyl methyl ether) (PVME) is added to the polymerization medium. This PVME stabilized submicronic PANI, for example $PANI(HCl)_{0.5}$, is then dispersed using ultrasonics or by other suitable method in a solution of the matrix polymer. The dispersion medium must be good solvent for PVME in order to avoid aggregation of the colloidal particles. Blends with poly(vinyl chloride) (PVC), polystyrene (PS), poly(vinyl acetate), and poly(methyl metacrylate) were prepared by casting from THF solution. They all exhibited extremely low percolation threshold (between 0.025 and 0.04 wt%). Blends with poly(vinyl alcohol) were prepared by casting from aqueous solutions [272].

Alternatively, blends exhibiting low percolation threshold can be prepared using counter-ion-induced solution processibility of PANI described above. In this case PANI doped with functionalized sulfonic or phosphonic acids or phosphoric acid diesters is co-solubilized with the matrix polymer in the same solvent, usually *m*-cresol (MC), 2,2′-dichloroacetic acid (DCAA) or other. Such solutions are then used for film casting. Blends of doped PANI with poly(methyl metacrylate) (PMMA), polystyrene (PS), cellulose acetate (CA) and other matrix polymer were prepared [271,275,276].

Blends of PANI with conventional polymers exhibiting low percolation threshold are very valuable materials because they combine high transparency in the visible part of the spectrum with high electrical conductivity. It should be mentioned here that in the majority of blends studied the mechanical percolation threshold is one order of magnitude higher than the electrical one. Thus it is possible to obtain transparent, conductive materials with mechanical properties characteristic of the insulating matrix polymer [273].

Blends of poly(aniline) with industrially used engineering plastics can also be prepared by thermal processing. This method has some advantages as compared to solution processing because it is simpler and requires no solvent. One must however be aware of the fact that the lowest percolation thresholds obtained for thermally processed blends are at least one order of magnitude higher than the lowest percolation thresholds in solution-processed blends. Moreover in the overwhelming majority of cases the threshold exceeds 20 wt% [277].

Blends of PANI with thermoplastic polymers such as polyolefines, poly(styrene), poly(vinyl chloride) and others were prepared by extrusion and more precisely using a twin-screw extruder with the possibility of a variable mixing time [278,279]. The use of functionalized protonating agents from the same group of compounds which induce solution processibility of PANI facilitates thermal processing of blends. These are sulfonic or phosphonic acids or phosphoric acid diesters. For blends with low and high density polyethylene as well as with polypropylene low percolation thresholds (usually below 5 wt%) are obtained if significant amounts of a compatibilizer is added to the blending mixture. Among all compatibilizers tested esters of gallic acid lead to the lowest percolation threshold in the resulting blend [278]. Blends of plasticized-PVC with poly(aniline), protonated with phosphoric acid esters, show higher percolation threshold, however it does not exceed few percent [280].

The preparation of blends with those conducting polymers which are infusible and insoluble requires the application of special techniques. The use of stabilized colloidal dispersion of doped-PANI in the preparation of its blends with industrial polymers, described previously in this section of the paper, also belongs to this class of processing techniques. It was described together with solution processing of PANI because of their close similarity. There exist other techniques for preparation of blends with intractable conductive polymers. For example, heterocyclic conductive polymers (poly(thiophene), poly(pyrrole), poly(furan) and their derivatives) as well as poly(aniline) can be electropolymerized within the porous insulating polymer matrix deposited previously on the anode [281]. Other techniques involve molecular dispersion of the oxidizing/polymerizing agent within the insulating polymer matrix

followed by its exposure to the monomer vapor or to a solution of the monomer in a suitable solvent [282]. In this case the monomer slowly penetrates the insulating polymer matrix and undergoes polymerization in situ within the matrix. Poly(vinyl alcohol) (PVA) or poly(ethylene oxide) (PEO) are very suitable matrices for the preparation of such blends because they form molecular complexes with $FeCl_3$ which is a convenient oxidizing agent for the polymerization of heterocyclic conductive polymers [283,284].

To summarize, within the last 10 years significant progress in the processing of doped conjugated polymers have been observed. Presently fabricated conductive polymers combine good mechanical properties with high conductivity. They can be mixed with thermoplastics, elastomers and other polymeric matrices to give blends with low percolation threshold. Finally, they can be deposited as conductive layers on polyamide or polyester fibers or films exhibiting good adherence to the substrate.

3.4. Application of doped conjugated polymers

In the most general way, two broad categories of the application of doped conjugated polymers must be distinguished. The first category involves all applications, which exploit those specific physical properties of the polymer, which are the consequence of the doping process. Thus, this category embraces the application of doped conjugated polymers as organic conductors in the fabrication of conductive layers, fibers, antistatic coatings as well as transparent electrodes. Doped conjugated polymer based radar absorption materials (RAM) also belong to this category as well as conjugated polymer-supported heterogeneous catalysts obtained via the doping reaction. The second category involves these applications, which exploit the changes in the physical properties of conjugated polymers, which accompany the doping process. These are optodes, chemical and electrochemical sensors including 'electronic noses', conjugated polymer based-gas separators. The use of conjugated polymers in corrosion inhibition also falls in this category.

The most obvious application of doped conjugated polymers is their use as conductors which combine high electrical conductivity with excellent mechanical properties of plastics. This progress was achieved by appropriate polymer and dopant engineering. Free standing films of presently fabricated polymeric conductors show conductivities of several hundreds $S.\,cm^{-1}$. In modern technology there exist a great demand for optically transparent conductors. Due to high molar absorption coefficient in the visible range of the spectrum doped conjugated polymers are transparent only in extremely thin layers. However, as already stated, blends of doped conjugated polymers with insulating polymers frequently show extremely low percolation threshold for electrical conductivity. In such cases sufficiently high conductivity of the order of few $S.\,cm^{-1}$ can be achieved together with optical transparency. In fact many doped conjugated polymers are available commercially in a form of pastes or suspensions ready for use. These are for example doped poly(3,4-ethylenedioxythiophene) and various types of doped poly(aniline). Similarly as in the case of undoped conjugated polymers, the application of doped polymers in electronics and microelectronics steadily increases. For example they are used on an industrial scale in tantalum/tantalum oxide capacitors as layers improving the electrical contacts between the porous dielectric oxide and the counter-electrode. The use of polymeric conductors significantly improves the performance of such capacitors [285,286]. One must note here that the annual production of such capacitors is of the order of several billions. The detailed description of the use of doped conjugated polymers in microelectronics is out of the scope of this article. The readers interested in this subject are referred to several excellent review papers, for example [287].

Synthetic polymers produced industrially are insulators exhibiting extremely low conductivity, usually below 10^{-12} S. cm^{-1}. For this reason in many applications they require conductive admixtures or coatings, which facilitate charge dissipation, especially in cases where charge accumulation may be dangerous. Coating of synthetic fibers and textiles with conductive layers constitutes a significant technological problems for many decades. Initial technologies involved electrodeless deposition of metals in the fiber surface using noble metal catalysts. Although metal covered fibers and textiles exhibit high surface conductivity they frequently suffer from poor metal adhesion. Other conductors like copper sulfide can also be used for this purpose. Although in this case the surface conductivity of the coated fibers is lower, it is still sufficiently high for charge dissipation purposes. Doped conjugated polymers offer an interesting alternative to the above described systems since their application results in the fabrication of 'all-polymer' conductive fibers without all drawbacks of polymer–inorganic interface. Surface conductivity of doped poly(pyrrole) or doped poly(aniline)-covered fibers can easily reach 0.2 S. cm^{-1} [288,289] which is less than in the case of metallized fibers but much more than the conductivity required for charge dissipation. Moreover by changing the deposition procedure the surface conductivity can be varied over several orders of magnitude. Initially used deposition methods involved in situ polymerization of suitable monomers, mainly pyrrole and aniline [290]. Both aniline and pyrrole readily polymerize in aqueous solution to give doped polymers in a one step reaction. Moreover, the polymerization rate may be controlled by the changes in the composition of the reaction mixture and/or by the addition of admixture which modify the polymerization [291]. If proper conditions are selected the polymer formed does not precipitate but rather deposits on the fiber surface in a form of a well adhering layer.

The simplest method of the fabrication of conductive and charge dissipating fibers is the deposition of conjugated polymer layers from solution. It is preferable to process the polymer in its doped, i.e. conductive state because processing of undoped polymers requires an additional operation of post-processing doping. Unfortunately systems that can be processed in the doped state are rare and in their overwhelming majority are limited to poly(aniline) doped with functionalized acids. One must also note that industry is rather resistant to introduce the deposition from solution if the solvent is 'exotic' or toxic.

The solution and thermal processibility of doped conjugated polymers enables not only the deposition of conductive layers on insulating fibers but also to produce conducting fibers from blends consisting of doped conjugated polymers and insulating polymers [292,293] as well as fibers of pure conjugated polymers in their doped, i.e. conducting state [294,295].

Dissipative properties of doped conjugated polymers blends with industrial polymers as well as conjugated polymers coated synthetic fibers or textiles allow a large number of technological applications, for example in the fabrication of conveyor belts, carpets, filtration devices, to name a few. The range of obtainable conductivities in doped conjugated polymers and their blends makes also these materials attractive for application as resistive heaters although only in cases where a rather low power per m^2 is required [296]. Significant research effort has already been directed towards the use of doped conjugated polymers as components of radar absorbing materials. Surprisingly the number of papers devoted to this subject is relatively low [297]. This is probably due to military nature of this research. One must stress that with respect to this type of application doped conjugated polymers exhibit appropriate level of conductivity as well as relatively flat attenuation over a wide range of frequencies.

Conjugated polymers doped with large anions such as for example heteropolyanions of Keggin-type, $[XM_{12}O_{40}]^{n-}$, represent a new class of electrocatalysts and heterogeneous catalysts. These materials

differ in their electrochemical doping–dedoping mechanism as compared to polymers doped with small dopants. Typical p-type doping of a conjugated polymer consists of the insertion of anions into the polymer matrix whereas the dedoping leads to their removal from the matrix. Since heteropolyanions are extremely bulky, they are immobilized in the polymer and upon dedoping they remain in the polymer matrix whereas the neutrality of the system is preserved by insertion of a small cation, for example Li^+, originating from the electrolyte. Dedoping results in turn in the expulsion of this cation. Thus by doping with heteropolyanions we can convert p-type doped electroactive polymer into a cation inserting/expulsing system [298]. This has important consequences from the point of view of electrochemical properties and facilitates their applications for example as selective membranes or sensors.

Gomez-Romero [226] classifies heteropolyanion doped conjugated polymers as organic–inorganic hybrids rather than doped polymers. Such approach is especially appropriate for surface doped conjugated polymers, which are real hybrid materials. Such hybrids are excellent polymer supported heterogeneous catalysts in several industrially important reactions such as alcohols conversion or olefin oxidation [299]. The main advantage of these new systems over the classical ones is molecular dispersion of the catalytic active species via the doping reaction as well as their chemical bonding to the support which prevents them from desorption. Several surface doped conjugated polymers were tested as heterogeneous catalysts [228,231,232,300]: poly(acetylene), poly(aniline), poly(pyrrole) and poly(azomethine)s, to name the principal. For example poly(acetylene) doped with anions originating from $H_3PMo_{12}O_{40}$ is a very efficient catalysts for ethanol conversion giving acetaldehyde as the major product which is formed on redox centers while ethylene and diethyl ether, i.e. products of acid–base catalysis, are formed in smaller quantities [228]. Conjugated polymers containing basic centers in their chains (poly(aniline), aromatic poly(azomethine)s) also exhibit extremely interesting catalytic behavior [231,232]. They can be doped with heteropolyanions via protonation with the corresponding heteropolyacids. It turns out for example that the conversion of 2-propanol with the use of such catalysts gives different products depending on the doping level. For low doping levels the catalyst gives only acetone with almost 100% selectivity. On the other hand for high doping level the catalyst produces propylene, also with almost 100% selectivity. This observation proves that at low doping level protonation of the polymer is very efficient and as a result all acid centers are blocked. At high doping levels the protonation is much less effective and the dopant molecule can act as a Brönsted acid giving the product of the acid-type catalysis.

The above catalysts can also be used in the reactions of olefin oxidation. In the oxidation of propylene they give hexadiene with selectivity exceeding 96%, which is the product of dehydrogenation type oxidation. The oxidation is 100% non-destructive, i.e. in no case C–C bond is broken [232]. Other oxidation products are propyl aldehyde, acetone and benzene. To summarize, these new conjugated polymers supported catalysts offer a unique possibility to modify their selectivity towards a given product in a practically continuous way by changes in their doping level, which are easy to control.

As it has already been stated, several important applications of conjugated polymers exploits the changes in their chemical or physical properties induced by doping. For example conjugated polymers exhibit distinctly different optical properties in their undoped and doped states. The doping associated optical changes can be induced electrochemically leading to so-called ‘electrochromic effect’ [301]. Electrochromic windows operate on this principle. Usually, in a sandwich-type system, thin layer of a conducting polymer electrode, suitable electrolyte and a transparent counter-electrode are assembled. Application of the voltage between the electrodes induces doping of the polymer and by consequence the change in its color.

Doping induced spectral changes constitute also the basis for the functioning of so-called pH optodes, i.e. devices which measure pH optically. It is known that the doping level of poly(aniline) depends strongly on the pH of the medium being in contact with the polymer. Thus pH optodes based on thin layer of poly(aniline) can be constructed [302–305]. One must note that, in the case of this polymer, the most significant doping induced spectral changes occur in the near-infrared (NIR) part of the spectrum. This is very fortunate because nature practically did not develop chemical compounds absorbing in this spectral range. Poly(aniline)-based optodes can therefore operate without any interference from the constituents of the solution studied. Solution processibility of poly(aniline) facilitates its deposition in a form of thin layer of high optical quality on a suitable support or on an optical fiber. pH probing consists of measuring absorbance for one or few λ from the NIR part of the spectrum which covers the region of doping induced changes. One must however note that pH optodes frequently suffer from the hysteresis effect. For a given pH the absorbance differs depending whether we are in increasing pH or decreasing pH mode [303]. The problem of the hysteresis can be easily resolved by a pre-treatment of a given optode in a solution of $pH = 0$ for few seconds. It constitutes however a serious problem in systems where pH must be monitored in a continuous manner and where random fluctuations of pH are expected.

Another important application of conjugated polymers which exploits the doping process is their use as membranes for gas and liquid separations [306–309]. In general polymers are excellent materials for the fabrication of such membranes. First, they have film forming properties and can be produced in sheets of large surface area. Second, very frequently their selectivity and permeability can be controllably modified by changing their supramolecular structure and/or morphology. In the case of conjugated polymers the morphology can be altered by consecutive doping–dedoping cycles. One must state here that conjugated polymer films used as membranes for gas separation cannot show microporosity, which leads to Knudsen-type diffusion. This is not always the case since many conjugated polymers are obtained as more or less porous materials. Poly(aniline) however, upon casting from NMP solutions, gives dense pore-free films suitable for the fabrication of membranes for gas separations. As cast film of PANI base is permeable to for example O_2/N_2 mixture showing higher permeability to oxygen with selectivity coefficient α close to 10. Protonation of as-cast films in aqueous solutions of HCl decreases both permeability and selectivity. Evidently the void space between PANI chains is now filled with hydrated chloride ions, which make the diffusion of gases more difficult. Dedoping of fully HCl protonated PANI with aqueous ammonia solution leads to a significant increase of permeability and gives the selectivity coefficient close to that measured for the pristine undoped film. This is not unexpected since PANI after HCl doping–undoping cycle is less crystalline and exhibits more open morphology as compared to pristine as-cast polymer. Partial redoping of the dedoped films produces a membrane which shows the highest selectivity for O_2/N_2 of any polymer [306]. However its permeability is lower than that measured for polysulfone-based membranes. Some improvement in permeability can be achieved by blending poly(aniline) with polyamic acid [310,311]. Other conjugated polymers such as poly(pyrrole) and poly(*p*-phenylene) derivatives were also investigated as gas separating membranes [306,312].

Pervaporation, i.e. the process in which the components of liquid mixture are separated allowing the passage of one component through the membrane, is another domain of chemical engineering which may exploit particular properties of conjugated polymers [313]. In this case the hydrophilicity or hydrophobicity of a particular membrane can be adjusted by appropriate functionalization of the polymer backbone or by the selection of appropriate functionalized dopant.

There are several other possible applications of doped conjugated polymers which are not discussed in

this review. For example the authors have deliberately decided no to discuss either the applications of conjugated polymers as electrochemical sensors for chemical and biological sensing or their use as corrosion inhibitors. The selection is purely subjective and reflects scientific interests of the authors.

4. Polymeric superconductors

Before discussing the superconductivity of conjugated polymers, it is instructive to describe briefly the historical development of the studies on the superconductivity of low molecular weight organic conductors. The first organic superconductor was discovered in the early 1980s [314]. It was prepared by electrochemical oxidation of tetramethyl tetraselena fulvalene (TMTSeF) to give an ion radical salt of the following stoichiometry $(TMTSeF)_2^+ \cdot X^-$ (where X^- is a monovalent anion of ClO_4^-, PF_6^- or other type). TMTSeF is a derivative of tetrethiafulvalene (TTH) which was the electron donating component of the first organic metal, i.e. charge transfer complex of TTF–TCNQ (where TCNQ is the abbreviation for tetracyoanoquinonedimethane — a well-known organic acceptor). In the years which followed several new ion-radical salts were discovered. The success in the preparation of organic superconductors,

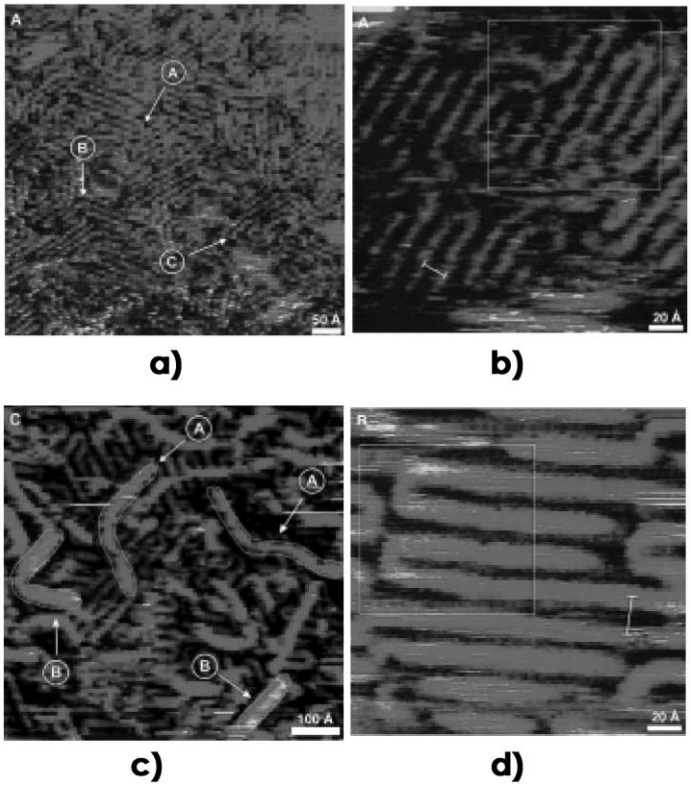


Fig. 21. (a) STM images (600×600 Å^2) of the long-range ordering in P3HT thin films on HOPG, (b) STM images (200×200 Å^2) of the long-range ordering in P3HT thin films on HOPG, (c) STM images (1000×1000 Å^2) of the long-range ordering in P3DDT thin films on HOPG, (d) STM images (200×200 Å^2) of the long-range ordering in P3DDT thin films on HOPG. (Reproduced with permission from Angew Chem Int Ed 2000;39(15):2680–4. Copyright 2000 Wiley-VCH.)

among others, was based on the fact that single crystals of sufficient quality to observe superconductivity could be grown on the electrode if sufficiently low current densities were used. The preparation of such highly ordered structures is of course much more difficult in the case of macromolecular systems. Therefore up to 2001 the only known case of a polymeric superconductor was poly(sulfur nitride) $(SN)_x$. This inorganic polymer, which becomes superconductor at extremely low temperature, i.e. $T_c = 0.26$ K, can however be prepared in a form of single crystals via solid-state polymerization of S_2N_2 [7]. The preparation of ordered layers of conjugated organic polymers is of course much more difficult. First chains with highly regular microstructure and low polydispersity must be prepared. Second, special solution processing conditions must be used which facilitate the crystallization of ordered structures. Then chemical or electrochemical doping must be carried out in order to create free charge carriers. The latter process is the weakest point of the whole procedure because doping induces disorder even in cases where it was carried out in solution using, counter-ion induced processibility. Solution processed doped polymers are only partially ordered and their crystallinity index usually does not exceed 40% [315].

From this point of view, the approach towards superconductivity of conjugated polymers presented by the group of Bell Laboratories was quite revolutionary [6]. In recent years it has been demonstrated that substituted poly(thiophene)s with high regularity of the polymer chain such as, for example, previously mentioned regioregular poly(3-alkylthiophene)s may form self-organized structures of remarkable crystallinity if deposited in the form of thin films on an appropriate substrate (see Fig. 21) [316]. Of course any chemical or electrochemical doping of such thin films would inevitably lead to a significant worsening of this order. The crucial point in the discovery of conjugated polymer superconductivity was to introduce charge carriers electronically without the use of chemical or electrochemical doping. This was achieved in so-called field-effect transistor (FET) configuration. Typical FET (see Fig. 10) consists of three electrodes. Two of them (source and drain) are deposited on a semi-conducting layer whereas the third one (gate) is separated from the semiconductor material by a thin layer of a dielectric, for example Al_2O_3. The configuration of the FET used for the studies of poly(3-hexylthiophene) superconductivity was slightly different. As in typical FETs the gate electrode was separated from the polymer semi-conducting layer with a thin layer of Al_2O_3 but the source electrode as well as the drain one were splitted into two electrodes in order to make possible in situ conductivity measurements by 4-probe technique which eliminates the influence of the contact resistance (see Fig. 22) [317–319]. The advantage of FET configuration is based on the fact that p-type charge carriers (holes) can be injected into the polymer layer electronically. Moreover their concentration can be precisely controlled over a very wide range by the applied gate bias. For low hole densities the polymer exhibits thermally activated conductivity characteristic of semiconductors. At higher hole densities the semiconductor to metal transition occurs and finally at

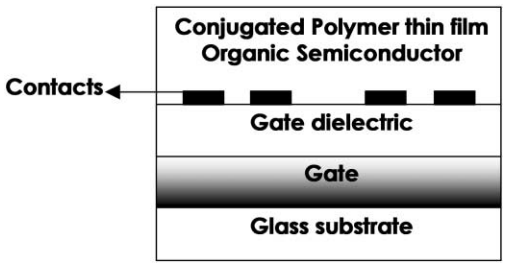


Fig. 22. Schematic structure of the regioregular poly(3-hexylthiophene) FET.

densities exceeding 2.5×10^{14} cm^{-2} poly(3-hexylthiophene) becomes superconducting at 2.35 K. The morphology of thin layers of superconducting poly(3-hexylthiophene) is complex. It consists of highly ordered zones, which become superconducting and less ordered zones, which do not show superconductivity. The percolation of superconducting zones results in macroscopic superconductivity.

Gate-induced superconductivity of poly(3-hexylthiophene) is the first example of the superconducting behavior in organic polymers. This phenomenon did not however appear *Deus ex machina* but was rather the consequence of systematic studies of Schön et al., who previously discovered superconductivity in low molecular weight compounds of acene series [320,321].

To date no chemically or electrochemically doped conjugated polymer was found to be superconducting. This is probably due to the fact that doping and processing techniques developed to date do not lead to supramolecular structures sufficiently ordered to assure the formation of a continuous network of superconducting zones. The authors of this paper strongly believe, however, that quick progress in this area of materials research will lead to chemically doped conjugated polymer superconductors in the near future.

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