Structure and Properties of Conducting Polymers

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ABSTRACT

A review of structure and properties of conducting polymers is presented. Special emphasis is put on computational methods of vibrational spectroscopy of conducting polymers, and on the modified extended Hückel band structure calculations for conducting polymers and quasi-one-dimensional (Q1D) graphites.

1. INTRODUCTION

Polymers are macromolecular chains consisting of a great number of repeating molecular units (monomers), in which the atoms are strongly joined by covalent bonding. In contrast to biopolymers which have, as a rule, strictly fixed molecular weights, synthetic polymers are a mixture of macromolecular chains of different molecular weights. All of the polymers have a complex three-dimensional (3D) structure dependent on their chemical composition [1]: in thermoplastics, the chains are held together only by weak Van der Waals bonds, enabling their plastic, ductile behavior; in thermosets, cross-linking agents rigidly bond the chains together by covalent bonds producing improved strength; in elastomers, some cross-linking is accomplished providing the unique elastic properties.

Polymers are lightweight, corrosion-resistant materials having, typically, low strength and stiffness, but are not suitable for use at high temperatures. However, most polymers are relatively inexpensive and can be readily formed into a variety of shapes, ranging from plastic bags and mechanical gears to bathtubs. Polymers also can have a variety of useful physical properties. Some, for instance, are transparent and, therefore, can replace glass in a number of applications. Some polymers have a very low coefficient of friction, others have the ability to convert light into electricity, and still others provide the basis for nonstick cookware. Polymers are used in an amazing number of applications including toys, home appliances, structural and decorative items, coatings, paints, adhesives, automobile tires, foams, packing, and many others.

Because their electrons are involved in covalent bonding, polymers normally have a band structure that gives a large energy gap and a very low electrical conductivity. As a result, polymers are frequently used in applications that require electrical insulation, preventing short circuits, arcing, and safety hazards [2].

In some cases, however, the low conductivity may be a hindrance. For example, static electricity can accumulate on housings for electronic equipment and damage the internal solid-state devices. If a lightning strikes the polymer matrix composite wing of an airplane, severe damage can occur. To minimize such problems, electrically conducting polymers could be decoratively finished by electroplating, or new polymer semiconducting devices could be developed for unique combinations of properties and applications.

Some techniques have been used to permit traditional polymers to become somewhat more conductive. Polymers have been coated with more conductive materials such as nickel and zinc. Conductive fillers, either in particulate or fiber form, have been introduced to produce conducting polymer matrix composites; incorporation of nickel-plated carbon fibers provides a unique method of combining high stiffness with conductivity. Hybrid composites containing metal fibers along with normal carbon, glass, or aramid fibers have been considered for lightning-safe aircraft skins.

Other polymers, so called conducting polymers, can be made more conductive by doping or processing techniques [3]. When such conjugated polymers, with π-electron states delocalized along the

polymer chain, are doped with donor or acceptor agents - electrons are able to jump freely from one atom to another along the backbone of the chain, increasing the conductivity near to the range of metals. In this paper we shall concentrate on such a class of polymers, their structure and properties.

A number of potential applications for the doped conducting polymers have been suggested [3]: antistatic coatings, fuel cell catalysts, solar electrical cells, photoelectrodes in a photogalvanic cells, protective coatings on electrodes in photoelectrochemical cells, electrodes in lightweight inexpensive batteries, and possible use as active materials in electronic or optical devices, now designated as "molecular electronics".

2. STRUCTURE AND PROPERTIES OF CONDUCTING POLYMERS

A significant impulse towards investigations of conducting polymers was given by the theoretical hypothesis of Little, which predicted high-temperature superconductivity in linear organic chains with polarizable side groups [4]. Although expectations born by Little's hypothesis have failed to date, numerous efforts of chemists on synthesis of quasi-one-dimensional (Q1D) conductors and physicists on investigations of these materials gave rise in 1973 to the discovery of inorganic polymer polysulfurnitride, $(SN)_n$, cf. Fig. 1, conductive at room temperature [5] and superconductive at 0.3 K [6].

Fig. 1 Structure of conducting and superconducting inorganic polymer, polysulfurnitride.

Shortly afterwards, considerable attention was directed toward the study of conducting organic polymers, following the discovery of Shirakawa *et al.* [7] and Ito *et al.* [8], who found that *trans-* and *cis-*polyacetylene, $(CH)_n$ or PA, cf. Fig. 2(a,b), could be prepared as films having a metallic luster. In 1977, it was discovered that the conductivity of PA could be increased by 13 orders of magnitude by doping it with various donor (alkali metals) or acceptor (halogens, AsF_5) species to give n-type or p-type semiconductors and conductors [9]. Later on, several different procedures have been developed by Naarmann and Theophilou [10] to synthesize *trans*-PA which, after orientation by mechanical stretching and doping with a saturated solution of iodine in CCl_4, gave metallic conductivities parallel to the direction of stretching $\sim 10^5 \ (\Omega cm)^{-1}$. Although many conducting polymers have been since investigated, doped polyacetylene remains the most extensively studied and understood organic polymer discovered to date [11].

A number of other organic polymers have been synthesized and evaluated as conductors upon doping: polypyrrole, PPY [12], polythiophene, PT [13], poly(p-phenylene), PPP [14], poly(p-phenylene sulfide), PPS [15], poly(p-phenylene vinylene), PPV [16], polyaniline, PANI [17], and many others [3]. Most of these polymers are based on aromatic ring systems, cf. Fig. 2(c-h). Unless doped, all of these conjugated polymers remain insulators, having a band gap >1.5 eV; $(SN)_x$ being an exception. However, none of these polymers, when doped, approach the conductivities of doped PA, lagging behind at least two orders of magnitude, $\sim 10^3 \ (\Omega cm)^{-1}$. The ultimate goal of such syntheses is achievement of the most conducting polymer - but also chemically stable, easily processable, mechanically strong and cheap.

To obtain a higher conductivity it is necessary to increase both the concentration and mobility of carriers. For a higher concentration of holes, i.e. electrons, a lower ionization potential, i.e. electron affinity is considered favourable as well as a lower energy gap. On the other hand, chemical and spatial regularities of polymer contribute to its higher mobility (as carriers are localized by defects), planarity and larger width of the highest partly filled band (which facilitate the π-electrons delocalization along the polymer chain). Quantumchemical calculations of the electronic band structure accomplished on many pristine conjugated polymers [18,19], enable the estimation of above parameters - and some correlation between experiment and theory exists. However, these conditions are neither necessary nor sufficient, and do not enable the unequivocal claim that some polymer will become conductive upon doping, just on the basis of calculated parameters.
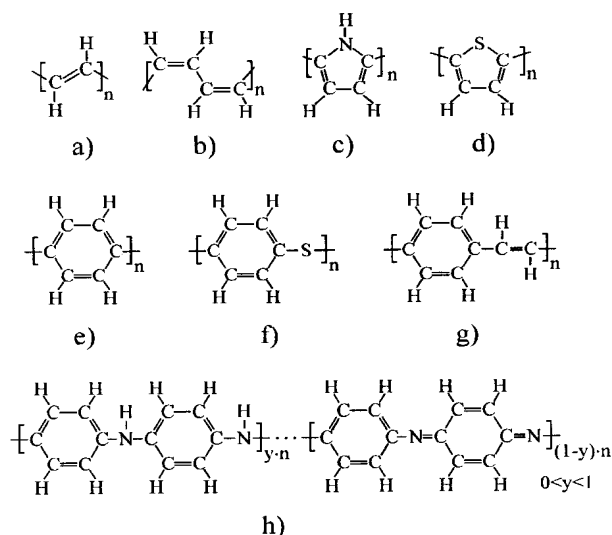
Fig. 2 Pristine structures of most significant conducting polymers: (a) trans-polyacetylene; (b) cis-poly-acetylene; (c) polypyrrole; (d) polythiophene; (e) poly(p-phenylene); (f) poly(p-phenylene sulphide); (g) poly(p-phenylene vinylene); and (h) polyaniline.

There are some conducting polymers with nonplanar structures (PPS [20], PPP [21,22], PANI [23], and possibly cis-PA [24]). Also, spatial regularity (crystallinity) of undoped and doped polymers are not necessary; even more, practically in most cases registered to date undoped polymers were polycrystal or amorphous, while doping introduced additional degree of disorder [25]. However, this does not mean that crystallinity of undoped and doped polymers would not give much higher values of electrical conductivity (comparable with copper), as it is the case for stretched PA [10] and intercalated graphite (of very regular structure) [26]. Therefore, spatial regularity of undoped polymers can be adopted as a reasonable initial assumption in theoretical studies.

Yet, it should be pointed out that a "rigid" polymer model has a limited applicability to doped polymers. Although such a model is reasonable in classical semiconductors (Si, Ge, ...) with low dopant concentrations, in the case of conducting polymers with dopant concentration up to 50% it has a limited notion, and can be applied only to lowly doped polymers (with dopant concentrations less than a few percents). That is to say, theoretical [27] and experimental [28] investigations of lithium doped $trans$-PA imply significant changes in spatial structure (equalization of C-C lengths) and electronic band structure (closing of energy gap E_g) under the charge transfer from lithium to polymer of only 0.1 e per carbon atom in the chain, which suggests that under high doping levels the polymer becomes a metal rather than a degenerate semiconductor. This mechanism of conductivity increase was also suggested on purely symmery arguments [29].

Anisotropy of electrical and optical properties is relatively weak (it is greater along the chain up to order of magnitude [30-35]), which is the consequence of shorter polymeric segments of nondisturbed conjugation and significant overlapping of electronic orbitals of adjacent chains. This is in accordance with the general conclusions on the stability of quasi 1D-systems in respect to metal-insulator phase transition [36,37].

Stability of doped polymers in air is different: it is the greatest in PANI [17], PPY [12], and PT [13] (almost indefinite after initial oxidation), somewhat worse in acceptor doped PA [30] and PPP [21], and very poor in these two donor-doped polymers as well as in PPS [31]. On the other hand, PA and PPP, doped with AsF_5 and sank in water, do not change electrical conductivity at all [14].

Thermal stability is the greatest in PPP [21] (up to 450 °C in air), PANI [38], and PPY [12] (up to 300 °C in air), while it is the worst in PA [30] (stable to 150 °C in air) and PPS [32] (stable to 300 °C in inert atmosphere).

Processability is also different: PA [30] and PPY [12] are insoluble and nonmeltable; PPP is also insoluble and nonmeltable, but it can be processed by techniques of powder metallurgy owing to a high thermal stability above 500 °C in vacuum [14]; PANI [17] and PPS [32] are currently the only soluble and meltable conducting polymers. Solubility and meltability of undoped PANI and PPS are presumably a consequence of a nonplanar elastic structure of the chains.

Optical absorption measurements on weakly doped samples (PA [34], PPY [12], PPP [33], PPS [31], and PANI [39]) show several maximums, one of them corresponds to the single one in undoped samples and defines the energy gap of pristine materials, while the others imply the existence of energy states inside the energy gap. The existence of novel energy states in weakly doped polymers is interpreted by soliton [40] and polaron [41] models, both of them obtained as a solution of the Hamiltonian model with electron-phonon interactions included.

3. VIBRATIONAL SPECTROSCOPY OF CONDUCTING POLYMERS

Very important experimental methods used in the investigation of polymers are vibrational spectroscopy methods: infrared spectroscopy (IR) and Raman spectroscopy [42]. With these experiments it is possible to investigate even the structure of noncrystalline polymers. However, these experimental methods must be accompanied by a calculation of vibrational properties, which includes calculation of positions and intensities of vibrational spectral bands. Then, it is possible to form complete spectral curves.

Vibrational spectra of many polymers, including those with extended π-electron conjugation, have been successfully interpreted [43] on the basis of the following theoretical model: (a) a single chain is considered which is infinite, extended, and translationally periodic; (b) the electrons and the nuclei are decoupled adiabatically; (c) anharmonic effects are neglected; (d) the force constants and electro-optical parameters in the framework of natural (internal) vibrational coordinates (valence bonds and angles, and out-of-plane dihedral and bond-plane angles) are assumed to be fairly local (i.e. independent of the structural details except for the location and the type of the few nearest neighbors), and hence they can be transferred from small molecules of appropriate stereochemical structure; and (e) the IR intensity computations are based on the valence-optical model [44,45] (unfortunately, an analogous procedure for obtaining Raman spectra is much less efficient, mainly due to a much greater number of the corresponding electro-optical parameters with respect to the infrared ones: therefore, the Raman intensities are not calculated).

Along these lines, we have computed the vibrational spectra of pristine *trans*-PA (Fig. 2(a)), PPP (Fig. 2(e)), and PPV (Fig. 2(g)), transferring the force and electro-optical fields from *trans*-hexatriene, toluene, and p-divinil benzene, respectively.

Our results on PPP are in a good agreement [46,22] with the observed IR and Raman spectra. Hence, one can reasonably view PPP as a simple concatenation of many identical phenyle-like structural elements.

However, in the case of *trans*-PA, two pronounced non-additive effects appear in the polymer, in contrast to shorter oligomers: the frequencies of the two strongest resonant Raman bands (corresponding to two "Peierls" modes, which give rise to metal-insulator structural phase transition in pristine *trans*-PA, as was suggested on purely symmetry grounds [29]) are lowered ~10-15%, and the intensity of the supposedly strongest IR absorption band (corresponding to the in-plane C-H bending vinylene mode) is dramatically reduced [47]. Strong electron-phonon coupling is believed to cause the first effect [48]. The origin of the second effect is interpreted as a consequence of a delocalized π-electron system [49].

To acquire some additional information, we have studied the vibrational spectra of PPV, that is intermediate in structure between PPP and *trans*-PA. No significant lowering of the frequencies of principal Raman features is observed, but IR in-plane C-H bending vinylene mode, is significantly reduced [50], like in *trans*-PA. As a consequence, the PPV is an example of a pristine polymer without electron-phonon

coupling, but with a well delocalized π-electron system – which can be the cause of an almost absent experimental IR in-plane C-H *trans*-vinylene band.

Our analogous calculations on *cis*-PA [24,51], PPY [52], and leucoemeraldine form of PANI [53] revealed the absence of both electron-phonon coupling and π-electron delocalization in these conjugated polymers.

4. MODIFIED EXTENDED HÜCKEL BAND STRUCTURE CALCULATIONS OF CONDUCTING POLYMERS AND Q1D-GRAPHITES

Electronic band calculations are even more important for theoretical investigation of conducting polymers [18,19,54] and related quasi one-dimensional graphites [55-59], as they provide the electronic density of states (DOS).

One of the simplest and quickest methods for such calculations is the extended Hückel method (EHM), initially adopted for small molecules [60]. The extension of EHM method on finite periodical structures is based on the mathematical analogy between EHM and calculation of normal vibrations, which can be reduced to the matrix eigenvalue problem [43,61].

In this section we shall discuss our EHM calculations for *trans*-PA, *cis*-PA, PPP, and several Q1D-graphites: polyacene (PA), polyacenacene (PAA), polyphenanthrene (PP), polyphenanthrophenanthrene (PPhP), and polyperinaphthalene (PPN) [59]. The change in energy gap due to the growth of the Q1D-graphites in the two-dimensional direction, starting from *trans*-PA, *cis*-PA or PPP, will be discussed - with the aim of designing intrinsically metallic Q1D-graphites.

Q1D-graphites are of high potential interest as their structures are in-between those of polyacetylene and graphite. Especially, since the Q1D graphites consist of aromatic rings, they are expected to be more stable against oxygen in the air than polyacetylene, which is the case for poly(p-phenylene) and graphite. Besides, some of the Q1D graphites are expected to be intrinsically conductive, like graphite.

The structures of polyacene (PA) and polyacenacene (PAA) have laddered skeletons of two and three *trans*-PA chains, respectively. On the other hand, the structures of polyphenanthrene (PP) and polyphenanthrophenanthrene (PPhP) are the corresponding laddered versions of *cis*-PA chains. Also, polyperinaphthalene (PPN) (frequently also referred as polyperylene) can be considered as a graphitized version of PPP. The structures of these polymers are presented in Fig. 3, with the unit cells employed in the present calculation.

The calculated DOS histograms as well as energy gaps, for polymers shown in Fig. 3, are presented elsewhere [59].
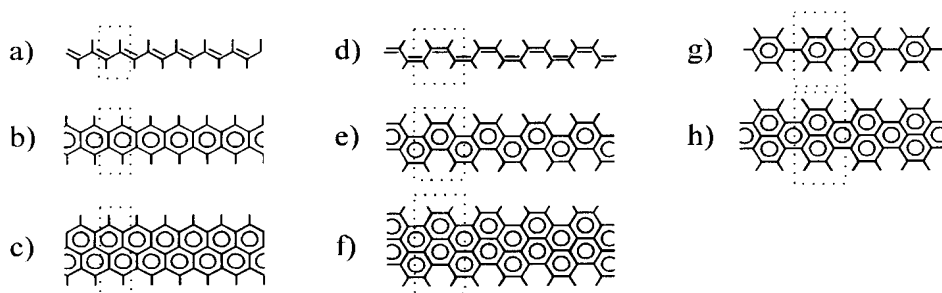

Fig. 3. Schematical drawings of (a) trans-polyacetylene (*trans*-PA), (b) polyacene (PA), (c) polyacenacene (PAA), (d) cis-polyacetylene (*cis*-PA), (e) polyphenanthrene (PP), (f) polyphenanthrophenanthrene (PPhP), (g) poly(*p*-phenylene) (PPP), and (h) polyperinaphthalene (PPN), with the unit cells employed in the present calculation.

The calculation reveals that PP and PPhP are intrinsically semiconducting materials, while PA, PAA and PPN are typical members of the Q1D-graphites, without an energy gap.

By inspection of the *trans*-series graphitization process, it appears that the energy gap vanishes in both PA and PAA, making them typical members of the Q1D-graphites.

On the other hand, the energy gap in the *cis*-series is initially enlarged after graphitization to PP, being then almost halved with further graphitization to PPhP due to a two-dimensional (2D) expansion of the Q1D-structure in the direction of 2D-graphite.

Finally, the graphitization of PPP to PPN gives rise to an abrupt vanishing of the energy gap, although with relatively low electronic DOS above the Fermi level, implying semimetallic nature of PPN.

The above method enables [61] quick qualitative estimations of the main characteristics of polymer electronic structure, being so very convenient for prognosis of electronic properties of novel organic materials. The employed scheme has an advantage in respect to other quantumchemical methods also because it basically treats finite fragment of polymer (oligomer), i.e. it does not use the cyclic boundary conditions. This distinguishes the present method from solid state zonal methods, and brings it near to the cluster quantumchemical methods.

However, cluster methods necessarily require the convergence investigation of results in respect to dimensions of the cluster [62]. This frequently appears to be a very complex procedure, as enlargement of the cluster dimensions also increases the order of matrices, which exceedingly complicates the calculations. The advantage of the present method is that it does not increase the order of diagonalized matrices, but only linearly increases the number of corresponding diagonalizations, which themselves all have the matrix orders limited by dimension of the polymer unit cell. In this way it is also relatively easy to investigate the dependence of electronic structure characteristic on the length of oligomers [61]. A saturation usually begins for $N=30-50$ unit cells.

The present EHM method can also be easily employed on real polymers with some side groups, by applying the perturbation method [61]. Besides, it can be easily generalized on 2D and 3D structures, enabling a simple simulation of a real environment [61,63].

CONCLUSION

In this article, a review of physical properties of conducting polymers was presented. Special emphasis was given on computational methods of vibrational spectroscopy, as a very powerful tool in investigation of stereochemical structure, electron-phonon coupling, and π-electron delocalization of conducting polymers. Also, modified extended Hückel band structure calculations for conducting polymers and quasi-one-dimensional graphites were thoroughly discussed, as being very convenient for a quick prognosis of electronic properties of novel organic materials.

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