

Charge distribution in model organic polymers

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Dedicated to Academician V Kellö, in honour of his 70th birthday

The electron structure, *i.e.* the distribution of Wiberg indices of respective bonds and the charge values of individual atoms, contained in the model structures of polymer compounds of the poly(*p*-phenylene), poly(*p*-phenylene oxide), poly(*p*-phenylene sulfide), poly(*p*-phenylene selenide), poly(2,6-dimethylphenylene oxide), polyazomethine, cyclic polynitrogen and poly(dibenzofuran) types of the system, have been studied. In the case of thermal polyacrylonitrile destruction the cyclic polynitrogen radical developed has been found to have the most favourable electron distribution ensuring all assumptions for the higher electron conductivity.

Исследованы электронные структуры, т.е. распределение индексов Виберга химических связей и величины зарядов отдельных атомов, содержащихся в модельных структурах полимерных соединений типа поли(*n*-фенилен), поли(*n*-фениленоксид), поли(*n*-фениленсульфид), поли(*n*-фениленселенид), поли(2,6-диметилфениленоксид), полиазометин, циклический полиазот и поли(дибензофуран). В случае термического разложения полиакрилонитрила обнаружено, что образующийся циклический полиазотный радикал располагает наиболее выгодным электронным распределением для выполнения предпосылок для более высокой электропроводности.

In the recent years there have been a growing number of theoretical and experimental works dealing with the high-molecular compounds of special properties such as elevated thermal stability, low flammability, and magnetic and semiconductive properties [1—8]. Nowadays the problem of preparation of polymers of particular, mainly semiconductive and superconductive properties has become one of the new trends in the polymer chemistry and physics.

Semiconducting organic polymers exhibit conductivities from 10^{-9} to 100 S cm^{-1} [9]. These polymers can be classified into three groups based on their chemical structure [9]:

1. Composite polymers which combine graphite-like structures with metal particles;

2. polymeric charge-transfer complexes in which a metal ion or an anionic species such as the iodide ion I_3^- or an organic acceptor such as trinitrofluorenone interacts with the polymer main chain by alternating the molecular orbital arrangement through electron interactions;

3. conjugated polymers which show semiconducting properties because the π -orbital overlap along the unsaturated polymer chain allows conduction electron to interact with neighbouring π -orbitals on adjacent carbon atoms.

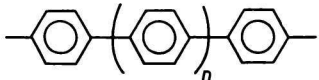

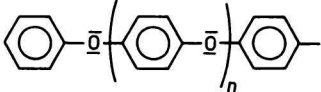
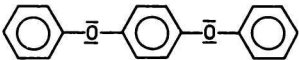
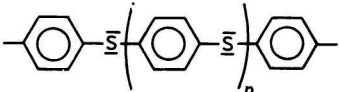

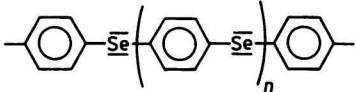

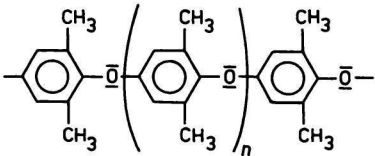
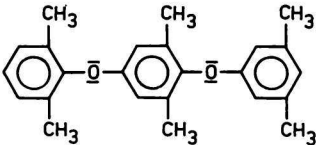
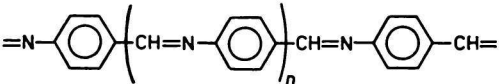

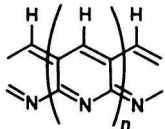
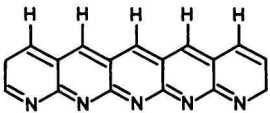
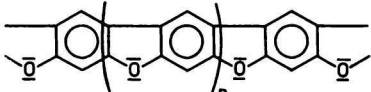
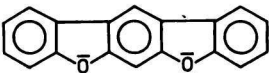
The purpose of this paper was to find out the relationship between the electron structure of the model compounds and the electric conductivity measured in our laboratory or given in the literature.

Computational method, criteria of conductivity

In quantum-chemical high-molecular calculations a compromise should be made between the accuracy of the employed method on the one hand, and the claims made upon the capacity and the computer time on the other. Therefore, in the paper presented the semiempirical INDO method capable of providing the physically actual trends in the study of a number of similar systems has been used, its claims to the computer time and to the computer capacity being also in our conditions acceptable [10—12].

A direct calculation of electron-density distribution within the high-polymer molecules performed by quantum-chemical methods is at present unrealizable due to the restricted speed and capacity of computer. Therefore, for the polymer systems investigated we have chosen the model ones according to Table 1. The central fragments of indicated model systems reproduce satisfactorily the electron-density distribution of the respective polymer-system fragments. It follows that the model systems are suitable for studying the conductivity properties of the appropriate polymer systems. The electron-density distribution in these systems, having a great influence upon the values of all physical quantities, is strongly dependent upon geometrical characteristics. Consequently, the geometries of individual systems were optimized during calculations. As the systems involve a variety of geometric degrees of freedom, the particular systems symmetry was exploited during optimization, the most significant geometric parameters being optimized (minimum value of the total energy). Considering the possibility of applying the shear stress action during the final treatment of the materials studied, one may assume their quasilinear and planar structures, which is simultaneously in agreement with the principle of the closest arrangement displayed in the solid phase. Hence, for all systems studied only their planar structures were taken into account. The correctness of the above-indicated assumptions can be illustrated by the following example: the aromatic rings of a gaseous biphenyl are turned one to another by 45° ; in the liquid polyphenylenes the mutual angular rotation of the aromatic rings is 33° , meanwhile in the crystalline state it is only 3° [13].

Table 1
A survey of model compounds studied

| Polymer | Model system |
|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
|  PPP |  |
|  PPO |  |
|  PPS |  |
|  PPSe |  |
|  PDMPO |  |
|  PAZM |  |
|  CPN |  |
|  PDBF |  |

In this paper eight polymeric systems have been studied, namely: the poly(*p*-phenylene) (PPP); poly(*p*-phenylene oxide) (PPO); poly(*p*-phenylene sulfide) (PPS); poly(*p*-phenylene selenide) (PPSe); poly(2,6-dimethylphenylene oxide) (PDMPO); polyazomethine (PAZM); cyclic polynitrogen (CPN); and poly(dibenzofuran) (PDBF) systems, respectively. These polymers are all structurally similar in that they possess conjugation along the backbone and the carriers created upon redox doping can attain a significant inter- and intrachain mobility along the delocalized orbitals [8].

The conductivity in the conjugated π -electron systems is induced by a considerable mobility of the conjugated π -electrons. On these grounds, the conductivity of the systems examined can be estimated, from the aspect of quantum chemistry, by means of the following criteria:

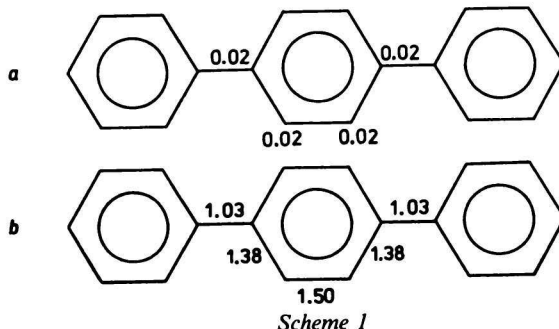
1. By means of a bond order of particular bonds which are mediators of conductivity [14]. The higher the bond order of an appropriate bond, the higher is also the π -electron density between the appropriate pair of atoms. The bond order of the pertinent bond can be characterized either by means of the Wiberg indices or by means of the two-centre part of the total energy of the system representing a contribution of the given bond to the total molecular energy.

2. Another criterion describing the conductivity is the electron-density value of individual atoms of the system. The higher and closer the electron densities on the individual atoms in the whole conjugated system, the lower can be expected the potential barriers in transmitting the electrons through the π -electron skeleton [14].

From these aspects it follows that the ideal systems will be those with equal bond orders of individual bonds and equal charge distribution on the individual atoms taking part in the conductivity process. Simultaneously, it is necessary that the charge values as well as the Wiberg indices be maximum.

Results and discussion

The model system of a PPP chain yields a desirable electron-density distribution within the individual aromatic rings, the charges of individual carbon atoms displaying relatively low values and being practically equal (Scheme 1).



The charge values of atoms (in $|e|$) (a) and the Wiberg indices of individual bonds (b) for the central fragments of the PPP system in the optimum geometry

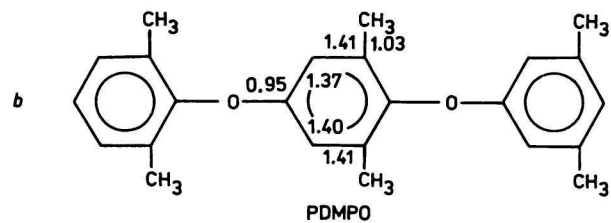
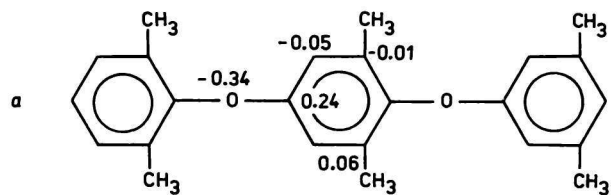
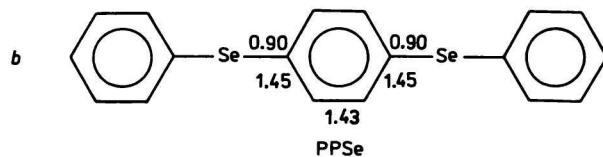
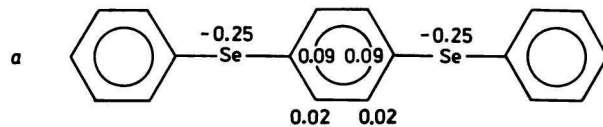
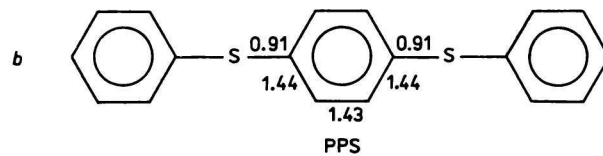
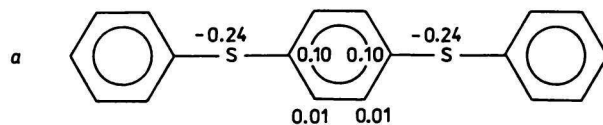
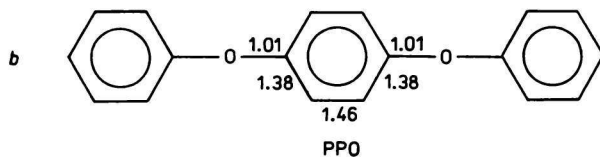
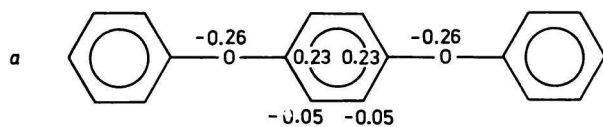
This means that the potential barriers to the transmission of conducting electrons will be minimum. The Wiberg indices values of individual bonds refer to the fact that in the aromatic phenyl-system ring the aromaticity of the benzene system is relatively well retained. It appears that the critical point in the conductivity chain is the bond connecting individual phenyl rings, being, despite a planar arrangement, only partially engaged in the conjugate system.

In the case of model PPO, PPS, PPSe, and PDMPO systems, respectively, the aromatic character of individual phenyl rings will be, to a great extent, retained similarly as in the previous case, which is detrimental to extending the conjugate system over the heteroatomic bridge (Scheme 2). Therefore, the critical point in the conductivity chain will be that occupied by the bonds uniting individual phenyl rings through the appropriate heteroatom. The substitution by methyl groups performed in the case of the PDMPO system results in the increased alternation of charge density in the individual atoms, which is associated with the higher potential barrier in this system. Also, the Wiberg indices values are pointing to the increased conjugation of bonds in the aromatic rings of this system compared to the unsubstituted system, which is, however, detrimental to the higher weakening of the C—O bond. This suggests that this feature is more critical in view of the feasible electrical conductivity.

Similarly as in the previous case, the conjugate system of individual aromatic rings is relatively well preserved also in the PAZM system. This means that the azomethine bridge will be considered, from the standpoint of conductivity, as the critical point, particularly the C—C and C—N bonds exhibiting only the partially dual character (Scheme 3). In the points considered also the alternation of charge density proceeds, which indicates, at the same time, that the potential barriers in those bonds of the chain exist.

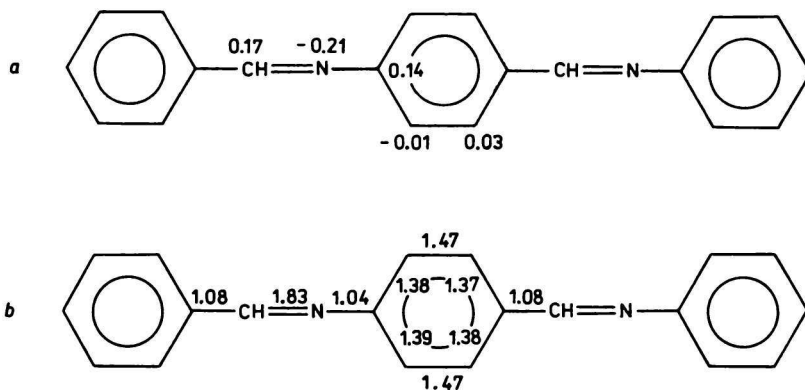
From the conductivity point of view the CPN system (Scheme 4) seems to be useful. Here, in the "upper" C—C chain a remarkable conjugation takes place, the charges of individual atoms being rather small and practically identical, which refers to the minimum potential barriers in this chain. As much greater alternation of charge density as well as the minor conjugation of the π -electron system occurs in the "lower" C—N chain, it can be assumed that the "upper chain" will represent a conductive path of the polymer.

The similar situation but somewhat less favourable occurs in the case of the PDBF system (Scheme 5) in which the "upper" path with its small and approximately identical charges of the individual carbon atoms appears to be, from the conductivity point of view, more convenient. However, here the partial alternation of π -electron density takes place, which is, in terms of conductivity, unfavourable. In the "lower" chain the situation is much more undesirable from the aspect of both the π -electron conjugation and the charge-density distribution along the polymer system.



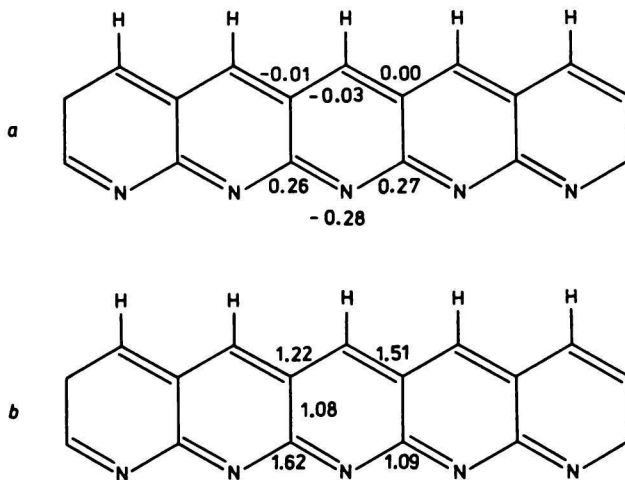
Scheme 2

The charge values of atoms (*a*) and the Wiberg indices of individual bonds (*b*) for the central fragments of the PPO, PPS, PPSe, and PDMPO systems in the optimum geometry



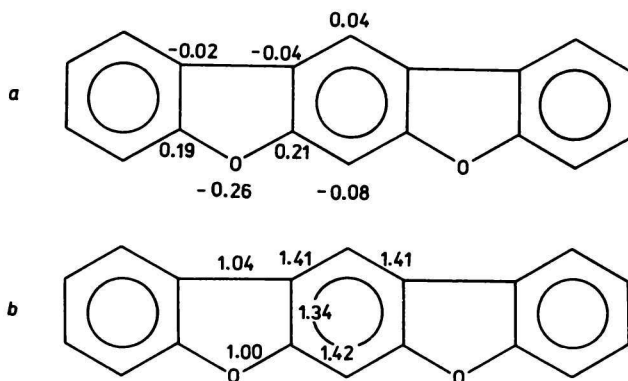
Scheme 3

The charge values of atoms (*a*) and the Wiberg indices of individual bonds (*b*) for the central fragments of the polyazomethine system in the optimum geometry



Scheme 4

The charge values of atoms (*a*) and the Wiberg indices of individual bonds (*b*) for the central fragments of CPN in the optimum geometry



Scheme 5

The charge values of atoms (a) and the Wiberg indices of individual bonds (b) for the central fragments of the PDBF system in the optimum geometry

Table 2

Conductivities (S cm^{-1}) of polymers

| Polymer | Conductivity | Ref. |
|----------------------|-----------------------|-------------|
| PPP ^a | 500—1000 | [8, 15, 16] |
| PPS ^a | 1—100 | [8, 15, 16] |
| PPO ^a | 10^{-3} | [15] |
| PPO | 10^{-13} | This paper |
| PAN ^b | 10^{-6} — 10^{-3} | [18, 19] |
| PTClPSe ^c | 9×10^{-9} | [17] |
| PTClPSe | 1.5×10^{-11} | [17] |

PTClPSe — poly(tetrachloro-*p*-phenylene selenide); PAN — polyacrylonitrile.

a) Doped with AsF_5 ; b) pyrolyzed; c) doped with I_2 .

The published results of conductivities of the above-mentioned polymers are listed in Table 2.

One may conclude from our calculations that from the studied systems the best conducting properties should be exhibited by CPN in the undoped state, and the best insulating ones by PPO.

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