20 Years of Reticulate Doping – Beyond Conductive Properties[*]

by J.K. Jeszka

*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,
ul. Sienkiewicza 112, 90-363 Łódź, Poland, E-mail:jkjeszka@bilbo.cbmm.lodz.pl.
Department of Molecular Physics, Technical University of Łódź, 90-924 Łódź, Poland*

The most interesting results obtained during 20 years of studies on reticulate doped polymers preparation and properties are reviewed. All developed methods of preparation are described and the influence of different parameters on the properties of obtained materials is briefly discussed. The stress is put not so much on the electrical properties but on the aspects of preparation and on the properties, which are interesting but deserved less attention till now like structure, morphology and composition of the microcrystals and their transformations, optical, magnetic and other properties.

Key words: reticulate doping, reticulate doped polymers, conductive polymer composites, organic conductors, molecular metals, organic superconductors, crystallization, ion exchange, polycrystalline layers

1. Introduction

The interest in organic conductors – charge transfer (CT) complexes was largely stimulated by the discovery of highly conductive complexes, which show metal-like temperature dependence of electrical conductivity in a broad temperature range – organic metals [1]. There was a great hope that organic conductors can find in the near future practical applications, especially if Little's idea of excitonic coupling mechanism leading to high temperature superconductivity in organic systems [2] would come truth. All the studies were performed on tiny single crystals or compacted pellets. Neither of these forms seemed suitable for applications, mostly due to their poor mechanical properties. One of possible solutions was embedding such conductive CT complexes into a polymer, thereby combining high electrical conductivity of CT complex and good mechanical properties of a polymer matrix. First attempts were not really successful. To obtain conductive material high loadings (*ca*. 15%) were necessary and the properties were poor [3]. This approach was to find a good solvent and a polymer that could accommodate a lot of CT complex molecules. We tried at first to follow the same way using recently discovered organic metal TTT-TCNQ$_2$ (tetra-

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[*]Dedicated to the memory of Professor Krzysztof Pigoń.

thiotetracene-tetracyanoquinodimethane) (chemical structures of the compounds investigated can be found in Table 1). It was poorly soluble and it was our luck. We had to use a low concentration but we obtained a surprisingly well conductive material! This was the discovery that was the beginning of a new class of conductive polymer composites: reticulate doped polymers (RDP) [4,5].

Since then over 70 scientists from different laboratories in 15 countries published well over 100 papers exploring the possibilities opened by this approach and trying to explain different physical aspects of the phenomenon of reticulate doping. The purpose of this paper is to summarize briefly all aspects of reticulate doping and the most important results obtained during 20 years that passed since the first pioneering paper [4] appeared.

Although reticulate doping was at the beginning oriented mainly towards preparation of useful conductive materials, it turns out that behind simple application aspects there is a wealth of interesting phenomena and properties. Even if it is difficult to suggest for them some application at the moment, they are interesting from scientific point of view expanding our knowledge of new, often unexpected phenomena, which are observed when organic additive synthesis and/or crystallization proceeds in the presence of a polymer. The purpose of this work is to review the most interesting findings (especially these not lying in the main stream of interest – conductivity).

2. General

The general idea behind the slightly misleading term "reticulate doping" is that (contrary to inorganic semiconductors) the active "dopant" forms a separate reticulate phase, which penetrates an inert matrix or at least its surface layer. The electroactive phase is usually a conductive CT complex. The inert matrix till now was always a polymer. Such phase separated composite systems were of course known before, *e.g.* metals or carbon blacks were used as conductive phase. The originality of reticulate doping consists in formation of the conductive phase crystals and of their network *in situ*. This was the main difference as compared with two-phase systems prepared by mixing of polymers with a conductive phase – crystallization *in situ* during polymer matrix solidification leads to a specific organization of the conductive phase within the matrix and allows its control. Indeed, by proper adjustment of the crystallization conditions, it is possible to control the size of dopant grains, their form (aspect ratio) and connectivity of the conductive phase. Practically unlimited possibilities of changing composition of the system: using different conductive complexes, polymers and solvents makes this method very flexible.

This basic approach was used in two variants called one-step and two-step method, which led to three dimensional and two dimensional networks respectively. Because both preparation technique and morphology of the obtained materials are different, they will be discussed separately.

About 50 organic conductors or semiconductors and a dozen of polymer matrices have been used to obtain conductive composites of different mechanical, electrical

Table 1. Most important reticulate doped systems developed (having outstanding properties or studied in more detail) classified by the organic donors used. Additive concentration is typically around 1 wt.% (0.3–2.0 wt.%) and conductivity 10^{-3}–10^{-2} S/cm for bulk conductive and 10^{-4}–10^{-3} S/cm for surface conductive materials (if not specified).
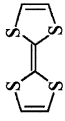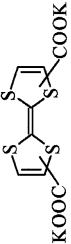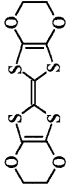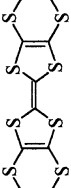
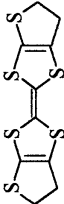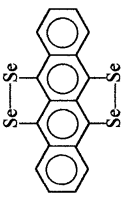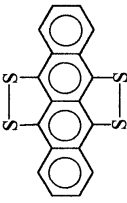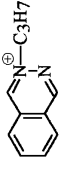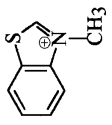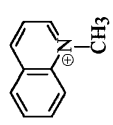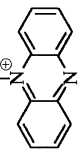| Abbreviation	Current name and chemical structure	Acceptors	Polymer matrices	General characteristic and properties studied in detail
TTF	tetrathiafulvalene	TCNQ I	PE PVDF PC, PS PC PC	bulk-conducting [19,48,72], in PVDF exceptionally high conductivity (up to 1 S/cm metallic down to 250 K [48]), $\sigma(T)$, $\sigma(\omega)$ [52–54,73], morphology and σ dependence on casting conditions [19,72], junctions [68–70], sensors [68] surface-conducting [9,24], magnetic properties (ESR) [60] surface-conducting, [25], thermoelements [71]
TTF-DC	dipotassium tetrathiafulvalene dicarboxylate	$K_3Fe(CN)_6$	PVA	bulk conductive (10^{-2} S/cm for 5%), water-born [61] conductivity *vs.* casting temperature, ESR, NIR at r.t.
BEDO-TTF or **BO**	bis(ethylenedioxy)-tetrathiafulvalene	Br I	PC PC PMMA	surface conducting (10^{-2} S/cm), metallic down to 100 K, colourless, exceptionally high transparency [28,31] surface conducting (10^{-3} S/cm), metallic down to 4 K [28,31,47] dependence of properties on preparation conditions [28] network transformations by ion exchange [42]
BEDT-TTF or **ET**	bis(ethylenedithio)-tetrathiafulvalene	I	PC PMMA PS	surface conducting, films with α-ET_2I_3 [25–27,74], α_T-ET_2I_3 [25–27,74], α_T-ET_2I_3 [25–27] and β-ET_2I_3 [29,32] crystal structures of the salt were obtained, α- to α_T-phase transformation by annealing [27,41,56], films with α_T- and β- form metallic, in the case of α_T onset of superconducting transition 5–6 K [27,55] ($\sigma(T)$ [25–27,74], $\sigma(\omega)$ [26,27,75], optical (UV-Vis-IR) magnetic properties [62], morphology (STM,AFM,SEM) [33,34] ion exchange [37]

Table 1 (continuation)

BET-TTF or **BET**	bis(ethylenethio)-tetrathiafulvalene	I Br IBr	PC	surface conducting (10^{-2}), metallic down to 4 K, transparent [36,40] σ(T), dependence on preparation conditions [36] (for Br)
TSeT	tetraselenotetracene	Cl	PC	bulk conducting (up to 10^1), metallic down to 60 K [22], highly transparent, stable, commercial (Ciba-Geigy), free standing films, coatings, LC display electrodes [11,17,38], σ(T), σ(ω) [11], optical properties, mechanical properties and resistance to bending [17]
TTT	terathiotetracene	TCNQ	PC PMMA PVDF PP PS' PVC ABS epoxy resins	bulk-conducting [4,5,12,14,76] and surface-conducting [9,24], anisotropic systems (electrical [50,51] and optical [63] anisotropy), σ(T) [52,54], σ(ω) [53,54], [4,15] concentration dependence of morphology [15,20] and electric properties [4,12,15,21], influence of casting parameters and of polymer matrix [12,15,19]
		I	PC	surface-conducting[25,26], σ(T), σ(ω) dependence on preparation conditions [26]
		CuCl$_2$	PC	bulk conductive, can be spray deposited [17]
PrPht	N-propylphtalazinium	TCNQ	PC	bulk conducting, exceptionally high conductivity as compared with pure salt (below 200 K higher than that of single crystals) [43], σ(T), magnetic properties vs. temperature [43]

Table 1 (continuation)

MBT	N-methylbenzothiazolium		TCNQ	PS CA	bulk-conducting (10^{-3} S/cm) [10,77], probably produced but not commercialized by Bayer AG $\sigma(T)$ [75], morphology
NMQ	N-methylquinolinium		TCNQ	PS PC CA	bulk-conducting (10^{-4} S/cm) [10,77], probably produced but not commercialized by Bayer AG, $\sigma(T)$ [77], morphology
NMP	N-methylphenazinium		TCNQ	PC PMMA PVB polyacetals epoxy resins	bulk-conducting (10^{-4} S/cm for 4%) [23,76,78,79], concentration and casting conditions dependences, optical properties, morphology

Legend: Abbreviations used for other compounds

TCNQ – 7,7,8,8-tetracyanoquinodimethane, ABS – acrylonitrile-butadiene-styrene copolymer, CA – cellulose acetate, PC – poly(bisphenol-A)carbonate, PE – poly(ethylene), PMMA – poly(methyl methacrylate), PS – poly(styrene), PP – poly(propylene), PVA – poly(vinyl alcohol), PVB – poly(vinyl butyral), PVC – poly(vinyl chloride).

and optical properties. Some of the materials developed were patented [5–12] and produced for several years. Bulk conductive systems have received at first bigger attention, both from scientific and practical point of view. Early results are reviewed more or less extensively in [13–15]. From the application point of view, the most attractive feature of RDP is the very low percolation threshold (below 1 wt.%.), which in turn results in high transparency and negligible deterioration of mechanical properties of the conductive films as compared with pure polymer matrix. The most serious disadvantage is their rather low resistance to organic solvents, which is inherently related to the wet method of preparation.

3. Preparation and morphology

3.1 3D networks – bulk conductive systems.

3.1.1 Preparation – one step method. In materials belonging to these classes a 3D network of additive crystallites penetrates the bulk of a polymer matrix. It is achieved by preparing a solution containing the additive and the polymer in a common solvent and casting a film in appropriate conditions. The composition of the solution, temperature and the solvent evaporation rate must be chosen so that the additive crystallization begins at an appropriate stage of the solvent evaporation and proceeds in non-equilibrium conditions. Because of the several parameters which influence the crystallization obtaining of a good material is usually a matter of both knowledge and art. The influence of different parameters on the network morphology was extensively studied by A. Tracz who developed also a mathematical model of the composite film casting [15,16]. The most important conclusion is that the crucial parameters are crystallization rate and supersaturation at the beginning of crystallization, which in turn are controlled to a large extent by viscosity (beside of solvent evaporation rate and temperature). It is the interplay of viscosity that increases rapidly in the last stage of film formation and of the additive crystallization rate, which determines the habit of the crystals as well as their aspect ratio and, therefore, the percolation properties of the network.

These findings can be used as guidelines, but still different systems can behave in a somewhat different way and the choice of casting conditions can be additionally limited by the requirements of good polymer film quality, its thickness, casting time and so on.

In particular the importance of the film thickness was usually underestimated. It is shown in [15,16] that the thickness of the cast solution is also an important parameter, which influences the crystallization conditions and, thereby, network morphology (sometimes also its composition). In most studies the films were 15–30 µm thick, cast in a usual way. In some cases it was shown that different techniques could also be used. Some systems with TTT salts or TTF-TCNQ were prepared as very thin films by spin-casting or doctor blade technique [17,18]. In the case of $TTT(CuCl_2)_{0.45}$ or tetraselenoteracene halides (*e.g* $(TSeT)_2Cl$) spray deposition can also be used [17].

3.1.2 Morphology. For most of the systems studied the morphology of the crystalline conductive network was studied using optical microscopy. Because the additive crystals are embedded in the polymer matrix, the studies using electron microscopy are difficult and are very scarce. Even spin cast films are too thick for transmission microscopy and only in some systems the crystals can be observed on the surface using standard scanning electron microscope [19]. The best results were obtained using TEM, provided with a scanning attachment, which allows using high energy electrons which penetrate deeper into the polymer matrix [20]. These studies revealed nanoscopic structure of the networks of TTT-TCNQ, which consisted not of branched microcrystals, as suggested by optical microscopy, but bundles of several μm long and only *ca*. 200 nm thick whiskers [20–22]. At this time it was not realised that these were one of the first organic nanowires obtained.

Most images in the literature presented the morphology of the best conductive systems obtained by the authors. Generally good results, *i.e.* conductive systems at low additive content, were obtained for additives, which form crystals of high aspect ratio (as expected from percolation theory). An additional feature observed in most cases was branching of microcrystals, leading in many cases to dendritic structures although *e.g.* in [11,17] branching is not observed and percolation threshold is low. The influence of casting conditions on film morphology is best documented in [15,16]. For the same system polymer-solvent-additive, the crystal form strongly depends on the crystallization conditions. The rule is that the more rapid and the more effective is the network formation, which is due to growth of non-equilibrium forms of very high aspect ratio – long branched needles or whiskers. Topology of such networks could be described in terms of fractal theory, but because of the difficulty in detailed imaging of the network only few attempts have been made [23].

3.2   2D networks – surface conductive systems.

3.2.1 Preparation – two step method. In the materials belonging to this class a quasi-2D network of additive crystallites penetrates the bulk of polymer matrix. It is achieved in a two-step process: first preparing a solution containing the additive and the polymer in a common solvent and casting a film at elevated temperature. The composition of the solution, temperature and solvent evaporation rate must be chosen so that the additive crystallization does not take place. The film obtained contains a "molecularly" dispersed additive, so its electrical conductivity is practically the same as that of pure polymer. Such film is in the second step treated with a solvent vapour, which increases the molecular mobility and results in swelling of the polymer matrix and controlled crystallization of the additive in the surface layer of the film. Under appropriate conditions, the network is continuous and after drying a surface conductive material is obtained [9,24].

Another procedure developed later [25] is to start with a solid solution of a donor alone and to treat it with mixed vapours of a solvent and of a volatile electron acceptor, like iodine or bromine. This method was the most widely used, because it allowed using as additives an interesting class of molecular metals and superconductors,

based on bis(ethylene(tetrathiofulvalene)) abbreviated as BEDT-TTF or ET [25-27] and its oxygen substituted analogue BEDO-TTF or BO [28].

In both methods there are three most important parameters, which should be optimized: kind of the solvent (or mixture of solvent), the treatment time and the vapour partial pressure. Usually procedure is such that the solvent, which allows some flexibility in other parameters, is selected first and then the optimum time is found. In the case of treatment with acceptor vapours, solutions *e.g.* of iodine in methylene chloride are used, thus an additional very important parameter is the acceptor concentration [25–29]. Vapour treatment is usually performed at room temperature, but in principle the temperature can also be changed to control better the crystallization conditions and in some cases to obtain crystallization of a different phase. This approach was successfully used to obtain directly the superconducting β-ET$_2$I$_3$ form [30] (elevated temperatures *ca*. 90°C) and transparent colourless BO iodide (low temperatures) [31]. It is also possible to swell the pristine polymer film with a liquid solvent, usually with appropriate mixture of solvents, containing (if needed) an electron acceptor. This method gives conducting films with less uniform properties and it was used only for TTF-TCNQ [8] and non soluble organic superconductor ET$_2$CuNCS [32].

3.2.2 Morphology. Micro- or nanocrystals forming 2D networks on the film surface are generally much smaller and they can hardly be visible under optical microscope. Their morphology was, therefore, studied using first SEM [20,28–30] and later AFM and STM [33,34]. In most cases the microcrystals have a form of platelets (sometimes elongated but not needles) lying flat parallel to the surface of the film, so the material is highly anisotropic. The network is therefore quasi-2D not only from the point of view of electrical conductivity, but also from the point of view of the orientation of the crystal c-axis perpendicular to the platelet plane, which is usually the plane of high conductivity.

Therefore, such a RD film is as a matter of fact composed of an insulating polymer support (which is practically additive-free) and a submicrometer layer of oriented nanocrystals on one surface. This led Laukhina *et al*. to use the term "bilayered films" (BL) as equivalent of RDP films, obtained using two step method [35,36]. The high orientation of nanocrystals allows X-ray studies of the subtle changes of the crystal structure *e.g.* [34,37]. All the imaging techniques mentioned above allow visualization of the film surface. To find out if there are microcrystals lying deeper in the polymer, etching techniques must be used. Using chemical and plasma etching it has been found that there are also somewhat deeper laying, usually bigger, well formed microcrystals [34].

It was evident from the beginning that some crystals are not covered by the polymer, because the good electrical contact to such systems can be obtained by gentle touching with a thin metal wire. It was, however, surprising that so many crystals are on the surface that even STM observations (which require in principle that the sample is conductive on all its surface in submicrometer scale) are possible [34]. Morphology of 2D networks is different in some systems (*e.g.* PC/TTT-TCNQ), where the addi-

tive also forms platelets (contrary to 3D systems with the same CT complex), but these platelets are oriented perpendicular to the film surface [20].

3.2.3 Role of the solvent. In the case of the two step method, the role of the solvent is different in the two steps. In the first step a good solvent should be chosen, because it enables an easier preparation of the solid solution (polymer film with molecular dispersion of the additive). It is generally much easier if a donor (or acceptor) and not a CT complex is to be dissolved. In the second step, when the film is treated with solvent vapours, solubility of the additive must be low, thus, poor solvents give good results. It is not of primary importance, if the additive solubility is so low that the pristine film has to be obtained at high temperature. It is also important if the solvent is a good or poor solvent of the polymer, because it determines the quality of the network in a different way for different additives.

For instance in the one of the most thoroughly studied system PC+ET_2I_3 it has been found that the best results are obtained using methylene chloride and tetrahydrofurane, while treatment with for instance chlorobenzene results in crystallization of the organic metal (as confirmed by UV-Vis-NIR spectra), but the crystals do not form a conductive network. Ethylenechloride or 1,1,2-trichloroethane give (at room temperature) the films, which become conductive only after additional annealing. It is due to a too high iodine content in the microcrystals, but reduction of iodine concentration also yields non conductive films, because additive crystallization takes place also deep within polymer film (see [25,29] for more detailed discussion). The kind of solvent can also have an influence on the crystal structure *e.g.* only a small amount of o-dichlorobenzene in the film (cast from this solvent) leads to crystallization of β-ET_2I_3 instead of α-ET_2I_3 [29]. Generally, it seems that in the case of plate-like crystals good quality, well oriented networks are obtained when the crystallization proceeds on the phase boundary solvent vapour/solution. The author's experiments on ET solution without polymer placed in I_2 vapours, in which a layer of ET_2I_3 crystals formed at the interface, confirm this hypothesis. On the other hand, in the case of well soluble complexes, swelling with poor solvents of the polymer or even solvents that can only slightly swell the matrix, leads to conductive networks. For instance, in the case of PC/TTF-TCNQ system conductive networks were obtained by swelling with acetone or dioxane.

3.3 Other preparation methods. Reticulate doped polymers were also obtained using modified methods which should be briefly described. To obtain bulk conductive systems, using practically insoluble salts, people from Ciba-Geigy laboratories modified the one step method. TSeT halides networks in polycarbonate were obtained by selective chemical redox reaction during film casting. TSeT was oxidized *in situ* with organic perhalides. The driving force is the insolubility of the salts formed, so the growth of the microcrystals starts immediately after addition of halogenacceptor. In such a case the morphology of the network is not influenced by the type of polymer or solution viscosity [38] (contrary to usual situation in the one step method). Bulk conductive 3D conductive networks can also be obtained in two steps. Some organic electron donors (*e.g.* TTT) can crystallize in polymer matrices forming

non-conductive, one-component continuous networks. Such networks can be subsequently rendered conductive by treatment with gaseous acceptor *e.g.* iodine. An important point is that donor microcrystals are transformed into corresponding CT complexes without loosing continuity and connectivity of the network [34]. The term 'three-step method' has been recently used by Laukhina *et al.* [40] to describe the two step method, followed by transformation of the conductive material *in situ*. This approach was used first to obtain organic superconductor network by phase transformation upon annealing at elevated temperature [27,41]. This term can also be used in the future (but till now it was not) to describe a two-step method, followed by network transformations by ion exchange (as described in [42]).

3.4 Network composition. Many organic donors and acceptors can form crystals of different stoichiometry, depending on crystallization conditions and donor-to-acceptor (D-A) ratio in the solution. As the crystallization conditions during RDP preparation are non-equilibrium and change in time, it should be expected that stoichiometry can be different from the input D-A ratio. Especially in 2D systems, prepared by treatment with solvent/halogen vapours, the acceptor concentration in the swollen layer depends on the distance from the surface and changes in time. Generally, it is difficult to prove real stoichiometry. In 3D systems in no case a direct evidence from X-ray diffraction could be obtained. Indirect arguments were provided in many systems by studying conductivity dependence on donor-to-acceptor ratio. In few cases the conductivity alone proves formation of a new, unknown before well conductive phase: when RDP conductivity at low loading is similar or higher than conductivity of pure additive crystals [43,44]. In some cases it is possible to determine stoichiometry by UV-Vis spectra. The difference in absorption between complexed and neutral molecules must be big enough to be used for quantitative measurements (usually it is not, because of overlapping of absorption maxima of different components). Such analysis was, therefore, done only in few cases, the best documented being TTT-TCNQ in PC [45]. The most interesting result shown in this paper is that for the same input D-A ratio, the network stoichiometry strongly depends on the casting temperature *i.e.* on the crystallization rate. Different stoichiometry of whiskers was confirmed latter by ESR studies [46].

In the 2D systems with halogen acceptors (mostly iodine) it was shown that the stoichiometry of the crystals, being formed, depends on halogen concentration during vapour treatment. In particular, using too high concentration leads to formation of non-conducting salts. However, in this case, due to high orientation of microcrystals, it is possible to use UV-Vis and Raman spectra as well as X-ray diffraction to identify the not only the stoichiometry but even the crystal form (α, β *ect.*). More detailed up to date discussion of the influence of different phenomena can be found in [27,33,34].

3.5 Network transformations. Reticulate doping technique is unique in providing an organized stabilized assembly of micro and nanocrystals of usually well defined size and orientation. Especially in the case of 2D networks, these crystals are well oriented and located in the surface layer or directly on the surface. It provides a unique opportunity to perform and study their properties and transformations. Con-

trary to millimetre-size crystals such submicroscopic, often less than 50 nm thick crystallites, usually transform quickly, completely and the crystal "survives" phase transformations. In other cases the network can recrystallize, which leads to new microcrystalline network.

The most thoroughly studied transformation was the temperature induced transformation of the kinetically favoured α-phase to superconducting β- or α_T-phase of Et_2I_3 (see [27] for a more extensive discussion). Even more interesting is, however, the possibility of ion exchange without loosing continuity of the network. Different aspects of this phenomenon are discussed in [34,42,47].

3.6 The role of polymer matrix. The fact that not only mechanical properties of the film, but also the morphology of the conductive network depends on the chemical structure of the polymer matrix was discovered at the very beginning. The fundamental role of the "inert" polymer in the reticulate doping process is something that makes this technique particular and flexible. Contrary to widely used methods of mechanical mixing of polymers with fillers in RD, the polymer matrix is not just an inert binder. Of course in the solid film its role is similar – it determines the mechanical properties and to a large extend resistance to heat, solvents *etc*. However, in RD the polymer-solvent system is an active component, controlling the additive crystallization. Starting solutions contain usually around 5% of the polymer used, so it is the solvent that determines the additive solubility. However, the requirement of high viscosity during additive the crystallization imposes that the polymer concentration at this stage of solvent evaporation is much higher (of the order of 50%) and growing up to around 95% at the moment of solidification when further crystallization is hindered. It means, that the kind of polymer (its polarity specific interactions) has a dominant influence on the additive solubility and, therefore, crystallization conditions at this stage. It has been found that in some polymers *e.g.* chlorinated PS crystallization of the same additive that formed microcrystals in PS was practically not observed, in spite of using the same or even higher concentration. Chemical structure and stiffness of the polymer chain has also, beside of molecular weight, a profound influence on the solution viscosity. Very recently it has been found, that also mechanical stress of the polymer matrix, due to its contraction during solidification or cooling, can have a profound influence on the additive crystals properties (see [34] for detailed discussion).

3.6.1 Semicrystalline polymeric matrices – mutual influence on crystallization of an additive and the polymer. Semicrystalline polymers can also be used as macromolecular matrices [19] and in such case crystallizations of the two components influence each other. From the point of view of the network formation, the crystallization of the polymer matrix is generally advantageous, because the low molecular weight additive is "pushed out" of the growing polymer crystallites and the effectiveness of its crystallization is high. In polyolefines (PE, PP) practically all the amount of the additive crystallizes as evidenced by UV-Vis spectra. In the case of polymers, which can be used either as amorphous or as semicrystalline (*e.g.* PS), this effect and its influence on the network morphology is most clearly observed. In principle, depending on the casting conditions it is either the additive or the polymer

which crystallizes first [19]. In most cases, however, the networks which have good connectivity are obtained under such conditions that the additive crystallizes first. In such a case, the influence of the additive network on polymer crystallization is also observed, leading to modified film properties. Transcrystallization of the polymer on organic conductor micocrystals has been observed in PE, PP isotactic PS and PVDF. More detailed studies have been performed on PVDF, where the presence of TTF-TCNQ network was found to lead also the preferential crystallization of PVDF, as a piezoelectric β-phase, instead of electrically non-active α-phase [48]. An influence of TTF-TCNQ network on crystallization of PE and on mechanical properties of the films (also oriented by stretching) was also studied [49]. Nucleation of polymer crystallization on the microcrystals of the additive can have an important influence on polymer film properties. For instance polypropylene films cast with 1% of TTF-TCNQ have good mechanical properties, while cast at the same conditions without the additive are granular, non continuous.

3.7 Anisotropic networks. The possibility to control network formation by changing crystallization conditions was also used to obtain highly anisotropic networks and thereby films of high electrical and optical anisotropy [50,51]. The method developed was called zone casting technique. It consists in a continuous providing of solution, being cast on a moving support using a flat nozzle. Solvent evaporation takes place in a narrow zone of solution meniscus and the resulting gradient of the additive concentration makes the crystallization conditions highly anisotropic with preferential crystal growth the direction of move. In these experiments PC, PE and PP were used as polymer matrices and TTT-TCNQ or TTF-TCNQ as conductive phase [50,51].

4. Properties

4.1 Electrical properties.

Electrical conductivity was always considered to be the most interesting property of RDP and it is reported in practically all papers on these materials. However, systematic studies involving temperature and frequency dependence are scarce. The most complete and detailed investigations were carried by Ulański *et al*. for selected systems [52–54 and references cited therein]. There are several aspects of electrical properties of such systems that are interesting and astonishing: low percolation threshold (even below 0.003 [21]), network continuity and surprisingly high conductivity (often higher than the upper limit obtained using Clausius-Mossotti approximation). Detailed results for different systems and their discussion can be found in [12–14,52,54] and it will not be presented here. It is worth to note that also supported current densities are surprisingly high (15–25 A/cm^2 at 1% additive content [17]). It means that the current densities in the conductive crystals must be of the order of at least 2000 A/cm^2 (similar estimation for different systems was made in [52,54]). This can only be possible, because of an efficient dissipation of Joule's heat, due to embedding of the microcrystals in a polymer matrix.

In recent years most of the effort was, however, devoted to surface-conducting systems, in which conductive networks are formed of 2D organic metals and especially superconductors. First fully organic composite, showing superconductive transition, was obtained by thermal transformation of α-ET_2I_3 into superconductive β-phase (called usullay α_T) [55]. Properties of the obtained materials and different aspects of film preparation and transformation to the superconductive phase studied, using different techniques, are summarized in [27]. The most interesting point is that in spite of polycrystalline morphology of the network and its recrystallization during thermal transformation [34,56], an onset of superconductive transition at around 4K is observed in d.c. measurements [55] (in spite of several attempts by different groups it was never achieved in polycrystalline layers without a polymer matrix [27]). The fact, that the transition temperature was lower by *ca*. 3 K as compared with single crystals transformed in the same way, was recently explained by Tracz [57,58] as due to the pressure of the polymer matrix at low temperatures, due to different thermal expansion factors of the organic metal and the polymer matrix. Generally, it should be stressed that properties of the 2D networks, formed of organic conductors in which electronic structure is quasi-two dimensional, are not much different from the corresponding single crystals. It is not the case if the crystals are quasi-1D conductors, because in such case the network properties are much more sensitive to defects. Thermoelectric power and its temperature dependence has been measured only in several systems [59], although it provides a valuable information, complementary to conductivity. This is due to different weight contribution of imperfect network elements. The sign of thermopower can show metallic character of dominant network elements in spite of semiconductor-like temperature dependence of conductivity (*e.g.* in PE+TTF-TCNQ).

4.2 Magnetic properties.

The magnetic properties, mostly electron spin resonance (ESR) are a useful and sensitive tool, giving insight into properties of the crystalline network, because most of organic conductors give strong ESR signals, while neutral molecules including polymer matrix give only negligible impurity signals. It is, therefore, surprising that there are only few papers in which this technique was used. Thorough studies were done for TTT-TCNQ and TTF-TCNQ networks in PC [46,60]. It was shown that detailed analysis of ESR spectra can provide information on the stoichiometry of the crystals, concentration of defects and average orientation. The conclusions, which probably apply also to other similar systems, were that (a) orientation of the microcrystals in the plane of the film is high (higher than expected, also in the case of 3D networks), (b) concentration of defects, generally quite high 1–3% (as expected for non-equilibrium crystallization), is non-uniform and perfection of the structure of a considerable part of the network is quite good (below 0.2% of defects). ESR studies of the networks of cation radicals TTF dicarboxylate in poly(vinyl alcohol) have also shown high orientation of the microcrystals in the plane of the film [61]. By comparison with single-crystal data on g-factor splitting and temperature dependence of linewidth and spin susceptibility, one can identify the crystal phase and/or stoi-

the additive degradation, which is responsible for deterioration of the material properties, although in many RDPs even after annealing for weeks the conductivity decreases, but still remains high (*e.g.* [17]). In the commercial films produced by CIBA-Geigy (TSeT)$_2$Cl (stable even above 470 K) was used.

Resistance to organic solvents, similar to those used for preparation, is of course low. In most cases it is the polymer matrix, which is much more sensitive than the additive. Most of the systems studied are resistant to water. Recently RDP were obtained also from water solutions [61] and these are more resistant to organic solvents, but of course not to water. These systems based on poly(vinyl alcohol) are also biocompatible. Last but not least it should be mentioned that diffusion controlled crystallization allows a reduction of the size of the crystals obtained down to nanoscopic level [20,21,34,64]. This possibility has been little exploited till now and new properties of organic conductors related to nanosize can be found.

5. Applications

The first and the simplest idea of application was to use RD polymer films, as antistatic films mostly for packaging sensitive electronic elements. Also for shielding and absorbing of electromagnetic radiation (first of all in military applications) conductive needles embedded in an insulating matrix are a material of choice. No information on such applications was, however, widespread.

High transparency of some RDP's (up to 95% both for 2D and 3D systems) makes them potentially interesting for preparing electrodes in displays, based on liquid crystals and smart windows [17]. Of several attempts [17,65–67] only Ciba-Geigy [17,67] presented displays some 200 cm^2 big. The biggest problem in this case is generally the low resistance of organic conductors to chemical and especially electrochemical degradation, due to ions present in liquid crystals. The organic conductor used must be very stable or it must be protected by an additional layer, which however, is not much discouraging since ITO electrodes are usually also covered by a polymer layer.

Several papers were devoted to studies of heterojunctions of RDP with metals or inorganic semiconductors [68–70]. Rectifying junctions (rectification ratio up to 10^4) were obtained with some metals and especially with Si. Such junctions are more sensitive to some gases than the conductivity of the film itself and sensor properties were studied [68]. Gas sensors can also be made using single component networks [39], in which the conductivity changes by several orders of magnitude on doping (as documented for iodine) and transformations of 2D networks especially of BO salts, which can be reversibly cycled between forms which differ in conductivity and optical properties [42]. Different thermoelectric power makes possible the preparation of thermocouples based on two different RDP films or RDP and metals [71]. Such thermocouples are flat and very thin (below 40 μm), so they can be useful for measuring temperature gradients between flat surfaces.

6. Conclusions

The purpose of this work was to present a concept, which led to production of materials using a unique feature of organic conductors – solubility in organic solvents and controlled crystallization and the most important results, collected in Table 1. Summarizing briefly 20 years of studies we find that many ways, leading to new possibilities and new phenomena, have been exploited to a limited extend. From the scientific point of view, it should be stressed that especially the two-step method provides highly oriented polycrystalline layers that show the properties very similar to those of single crystals. It gives a unique possibility to study properties of the crystals and their interactions with environment.

At the moment it seems that the immense progress, made in last years in developing new materials based on organic conjugated polymers, rewarded in 2000 with the Nobel Prize, has took most of the potential market and interest for organic conductors. However, the systems involving low molecular weight "organic metals" have still a considerable potential, also from practical point of view.

REFERENCES

1. Coleman L.B., Cohen M.J., Sandman D.J., Yamagishi F.G., Garito A.F. and Heeger A.J., *Solid State Commun.,* **12**, 1125 (1973).
2. Little W.A., *Phys. Rev.,* **134A**, 1416 (1964).
3. Mizoguchi K., Kamiya T., Tsuchida E. and Shinohara I., *J. Polym. Sci., Chem. Ed.,* **17**, 649 (1979).
4. Jeszka J.K., Ulański J. and Kryszewski M., *Nature*, **289**, 390 (1981).
5. Jeszka J.K., Ulański J. and Kryszewski M., Polish Pat. P-116850 (1979).
6. Tracz A.T., Pakula T., Ulański J. and Kryszewski M., Polish Pat. P-231177 (1981).
7. Pęcherz J. and Kryszewski M., Europ. Pat. EP-OS174871 (1984).
8. Kim O.-K. and Fox R., US Pat. 4622226 (1985).
9. Kryszewski M., Jeszka J.K., Ulański J. and Tracz A., Europ. Pat EP-0134026 (1987).
10. Hocker J., Dhein R. and Merten R., Europ. Pat. EP- 0034300 (1980).
11. Finter J., Hilti B., Mayer C.W., Minder E. and Pfeiffer J., Europ. Pat. EP-285564 A1 (1988).
12. Kryszewski M., Jeszka J.K., Ulański J. and Tracz A., *Pure Appl. Chem*., **56**, 355 (1984).
13. Heywang G., "Elektrisch leitende Kunststoffe", Mair H., Roth S. (Eds.), Munich, 1989, p. 347.
14. Ulański J. and Kryszewski M., "The Encyclopedia of Advanced Materials", Bloor D., Brook R.J., Flemings M.C. and Mahajan S. (Eds.), Pergamon Press, Oxford, 1994, vol. 3, pp. 2301.
15. Tracz A. and Kryszewski M., *Macromol. Chem. Suppl*., **15**, 219 (1985).
16. Tracz A., PhD Thesis, Centre of Molecular and Macromolecular Studies, Łódź, Poland (1988).

17. Bleier H., Finter J., Hilti B., Hofherr W., Mayer C.W., Minder E., Hediger H. and Ansermet J., *Synth. Met.*, **55-57**, 3605 (1993).
18. Jeszka J.K. and Tracz A., unpublished results.
19. Tracz A., Jeszka J.K, Ulański J. and Kryszewski M., *Chemtronics*, **1**, 50 (1986).
20. Jeszka J.K., Kobayashi T., Tracz A., Ulański J., Kryszewski M. and Yamamoto N., *Synth. Met.*, **35**, 215 (1990).
21. Tracz A. and Jeszka J.K., *Synth. Met.,* 41–43, 1831 (1991).
22. Finter J., Mayer C.W., Ansermet J.P., Bleier H., Hilti B., Minder E. and Neuschafer D., *Synth. Met.*, **41–43**, 951 (1991).
23. Srivastava D.N. and Singh R.A., *Synth. Met.*, **96**, 235 (1998).
24. Jeszka J.K., Tracz A., Ulański J. and Kryszewski M., *J. Phys. D:Appl. Phys.*, **18**, L167 (1985).
25. Jeszka J.K. and Tracz A., *Polym. Adv. Technol.*, **3**, 139 (1992).
26. Jeszka J.K*., Mat. Sci. Forum*, **191**, 141 (1995).
27. Ulański J., Tracz A., Jeszka J.K., Laukhina E., Khomenko A., Polanowski P., Staerk D. and Helberg H.W., Electrical and Related Properties of Organic Solid State, Kluwer Acd. Pub., Dordrecht, 1997, p. 241.
28. Jeszka J.K., Tracz A., Sroczyńska A., Kryszewski M., Yamochi H., Horiuchi S., Saito G. and Ulański J., *Synth. Met.,* **106**, 75 (1999).
29. Tracz A., Jeszka J.K., Sroczyńska A., Ulański J. and Pakuła T., *Adv. Mat. Opt. Electr.*, **6**, 335 (1996).
30. Jeszka J.K., Tracz A., Sroczyńska A., Ulański J., Müller H. and Kryszewski M., *Synth. Met.*, **103**, 1820 (1999).
31. Tracz A., Jeszka J.K., Sroczyńska A., Schrader S., Ulański J. and Kryszewski M., *Adv. Mat. Opt. Electr.*, **6**, 330 (1996).
32. Jeszka J.K., Sroczyńska A., Tracz A. and Müller H., *Synth. Met.,* **94**, 31 (1998).
33. Tracz A., Jeszka J.K., Pakuła T. and Rabe J.P., *Synth. Met.,* **94**, 17 (1998).
34. Tracz A., this issue, *Polish J. Chem.*, **76**, 457 (2002).
35. Laukhina E., Tkacheva V., Shibaeva R., Khasanov S., Rovira C., Veciana J., Vidal-Gancedo J., Tracz A., Jeszka J.K., Sroczyńska A., Wojciechowski R., Ulański J. and Laukhin V., *Synth. Met.*, **102**, 1785 (1999).
36. Mas-Torrent M., Laukhina E., Rovira C., Veciana J., Tkacheva V., Zorina L. and Khasanov S., *Adv. Funct. Mater.*, **11**, 299 (2001).
37. Tracz A., *Synth. Met.*, **109**, 236 (2000).
38. Krohnke Ch., Finter J., Mayer C.W., Ansermet J., Bleier H., Hilti B., Mayer C.W., Minder E. and Neuschafer D., *Cont. Topics in Polym. Sci.,* **7**, 111 (1988).
39. Jeszka J.K., *Polym. Adv. Technol.,* **5**, 236 (1994).
40. Laukhina E., Rovira C. and Ulański J., *Synth. Met.,* **121**, 1407 (2001).
41. Ulański J., Jeszka J.K., Tracz A., Glowacki I., Kryszewski M. and Laukhina E., *Synth. Met.*, **55–57**, 2001 (1993).
42. Tracz A., *J. Appl. Polym. Sci.*, in press.
43. Tracz A., Jeszka J.K., Ulański J., Boiteux G., Firlej L., Graja A. and Kryszewski M., *Synth. Met.*, **24**, 107 (1987).
44. Pęcherz J., Firlej L., Jeszka J.K.,Ulański J. and Kryszewski M., *Synth. Met.*, **37**, 189 (1990).
45. Tracz A., Jeszka J.K., Shafee E.El., Ulański J. and Kryszewski M., *J. Phys. D:Appl. Phys.*, **19**, 1047 (1986).
46. Jeszka J.K., *Synth. Met.,* **59**, 151 (1993).
47. Tracz A., Jeszka J.K., Sroczyńska A., Ulański J., Płocharski J., Horyuchi S., Yamochi H. and Saito G., *Synth. Met.* **86**, 2173 (1997).
48. Choi C.H., Tracz A., Jeszka J.K., Boiteux G., Seytre G., Ulański J. and Kryszewski M., *Synth. Met.* **37**, 181 (1990).
49. Genetti W.B, Lamirand R.J. and Grady B.P., *J. Appl. Polym. Sci.,* **70**, 1785 (1998).
50. Burda L., Tracz A., Pakuła T., Ulański J. and Kryszewski, *J. Phys. D:Appl. Phys.*, **16**, 1737 (1983).
51. Tracz A., Shafee E.El, Ulański J., Jeszka J.K. and Kryszewski M., in Electronic Properties of Conjugated Polymers, H. Kutzmany, M. Mehring and S. Roth (Eds.), Springer Verlag, Berlin, Heidelberg, 1989, p. 442.
52. Ulański J., *Synth. Met.*, **39**, 13 (1990) and *ibid*. p.25.
53. Ulański J., Lupke G., Dressel M. and Helberg H.W., *Synth. Met.*, **37**, 165 (1990).

54. Ulański J., *Zeszyty Naukowe Politechniki Łódzkiej*, **610**, (1990).
55. Laukhina E.E., Merzhanov V.A., Pesotskii S.I., Khomenko A.G., Yagubskii E.B., Ulański J., Kryszewski M. and Jeszka J.K., *Synth. Met.,* **69**, 797 (1995).
56. Ulański J., Tracz A., Jeszka J.K., Laukhina E. and Pakula T., *Synth. Met.,* **85**, 1591 (1997).
57. Tracz A., *Synth. Met.*, **123**, 477 (2001).
58. Tracz A., Wosnitza J., Barakat S., Hagel J. and Müller H., *Synth. Met.*, **120**, 849 (2001).
59. Jeszka J.K., Tracz A. and Kryszewski M., *Synth. Met*., **55–57**, 109 (1993).
60. Jeszka J.K., *Synth. Met.,* **45**, 15 (1991).
61. Hong Y., Benz M.E. and Miller L., *Synth. Met.,* **68**, 281 (1995).
62. Laukhina E., Ulański J., Khomenko A., Pesotskii S., Tkachev V., Atovmyan L., Yagubskii E., Rovira C., Veciana J., Vidal-Gancedo J. and Laukhin V., *J. Phys. I France*, **7**, 1665 (1997).
63. Tracz A., Shafee E.El., Ulański J. and Kryszewski M., *Synth. Met*., **37**, 175 (1990).
64. Jeszka J.K., Tracz A., Wostek D., Boiteux G. and Kryszewski M., *Synth. Met*., **71**, 2205 (1995).
65. Resnikov Y., Tracz A. and Kryszewski M., Sov. Pat. SU 1646403.
66. Galloppa A., Cataldo F., Campoli F., Beccherelli R., d'Alessandro A., Ferrara V. and Maltese P., *Mol. Cryst. Liq. Cryst*., **290**, 129 (1996).
67. Fergason N.S. and Fan N.S., Europ. Pat. EP 357234 A2 (1989).
68. Remaki B., Jullien D. and Jouve C., *Sensors Actuat. A*, **33**, 85 (1992).
69. Jeszka J.K., Tracz A., Boiteux G., Seytre G. and Kryszewski M., *Synth. Met*., **71**, 2205 (1995).
70. Jeszka J.K., Tracz A., Boiteux G., Seytre G. and Kryszewski M., *Acta Phys. Polonica A*, **88**, 533 (1995).
71. Tracz A., Jeszka J.K. and Kryszewski M., *J. Appl. Polym. Sci.,* **52**, 1005 (1994).
72. Tracz A., Ulański J and Kryszewski M., *Polym. J.*, **15**, 635 (1983).
73. Jouve C., Jullien D. and Remaki B., *Synth. Met*., **66**, 197 (1994).
74. Polanowski P., Tracz A., Ulański J. and Dormann E., *Synth. Met.,* **109**, 235 (2000).
75. Polanowski P., Ulański J., Wojciechowski R., Tracz A., Jeszka J.K., Matejcek S, Dormann E., Pongs B. and Helberg W., *Synth. Met.*, **102**, 1789 (1999).
76. Quill K., Underhill A.E. and Kathirgamanathan P., *Synth. Met.*, **32**, 329 (1989).
77. Hocker J., Jonas F. and Müller H.-K, *Angew. Makromol. Chem*., **145/146**, 191 (1986).
78. Kim O.K., *Org. Coat. Appl. Polym. Sci. Proc.,* **48**, 652 (1983).
79. Kim O.K., in "*Polymers in Electronics*", Davidson T. Ed., *ACS Symp. Ser.*, **242**, 41 (1984).