

STRUCTURE AND ELECTRICAL PROPERTIES OF POLYMERS WITH AMORPHOUS
AND CRYSTALLINE DOPANTS

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Abstract - Polymers are usually dielectrics. The specific chemical constitution of polymer chains makes it possible to obtain semiconducting systems which after suitable doping in the solid state can be transformed into systems which exhibit high electric conductivity eg. polyacetylenes. However these interesting materials are unstable in ambient conditions. Taking into consideration the basic knowledge of highly conducting CT complexes of low molecular weight compounds - organic metals - a new class of conducting polymeric materials has been obtained with a correlated network of crystalline, conducting CT complexes grown in different inert polymers. These systems exhibit a high conductivity in the dark at a concentration of additives as low as 1 wt% and are very stable in ambient conditions. The preparation, structure, and the electrical and mechanical properties of these systems are discussed and compared with those obtained when low molecular weight CT complexes are molecularly dispersed in polymers leading only to enhanced photoconductivity. These new systems are also compared with the mixtures obtained using CT complexes and polymers which exhibit high conductivity only when the concentration of additives is of the order of 30 wt% which leads to an important change of all properties of the system. The discovered highly conducting systems open a new field in polymer science and organic solid state physics because a variety of CT complexes and polymer matrices can be used and various isotropic and anisotropic systems can be obtained. Studies on these materials will shed light on the basic problems of charge transport in such systems and will lead to novel materials with possible practical applications showing the importance and specific properties of organized molecular assemblies in polymer matrices.

INTRODUCTION

Many polymers exhibit some properties characteristic of metals. These include good strength, elasticity, frictional resistance, toughness, etc. and because of the ease of preparation and processing and low density, such polymers have long replaced metals in many applications. Only the most important property of metals, electrical conduction, was not obtained in polymers until very recently. Attempts to prepare polymers which exhibit high electrical conductivity have been made by many academic and industrial centers. The significance of this question is clear because one would like to process such materials in the form of films or fibers using well known technologies of the plastics industry. Numerous studies carried out by chemists and physicists have led to the preparation and characteristics of macromolecular materials which exhibit semiconducting properties. From monographs (Ref.1-3) and review articles (Ref.4-6) which are quoted here only as an example it can be gleaned that ideas related to the relationship between molecular constitution and physical structure of macromolecular solids are not fully developed, although much basic knowledge has been acquired. Macromolecules with an extended π -electron system were synthesized in the hope that delocalization of the electrons would lead to a high concentration of free charge carriers. The low conductivity of

polymer Π -bonded systems observed experimentally was attributed to many factors eg. breaks in the Π -bonding, chain ends etc. It is now known that polymers with polyconjugated structures in the main chain are insulators in the ground state and illumination produces only a limited number of free carriers because of exciton formation. The thermal excitation of an electron from the valence band into conduction band is practically excluded. The stimulus for the present research in the area of semiconducting and conducting polymers comes from solid - state and semiconductor physics. New insights were introduced by the studies on "organic metals", i.e. organic compounds which exhibit electrical properties resembling those of metals (Ref.7) as well by the investigations on doped poly(acetylene) (PA). It was shown (Ref.8) that semicrystalline PA, a semiconductor with a relatively large band gap, exhibits a dramatic increase of specific conductivity when doped with strong oxidizing or reducing agents. Data concerning the electrical and optical properties were interpreted in the framework of theories of phase transition from semiconductor to metal. It was shown in analogy to e.g. silicon which upon doping with donors or acceptors can be transformed into a conducting state. Another analogy ought to be mentioned concerning the amorphous semiconductors which change their electrical behaviour upon doping. Similarly, poorly conducting amorphous polymers (even insulators) may be transformed into very interesting photoconductors by suitable molecular doping. Taking into consideration the above given remarks, doping of polymeric systems in order to obtain amorphous photoconductors or semicrystalline high molecular weight photoconductors is an important way of modifying their electrical properties. The dopants are effective mainly due to their interaction with the matrix which may be analysed in terms of charge transfer, or in terms of oxidation or reduction reaction with suitable polymeric matrix e.g. PA. These reactions are also usually called doping. The formation of CT complexes between two polymers is a rather unusual situation and thus more attempts at modifying the electrical properties of polymers by doping with low molecular weight compounds were made. Two aspects are worth mentioning. Firstly the added CT complexes are molecularly dispersed in the polymer matrix forming solid solutions. Secondly the additives are dispersed in the form of crystallites with different structures and morphologies. This paper will discuss the basic concepts and results of studies on polymers with molecularly dispersed charge transfer complexes and on polymers with crystalline CT complexes formed by the additives leading to conductive systems. Special emphasis will be placed on the latter systems because the former ones have been extensively discussed in our previous paper (Ref.6) and by other authors (Ref.4-9). The molecularly dispersed CT complexes in polymers are discussed here only in brief to show the particular differences between these two types of system related to the crystalline structures which can be controlled by the proper selection not only of the CT complex components and polymer but also by specific crystallization. Moreover structural and functional features common to organic metals and crystalline doped conductive systems will be indicated.

MOLECULARLY DISPERSED CT COMPLEXES IN POLYMERS

The very weak intermolecular interactions in molecular solids result in very narrow and separated energy bands. This means that the properties of noncrystalline or semicrystalline organic solids are determined by the molecules themselves, with dynamic charge transfer being due to charge exchange between the neighbouring molecules. These effects influence carrier generation (or photogeneration) and transport of charge carriers (Ref.10). Polymers generally belong to the group of amorphous or semicrystalline organic solids and their electrical properties make it possible to classify them as dielectrics whose conductivity may be appreciably enhanced by suitable illumination. Extensive studies on the electrical properties have been performed on polymers based on carbazole such as poly(N-vinyl carbazole) (Ref.4,11,12) and on model systems: N-isopropyl carbazole (NIPC) or triphenyl amine (TPA) dissolved in polycarbonate polymer (bisphenol A-polycarbonate) (PC). The basic transport properties in these disordered solids are already known. It has been shown using different techniques that charge transfer occurs by thermally activated hopping. The drift mobility and its activation energy are field dependent. Carrier hopping through a random medium is described taking into consideration the fluctuation of hopping times due to positional and orientational disorder of the molecules that provide the hopping sites leading to featureless current transients in time-of-flight experiments. Such current transients are indicative of "dispersive transport" which can be elucidated in terms of the general framework given by Scher and Montroll (13) and further developed by other authors. While it is not necessary to refer to the comprehensive theoretical

background developed for the explanation of transport and carrier generation in organic doped disordered systems, it seems interesting to note that the CT complex formation between polymer donor (e.g. PVK) and added acceptor (e.g. TNF) is of basic importance. Usually the particular CT complex has little activity unless it is excited by light. Detailed studies on the efficiency of generation and their field dependence can be elucidated in terms of Onsager's model but there are still some problems with the physical description of the photogeneration process and its relationship to bulk or macroscopic transport properties. Because polymers are mainly photosensitive to UV-radiation, an enormous literature has been devoted to extending the spectral sensitivity to a more useful visible region by addition of dye molecules (sensitization). All of the above remarks on molecularly doped polymers are also valid for macromolecular systems doped with both low molecular weight donors and acceptors. This approach and idea have been clearly recognized in the past and they have been studied using many reasonably characterized polymers and molecular dopants. The materials produced are soluble in organic solvents and they can thus be investigated in the form of films making possible elucidation of the underlying mechanism. The advantage that such doped materials offer is that both neutral and charged species (either cation or anion) or excited molecules can be dispersed in a rather high concentration as a homogeneous single phase. They exhibit also good stability and very interesting magnetic properties as investigated by E.S.R. However, it should be mentioned that the complexity of disordered systems makes a quantitative analysis of their properties very difficult and for that reason studies of these materials are not only currently relevant but also necessary. The ability to observe and identify many phenomena makes it possible to use molecularly doped polymers to elaborate new techniques for studying the mobility of charge carriers and its relation to the structure of trapping sites by means of thermally stimulated current method (TSC) (Ref.14). The theory of TSC transport peak was confirmed not only in studies of PVK but also of a model system-phenothiazine doped anthracene (Ref.15). Polymers doped with molecularly dispersed CT complexes are especially interesting because of their electrical and photoelectrical properties but several other physical properties are also changed by donor or acceptor additives (Ref.16,17) e.g. mechanical properties, thermal behaviour in terms of plasticization and or antiplasticization etc. All these materials show low dark conductivity although molecularly dispersed CT complexes enhance the conductivity of these systems. Attempts to obtain conductive, molecularly doped polymers have so far been unsuccessful even at rather high concentration. Considering the fact that crystalline organic metal consists of strong donors or acceptors one should expect that if it were possible to create this type of crystals in polymeric matrix one could increase the number of free carriers and improve the transport by the formation of a conducting paths. Actually polymers filled with conducting particles of carbon black or metallic powder are in common use but the required amount of conducting filler is large, usually exceeding 20 wt%, and changing completely all typical properties of polymeric systems. Recently we have proposed a method which enables one to obtain such composite materials which, while preserving good characteristics of organic polymers also show relatively high electrical conductivity. This new class of purely organic materials consist of a polymeric matrix in which a surprisingly small amount of well conductive organic CT complex is dispersed. The materials conduct electricity in spite of the additive content as low as 1 wt% because, due to a specific crystallization process, the crystalline CT complex forms a continuous conductive network in the bulk of the polymer matrix.

CONDUCTING POLYMERS WITH CRYSTALLINE NETWORK OF STRONG CT COMPLEXES

This section will be devoted to the preparation and some properties of these materials. In the first subsection the process of crystallization of low molecular weight additive in polymer matrix is discussed in more fundamental form and the conditions in which conductive network can be formed are defined. The second subsection deals with the influence of the components of the system on the crystallization process, on the possibility of making it conductive, and on its properties. Finally, in the last section we discuss the properties of the obtained materials and the conduction mechanism. More detailed experimental information can be found in other papers on this subject (Ref.18-24). Before going into the characteristics of preparation and properties of these systems it seems appropriate to give a few brief comments on organic metals and other polymers which exhibit very high electrical conductivity. The best known example of organic metal is the CT complex of tetrathiofulvalene (TTF) with tetracyanoquinodimethane (TCNQ) which can be obtained in the

form of single crystals. The packing of donor and acceptor molecules in separate stacks with partial exchange of charge was found to be the structural prerequisite for high conductivity of metallic character. The instability of many such crystals against moisture and oxygen as well as small size and brittleness have prevented practical application. Studies of different properties of these unique materials have led to substantial knowledge of the principles governing their behaviour thus it is obvious that attempts have been made to transfer them into polymer field. Although many macromolecular donors and acceptors are known, attempts to prepare CT complexes with such high electrical conductivity have not been very successful for reasons which can not be discussed here in detail. Some macromolecular systems have been obtained in recent years which show similar metallic conductivity. The structural nature of this type of conductivity is not entirely clear. Examples are the polymer $(SN)_x$ and doped poly(acetylene). It seems that the former is of theoretical interest only because of the many difficulties involved in its preparation and chemical instability. Poly(acetylene) doped with electron donors or acceptors becomes highly conductive and is of great interest both theoretically and from the point of view of expected practical applications. Among other reasons this is due to the fact that this polymer is obtained from acetylene by simultaneous polymerization and crystallization using known catalysts such as Ziegler-Natta-systems and to the straightforward nature of the methods of doping and handling as well as forming into films or other shapes. It is necessary to mention here that oxygen may enhance the conductivity if it acts on pristine PA in small quantities. At higher concentration and larger exposure times, and especially at higher temperatures, irreversible oxidation takes place and conductivity drops abruptly to that of semiconductor or insulator level. The same remarks is valid for other doped PA and this means that they are unstable in ambient conditions. Following the fundamental discoveries of Mac Diarmid and Heeger (8) other polymers which became conducting upon doping were found but their stability at ambient conditions is not very much different from that of PA, so they will not be discussed. We will concentrate on composites containing structurally correlated crystallites of "metallic" CT complexes within polymeric matrix at low concentration. These systems are stable in the ambient atmosphere preserving all properties characteristic of polymers.

Crystallization mechanism

The process which gives as the final product a polymer film with low-molecular-weight dopant dispersed in the form of microcrystals is called throughout this paper crystallization in polymer matrix, but in reality the situation is much more complicated. In solid polymers even above the glass transition temperature the diffusion of bulky molecules is strongly hindered and in fact crystallization takes place in a polymer solution. Crystallization of low-molecular-weight additives can occur in a broad range of polymer concentrations but what makes the process particularly interesting is the unusual morphology of the CT complex crystallites in samples obtained in some specific conditions which makes them conductive at surprisingly low additive concentration. In what follows we shall discuss also some more general problems but let us first concentrate on the conditions which must be fulfilled for the formation of a conductive network to occur. Conductive films can be obtained using complexes of different chemical constitution crystallized in a range of polymer matrices, using different solvents, but for the sake of clarity the discussion of the influence of different factors will be illustrated with the results obtained for the complex tetrathiotetracene (TTT) with TCNQ in PC unless the role of the polymer matrix itself is discussed. The process of crystallization during film casting is influenced by many factors. Microscopic parameters which govern the process are supersaturation and viscosity of the medium but from the experimental point of view each of them is related to the composition i.e. properties and the actual concentration of the CT complex components, of the polymer and of the solvent, to the cast temperature and to the solvent evaporation rate. Quantitative description of this process is extremely difficult because the parameters are interrelated to some extent and change in time in a fashion that makes measurements very difficult to perform. As a result of the evaporation of the solvent the concentration of the CT complex and the viscosity of the polymer solution increase and the composition i.e. solvent-to-polymer ratio, being initially of the order of 20, falls down to about 0.1 and less. This means that in the initial stage the solubility of the complex in the solvent is dominant while in the final stage the polymer is at least of comparable importance. Comparing the specific conductivities of the samples exhibiting different morphology of the CT complex crystallites it can be deduced that

nonequilibrium forms of crystallites like dendrites and whiskers are the most favourable. More detailed model considerations of the conditions in which such crystallization occurs in different systems have been published in other paper (Ref.20). Without going into the details involved we can say that fast, nonequilibrium crystallization occurs if the precipitation of the CT complex i.e. beginning of its crystallization takes place in the last stage before film solidification, when the solution attained relatively high viscosity and if evaporation of the solvent is fast enough. The viscous medium hinders diffusion of the additive molecules to the crystallization front of the already grown crystals if they are separated enough and considerable local supersaturation takes place. This induces the appearance of new crystallization centres as well as secondary nucleation on crystal faces i.e. branching, and fast spontaneous crystallization.

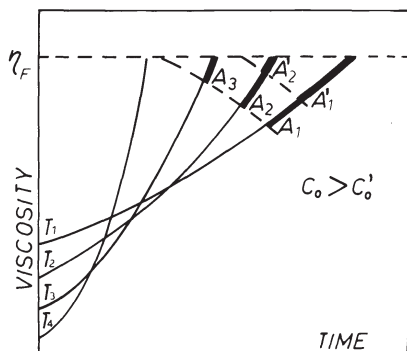


Fig. 1. Schematic dependence of solution viscosity on evaporation time at different cast temperatures; $T_1 < T_2 < T_3 < T_4$. Points A and A' indicate the beginning of CT complex crystallization for two different initial concentration of the dopant in the solution, C_0 and C'_0 respectively.

The process of film casting is depicted schematically in Fig. 1. The viscosity of the solution increases with time as the solvent is evaporated. The limiting viscosity η_F denotes a viscosity at which the diffusion of CT complex molecules is so slow as to preclude further crystallization. Points A and A' on the curves drawn for different temperatures indicate the critical concentration of the CT complex in solution i.e. the beginning of its precipitation at a given temperature for two different initial concentrations of the additives C_0 and C'_0 respectively ($C_0 > C'_0$). One can see that for concentration C_0 at lower temperatures (say T_1 in Fig. 1.) the crystallization begins at relatively low viscosity and because of the slow evaporation of the solvent at low temperatures a relatively big, poorly branched crystals of the CT complex are formed. Such situation occurs for the system PC+1 wt% of TTT·TCNQ cast from o-dichlorobenzene if the film is obtained at temperatures of the order of 90°C and less. The resultant morphology is presented in Fig. 2a. At the optimum temperature (say T_2 in Fig. 1) the medium viscosity at the point A_2 is higher and the evaporation is faster which leads to the nonequilibrium crystallization described above yielding, in the case of PC+1%TTT·TCNQ, correlated dendritic structures contacting each other and forming conductive network. This morphology obtained in the optimum temperature range 115-120°C, is represented in Fig. 2b.

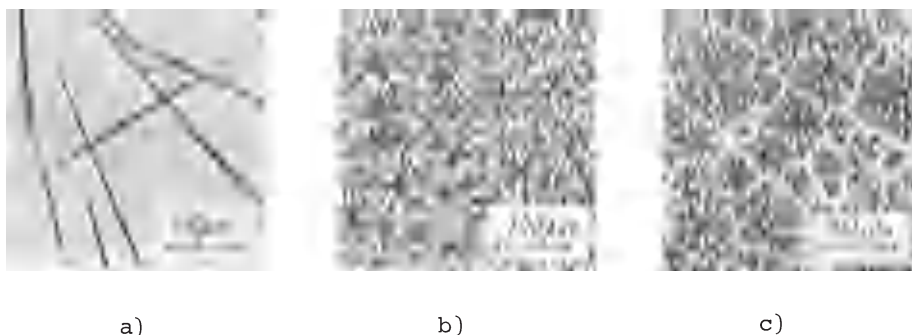


Fig. 2. Micrographs of polycarbonate films containing 1 wt% of TTT·TCNQ CT complex cast from o-dichlorobenzene at different temperatures: a) 85°C (too low), b) 120°C (optimum), c) 145°C (too high).

For still higher temperatures (say T_3 in Fig. 1) the crystallization starts too late when the medium viscosity is high and increases quickly. The crystallization process is then stopped before a continuous network can be formed and a considerable fraction of the CT complex components remains more or less molecularly dispersed in the matrix. The corresponding picture for PC+1 wt % of TTT·TCNQ system is presented in Fig. 2c. One can see that nonequilibrium dendritic structures are poorly developed and do not contact each other. As the cast temperature is further increased (say to T_4 in Fig. 1) the fraction of the additive which remains dispersed in the polymer matrix and does not form any crystalline forms, at least such as would be visible under optical microscope, increases to yield in the case of PC+1wt% TTT·TCNQ system at temperatures of the order of 160°C and more, homogeneous films. Its specific conductivity is practically the same as that of the additive-free polymer. In the preceding discussion it was assumed that the solvent evaporation is homogeneous. This is of course only an approximation. In a standard casting process, evaporation is roughly homogeneous in the plane of the film but not in the direction perpendicular to its surface. The concentration increase is faster near the free surface of the film especially for high evaporation rates and high viscosities. This difference may lead in some cases to different morphologies of the CT complex crystallites and to different conductivities on both sides of the film. Very interesting results can be obtained if a concentration gradient in the direction parallel to the film surface is induced by zone solvent evaporation. If the conditions are adjusted so that the narrow zone of the CT complex precipitation moves as fast as the crystallites grow, an anisotropic structure is formed exhibiting also a very large anisotropy of electric conductivity. Again, different morphological structures with different anisotropy can be obtained depending on the conditions. The methods of obtaining such materials and their properties are more extensively discussed in our previous work (Ref. 19). A typical micrograph of such an anisotropic film is presented in Fig. 3.



Fig. 3. Micrograph of PC+1wt% of TTT·TCNQ system with anisotropic conductivity. The film was obtained from *o*-dichlorobenzene using zone-solidification technique.

The casting temperature influences the crystallization process in a complicated way because it has a strong hold on several factors: solubility of the additives in the solvent and in polymer solution, equilibrium constant of the CT complex formation, the rate of diffusion, directly and via temperature dependence of the solution viscosity and evaporation rate at least unless special precautions are taken. The dependence of the specific resistivity on

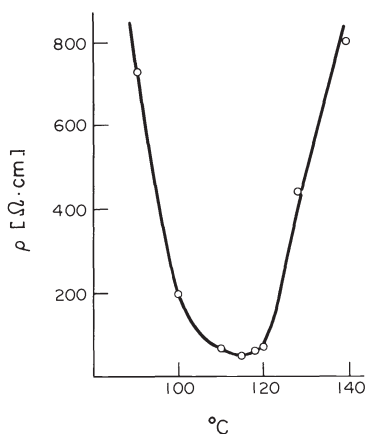


Fig. 4. The dependence of the specific resistivity ρ of PC+1wt% of TTT·TCNQ system cast from *o*-dichlorobenzene on the cast temperature. The resistivity was measured at room temperature using four-probe technique.

the cast temperature, corresponding to morphological structures presented in Fig. 2 is shown in Fig. 4. One can see that in the optimum cast temperature range the resistivity is low and roughly constant while as the cast temperature is decreased or increased it rises rapidly.

Further experimental support for the model considerations presented above is provided by the studies of the conductivity of the cast solutions during solvent evaporation up to solidification of the film. The current flowing in the solution was measured using thin steel electrodes mounted onto a glass substrate. The crystallization process was simultaneously observed under microscope. The electric field strength applied was very small (~ 1 V/cm) to minimize any mass transport, which could affect the crystallization process. Representative plots of current vs. time for PC+1wt% of TTT·TCNQ system cast from *o*-dichlorobenzene and chlorobenzene at optimum temperatures and at a lower temperature are shown in Fig. 5. One can see that in the case of *o*-dichlorobenzene (curves 2 and 3) the current initially decreases. It can be explained by

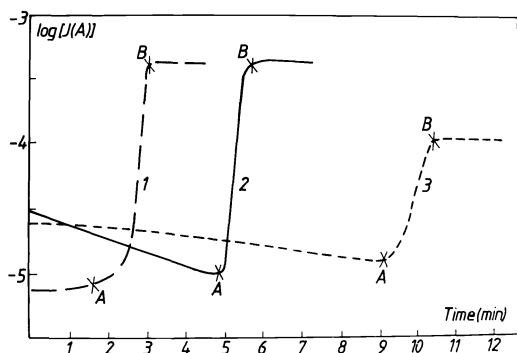


Fig. 5. The changes of current flowing through cast solution registered during solvent evaporation for PC+1wt% of TTT·TCNQ system (see text). Initial concentrations in the solvent: PC-4wt%, CT complex - 0.04wt %. Curve 1: solution in chlorobenzene cast at 110°C (optimum), curve 2 and 3: solution in *o*-dichlorobenzene cast at 120°C (optimum) and 85°C (too low) respectively.

a decrease of ionic conductivity due to increasing viscosity of the solution, which is still transparent and no precipitation is observed. At some moment, indicated by point A on the curve, the crystallites of the conductive CT complex appear and cause an increase in the conductivity of the system. This process is fast at optimum temperature (curve 2) and, as discussed above, leads to formation of the conductive network presented in Fig. 2b. It is completed at the moment indicated by point B. At lower cast temperature (curve 3), solvent evaporation takes longer time and the critical concentration is lower in agreement with the scheme illustrated by Fig. 1. Thus, crystallization begins when the solution has a lower viscosity and, taking much longer time due to lower evaporation rate, yields relatively big, needle-like crystals shown in Fig. 2a. They form a poor network which is the reason why the final current intensity is much lower in this case. In the case of chlorobenzene (curve 1) the evaporation rate is considerably higher due to the lower boiling point of this solvent (132°C comparing with 180°C for *o*-dichlorobenzene). Critical concentration of the TTT·TCNQ complex in chlorobenzene is lower so the viscosity of the solution at point A is also lower. An increase of the conductivity due to complex crystallization overlaps the decrease of the ionic conductivity in this case and no minimum on curve 1 is observed. However, in contrast to the *o*-dichlorobenzene solution cast at low temperature (curve 3) quick solvent evaporation in this case leads to local supersaturation and rapid nonequilibrium crystallization in a form of branched whiskers (see Fig. 8a). The obtained films have practically the same conductivity as those obtained from *o*-dichlorobenzene at the optimum temperature (see Table 1).

Composition of the system

Charge-transfer complexes. A number of conductive CT complexes and also other conductive compounds can be used to obtain conductive macromolecular materials according to the presented method. Modifications that can be necessary involve first of all the proper choice of polymer matrix and of the solvent to reduce the necessary additive concentration to low level. The low concentration of the additive sufficient to form a conductive network is especially attractive.

The concentration dependence of conductivity is presented in Fig. 6 for TTT·TCNQ in PC and in poly(methylmethacrylate) (PMMA) cast from *o*-dichlorobenzene.

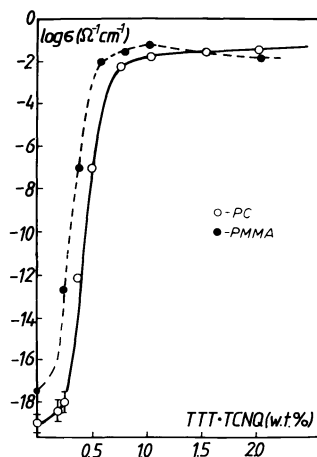


Fig. 6. The dependence of the specific conductivity of PC and PMMA films on the content of TTT·TCNQ CT complex. The films were cast from *o*-dichlorobenzene at optimum temperatures (see Table 1).

One can see that the concentration dependence of the specific conductivity has a threshold character, and is accompanied by increasing homogeneity of the crystallite network, which reaches its optimum at about 1wt% TTT·TCNQ content. Below this value the discontinuity increases rapidly and regions with few separated microcrystals extend more and more as the additive content is lowered, so that below 0.2% the conductivity of the material is virtually that of the additive-free polymer matrix. For higher concentration on the other hand much bigger and thicker crystallites also appear, consuming a lot of the added low molecular compounds. Apparently, the quality of the conductive network does not improve and the surplus material is not used effectively. Different problems arise when the best known organic metal tetrathiofulvalene (TTF)·TCNQ is used. Its solubility in common polymer solutions is so high that it does not crystallize at all at low concentrations. The problem can be overcome either by careful choice of the solvent and of the polymer matrix or by suitable casting procedure deduced from analysis of the scheme shown in Fig. 1 (Ref. 20). Without going into details let us note that it involves a rapid cooling of the solution previously thickened at high temperature or reduction of the pressure above the solution at low temperature. Both procedures lead to rapid supersaturation of the solution and fast, nonequilibrium crystallization of TTF·TCNQ, and yield materials with conductivities comparable to those of TTT·TCNQ systems. Some other less conductive CT complexes, e.g. TTT·TCNE, TTT·Chloranil were also used. In all cases materials with crystalline network penetrating the polymer matrix were obtained. The specific conductivity of these films is also lower, but these systems are interesting because they demonstrate that a variety of dopants can be introduced into the polymer by the method under consideration.

Polymers. Because of the very low content of the conductive additive it is the polymer matrix which determines the mechanical properties of the system, the temperature range in which it can be used, its resistance to water, organic solvents or light and many other properties. Most important however is its influence on the process of crystallization of the conductive CT complex, because this determines whether a given polymer can be used at all at least for a given CT complex. The preceding discussion of the crystallization conditions necessary to obtain a conductive network implies that the polymer used affects the crystallization process mainly through its dominant influence on the viscosity of the solution but also on the solubility of the additives. The influence on viscosity is related to the polymer-solvent interactions and to the molecular weight of the polymer used. Because high viscosity favours reticulated crystallization, a poor solvent should in fact be used and the molecular weight of the polymer should also be rather high. More detailed discussion of these parameters can be found in our other papers (Ref. 20 and 25). These conditions are however relatively easy to satisfy. The factor which usually limits the range of polymers that can be used as matrices is the solubility of the additives in these macromolecular systems. As has already been mentioned, the concentration of the polymer in the solution at the moment when crystallization begins should be high. If a given additive is well soluble in such a solution, it will begin to precipitate close to the limiting viscosity η_F (see Fig. 1), or will not precipitate at all. In either case an insulating film is formed.

This effect was observed for the TTT·TCNQ CT complex in a series of polymers: polystyrene (PS), copolymer styrene-chlorostyrene (PS-chS) and polychlorostyrene (PchS). The solubility of TTT·TCNQ increases with increasing chlorine content and the complex crystallizes, although not very well, in PS but neither in the PS-chS copolymer nor in PchS. It does not precipitate even in their 1:1 mixtures with PC. TTT·TCNQ does not crystallize either in PVK matrix which can be alternatively explained by the formation of a competitive CT complex PVK·TCNQ (Ref. 21). The polymer matrix has also a strong influence on the morphology of the CT complex crystallites. This effect can be clearly seen comparing micrographs of the same complex in different polymer matrices using the same solvent. In Fig. 2b and 7 abc morphologies of the TTT·TCNQ CT complex crystallized in PC, PMMA, PS and poly(oxyphenylene)(PPO) are shown.

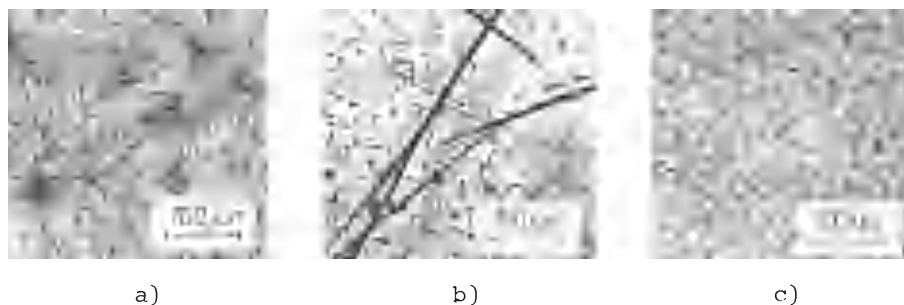


Fig. 7. Micrographs of PMMA (a), PS (b) and PPO (c) films containing 1 wt% of TTT·TCNQ CT complex cast from *o*-dichlorobenzene at optimum temperatures (see Table 1).

TABLE 1. The specific conductivities ($\Omega^{-1}\text{cm}^{-1}$) measured at room temperature of various polymers doped with 1wt% of TTT·TCNQ cast from different solvents at indicated, optimum temperatures.

Polymer	Solvent		
	chlorobenzene	<i>o</i> -dichlorobenzene	trichlorobenzene
PC	2×10^{-2} (110°C)	2×10^{-2} (120°C)	2×10^{-2} (125°C)
PMMA	2×10^{-2} (105°C)	5×10^{-2} (115°C)	
PS	$1,5 \times 10^{-3}$ (110°C)	3×10^{-3} (85°C)	$1,5 \times 10^{-3}$ (100°C)
PPO		2×10^{-4} (100°C)	

Specific conductivities and optimum casting temperatures for this group of systems are listed in Table 1 for different solvents. In the case of PC and PMMA (Figs. 2b and 7a), the relatively inert polymeric matrices make it possible to realize the optimum crystallization conditions in the manner described above. It follows that it is possible to cast the films at temperatures sufficiently high for spontaneous, rapid crystallization in viscous medium to yield dendritic structures forming conducting network. These films have the highest conductivity. In the case of PS (Fig. 7b) the optimum cast temperature is relatively low, because at higher temperatures CT complex precipitates very weakly due to its better solubility in polystyrene. At 85°C the solvent evaporates slowly and CT complex crystallizes in needle-like, equilibrium forms (however some finer structure, poorly seen on the micrograph, also arises affording contacts between the needles). The resulting conductivity is in this case at least an order of magnitude lower than that for PC or PMMA.

Solvents. The solvent used for film preparation is of crucial importance from the point of view of the resulting properties, although its residue in the final product can usually be lowered to negligible level by a proper vacuum drying procedure. The properties of this component, which is present in an amount exceeding by a wide margin all others in the initial stage of the casting process, determine not only the solubility of the CT complex in the medium and its

viscosity but also the temperature range available and the maximum evaporation rate at least in an open system. Micrographs of the films of PC+1wt% TTT·TCNQ and of PS+1wt% TTT·TCNQ cast from chlorobenzene at optimum temperatures (Fig.8) can be compared with those obtained from *o*-dichlorobenzene (Fig. 2b and 7b).

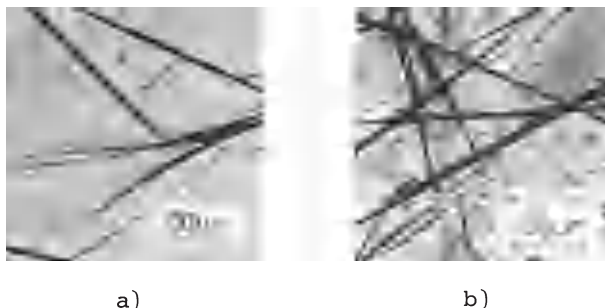


Fig. 8. Micrographs of PC (a) and PS (b) films containing 1 wt% of TTT·TCNQ CT complex cast from chlorobenzene at optimum temperatures (see Table 1).

It can be seen that the morphology of CT complex crystallites differs considerably in different solvents. The cast temperatures (Table 1) are different and they are chosen so that the conductivity is the highest for the fixed composition. The solubility of the CT complex in chlorobenzenes increases as the number of chlorine atoms in the molecule rises. For solvents with high boiling point (*o*-dichlorobenzene and chlorobenzene), the cast temperature for inert polymer matrix (PC, PMMA) can be high enough to induce reticulated crystallization. For PS, however, the cast temperature can not be raised in these cases due to better solubility of the CT complex in PS.

Conduction mechanism

The close relationship between morphology of CT complex crystallites and conductivity for different systems presented above indicates that electrical properties are determined mainly by the properties of the crystalline CT complex itself and by perfectness of the conducting network formed. However the polymer matrix, being essentially inert, influences not only the process of crystallization as it was already shown, but also some properties of the obtained conducting systems.

Current-voltage characteristics. The current-voltage dependences of well conducting samples (above $10^{-3} \Omega^{-1} \text{cm}^{-1}$) are ohmic in the investigated temperature range of $-196^{\circ} + 50^{\circ}\text{C}$. Maximum field strength which can be applied to these systems does not exceed 10^4V m^{-1} . At higher fields the Joule heat that evolves causes overheating in "weak" point and destruction of the crystalline path. Such a break in the conducting network, initially local, results in still higher current density flowing through neighbouring paths and further destruction of the network. Finally, a non-conducting region visible as a homogeneous path perpendicular to the field direction, crosses the film. For samples with lower conductivity, the current-voltage characteristics exhibit deviations from ohmic dependence for the field strength higher than 10^5V m^{-1} . These deviations, typical of polymers, are the consequence of the increasing role of the polymer matrix separating microcrystals as concentration of the crystalline CT complex decreases.

Temperature dependence of the conductivity. The plot of the ratio of conductivity at a given temperature to conductivity at room temperature vs temperature for different systems is shown in Fig. 9. In general this dependence is rather weak. The strongest dependence is observed for systems with poorly developed conducting network (like for PPO, compare Fig. 7c) because in this case the conductivity is controlled by polymeric layers disturbing the conducting paths. These can be regarded as energetic barriers and transport through these regions is thermally activated. For more perfect conducting network, like the one in PMMA (see Fig. 7a), the temperature dependence of conductivity is weaker, although it is still positive, contrary to metal-like dependence of the single crystals of the conducting CT complexes ("organic metals"). Similar conclusions were drawn also from the fact that the temperature dependence of the conductivity increases with decreasing CT complex content (Ref. 18). The changes of the conductivity are also affected by thermal expansion in all cases, and the expansion of polymeric matrix separating crystallites seems to

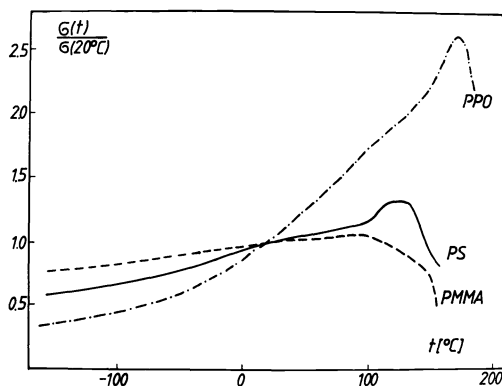


Fig. 9 The temperature dependence of the conductivity of different polymers containing 1 wt% of TTT·TCNQ CT complex cast from o-dichlorobenzene at optimum temperatures (see Table 1).

be especially important. This effect is probably responsible for the irreversible lowering of the electrical conductivity in samples heated over the glass transition temperature of the polymer matrix. (Fig. 9). Heating to still higher temperatures can lead to dissolution of the CT complex microcrystals in the polymer matrix. After cooling down the additives remain molecularly dispersed in the polymer because high viscosity of the matrix prevents recrystallization.

The temperature dependence of the conductivity of anisotropic systems. Figure 10 shows the Arrhenius plots for the conductivity in the direction parallel to the conduction paths (curve 1, compare for structure Fig. 3) and in the perpendicular direction for two samples with higher (curve 2) and lower (curve 3) density of branchings, i.e. with lower and higher anisotropy, respectively. The highest activation energy as well as the lowest conductivity in the last case is evidently caused by lack of effective links in this direction between nearly parallel conducting paths confirming the above presented conclusion on the important role of the structure of the conducting network.

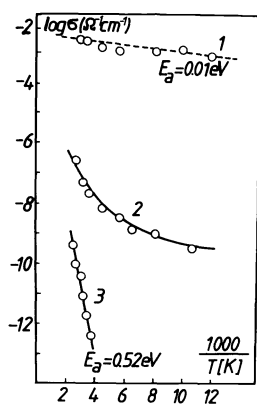


Fig. 10. Arrhenius plots for the conductivity of the anisotropic PC films containing 1wt% of TTT·TCNQ CT complex: in the direction parallel to the crystal columns (curve 1) and in the direction perpendicular to the crystal columns for samples with higher (curve 2) and lower (curve 3) density of branches.

Hall effect measurements. The high conductivity of polymer films of that type made it possible to carry out measurements of the Hall effect for the PC+1wt% TTT·TCNQ system (Ref. 18). At room temperature in magnetic field of 10 T the mobility of $9 \times 10^{-2} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and density of charge carriers of the order of 10^{18}cm^{-3} were estimated. The majority charge carriers were found to be electrons. Assuming that each of the TTT·TCNQ complexed molecules yield one carrier and taking the value of conductivity of $2 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ one can calculate for this system the corresponding values of the order of $10^{-2} \text{cm}^2 \text{V}^{-1}$ and 10^{19}cm^{-3} respectively. Thus, without going into detailed interpretation of the Hall effect in unhomogeneous materials (see e.g. Ref. 26), one can accept the obtained values as reasonable approximation.

The mechanical properties. Generally the mechanical properties of the considered conducting polymers are practically unchanged as compared with pure polymer films cast under the same conditions, because of low dopant content. Some antiplasticization effect caused by CT complex was observed at higher concentrations of molecularly dispersed additives (Ref. 16 and 17). However, stretching of the conducting samples causes deformation of the conducting network and consequently changes of the conductivity. At small elongations, below 2%, the change of the resistance of the sample is very small and reversible. At elongations of up to 6%, the resistance increases still only by a few per

cent, but these changes are irreversible. At still higher elongations the resistance of the sample increases abruptly. The highest elongation was obtained by drawing the film at elevated temperature through an appropriate flat die. At 50% elongation the conductivity of the sample decreases by about 2 orders in magnitude and exhibits some small anisotropy, i.e. conductivity in the drawing direction is 2-3 times higher than that measured perpendicularly. This effect indicates that stretching breaks the contacts between the crystallites and induces their small orientation.

Properties of CT complex crystallized in polymer matrix. The properties of CT complex crystals formed in the polymer matrix are expected to be different from those of well formed, pure single crystals used to study the properties of "organic metals". Due to the fast, nonequilibrium crystallization, the perfection of crystalline structure is very poor. ESR experiments on PC+1wt% TTT·TCNQ cast from o-dichlorobenzene show that only at the lowest cast temperature is the crystalline order clearly reflected in the form of ESR signals (Ref. 27). In samples of the same composition but cast from chlorobenzene, the crystalline splitting is observed for all investigated cast temperatures, but it should be kept in mind that in this solvent a considerable part of the material always forms relatively big needle-like crystals and the signal due to whiskers can be too weak to be seen even if its form is different. Measurements of the specific conductivity of needle like crystals isolated from PC matrix have shown that even for these crystals the specific conductivity is about an order of magnitude lower ($<10\Omega^{-1}\text{cm}^{-1}$) than that reported in the literature, which is also indicative of poor crystal perfection (Ref. 28). It is also interesting to note that the stoichiometry of the TTT·TCNQ complex crystallized in polymer matrix differs from the 1:2 ratio which was found in the case of crystallization from neutral components in pure solvent (Ref. 28), being closer to one-to-one. This conclusion was drawn from the results of elemental analysis of microcrystals isolated from polycarbonate by elution of the polymer with methylene chloride and measurements of conductivity of PC+TTT·TCNQ samples with different donor-to-acceptor molar ratio. Two series of samples were investigated: either TTT content was kept constant and TCNQ content was changed or total amount of both components was kept constant and equal 1 wt% but TTT/TCNQ molar ratio was changed. In both cases the minimal resistivity of the doped polymer was achieved at a 1:1 donor-to-acceptor ratio.

Percolation threshold. As one can deduce from the conductivity vs. content of additives plots (Fig. 6) a dramatic increase of conductivity occurs in these systems at concentrations above 0.2% of the conducting compound. The abrupt changes of conductivity in heterogeneous systems containing components with different conductivities can be interpreted in terms of the percolation theory which expects the appearance of such a threshold at critical concentration. We do not know any other system in which the percolation threshold would be observed at such a low amount of the conducting filler. The Clausius-Mossotti approximation which according to Landauer argumentation (Ref. 27) describes maximal and minimal bounds for the conductivity of mixtures, yields $\sigma_{\text{max}} \approx \sigma/150$ at 1% of conducting component in an insulator, where σ is the conductivity of the conducting component. The conductivity of TTT·TCNQ microcrystals isolated from polymer matrix was found to be of the order $10\Omega^{-1}\text{cm}^{-1}$ (Ref. 27), thus $\sigma_{\text{max}} = 0.07\Omega^{-1}\text{cm}^{-1}$. The conductivity of our best conducting system - PMMA+1% TTT·TCNQ - is $0.05\Omega^{-1}\text{cm}^{-1}$, i.e. very close to that absolute limit. One can argue that the conductivity of very thin and long microcrystals observed in PMMA can be higher than the conductivity of needle-like, relatively big microcrystals which can only be isolated and measured. Nevertheless the effectiveness of the utilization of the CT complex in these systems seems to be very high. Exact description of the dependences shown in Fig. 6 in terms of the percolation theory is very difficult. Apart from complications arising from the peculiar correlation of microcrystals arrangement, branching and broad distribution of microcrystals sizes, there are two disadvantages which limit the possibility of theoretical fitting experimental points: a/ some unknown part of the additives remains molecularly dispersed in the matrix and is inactive. This part is relatively bigger for smaller concentrations of the dopant, i.e. the exact position of the experimental points in Fig. 6 in relation to X-axis is unknown, b/ the morphologies arising at different concentrations of the dopant are different and unique. Samples with different amounts of the dopant are independent entities and it is impossible to simulate the microcrystalline network observed at higher concentration by addition of some elements to the network obtained at lower concentration, a common procedure in any percolation theory considerations. To estimate the percolation threshold the following line of argument can be used. Consider a system with dendrite-type morphology of crystalline network, say PC+1% TTT·TCNQ, cast from o-dichlorobenzene at 120°C (Fig. 2b). Because the conducting network is completed at 1% of the dopant /saturation effect is observed for higher concen-

trations, compare Fig. 6/, it can be assumed that the density of microcrystals in individual dendrite is sufficient to make contacts with the neighbouring dendrites. Thus we can treat the polymeric "sphere" with dendrites inside as a new conducting phase. Then, because the percolation threshold for the conducting spheres dispersed in insulating matrix occurs at ca. 30 vol.% of spheres (Ref. 29), each containing 1% of the CT complex, one can obtain a percolation threshold of the order of 0.3%. Obviously this model can be used only to demonstrate that percolation threshold can occur at such a low amount of the dopant. In the case of whisker-type morphology, like the one shown in Fig. 8a, comparison with the literature data (Ref. 30) indicates that for percolation threshold to occur below 0.5% of randomly dispersed fibers, the aspect ratio of the whiskers should be unacceptably high, of the order of 10^4 . This implies that there is some correlation of distribution which makes more effectively continuous network than does statistical mixing.

CONCLUDING REMARKS

The above discussion is not intended to be a thorough review of all of our results in the field of molecular and crystalline CT complexes doped polymers. Conducting systems can be obtained from a variety of crystalline CT complexes and polymeric matrices. We have also prepared conducting systems with high molecular weight additives e.g. TCNQ salts containing sulphur atoms and aliphatic chains or aromatic rings in the main chain (Ref. 31) which are able to crystallize in polymeric matrix forming a network of conductive paths. In many ways their properties correspond to those discussed above. In this case, depending on the components and casting conditions, different structure can be obtained governing the electrical and mechanical properties. Anisotropic structures are more difficult /but not impossible/ to prepare. The crystallization of conducting or non-conducting additives in the polymer matrix, e.g. diacetylenes, and their subsequent polymerization induced e.g. by UV light results in similar anisotropic or isotropic, crystalline network changing the electrical and mechanical properties along the lines discussed above. Appropriate work is in progress at our laboratories. Species grown in the polymer matrix are not necessarily to be of the "microcrystal" type but may be a kind of self-assemblies of organic molecules of rich structure and properties. Such supra-molecular structures are known in various micelle-type organizations e.g. in biochemistry and may produce unusual electrical properties. The dimensionality of these assemblies and the nature of their morphology are not known but they have important consequences and further experiments will shed light on the properties of these materials in which quasi-molecular order seems to be of importance (Ref. 32).

It seems necessary to compare the systems containing low concentration of network-forming crystalline conducting additives discussed above with other heavily doped polymers or polymer mixtures with conducting particles. Because of large amount of I_2 in poly(2-vinyl pyridine) or in PVK (Ref. 33, 34) these systems are not stable. Desorption of I_2 causes not only a change in the conductivity but also several technical difficulties. In the case of polymers with conducting fillers the mixture should contain 20 wt% or more of the filler which however results in deterioration of the mechanical and processing properties. The same applies to polymer mixtures with statistically dispersed microcrystalline CT complexes or mixtures with conductive salts with TCNQ. However, the resistivity of these materials was reported to be as low as $1 \Omega\text{cm}$ but the CT complex concentration reached up to 80 wt%. These systems were claimed to be uniform but the authors believed that fine crystals form conducting paths between the filler crystals. Similar results have been obtained by other authors (Ref. 35, 36, 37). The thermal and environmental stability of these systems is not known exactly.

Possible applications of conducting polymers with low content of crystalline CT complexes forming an appropriate structure will result from their low specific weight, typical properties characteristic of other commercial polymers, and any advantages they may have in production e.g. well known casting techniques. The possibility of obtaining large conducting areas at relatively low price seems to be important for preparation of conducting sheets for resistors, conducting coatings, solar cells, modified xerographic materials.

The presence of crystalline network and especially anisotropic systems in polymeric matrix can also modify considerably different physical properties e.g. increases the absorption of light and electromagnetic waves leading to production of different screens and protecting systems. The knowledge of these systems accumulated up to now is far from sufficient, but it is possible to predict several applications taking into consideration that both the bulk and the surface of these systems can be modified.

Last but not least is the significance of these systems for the basic studies on charge generation and transport because the dimensions of conducting crystallites can be of the order of assemblies thus reaching quasi-molecular scale.

In any case, research on the composition, preparation conditions, structure, electric and electronic properties of polymers with crystalline CT complex additives exhibiting high conductivity presents a considerable scientific challenge. Many interesting questions remain unanswered, but one can be confident that as our fundamental understanding of these systems grows, more refined assessment of such polymeric conducting materials will follow. The research activity of the last few years has unambiguously demonstrated that polymers with high conductivity can be obtained and that much progress can be made when enough imagination, knowledge and effort has been put into this field.

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