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Conducting polymer films with new organic donor MDT-TSF: preparation and properties

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Preparation and properties of surface-conductive polymer composites based on a recently synthesized electron-donor, methylenedithio-tetraselenefulvalene (MDT-TSF) are described. Polycarbonate and biodegradable polyester polylactide are used as polymer matrices. The obtained surface-conductive materials with MDT-TSF polyiodides show high, metal-like conductivities, indicating that MDT-TSF is one of the best donors for conductive composites.

1. Introduction

Conductive polymeric materials, including composites, are interesting from the viewpoint of many applications. Rendering conventional insulating polymers conductive can be achieved by preparing composite materials in which networks of various conductive materials are formed within polymeric matrices. One possibility is to use organic conductors, in particular highly conducting CT complexes and salts (organic metals). Solubility of these materials makes possible use of solution processing techniques, and several very efficient methods for growing *in situ* conducting networks in polymer matrix have been elaborated [1–3].

In particular, using the so-called two-step reticulate doping method [2] one can obtain well-formed nanocrystals (20–100 nm thick) in the surface layer of polymer films [1–6]. Due to a very high degree of orientation of the crystals (conducting plane in the plane of the film) and good contacts between them, properties of such polycrystalline layers are close to those of single crystals. Although conductive systems have been

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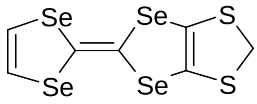
obtained using many different organic conductors including those showing metal-like temperature dependence of conductivity as single crystals, composites containing these materials are usually semiconductors. Only three systems have been found which are metallic in a broad temperature range [1, 3–7].

In this paper, we describe preparation and properties of composites based on a recently synthesized electron-donor methylenedithio-tetraselenefulvalene (MDT-TSF) [8–10]. By contrast to other donors used so far, MDT-TSF is asymmetric, metallic and even superconductive salts have been obtained by electrocrystallization [8]. Those materials show electronic and structural characteristics quite different from bis(ethylenedithio)–tetrathiafulvalene (ET) salts and constitute a new class of organic superconductors. In the present study, we employed polycarbonate and biodegradable polyester polylactide as polymer matrices and found that the obtained surface-conductive materials with MDT-TSF polyiodides show high, metal-like conductivities, indicating that MDT-TSF is one of the best donors that can be used to prepare conducting composites.

2. Experimental

MDT-TSF (scheme 1) was synthesized as described in [8, 11]. Poly(bisphenol A-carbonate) (Lexane) (PC) was provided by Goodfellow. L-Polylactide (PLA) was supplied by Cargill-Dow (Minnetoka MN). Electrical conductivities were determined using the four-point method with a Keithley 195A multimeter. UV-Vis spectra were recorded using a Specord UV-Vis spectrophotometer. The morphology was studied with a Nikkon Eclipse E400 Pol polarizing microscope and a Jeol JSM-5500 scanning electron microscope (SEM). Reagent-grade solvents (methylene chloride (MC) and chlorobenzene (CB)) and iodine were used as received. X-ray diffraction (XRD) was measured with a Siemens diffractometer using Cu (K_α) radiation. Raman spectra were recorded using a Jobin–Yvon T6400 apparatus equipped with a confocal microscope. The excitation wavelength was 514.5 nm.



Scheme 1. Chemical formula of MDT-TSF

To prepare conductive composites, so-called modified two-step method of reticulate doping has been used [1–3]. In the first step, polymer films containing 2 wt. % of MDT-TSF were obtained by casting a common solution in CB at 360 K. The additive was molecularly dispersed in the polymer matrix and the films so obtained were non-conductive. PC films cast in such conditions were amorphous while those of PLA were semicrystalline. One surface of these films was then treated with vapours of iodine solutions in MC. MC swells the polymer film and enables a reaction between MDT-TSF and iodine. The salt crystallizing *in situ* forms conductive network of microcrystals in the surface layer of the polymer film.

3. Results and discussion

Figures 1 and 2 show morphologies of conductive networks of MDT-TSF-iodide in PC films treated with MC/I_2 vapours for different times. After a short time a network of randomly oriented plate-like microcrystals is formed (Figs. 1a and 2a), similar to those observed in other systems [1–3]. However, after a longer time larger morphological structures appear: domains of higher optical anisotropy, resembling spherulites (Fig. 1b, c. Such a phenomenon has never been observed in similar composites until now. The mechanism of formation of the domain-phase is not clear and needs further investigations. We presume that it grows by recrystallization of micro-plates in the swollen surface layer of the polymer film, evidently nucleated in some places. The domains appear to be formed of smaller, hardly recognizable plates, forming long branched “wires” (Fig. 2b). This morphological change is also accompanied by changes of other physical properties of the films as discussed below.

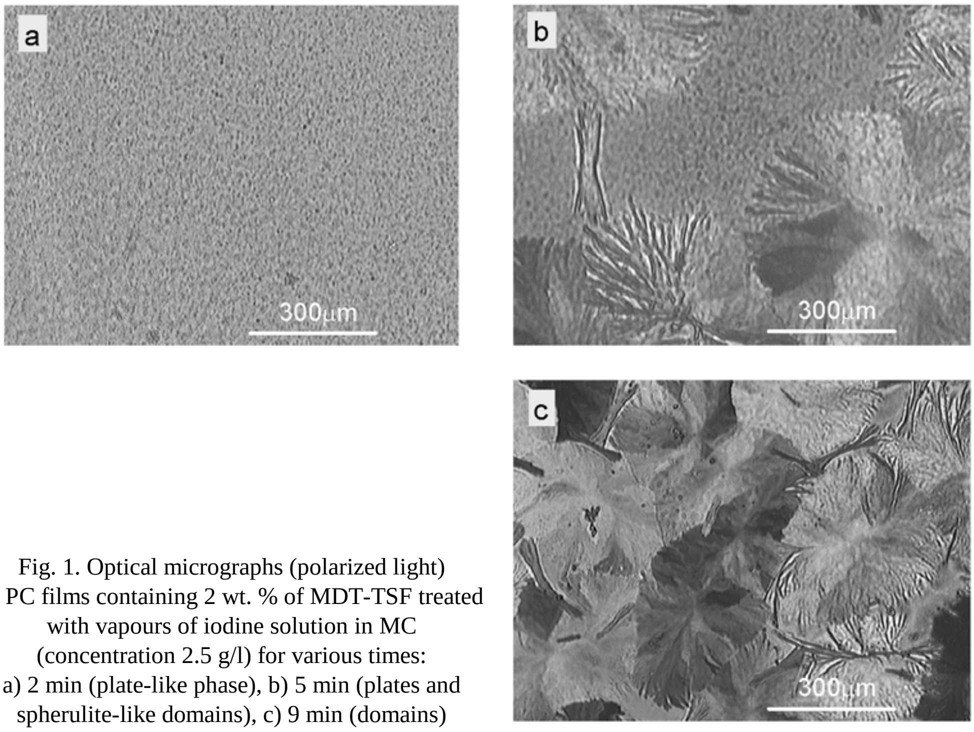


Fig. 1. Optical micrographs (polarized light) of PC films containing 2 wt. % of MDT-TSF treated with vapours of iodine solution in MC (concentration 2.5 g/l) for various times: a) 2 min (plate-like phase), b) 5 min (plates and spherulite-like domains), c) 9 min (domains)

On increasing the vapour treatment time (or the iodine concentration) the colour of the vapour-treated films changes from brown (random platelets) to olive (domains). It should be pointed out that (MDT-TSF)$I_{1.27}$ crystals obtained by electrocrystallization are also gold-olive [8]. Absorption spectra of the films with plates and with domain structures and of films before vapour treatment are compared in Figure 3. Formation of MDT-TSF salt results in a decrease of the absorption at 32 000 cm^{-1} related to neutral MDT-TSF (but not as pronounced as in other systems [2, 3]) and to a build-up of the absorption in the visible range related to I_3^- and MDT-TSF cation. The absorption bands strongly overlap (more than for surface conducting films with bis-(ethylenedioxy)-tetrathiafulvalene (BO) or ET polyiodides) and therefore it is not possible to identify peaks of I_3^- (in the range 16 000–21 000 cm^{-1}) and of donor radical cations. One can also see an increase of the base line due to light scattering by the microcrystals.

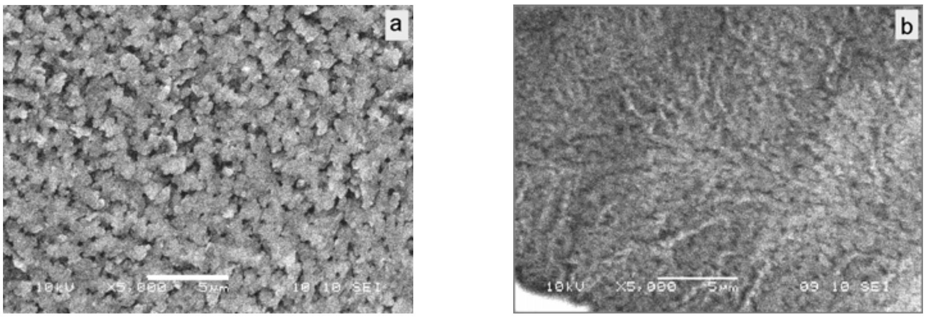


Fig. 2. SEM images showing plate-like phase (a) and domain (spherulite-like) phase (b) in PC films containing 2 wt. % of MDT-TSF treated with vapours of iodine solution in MC (concentration 2.5 g/l) for 5 min. Scale bar 5 µm

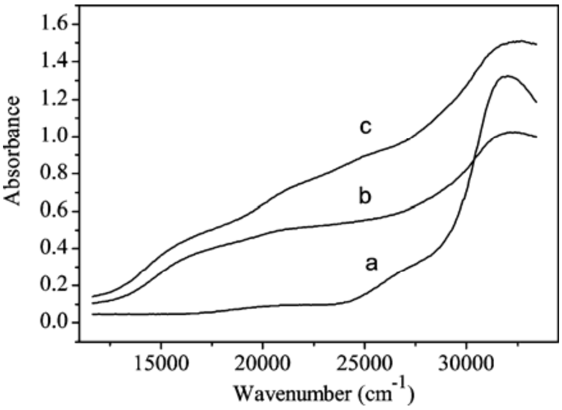


Fig. 3. Absorption spectra of PC film containing 2 wt. % of MDT-TSF: a) before treatment, b) after treatment with vapours of 2.5 g/l solution of iodine in MC for 2 min (plate-like phase), c) after treatment with vapours of 5 g/l solution of iodine in MC for 5 min (domain structures)

The surface conductivity of the films is strongly dependent on the composition of pristine films, on the kind of polymer matrix and on the vapour treatment conditions (iodine concentration, time, etc.). For a given iodine concentration, after some time the conductivity strongly increases and reaches a maximum (Fig. 4). This increase is related to formation of a conducting network. In the case of higher iodine concentration (e.g. 12 g/l), the conductivity decreases after reaching a maximum. This behaviour, which can be explained by formation of less conducting salts of higher iodine content, has also been observed in surface conducting reticulate doped systems with other donors, e.g. BO [6]. For lower iodine concentrations, the over-doping with excessive amounts of iodine does not occur and highly conducting films can be obtained in broad range of the vapour treatment time.

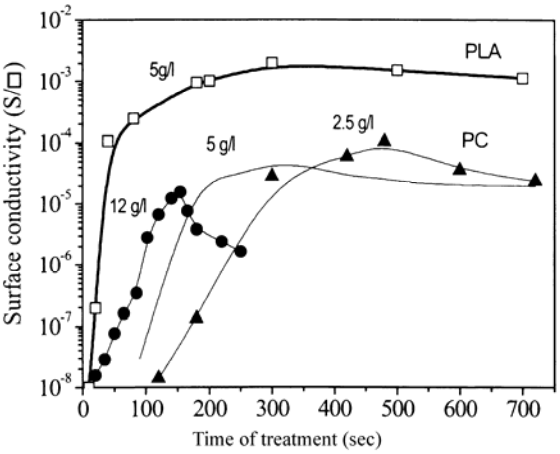


Fig. 4. Surface conductivity vs. vapour treatment time of PLA and PC films with 2 wt. % of MDT-TSF after treatment with vapours of MC solutions with various iodine concentrations (in g/l)

Although the plates formed after a short time of treatment seem to contact each other and form a continuous network (as can be seen in the SEM image in Fig. 2a), the conductivities of these films are poor. Only films containing the domain phase (like those shown in Fig. 2b) exhibit high conductivities (and also XRD maxima are clearly seen – vide infra).

Under appropriate vapour-treatment conditions, we obtained the surface conductivities of the order of 10^{-4} S/□ (percolation of the domain phase) in the case of PC matrix and even 10^{-3} S/□ in the case of PLA. However, the conductivities are still by at least two orders of magnitude smaller than those one could expect assuming that the thickness of the salt layer is ca. 200 nm (as estimated from the volume ratio of the salt and the polymer) and taking the value of specific conductivity for single crystals of the only known highly conducting MDT-TSF polyiodide, namely (MDT-TSF) $I_{1.27}$.

Highly conducting films obtained from both polymers show metal-like temperature dependence of conductivity in a broad temperature range, as is shown in Figure 5.

At the lowest temperatures a levelling of conductivity is observed. Such a behaviour has been observed in most composite systems obtained by this method and has been attributed to grain boundaries and temperature expansion coefficients. The temperature coefficient of conductivity is higher for the PLA films showing better conductivity at room temperature than the PC films (Fig. 5). For less conducting PC films, especially those in which the plate-like phase dominates, the temperature dependence of resistivity is semiconductor-like.

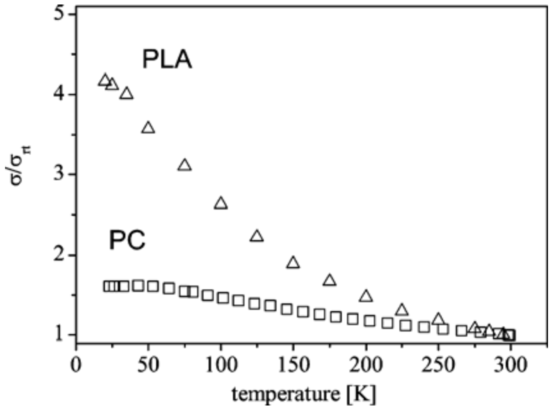


Fig. 5. Temperature dependence of relative surface conductivity for PC and PLA films with 2 wt. % MDT-TSF after treatment with vapours of iodine solution in MC (5g/l) for 6 min

Biodegradable polylactide used in this work is very good as a polymer matrix, forming films of very high conductivity, being, however, less suitable for investigations of properties of the conductive network because it is semicrystalline. The work on optimization of PLA composites and explaining the role of its crystallinity is in progress.

X-ray diffractograms of the PC films are presented in Figure 6, showing the formation of a crystalline phase of MDT-TSF salt after the vapour treatment. It is worth noting that in case of poorly conducting "brown films" obtained after short vapour treatment time (e.g., 2 min) and containing only plates, no pronounced X-ray diffraction peaks are observed. This can be explained by a small size (thickness) of crystallites and/or their poor perfection. The diffraction peaks can be seen only in films obtained after a longer vapour treatment (e.g., 3 min) and containing some domain structures (even isolated ones). One can see that the same family of peaks is observed independent on the vapour-treatment time. The intensity of the peaks increases with the vapour treatment time, i.e., with increasing amount of the domain phase (Fig. 6). The presence of only one family of peaks indicates a good orientation of the microcrystals in the film plane. On the other hand, a comparison of the structure of microcrystals in the conductive films and electrochemically grown (MDT-TSF)$I_{1.27}$ single crystals can be made using only one parameter – the interlayer spacing. In other similar systems, the observed diffraction peaks correspond to (00l) spacing in the c^* direction [3, 4, 6, 7, 12]. In the investigated MDT-TSF iodide composites, however, this is not the case. Single crystals obtained by electrocrystallization are orthorhombic, space group P_{nma}, with a = 4.013 Å, b = 12.539 Å and c = 25.620 Å, ab plane being the plane of high conductivity.

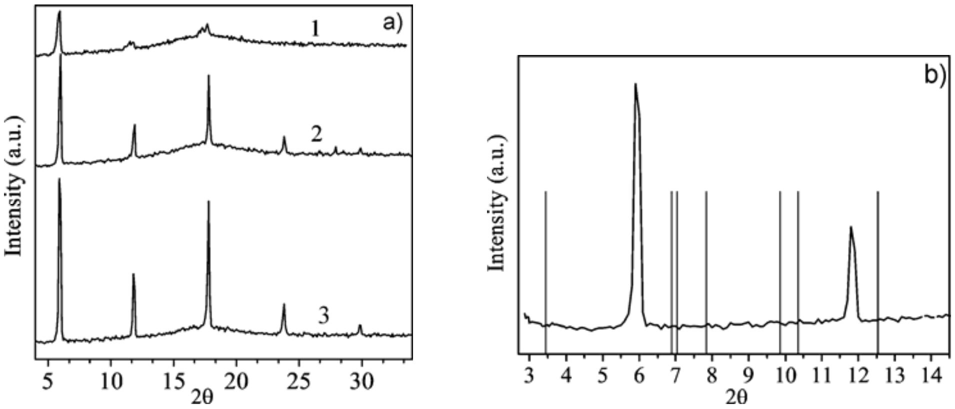


Fig. 6. X-ray diffraction patterns of PC with 2 wt. % of MDT-TSF after vapour treatment with iodine solution in MC (5 g/l) for various times: 1 – 3 min, 2 – 5 min, 3 – 8 min (a); a part of the diffractogram (3) displayed in a smaller 2θ range; the vertical bars represent the positions of all diffraction peaks expected in this 2θ range for (MDT-TSF) $I_{1.27}$, i.e. (001), (002), (010), (011), (012), (003), (013), (020), (004) (b)

In Figure 6b positions of peaks expected from random orientation of the (MDT-TSF)$I_{1.27}$ crystals (vertical bars) are compared with positions of the peaks obtained for a highly conducting film. In order to facilitate the comparison, the angular range in Figure 6b is limited to small values of 2θ. The positions of experimental and of all calculated reflexes are significantly different. This result indicates that the reaction of the neutral donor with I_2 in a swollen polymer surface yields crystals not only of different morphology but also of a different structure from those obtained in solution. The stoichiometry of the new salt in the polymer matrix is not known yet.

In order to check the actual iodine species in the conducting film, we performed Raman spectroscopy studies. This technique is a powerful tool for identification of I_3^-, both in single crystals of different highly conducting salts [13, 14] and in polymer composites [6, 15, 16]. An instrument equipped with confocal microscope was used in our studies. It was therefore possible to detect independently the Raman scattering from plate microcrystals and domains even though they were present in the same film (as in the case shown in Fig. 1b).

Resonant Raman scattering spectra of surface conducting PC and PLA films containing MDT-TSF iodide salts are shown in Figure 7. One can notice that each spectrum exhibits a strong band around 110 cm^{-1} and its overtones. The presence of a Raman scattering peak was observed in this range for various single crystals and for microcrystals in surface conductive composites with various donors [6, 13–16]. It has been unambiguously ascribed to the symmetric stretching vibrations of I_3^-. A closer inspection of the spectra in Figure 7 reveals, however, slight differences between the Raman scattering from the plates and from the domains. In the case of plates (curve 1) the maximum is at 108 cm^{-1}. In the case of the domain phase both in PC and in PLA films the maximum is observed at 105 cm^{-1}. In the domain phase, the Raman peak is only slightly asymmetric while in the plate-like microcrystals a shoulder is clearly seen at higher wave numbers. Such an asymmetry was observed for microcrystals of $(BO)_{2.4}I_3$ in polymer films (max. at 107 cm^{-1} [6]) and for single crystals of MDT-$ST(I_3)_{0.417}$ (max. at 104 cm^{-1}) [17]. The asymmetry could be explained by different molecular environments of I_3^- anions because I_3^- and BO or MDT-ST lattices are incommensurate. Although there are no structural evidences yet, the Raman spectra seem to indicate that also in the case of microcrystals in surface conducting PC and PLA films the donor and acceptor lattices are incommensurate.

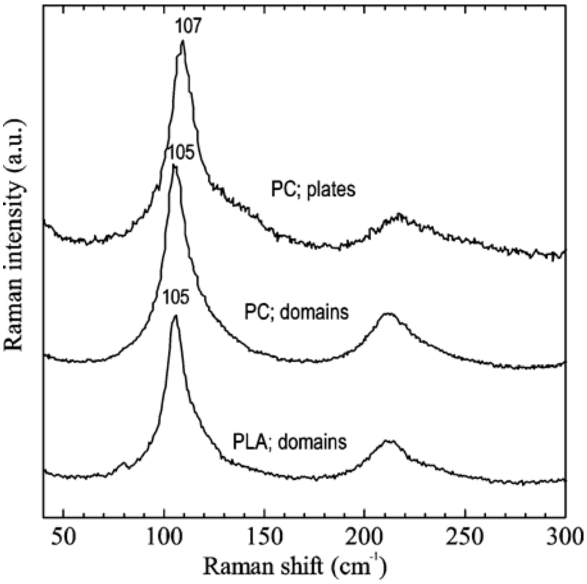


Fig. 7. Raman spectra of PC and PLA films with 2 wt. % of (MDT-TSF) treated with vapours of iodine solution in MC (2.5 g/l) for 5 min

4. Conclusions

Recently obtained asymmetric MDT-TSF donor is very well suited for fabrication of conductive composites using the two-step reticulate doping method. The reaction of the neutral donor with I_2 in swollen surface of PC or PLA films yields highly conductive microcrystals. Two morphological forms of conductive networks are obtained: random plate-like and spherulite-like domains. The percolation of the domains is a condition for high conductivity and its metallic temperature dependence. X-ray diffraction studies show that the structure of microcrystals in highly conducting domains is different from that of electrochemically grown single crystals of metallic (MDT-TSF)$I_{1.27}$.

The acceptor lattice in the new salts has been confirmed to be chains of I_3- as evidenced by the Raman studies. The two morphological forms of conducting networks have slightly different positions of the maxima ascribed to symmetric stretching vibrations of the triiodide anion. This indicates that the reaction of I_2 with MDT-TSF leads to formation of salts with various structures and stoichiometries as was found for other TTF derivatives. An unambiguous explanation of the crystal structure and properties of the networks of MDT-TSF salt forms needs further studies.

Biodegradable polylactide used in this work is very good as a polymer matrix, forming films of very high conductivity but, being semicrystalline, is less suitable for investigations of properties of the conductive network. The work on optimization of PLA composites and explaining the role of its crystallinity is in progress.

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