Ion Exchange in $(BO)_{2.4}I_3$ Microcrystals: A Method for Obtaining Colorless, Transparent, Metallically Conductive Polymer Films

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ABSTRACT: I obtained colorless, transparent, metallically conductive polymer films by anion exchange in the microcrystals of $(BO)_{2.4}I_3$ [BO = bis(ethylenedioxytetrathiafulvalene)], forming the conductive network in surface-conducting reticulate-doped polycarbonate (PC) films. Strongly absorbing I_3^- anions were replaced by I^- or Br^- anions, showing weaker absorption in visible light. Interestingly, this transformation proceeded without deterioration of the continuity of the network, and even the shape of the microcrystals was preserved. Particularly, the salt $(BO)_{2.4}I_3$ could be transformed to $(BO)_2Br(H_2O)_3$ or to $(BO)_2I(H_2O)_x$. I achieved this by immersing strongly colored $PC/(BO)_{2.4}I_3$ films in the KBr solution or by contact with a Cu plate in KI solution. Depending on the conditions of the ion-exchange reaction, colorless films showing metallic conductivity down to helium temperatures or showing semiconducting behavior below 100 K were obtained. Electrical properties of some systems are very sensitive to the partial pressure of water. The $(BO)_2Br(H_2O)_3$ and $(BO)_2I(H_2O)_x$ microcrystals could reversibly change their water content, as shown by comparative X-ray diffraction and electrical studies performed under reduced pressure or dry atmosphere and under ambient conditions. The controlled anion exchange presented in this article can be considered as a new effective way of modifying the polycrystalline networks of $(BO)_{2.4}I_3$ and other similar salts. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1465-1472, 2002

Key words: microstructure; X-ray; transparency

INTRODUCTION

Bis(ethylenedithio)–tetrathiafulvalene (ET) and bis-(ethylenedioxy)–tetrathiafulvalene) (BO) polyiodides form one of the most intensively studied families of two-dimensional organic conductors.[1] Some of the salts exhibit very interesting properties, such as metal-like conductivity or even superconductivity.[1,2] These salts are obtained in the form of tiny single crystals or microcrystalline powders, and therefore, the possible application of these interesting materials presents a serious problem.

Many studies have been carried out to obtain conducting ET and BO polyiodides in a form more applicable than single crystals, for example, in the form of polycrystalline layers.[3,4] In many cases, however, the materials with the desired properties have not been obtained. Particularly, the polycrystalline layers prepared by the evaporation of solid salts in high vacuum exhibited semiconducting behavior, whereas single crystals of $(BO)_{2.4}I_3$ or β-$(ET)_2I_3$ are organic metals.[1,2,5,6]

Metallically conducting networks of microcrystals of ET or BO polyiodides can be formed within the surface layer of polycarbonate (PC) films[7–10] by the so-called two-step reticulate doping technique.[11] Crystallization of the polyiodide occurs during the exposure of films containing 1–2 wt % of a molecularly dispersed donor, for example, ET or BO, to vapors of iodine solution in methylene chloride. Electrical and optical properties of the obtained surface polymer composites depend on exposure time and iodine concentration.[10–13] Also, other volatile acceptors such as Br_2[9] or IBr,[14] or other donors can also be used.[9,14,15]

Interestingly, the networks of ET or BO polyiodides formed within the surface layer of PC films can be modified by different methods. In such a way, the optical and electrical properties of the materials can be changed even after their preparation. Annealing PC films with α-$(ET)_2I_3$ (PC/α-$(ET)_2I_3$) results in a transformation to PC/β-$(ET)_2I_3$, which showed metallic conductivity and even an onset of superconducting transition (below 5 K), was found.[7] PC/α-$(ET)_2I_3$ films were transformed to PC/α-$(ET)_2IBr_2$ by reaction with Br_2.[16] In the latter case, not only the crystal structure but also the composition of the conducting salt was changed; nevertheless, the continuity of the conducting network was preserved.

From the point of view of optical properties, the most important feature of the $PC/(BO)_{2.4}I_3$ system, which is strongly colored (gray),[8,9] is the possibility of

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its transformation into a colorless form.[17] In previous studies, the discoloration has been performed electrochemically. The PC/(BO)$_{2.4}$I$_3$ film was used as an electrode (anode) in KI solution.[17] The transformed films showed metallic conductivity in a broad temperature range. It was assumed that the discoloration was due to removal of some unknown aggregates containing I$_3^-$; however, the structure and composition after the transformation were unknown.

It should be stressed that colorless film derived from PC/(BO)$_{2.4}$I$_3$, two important properties: metallic conductivity and high transparency, is unique among organic conducting materials or composites. Materials possessing these properties are very interesting as candidates for replacing the commonly used transparent indium tin oxide (ITO) electrodes in designing flexible, fully organic, optoelectronic systems.

In this article, the structure and properties of colorless films derived from PC/(BO)$_{2.4}$I$_3$ by new methods is discussed.

EXPERIMENTAL

BO was synthesized according to a method described earlier.[18] Poly(bisphenol-A carbonate) (PC), provided by BDH Chemicals Ltd. (Poole, UK), and other reagent grade chemicals, including methylene chloride, o-dichlorobenzene, iodine, and bromine, were used as received. Grey, PC/(BO)$_{2.4}$I$_3$ films were obtained by the two-step reticulate doping technique.[11] In the first step, I prepared polymer films with 1 wt % molecularly dispersed BO by casting from o-C$_6$H$_4$Cl$_2$ at 393 K. In the next step, these films were exposed to vapors of iodine solution (8 g/L) for 4 min. Under such conditions, the microcrystals of (BO)$_{2.4}$I$_3$ iodine salt were formed within the surface layer of the polymer film.[9]

The colorless films studied in this work were obtained by transformation of the PC/(BO)$_{2.4}$I$_3$ films with the following methods:

1. Immersion in KBr solution: PC/(BO)$_{2.4}$I$_3$ sample (5 × 15 mm) was immersed in KBr solution (0.1 g/mL) for several hours until it appeared completely discolored. After removal from the solution, the sample was washed in distilled water and dried in a stream of air. The samples discolored by this method are denoted as Im/KBr.

2. "Wet contact" with a Cu plate: First, a Cu plate (10 × 20 cm) was wetted with a droplet of KI solution (0.1 g/mL); then, the conducting surface of PC/(BO)$_{2.4}$I$_3$ film (5 × 15 mm) was gently pressed to it. After few seconds, as soon as the film became colorless and transparent, the sample was detached from the Cu plate and immediately washed in water and dried in a stream of air. The samples discolored by this method are denoted as Cu/KI.
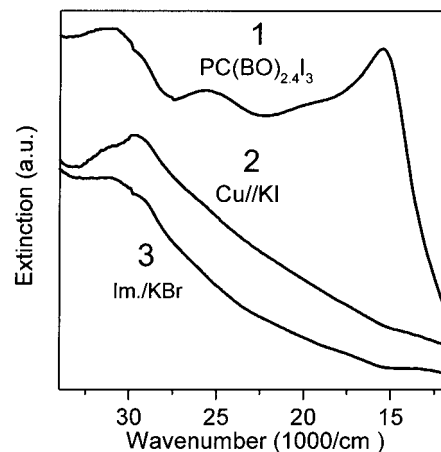

Figure 1 UV–vis absorption spectra of (1) obtained PC/(BO)$_{2.4}$I$_3$ gray film, (2) films discolored by wet contact with a Cu plate with KI solution, and (3) films discolored by immersion in KBr solution.

Some of the discolored films were further transformed by immersion in KBr or exposure to gaseous iodine. Composition of BO polyiodide microcrystals was studied with energy dispersive X-ray spectroscopy (EDX; magnification = 4000×, energy = 10 kV). X-ray diffraction studies under normal pressure or under vacuum (rotational pump, ~ 10^{-2} Pa) were performed with a Siemens diffractometer (Munich, Germany) with Ni-filtered CuK$_\alpha$ radiation (λ = 1.541 Å). Utraviolet–visible (UV–vis) spectra were recorded perpendicularly to the film surface with a Specord M-40 (Jena, GDR) Uv–vis spectrophotometer. Raman spectroscopy studies were carried out at room temperature with a Jobin-Yvon T64000 (Longjumeau, France) Raman microscope spectrometer. The power of the He–Ne laser beam was about 5 mW. Electrical resistivity measurements were performed by means of a four-probe method under vacuum with a Displex Closed Cycle Flow Cryostate DE-204SL (Advance Research Systems, Inc., Allentown, PA). In a special holder, four thin graphite electrodes were gently pressed against the 3 × 12 mm strips of the films. The resistivity was also measured by immersion of the samples equipped with four wire electrodes directly in liquid nitrogen. Air or Ar$_2$, used in some experiments, was dried by passing through a column filled with P$_2$O$_5$. Atomic force microscopy (AFM) studies were performed with an instrument constructed at the University of Lodz. The morphology of samples was also examined by means of scanning electron microscopy (SEM) with a Jeol ISM-5500 (Jeol Ltd., Akishima, Tokyo).

RESULTS

Optical properties

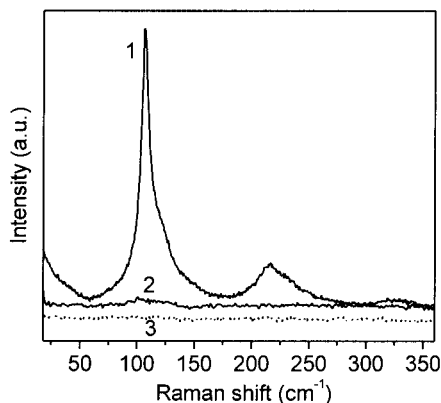The UV–vis absorption spectrum of the obtained PC/(BO)$_{2.4}$I$_3$ film and the spectra of discolored films are

Figure 2 Raman spectrum of (1) PC/$(BO)_{2.4}I_3$ gray film and the films discolored (2) by immersion in KBr solution or (3) by wet contact with a Cu plate with KI solution.

compared in Figure 1. The intense absorption band at about 15,600 cm^{-1} in the spectrum of the gray PC/$(BO)_{2.4}I_3$ film (curve 1) is assigned to the I_3^- anion.[8] As one can see, all discolored films showed a dramatic decrease in absorption in the visible range.

Important changes between the gray PC/$(BO)_{2.4}I_3$ films and the colorless films were observed in the Raman spectra (Fig. 2). Raman spectroscopy is a powerful tool for identification of I_3^- and other trihalides (e.g. I_2Br or IBr_2), both in single crystals of different salts[19] and in polymer composites.[14,20] The obtained gray PC/$(BO)_{2.4}I_3$ film showed a peak around 107 cm^{-1} (curve 1 in Fig. 2).

Analysis of the Raman spectra of other polyiodide salts,[21] indicated that this peak could be attributed to the symmetric stretching mode of I_3^-. Asymmetry of the absorption band (a shoulder at higher wave numbers) could be explained by the different molecular environment of I_3^- anions in the $BO_{2.4}I_3$ crystal because the I_3^- and BO lattices are incommensurate.[5] In all colorless films (curves 2 and 3 in Fig. 2), the peak at 107 cm^{-1} was not observed.

When the discolored films were exposed to I_2 vapors, they became strongly colored again. Their UV–vis and Raman spectra became similar to those before the discoloration; that is, the absorption bands related to I_3^- reappeared.

MORPHOLOGY

The AFM image of the obtained gray film PC/$(BO)_{2.4}I_3$ is shown in Figure 3(a). One can see a network of plate-like microcrystals. The thickness of the microcrystals was less than 50 nm. An image of the film discolored by immersion in KBr solution is shown in Figure 3(b). As one can see, the discoloration process did not change the morphology of the microcrystals.

This was in agreement with the morphological studies performed with SEM. In Figure 4, the boundary between colored and the discolored part of the film is

shown. As one can see in both parts of the film, the plate-like crystallites were similar. However, the contrast between the two parts of the film observed with the composition mode [Fig. 4(c)] indicated that the composition of the microcrystals in the colored and colorless parts of the film was different. Also, further transformation of films by immersion in KBr solutions or exposure to iodine vapors did not change the morphology of the microcrystals.

Composition

The EDX spectra of different films showed the peaks indicating the presence of C, O, Cl, S, and I or Br atoms. The presence of Cl was due to the trace amount of *o*-dichlorobenzene remaining in the polymer film. The I:S or Br:S ratios shown in Table I provide information about the average composition of the salt, that is, the BO:I or BO:Br ratios.
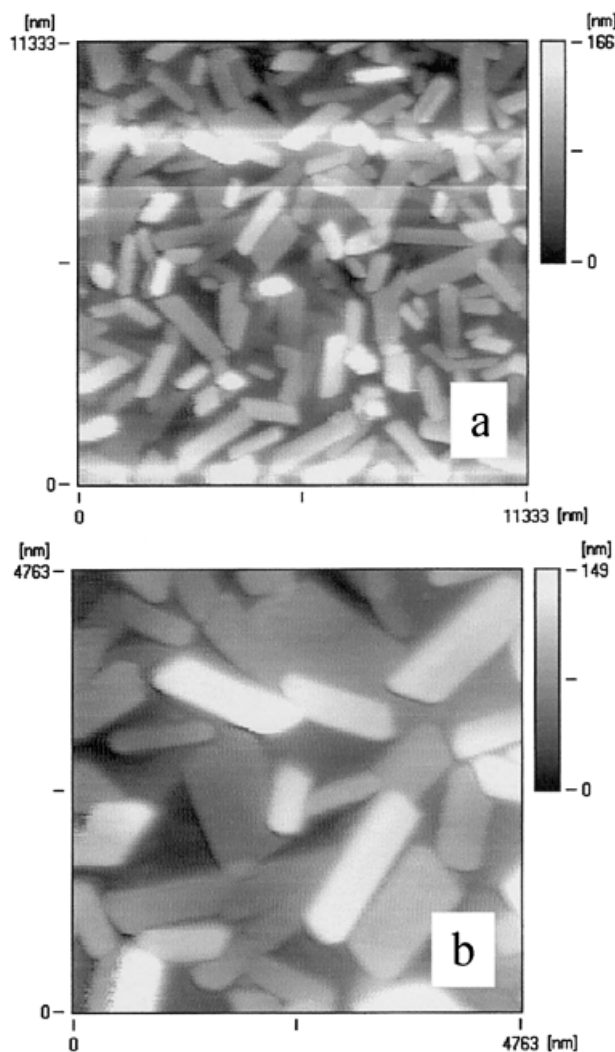

Figure 3 AFM images of the surface of (a) the obtained PC/$(BO)_{2.4}I_3$ gray film and (b) the film discolored by immersion in KBr solution.
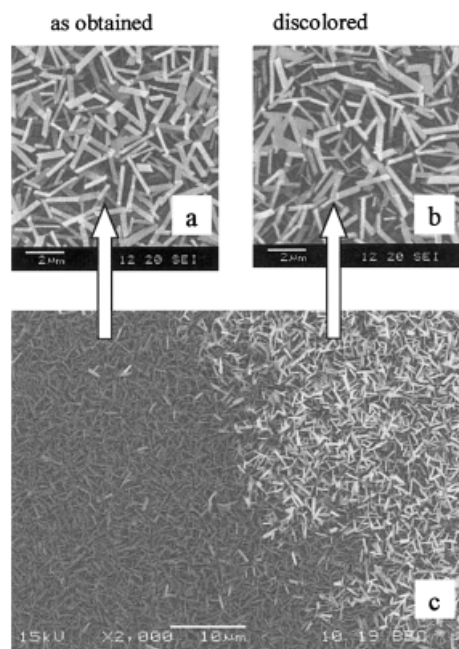
Figure 4 SEM images of (a) the boundary between the obtained PC/(BO)$_{2.4}$I$_3$ film and (b) the part of the film discolored by wet contact with a Cu plate with KI solution. The bottom image (c) and the upper images (a,b), showing the magnified areas of the two parts of the sample were obtained with back-scattered electrons mode (composition mode) and secondary electrons mode (topography mode), respectively.

The I:S ratio was 0.33 for the obtained films and agreed well with the 0.31 ratio expected for (BO)$_{2.4}$I$_3$. In the films discolored by immersion in KBr solution, not iodine but only bromine was detected. This indicated that the iodine was replaced by bromine. The ratio Br:S = 0.13 was very close to 0.125 expected for the stoichiometry BO:Br = 2:1. In the films discolored by wet contact with Cu, the S:I ratio was also about three times smaller than for PC/(BO)$_{2.4}$I$_3$. This meant that after discoloration, the amount of iodine decreased about three times, and the BO:I ratio was close to 2:1. The EDX analysis of the surface of the Cu plate that was in contact with the film indicated clearly that the iodine from (BO)$_{2.4}$I$_3$ salt reacted with Cu. The iodine in the films discolored by wet contact with Cu could be replaced by bromine when such films were immersed in KBr solution for about 30 min. In such films, the ratio Br:S = 0.12 also suggested that the stoichiometry BO:Br in the microcrystals was 2:1.

TABLE I
I:S and Br:S Ratios in Microcrystals in Different Films Studied with EDX

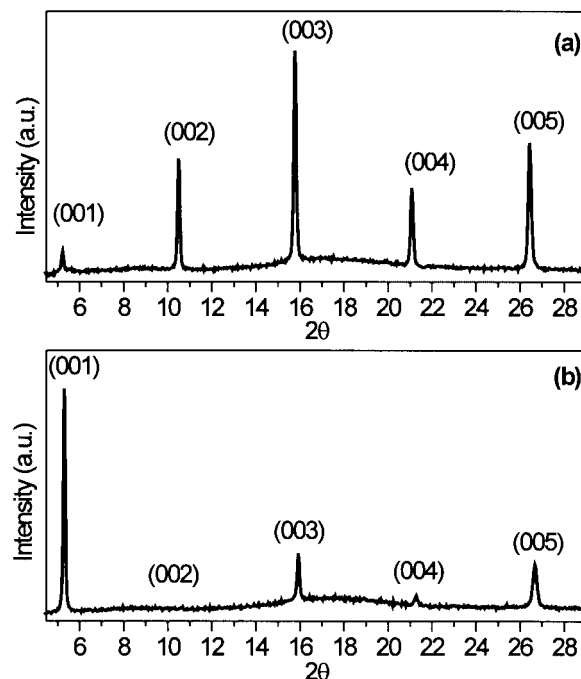| Sample	I:S	Br:S
Obtained	0.33	0.00
Im/KBr	0.00	0.13
Cu//KI	0.12	0.00
Cu//KI + KBr	0.00	0.12

Figure 5 Diffraction patterns of surface conductive polycarbonate films with BO: (a) obtained gray PC/BO$_{2.4}$I$_3$ and (b) film discolored by wet contact with Cu.

Structure

In Figure 5, the diffractograms of the obtained gray PC/(BO)$_{2.4}$I$_3$ film and one of the discolored films are compared. In both diffraction patterns, only the peaks related to the reflections from (001) planes were seen. This could be explained by the preferential orientation of the microcrystals with their c axis perpendicular to the film surface (like in others PC films with BO or ET salts.[9–12]). The comparison of the microcrystal structure in different films was, therefore, reduced to only one parameter: the interlayer spacing, d (the distance between the conducting sheets of cation). As one can see, the shapes of the diffractograms (the relative ratio of the peak's intensities), shown in Figure 5, were different. In the diffraction pattern of PC/(BO)$_{2.4}$I$_3$ film, the first peak corresponding to (001) reflection was the smallest, and the (003) dominated. In the diffractogram of the colorless films, the (001) peak was the most intense. The diffractograms of shape similar to that shown in Figure 5(a) were obtained also for films with BO$_2$Br(H$_2$O)$_3$.[9] The intensity of other peaks was much weaker, and the peaks (002) and (004) were hardly seen in most cases. Such shape of the diffractograms was characteristic of all colorless films. However, the exact positions of the peaks in the diffraction patterns of PC/(BO)$_{2.4}$I$_3$ and of the discolored films were slightly but significantly different. For films discolored by immersion in KBr solution, the diffraction from (001) planes was observed at higher 2θ than in the case of PC/(BO)$_{2.4}$I$_3$ film. All peaks were shifted proportionally, so these differences were best seen for
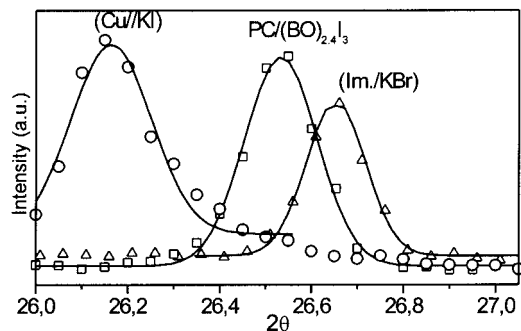
Figure 6 Diffraction patterns of (□) the obtained PC/$BO_{2.4}I_3$ film and the films discolored (△) by immersion in KBr solution and (○) by wet contact with Cu with KI solution. Lines represent the Gaussian fit to experimental points.

the (005) peak. It is clearly demonstrated in Figure 6, where the diffractograms of various systems are compared in a narrower 2θ range [(005) reflection]. As one can see for films discolored by immersion in KBr solution (△), the diffraction from (005) planes was observed at 26.64°, whereas for untreated PC/$(BO)_{2.4}I_3$ film (□), it was observed at 26.55°. This indicates that the microcrystals in the discolored film were formed of different BO salts with the d = 16.72 Å, slightly smaller than d = 16.77 Å for $(BO)_{2.4}I_3$. Interestingly, for the films discolored by wet contact with Cu with KI solution (○), the diffraction from (001) planes was observed at 2Θ smaller than for PC/$(BO)_{2.4}I_3$ film-[e.g., (005) at 26.16]. If this means that d in the microcrystals in the discolored films (d = 16.95 Å) was larger than in $(BO)_{2.4}I_3$ (d = 16.77 Å). The changes of the diffractograms [(005) reflection] of the discolored films after further modifications are shown in Figure 7. In Figure 7(a), the influence of immersing in KBr solution is illustrated. As one can see, the peaks in the diffraction patterns of the films first discolored by wet contact with Cu with KI solution was, after immersion in KBr solution, shifted toward higher 2θ. All the (001) peaks [only (005) shown in Fig. 7] were observed at the same positions as for PC/$(BO)_{2.4}I_3$ films directly discolored by immersion in KBr solution [compare Figs. 7(a) and 6]. In Figure 7(b), the the changes of the diffractograms of discolored films after recoloration by exposure to I_2 vapors are shown. As one can see, after recoloration, the diffraction peaks of the films discolored by wet contact with Cu or by immersion in KBr solution were shifted to the position corresponding to diffraction from $(BO)_{2.4}I_3$ (compare Figs. 7(b) and 6).

Electrical properties

The surface resistivity (ρ_s) of discolored films measured at ambient conditions was of the order of 10^3–10^4 Ω/square that is, it was only slightly higher than ρ_s of the obtained PC/$(BO)_{2.4}I_3$ films. Systematic mea-

surements of the temperature dependence of resistivity were performed under vacuum with a helium cryostat. The temperature dependences of ρ_s for the obtained PC/$(BO)_{2.4}I_3$ and for discolored films normalized at room temperature $[\rho_s(T)/\rho_s(300\ K)]$ are compared in Figure 8. As one can see, the films discolored by wet contact with a Cu plate (curves 2 and 3) showed metal-like temperature dependence of conductivity (down to the lowest temperature measured) similar to the obtained PC/$(BO)_{2.4}I_3$ films (curve 1). The CU//KI + Im/KBr films and the films discolored by immersion in KBr solution were metallic at higher temperatures but became semiconductive below 100 K (curves 3 and 4, respectively). The points in Figure 8 not belonging to the curves correspond to the measurements of resistivity performed on samples immersed in liquid nitrogen. For the obtained PC/$(BO)_{2.4}I_3$ or films discolored by wet contact with a Cu plate (Cu//KI), the values of $\rho_s(77\ K)/\rho_s(300\ K)$ measured in liquid nitrogen (diamond or triangle) and measured at 77 K in the cryostat under vacuum (curve 1 or curve 2) were similar. However, for the Cu//KI films subsequently immersed in KBr solution (big square) or for the films discolored by immersion in KBr solution (big circle), the difference between the values of $\rho_s(77\ K)/\rho_s(300\ K)$ measured in the liquid nitrogen were considerably smaller than in the cryo-
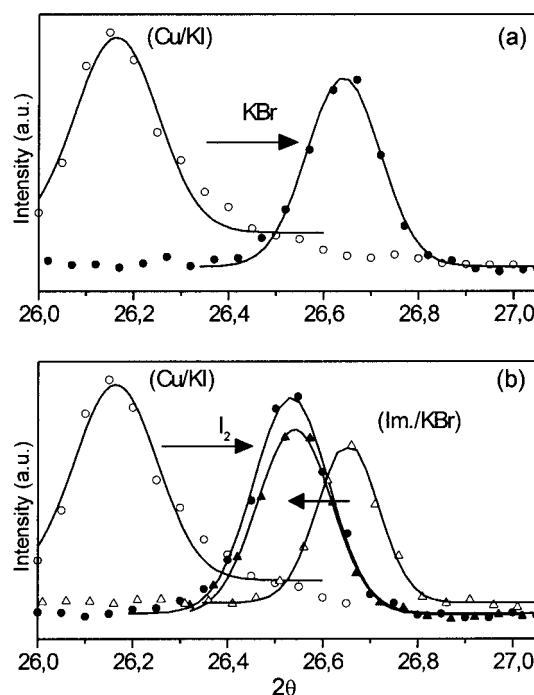

Figure 7 (a) Diffraction patterns of the film discolored by wet contact with Cu with KI solution (open symbols) before and (solid symbols) after immersion in KBr solution. (b) Diffraction patterns of films discolored open symbols by wet contact with a Cu plate with KI solution and by immersion in KBr solution (open symbols) before and (solid symbols) after exposure to I_2 vapors. Lines represent the Gaussian fit to experimental points.
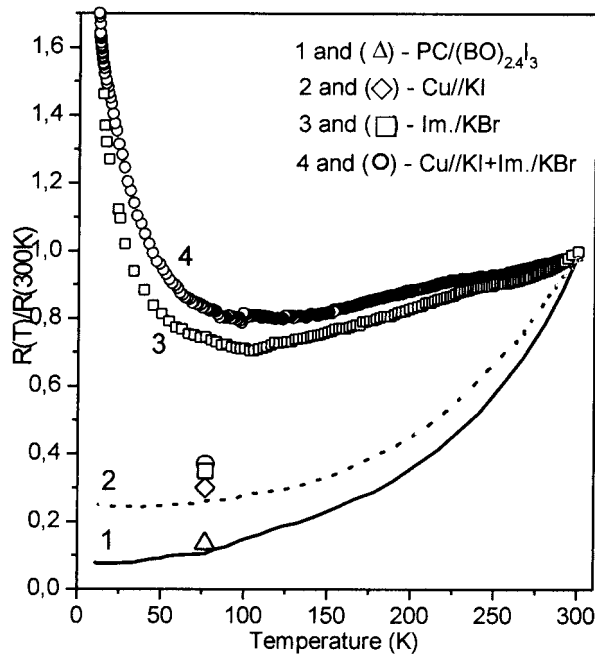
Figure 8 Temperature dependence of the relative e_s for the obtained $PC/(BO)_{2.4}I_3$ and different discolored films. The points not belonging to the curves correspond to the measurements of resistivity performed on samples immersed in liquid nitrogen.

stat under vacuum (curves 3 or 4). This results indicate the important influence of the reduced pressure on the electrical properties of some of the discolored films.

Influence of pressure and humidity on structure and electrical properties

For all discolored films, an increase in the resistivity at room temperature was observed when the pressure in the cryostat decreased. Films discolored by wet contact with a Cu plate showed an increase of about 1.2–1.5 times. For some films discolored by immersion in KBr solution, the increase in resistivity was even one order of magnitude. The increase in resistivity occurred during first 2 min of evacuation. However, when the air was let into the vacuum chamber, the resistivity of discolored samples returned after several minutes to the initial value. Interestingly, when the dry Ar gas or dry air was let into the chamber, instead of the ambient air, the resistivity was nearly the same as under vacuum. However, when the ambient (humid) air replaced dry air (or Ar), the resistivity decreased again and returned to the initial value. This suggests that the previously mentioned changes of electrical properties could be related to the changes in the amount of water incorporated in the discolored microcrystals. Some differences in the microcrystal structure under vacuum and in air were, therefore, expected. Indeed, for all discolored samples, the diffraction from (001) planes under vacuum was observed at higher 2Θ than under ambient conditions.

This indicated that d decreased under vacuum. The width of the diffraction peaks was bigger, indicating higher disorder in discolored crystals along their c^* axis. In some films, only the first, which was the most intense (001), peak could be detected. In Figure 9, the first diffraction peaks of different systems under ambient conditions (solid lines) and under reduced pressure (dashed lines) are compared. For the films discolored by wet contact with a Cu plate (Cu//KI), the spacing decreased by about 0.05 Å from $d = 17.00$ Å to $d = 16.65$ Å. The biggest decrease in d under vacuum by about 0.27 Å (from $d = 16.72$ Å to $d = 15.45$ Å) was observed for films discolored by immersion in KBr solution (or samples discolored by wet contact with a Cu plate and subsequently immersed in KBr solution).

The changes in d stimulated by the changes in the partial pressure of water were reversible. When the diffraction experiment for a given sample was performed under ambient conditions, the (001) reflexes were detected again at the previous positions (see dotted lines in Fig. 9).
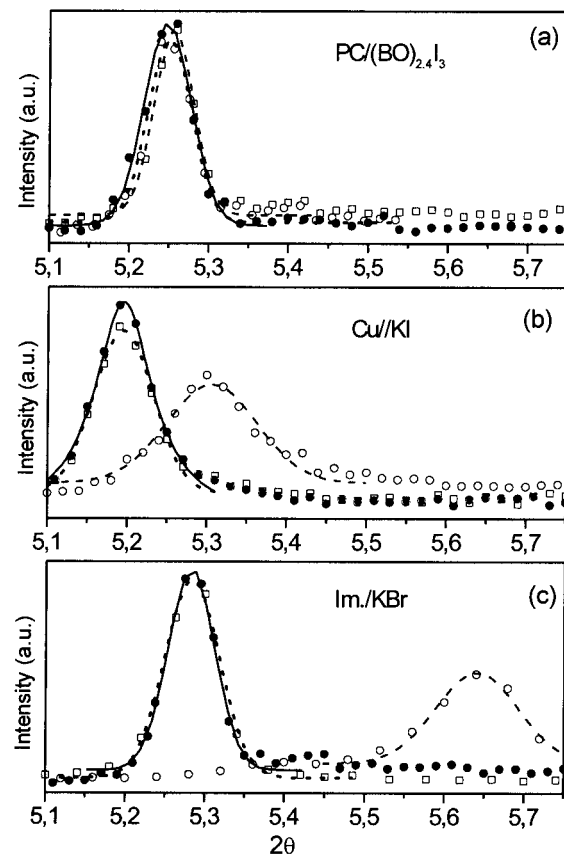

Figure 9 Diffraction patterns of (a) the obtained $PC/(BO)_{2.4}I_3$ film (b) the film discolored by contact with Cu in KI solution, and (c) the film discolored by immersion in KBr solution. Different lines represent the patterns obtained in the three successive diffraction experiments: (—) under ambient conditions, (– – –) under reduced pressure, and (. . .) after 30 min under ambient conditions.

DISCUSSION

The disappearance of the UV–vis absorption maximum at 15,600 cm^{-1} in the discolored films indicated that the microcrystals of $(BO)_{2.4}I_3$ were transformed to microcrystals that do not contain I_3^-. This conclusion was confirmed by the results of Raman spectroscopy of the discolored films, that is, the disappearance of the peak at 107 cm^{-1} related to the stretching mode of I_3^-. Also, the results of EDX studies proved that the discoloration process was accompanied by the decrease in iodine content in the microcrystals. The S:I or S:Br ratios close to 0.125 indicated that the stoichiometry BO:I or BO:Br in the discolored films was 2:1. This indicated that the microcrystals contained I^- or Br^- ions instead of I_3^-. Along with the orientation of the BO molecules, which prevented the absorption of the incident light normal to the film surface,[8] these anions did not absorb the visible light contrary to trihalides ones (I_3^- or Br_3^-), and therefore, the films were colorless.

When one takes into account that the BO:I or BO:Br ratio is 2:1, it seems that the $(BO)_2I$ or $(BO)_2Br$ salts should be considered as the product of the transformation of $(BO)_{2.4}I_3$ into "colorless form." However, no structurally characterized BO or ET conducting salts containing halogen anions alone are known. Therefore, $(BO)_2I(H_2O)_x$ or $(BO)_2Br(H_2O)_x$ should rather be taken into account as salts forming conducting networks in colorless film because the discoloration process occurs in water solution. Several conducting ET or BO salts are known, containing complex halogen anions, in which halogen ions and water molecules (or hydroxonium cations) are held together by hydrogen bonds, for example, $(ET)_4Cl_2(H_2O)_6$,[22] $(ET)_4Cl_2(H_2O)_4$,[22] $(ET)_3Cl_{2.5}(H_5O_2)$,[23] $(ET)_3Cl_2(H_2O)_5$,[24] $(ET)_3Cl_2(H_2O)_2$,[25] $(ET)_3Br_2(H_2O)_2$,[26] $(ET)_2Br(H_2O)_3$,[27,28] $(BO)_2Cl(H_2O)_x$,[22] $BO_2Cl_{1.28}(H_3O)_{0.28}(H_2O)_{2.44}$,[22] $(BO)_2Cl_x(H_2O)_y$,[29] and $(BO)_2Br(H_2O)_3$.[8] The crystals of these salts are usually unexpected products of the synthesis (e.g., due to air humidity[25]). In some cases, the exact content of water is still under debate.

The concept that the discolored films contained microcrystals with complex hydrated halogen was also supported by the sensitivity of their electrical properties and structure to the partial pressure of water. The poor stability of BO or ET salts containing water has been mentioned in some articles. For example, in the case of $(ET)_3Cl_2(H_2O)_2$, the dehydration process on heating was monitored by DTA.[22] In the case of $(BO)_2Br(H_2O)_3$, changes in electrical conductivity under vacuum and under pressure were reported.[30] Not reported, however, was the change in the crystal structure of BO halogen salts due to the loss of water molecules. Some structural changes at room temperature under vacuum were seen in Weissenberg patterns for a single crystal of $(BO)_2ReO_4(H_2O)$.[31] The authors suggested that these changes were due to water molecules going out from the crystal.

As evidenced by the AFM and SEM studies, the shape of the microcrystals remained unchanged after discoloration. This suggests that the changes of the anion composition and structure occurred via an intercalation mechanism. Such a mechanism was possible because $(BO)_{2.4}I_3$ salt is formed of alternating sheets of cation ($BO^{0.42+}$) and of anion (I_3^-). When one assumes that the reaction of anion exchange occurs only within the anion sheets, it is very likely that the conducting bands within the cation sheets (two-dimensional network of S…S and S…O interactions allowing the electron delocalization) would be preserved. This could explain why the films after discoloration were still conducting. However, the distance between the cation sheets (d) would have been dependent on the "thickness" of the anion sheets. Indeed, as evidenced by X-ray diffraction, d in the discolored films was different than in $BO_{2.4}I_3$.

The loss of water in microcrystals in all discolored films led to the decrease in d (Fig. 9). This could be explained by a decrease in the thickness of the anion sheets. In the case of the films discolored by wet contact with Cu, d under reduced pressure was similar to that in $PC/(BO)_{2.4}I_3$, and these films exhibited metallic conductivity. The structure and the electrical properties were not changed under reduced pressure, similar to $PC/(BO)_{2.4}I_3$ films. Probably the decrease in d in the microcrystals in these films was only due to the change in the water content in the anion layers, whereas the structure of cation sheets was the same as in $(BO)_{2.4}I_3$.

Under reduced pressure, d in the microcrystals in the films discolored by immersion in KBr solution was much smaller than in $(BO)_{2.4}I_3$, and the films showed semiconducting behavior below 100 K. One may speculate that in this case, the dehydration resulted also in some rearrangement within the sheets of BO molecules (e.g., an increase in the inclination of BO molecules), resulting in different electrical properties.

Under ambient conditions, d of the films discolored by immersion in KBr solution agrees with d in $(BO)_2Br(H_2O)_3$. This indicated that microcrystals of $(BO)_{2.4}I_3$ were transformed to $(BO)_2Br(H_2O)_3$. Under vacuum, however, these microcrystals transformed (reversibly) to an unknown salt with smaller d (Fig. 9). It should be stressed that BO (or ET) halogen salts containing hydrated Br^- or Cl^- anions only were structurally characterized up to date. The results presented in this article prove that conducting BO salts containing hydrated I^- anions [$(BO)_2I(H_2O)_x$] also exist; however, at present, it is not possible to give the unit cell parameters and the exact composition of these salts.

Although the optical properties of the colorless $PC/(BO)_2Br(H_2O)_3$ and $PC/(BO)_2I(H_2O)_x$ films are similar, the big advantage of the latter system is higher stability against reduced pressure and metallic behavior similar to $PC/(BO)_{2.4}I_3$. One should take into account

that the processes leading to the anion exchange and the sensitivity of some BO salts to the partial pressure of water reported in this article were not only related to polymer composite materials containing very thin microcrystals. In the interpretation of reflection spectra of single crystals, the presence of modified surface layers should be taken into account. Indeed, the differences in the Raman scattering and polarized reflectivity of $(BO)_2Cl(H_2O)_3$ or $(BO)_2Cl(H_2O)_3$ thin crystals studied under ambient conditions and in a vacuum were reported recently.[30,32]

The possibility of the observation of the dehydration processes for "bulky" single crystals would depend on the time scale of measurements. For example, in the case of a $(BO)_2ReO_4(H_2O)$ single crystal, the change in the structure under vacuum at room temperature was observed after 1 or 2 days.[31]

Other results not included in this article indicated that discoloration of gray films occurred also after immersion of $PC/(BO)_{2.4}I_3$ in pure water. By immersion in solutions containing Cl^- anions (e.g., NaCl or KCl), the triiodide anions in $(BO)_{2.4}I_3$ are replaced by chlorine anions. The discoloration occurs very fast in contact with different metals, in particular, with the conductive silver paint commonly used for attaching wire electrodes for conductivity measurements. In the latter case, if the contact is made even in pure water, the discoloration is very fast. If a $PC/(BO)_{2.4}I_3$ sample with a Ag electrode is left under ambient conditions, the film becomes colorless around the electrode after several weeks due to air humidity.

CONCLUSIONS

It was shown that the transformation of gray $PC/(BO)_{2.4}I_3$ film to colorless forms is related to the change of the composition and the structure of microcrystals. Strongly absorbing I_3^- anion was replaced by less absorbing $[I(H_2O)_x]^-$ or $[Br(H_2O)_y]^-$ anions. The controlled anion exchange presented in this article can be considered as a new effective way of modifying the polycrystalline networks of $(BO)_{2.4}I_3$.

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