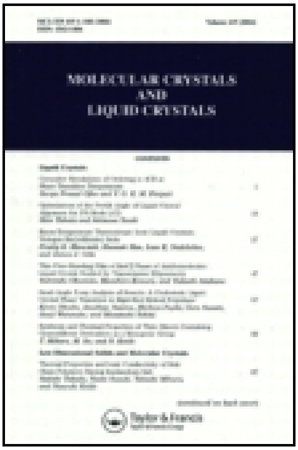

# Molecular Crystals and Liquid Crystals

# Raman Spectroscopy of Polymer Composites with Thin Layers of Bedt-Ttf Trihalide Salts

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# RAMAN SPECTROSCOPY OF POLYMER COMPOSITES WITH THIN LAYERS OF BEDT-TTF TRIHALIDE SALTS

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*Conducting polycrystalline layers in polymer composites have been prepared by a two step reticulate doping technique i.e. by exposing solid solution of bis-(ethylenedithiotetrathia)fulvalene (BEDT-TTF) in the polymer matrix to vapours of solvent containing $I_2$ or IBr. Characterisation of trihalide anion mixtures in the obtained layers of BEDT-TTF salts was completed by low frequency Raman spectroscopy. The surface morphology and the chemical composition of the layers were investigated by means of scanning electron microscopy with energy dispersive X-ray microanalysis and atomic force microscopy.*

*Keywords*: Raman spectroscopy; organic conductors; BEDT-TTF salts; conducting composites; AFM

## INTRODUCTION

The progress in the microelectronic and optoelectronic industry is in a great part based on the design of novel technologies and materials. From this point of view, organic conductors of different forms (single crystal, polycrystalline and composite materials) are of special interest.

We would like to thank to Dr. A. Tracz from Centre of Molecular and Macromolecular Studies, Polish Academy of Science, Lodz for help in the composite preparation. This work was supported by KBN (Poland) grant No 7 T08A 013 20 and RFBR No 00-03-3320 (Russia).

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The concept of material engineering involves modifications of the chemical and physical properties that may be achieved by exchanging either the entire molecules or just the atoms. Incomplete substitution leads to non-stoichiometric or mixed materials, whose physical properties can be modified *via* different substitution ratios.

In the wide range of conducting organic crystals a special attention is devoted to bis(ethylenedithiotetrathia)fulvalene BEDT-TTF trihalide salts mainly due to the unique properties of the superconducting $\beta$-(BEDT-TTF)$_2$I$_3$ salt [1–6]. The physical properties of these salts are changed by complete or partial substitution of the iodine atoms with smaller halogens (bromine and chlorine) and/or metals (gold and copper) [1–3,7–9]. The synthesis of a new material with higher $T_c$ does not automatically guarantee its application, since the form of the substances and processing difficulties are very often the factors limiting possibilities of practical applications. It is therefore interesting to combine the electrical properties of organic crystals with the mechanical properties of polymers by preparing composites. A modification of the two step reticulate doping technique (RDT) [10,11] is one of the promising methods that can be used, since it can yield materials that are relatively simple to prepare and not limited in size. This technique when applied to BEDT-TTF triiodide salts yields bilayered metallically conducting composites with metal-like properties showing an onset of superconducting transition [12,13]. Further applications of the two step RDT has yielded conducting polymer films with polycrystalline layers of BEDT-TTF trihalides containing different mixtures of anions [14–16]. In the present paper the anion mixture in the composites is characterised by Raman spectroscopy (RS) and energy dispersive X-ray microanalysis (EDX). Additionally, scanning electron microscopy (SEM) with EDX cartography and atomic force microscopy (AFM) are applied to complete the knowledge about the surface morphology of produced two-layered composites.

## EXPERIMENTAL

### Materials Preparation

In the first step of the RDT, the non-conductive, 15–120 μm thick, homogeneous, and transparent polymer films with molecularly dispersed BEDT-TTF (2 wt. %) are produced by casting. In the second step the film surface is exposed to the mixture of an acceptor-solvent vapours. The solvent ($CH_2Cl_2$) penetrates the film and the acceptor ($I_2$ or IBr) reacts with BEDT-TTF molecules forming the trihalide salt micro-crystals in the near-surface layer. Several different bilayered reticulate doped polymer (BRDP) films were prepared by using this technique:

i) The composites with α-$(BEDT\text{-}TTF)_2I_3$ were obtained by exposing at room temperature the polymer films containing 2 wt.% of BEDT-TTF to vapours of $I_2/CH_2Cl$ solution of two different concentrations: (15 mg/ml) for 6 minutes or (50 mg/ml) for 1 minute. Three polymers were used: polycarbonate (PC), poly(methyl-methacrylate) (PMMA), and polystyrene (PS) [17,18].

ii) The PC + β-$(BEDT\text{-}TTF)_2I_3$ BRDP composite was prepared by treatment of PC films containing 2 wt. % of BEDT-TTF with vapours of $I_2$/TCE solution (2.9 mg/ml) for 150 seconds at elevated temperature (378 K) [19] (β crystal phase obtained at elevated temperature is sometimes labelled β-$(BEDT\text{-}TTF)_2I_3$ [20]). Some of these samples were afterwards exposed for 10 minutes to vapours of $Br_2/H_20$ solution (0.1 mg/ml) at room temperature [15,21]. For our studies these composites were provided by Dr. A. Tracz from CBMiM - Polish Academy of Science.

iii) PC + BEDT-TTF/IBr composites were prepared by exposure of PC films containing 2 wt.% of BEDT-TTF with vapours of $IBr/CH_2Cl_2$ solution for 30, 60, 90, 120, 180, and 480 seconds at room temperature. The solution was prepared by diluting the 1.0 M IBr $CH_2Cl_2$ with pure $CH_2Cl_2$ at a 1:50 ratio giving concentration of 4 mg/ml.

## Experimental Conditions

Raman spectra were investigated using a Jobin–Yvon T64000 Raman spectrometer with confocal microscope, working in back-scattering mode. The Raman spectra of composites were taken at 20 K in a home-made liquid helium contact cryostat or at 80 K in a liquid nitrogen contact cryostat (Linkam THM 600 stage) using 458, 514, and 632 nm laser lines (spectral resolution 2 $cm^{-1}$). Also the $IBr/CH_2Cl_2$, $I_2/CH_2Cl_2$, and $Br_2/CH_2Cl_2$ solutions were investigated using the 514 nm laser. The laser beam power entering the apparatus optics was kept below 1 mW giving about 100 $kW/m^2$ energy density at the sample. Only low frequency spectral regions were recorded - *ca.* 20 500 $cm^{-1}$ range. For all the investigated BRDP composites the Raman spectra are non-sensitive to rotation of the sample around an axis perpendicular to the surface, due to the random orientation of the ***a*** and ***b*** crystallographic axes of the individual microcrystals (***c***-axis is perpendicular to the sample surface) [13,22].

Using JEOL scanning electron microscope model JSM-5800L with PGT microanalyses extension model IMIX-PTS the EDX microanalyses of sulphur, iodine, and bromine atomic concentration were conducted for PC + β-$(BEDT\text{-}TTF)_2I_3$ composites before and after treatment with $Br_2$ vapours as well as for the PC films containing 2 wt.% of BEDT-TTF before and after exposure to $IBr/CH_2Cl_2$ solution. The cartography images of the sulphur, iodine, and bromine, distribution on the surface of the PC + BEDT-TTF/IBr

BRDP composites were obtained. The dimensions of the micro-crystals in the polycrystalline layers were investigated by means of AFM working in tapping mode.

## RESULTS AND DISCUSSION

### BRDP Composites with $(BEDT\text{-}TTF)_2I_3$ Salts

Generally in the BRDP composites obtained at room temperature using $I_2/CH_2Cl_2$ solution the $\alpha$-$(BEDT\text{-}TTF)_2I_3$ phase is mainly present [12,13,22–24]. The sharp M-I transition (at 135 K) in single crystals [25] was observed for BRDP composites as a continues drop of the dc conductivity in a 80–140 K temperature range [12,13,22–24]. The reaction of BEDT-TTF and $I_2$ in a swollen film at elevated temperatures leads to the formation of conducting layer of the $\beta$- $(BEDT\text{-}TTF)_2I_3$ micro-crystals and the film shows metal-like dependence of conductivity down to 10 K [19,24].

In the spectra *(1a)* and *(1b)* (Fig. 1) of the PS + $(BEDT\text{-}TTF)_2I_3$ films evaporated from saturated (50 mg/ml) iodine solution the 108 and 117 $cm^{-1}$ bands are arising from the $I_3^-$ anions [26–28]. The recorded intensity of the 108 $cm^{-1}$ band (with overtones in a 217, 327, 437, 547, and 657 $cm^{-1}$ progression) differs for various places of the composite surface. Spectrum *(1a)* shows the highest, while spectrum *(1b)* the lowest recorded intensity of the 108 $cm^{-1}$ band with respect to the 117 $cm^{-1}$ band. The 29 and 117 $cm^{-1}$ bands in the spectra *(1a)* and *(1b)* represent the vibrational modes of the $\alpha$-$(BEDT\text{-}TTF)_2I_3$ single crystals [26,27]. The Raman spectra (Fig. 1 curve (2)) taken for the PC + $(BEDT\text{-}TTF)_2I_3$ composites (PMMA composites exhibits similar Raman spectrum) obtained from saturated (50 mg/ml) iodine solution show that the 108 to 117 $cm^{-1}$ band intensity ratio is lower than that observed for the PS composites. In spectra of the PC, PMMA and PS composites with $(BEDT\text{-}TTF)_2I_3$ obtained by evaporation with diluted iodine solution (15 mg/ml) there is only a very weak 108 $cm^{-1}$ band present as a shoulder on the low frequency side of the 117 $cm^{-1}$ band (see as example spectrum *(3)* in Fig. 1). The 29 and 117 $cm^{-1}$ band characteristic for the $\alpha$-$(BEDT\text{-}TTF)_2I_3$ phase are accompanied with overtones at *ca*. 90, 148, 178, 235 and 352 $cm^{-1}$. These overtones are also present in other spectra shown in Figure 1, but they are overlapped by the 108 $cm^{-1}$ band overtones. Two Raman bands at 108 and 120 $cm^{-1}$ originating form $I_3^-$ anion vibrations were found for the PC+$\beta$-$(BEDT\text{-}TTF)_2I_3$ BRDP composite obtained by evaporation at elevated temperature (curve *(4)* Fig. 1). The bands at 20–35 and 120 $cm^{-1}$ are characteristic of $\beta$-$(BEDT\text{-}TTF)_2I_3$ single crystals [26,27].

From the presented results one can conclude, that the relative intensity of the 108 $cm^{-1}$ band depends on the concentration of $I_2$ solution used for

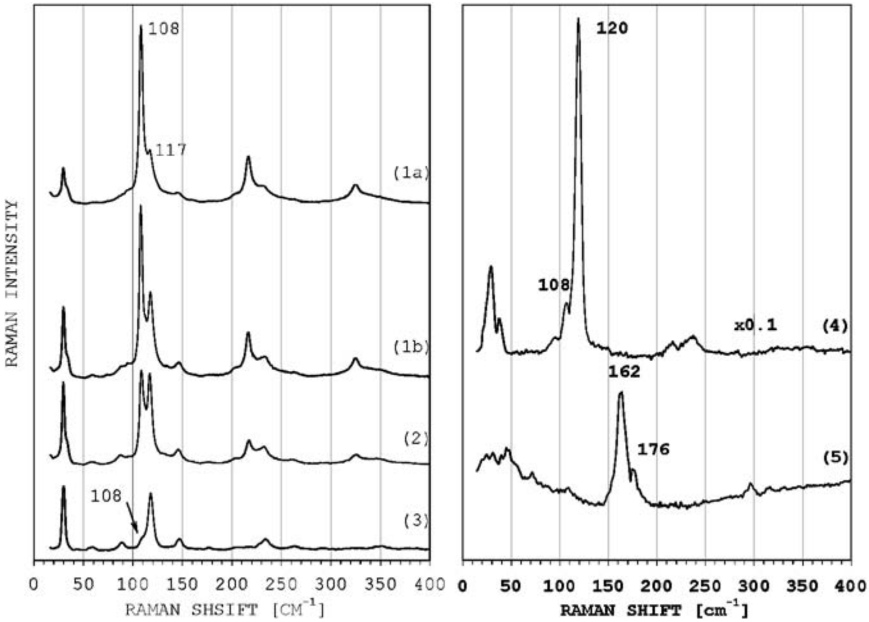

**FIGURE 1** Raman spectra taken using 514 nm laser line at 20 K for PS + α-(BEDT-TTF)$_2$I$_3$ *(1a)*, *(1b)* and PC + α-(BEDT-TTF)$_2$I$_3$ *(2)* obtained by evaporation at room temperature for 1 min from saturated I$_2$/CH$_2$Cl$_2$ (50 mg /ml) solution and for PC + α-(BEDT-TTF)$_2$I$_3$ *(3)* obtained by evaporation at room temperature for 6 min from diluted I$_2$/CH$_2$Cl$_2$ (15 mg /ml) solution. Spectra *(4)* and *(5)* were taken for 514 nm at 80 K for PC + β-(BEDT-TTF)$_2$I$_3$ obtained by evaporation at elevated temperature (368 K) for 2.5 min from I$_2$/C$_2$H$_3$Cl$_3$ (2.9 mg/ml) and the same sample after subsequent 10 min exposition to Br$_2$ vapours at room temperature.

the composite preparation and is higher for the BRDP composites evaporated from more concentrated I$_2$ solution. The position of this band seems to be independent on the micro-crystals phase as shown for α and β. The 108 cm$^{-1}$ band was also observed in the polycrystalline pressed pellet samples of α and β phases, as well as for the incommensurably modulated state of the β phase single crystals [26,29]. Furthermore it was already shown that the 108 cm$^{-1}$ band is disappearing when the BRDP composite with α-(BEDT-TTF)$_2$I$_3$ is annealed at temperatures lower than α to β phase transition [30]. We suppose therefore that I$_3^-$ anions giving rise to 108 cm$^{-1}$ band are present mainly on the surface of the micro-crystals or in the disordered interface between micro-crystals in the polycrystalline layer. Another possible explanation of the 108 cm$^{-1}$ band presence is based on the X-ray diffraction data [31,32]. This hypothesis assumes that disordered

$I_3^-$ anions are present inside the stressed micro-crystals because of the strains generated during the polymer film solidification.

## BRDP Composites with $(BEDT\text{-}TTF)_2I_xBr_{3-x}$ Salts

In Table 1 one can find EDX results of iodine, bromine, and sulphur atomic compositions before and after treatment with $Br_2$ vapours of the PC + $\beta$-(BEDT-TTF)$_2$I$_3$ composite. The stoichiometry of sulphur to iodine in the initial composite is $16/3 = 5.33$, as expected. After reaction with $Br_2$ the Br/I concentration ratio is equal nearly two, suggesting the formation of the $IBr_2^-$ anions, however, the S/(I+Br) ratio is much lower than for (BEDT-TTF)$_2$IBr$_2$ stoichiometry ($16/3 = 5.33$).

The Raman spectrum taken at 80 K for the 514 nm laser line for PC + $\beta$-(BEDT-TTF)$_2$I$_3$ films after exposition to $Br_2$ vapours (curve *(5)* in Fig. 1) is quite different from that taken before the treatment (curve *(4)* in Fig. 1). Two new bands at around 162 and 176 cm$^{-1}$ are observed. The former steams form $IBr_2^-$ anions, by comparison with spectra of the $\beta$-(BEDT-TTF)$_2$IBr$_2$ single crystals [26,27]. It is more difficult to attribute the 176 cm$^{-1}$ band. It can result from the $\Sigma_g^+$ mode of the $Br_3^-$ anions. However stoichiometry determined by EDX suggests that the ratio of iodine to bromine is nearly 1/2 therefore if the $Br_3^-$ anions are formed also the $I_2Br^-$ anions should be present.

An IBr/CH$_2$Cl$_2$ solution (4 mg/ml) has been prepared to obtain the polycrystalline layers of the BEDT-TTF trihalide micro-crystals with mixtures of the $I_3^-$, $I_2Br^-$ and $IBr_2^-$ anions directly in the second step of the RDT. The Raman spectra of IBr/CH$_2$Cl$_2$, I$_2$/CH$_2$Cl$_2$, and Br$_2$/CH$_2$Cl$_2$ solutions as well as for the pure solvent were recorded at room temperature using the 514 nm laser line (Fig. 2). Two bands at about 288 and 706 cm$^{-1}$, present in all spectra, result from the $CH_2Cl_2$ vibrations. For the I$_2$/CH$_2$Cl$_2$ solution the 210 cm$^{-1}$ band with overtones at *ca.* 420 and 630 cm$^{-1}$ represents the $\Sigma_g^+$ vibrational mode of $I_2$. In the spectrum of the Br$_2$/CH$_2$Cl$_2$ solution the 313 cm$^{-1}$ band is associated with the $\Sigma_g^+$ mode of $Br_2$. In the

**TABLE 1** The EDX Results of Iodine, Bromine, and Sulphur Compositions in the PC + $\beta$-(BEDT-TTF)$_2$I$_3$ BRDP film Before and after Treatment with $Br_2$ Vapours; Magnification of SEM was 1000 and the Electron Beam Energy 15 keV.

| | S[%] | I[%] | Br[%] | S/I | S/(I+Br) | Br/I |
|---|---|---|---|---|---|---|
| Non-treated | 84 | 16 | – | 5.3 | 5.3 | – |
| After treatment | 71 | 10 | 19 | 7.2 | 2.4 | 2.0 |

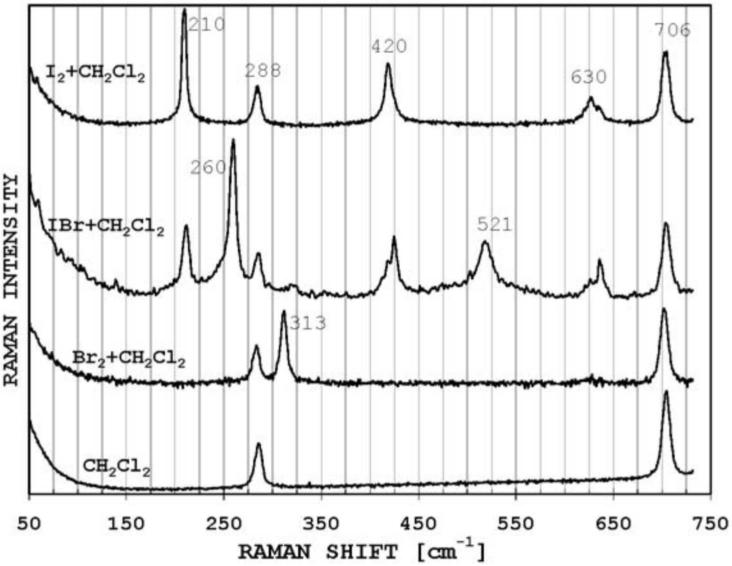

**FIGURE 2** The Raman spectra of the $I_2/CH_2Cl_2$, $IBr/CH_2Cl_2$, and $Br_2/CH_2Cl_2$ solutions as well as of pure $CH_2Cl_2$ taken at room temperature for the 514 nm laser line.

spectrum of the $IBr/CH_2Cl_2$ solution the band at $210\,cm^{-1}$ arises form the $I_2$ molecule vibration and the band at $260\,cm^{-1}$ with overtone at $521\,cm^{-1}$ originates from the IBr stretching $\Sigma^+$ mode. The IBr molecules seem to be dominant in the $IBr/CH_2Cl_2$ solution, since the peak at $260\,cm^{-1}$ is the most intensive, while the resonant condition is rather expected for the $I_2$ molecules. The present attribution is made on bibliographic data [33].

The results of EDX measurements of iodine, bromine, chlorine, sulphur, oxygen, and carbon atomic compositions for the PC + BEDT-TTF/IBr composites are listed in Table 2. For 10 keV the electron penetration depth is 1 µm, while for 20 keV the penetration is higher, *ca.* 3–4 µm. Chlorine detected by EDX originate form solvents used for the composite preparation. For all samples, except the non-evaporated film, the sulphur concentration measured at 10 keV is higher than that measured at 20 keV. It indicates that the BEDT-TTF molecules or radical cations (the sole moieties containing sulphur) are accumulated near the surface of the BRDP film, where the BEDT-TTF trihalide complex has grown. The sulphur content increases for the BRDP composites evaporated for a longer time, because more BEDT-TTF molecules diffuse to the surface. For the non-evaporated films the BEDT-TTF molecules are dispersed homogeneously in

**TABLE 2** The EDX Results, at 10 and 20 keV Electron Beam Energy and the 1000 SEM Magnification, of the Iodine, Bromine, Chlorine, Sulphur, Oxygen, and Carbon Composition in the PC + BEDT-TTF/IBr Composites Obtained by Evaporation with IBr/$CH_2Cl_2$ for Various Time Intervals.

| | 0 sec | | 30 sec. | | 60 sec. | | 90 sec. | | 120 sec. | | 180 sec. | | 480 sec. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [keV] | 10 | 20 | 10 | 20 | 10 | 20 | 10 | 20 | 10 | 20 | 10 | 20 | 10 | 20 |
| C(%) | 86.5 | 87.0 | 82.4 | 84.1 | 77.7 | 81.7 | 74.0 | 79.2 | 72.2 | 78.8 | 69.7 | 73.8 | 63.4 | 67.4 |
| O(%) | 12.4 | 12.3 | 12.1 | 13.0 | 11.6 | 13.0 | 11.4 | 13.0 | 10.3 | 13.1 | 7.7 | 10.1 | 6.2 | 8.6 |
| S(%) | 0.5 | 0.4 | 4.2 | 1.6 | 8.9 | 3.3 | 11.6 | 5.2 | 14.2 | 5.6 | 18.4 | 12.0 | 21.9 | 16.1 |
| I(%) | – | – | 0.3 | 0.1 | 0.7 | 0.3 | 1.1 | 0.5 | 1.4 | 0.5 | 2.0 | 1.2 | 3.4 | 2.7 |
| Br(%) | – | – | 0.2 | 0.1 | 0.5 | 0.3 | 0.9 | 0.5 | 1.2 | 0.6 | 1.7 | 1.1 | 4.6 | 3.4 |
| Cl(%) | 0.6 | 0.3 | 0.8 | 1.1 | 0.6 | 1.4 | 0.9 | 1.6 | 0.7 | 1.4 | 0.5 | 1.8 | 0.5 | 1.8 |
| Br/I | – | – | 0.7 | 1.0 | 0.7 | 1.0 | 0.8 | 1.0 | 1.17 | 0.9 | 0.85 | 0.9 | 1.4 | 1.3 |
| S/(I+Br) | – | – | 8.4 | 8.0 | 7.4 | 5.5 | 5.8 | 5.2 | 5.5 | 5.1 | 5.0 | 5.2 | 2.7 | 2.6 |

the polymer and the sulphur content determined at 10 and 20 keV is nearly equal to that calculated taking into account the film composition (2% wt. of BEDT-TTF in PC) *i.e.* 0.5%. The concentration of the iodine and bromine atoms, in the composites obtained by evaporation for time periods shorter than 180 seconds, seems to be identical, as expected from the IBr/$CH_2Cl_2$ composition. The concentration of iodine and bromine detected at 10 keV is higher than that detected at 20 keV, since most of these atoms are forming micro-crystals at the surface of the composite. For the sample evaporated for 180 seconds the S/(I+Br) ratio is nearly equal to that of $(BEDT\text{-}TTF)_2I_xBr_{3-x}$ salts. We presume that this sample contains the highest amount of micro-crystals with such stoichiometry. The composition and thus the stoichiometry of the sample evaporated for 480 seconds differs considerably from the other ones.

The EDX cartography images of iodine, bromine, and sulphur distribution in the near surface layer (1 μm in depth) of the PC + BEDT-TTF/IBr composites show homogenous distribution of iodine and bromine in the available spatial resolution range (which is however too low to see the micro-crystals). 10 $\mu m^2$ to 40 $\mu m^2$ needles of neutral BEDT-TTF are seen in the SEM image of the sample evaporated for 30 seconds ( Fig. 3*(a)*) and are reproduced perfectly in the sulphur EDX cartography picture. In the SEM image of the samples evaporated for 90 seconds the needles of the neutral BEDT-TTF are shorter but present in a higher quantity (Fig. 3*(b)*). It is difficult to conclude if needles of BEDT-TTF are formed during the second step of RDT or rather later when the polymer film was dried after the evaporation. For the sample evaporated for 180 as well as for 480 seconds

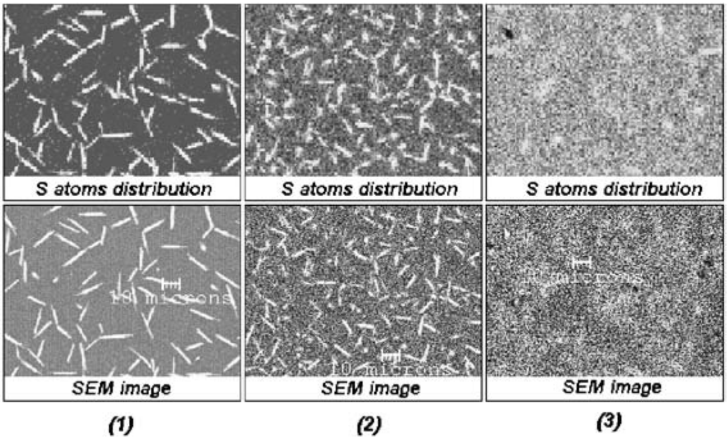

**FIGURE 3** EDX (at 10 keV) cartography of the sulphur (K-line) and corresponding SEM image (10 µm scale bar) for the PC + BEDT-TTF/IBr composites prepared during 30, 90 and 180 seconds *(1)*, *(2)*, and *(3)* evaporation time, respectively.

(Fig. 3*(c)*) one observe only some non-homogeneity in the sulphur distribution without any characteristic shapes.

In the AFM images *(a)* and *(b)* in Figure 4 the micro-crystals of the BEDT-TTF/IBr salts are present: smaller (0.2–05 µm) and bigger (1–15 µm) for the composites evaporated for 30 and 180 seconds, respectively. The thickness of the crystals present in image *(b)* can be estimated to be several

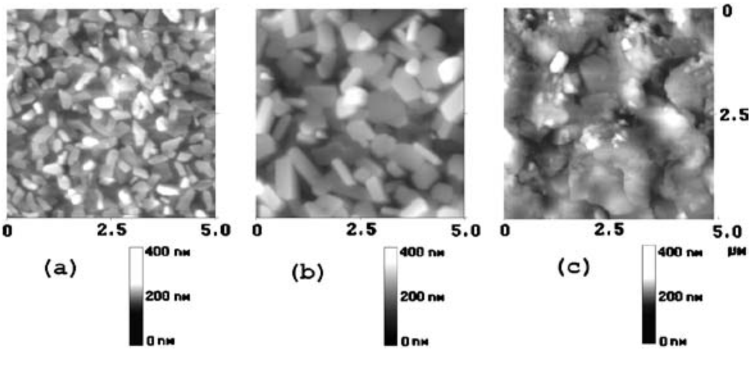

**FIGURE 4** AFM images (in the tapping mode) for the PC+ BEDT-TTF/IBr composites obtained by evaporation with $IBr/CH_2Cl_2$ for 30, 180 and 480 seconds *(1), (2)*, and *(3)* respectively.

tens of nanometers [21]. It is therefore obvious that the small diameters of the micro-crystals disable the spectroscopic studies from individual ones. The surface of the micro-crystals evaporated for 480 seconds (Fig. 4*(c)*) seems to be covered by some disordered material, as it was observed before for the PC + (BEDT-TTF)$_2$I$_3$ composites [22].

Figure 5 shows the Raman spectra taken for the PC + BEDT-TTF/IBr composites at 80 K for the 457, 514 nm laser lines and at room temperature for the 632 nm laser line. In the spectra taken from the composites evaporated for 60, 90 and 180 seconds three bands at about 119, 137 and 161 cm$^{-1}$ are seen for all laser wavelengths. These bands are the most intensive in the spectra recorded from the sample evaporated for 180 seconds. This is probably due to the highest content of the BEDT-TTF trihalide salt formed in this polymer composite. The relative intensities of the observed bands are different depending on the laser wavelength. This resonance effect is quite similar to that observed for the $\beta$-(BEDT-TTF)$_2$Br$_{1.45}$I$_{1.55}$ single crystals [34]. We assign the 119, 137, and 161 cm$^{-1}$ bands in the spectra from Figure 5 to the I$_3{}^-$, I$_2$Br$^-$, and IBr$_2{}^-$ anions, respectively. The Raman spectra of the composite evaporated for 480 seconds is quite different. This is not surprising, since the EDX results indicated different halide composition and AFM showed different surface morphology. A new band at 179 cm$^{-1}$ is dominant, especially in the spectrum taken for the 632 nm laser line. The 179 cm$^{-1}$ band was found also for

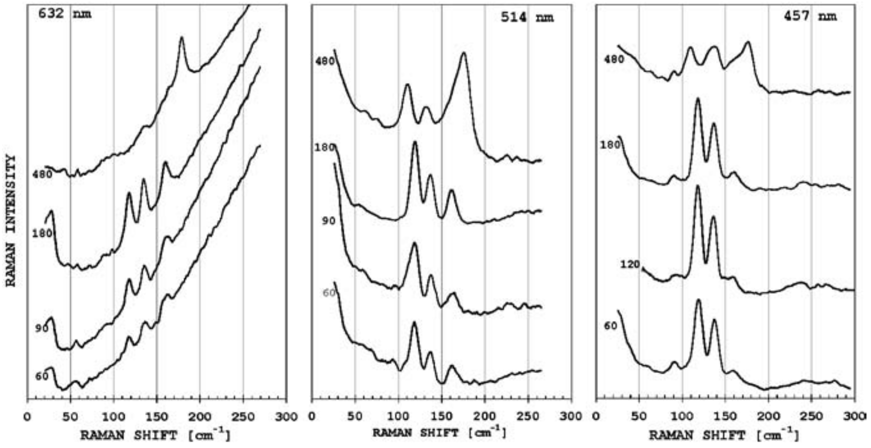

**FIGURE 5** The Raman spectra taken for the PC + BEDT-TTF/IBr composites exposed for 60, 90, 180 and 480 seconds to the vapours of the IBr/CH$_2$Cl$_2$ solution (4 mg/ml). The spectra are taken at 80 K for the 457, 514 laser lines and at room temperature for the 632 nm line.

the PC + $\beta$-(BEDT-TTF)$_2$I$_3$ film kept for 10 min in the Br$_2$ vapours. We suppose that the most plausible attribution of this band is the $\Sigma_g^+$ mode of the Br$_3{}^-$ anions.

## CONCLUSION

It has been shown that the two step RDT can yield polymer composites with a thin polycrystalline layer of BEDT-TTF trihalide salt that contains the mixture of trihalide anions. We have found that (BEDT-TTF)$_2$I$_x$Br$_{3-x}$ stoichiometry is dominant in the composite prepared in optimal conditions. The Raman bands of these composites were attributed to I$_3{}^-$, I$_2$Br$^-$, and IBr$_2{}^-$, indicating presence of a mixture of the symmetrical and non-symmetrical anions. The new 179 cm$^{-1}$ band found for some composites is ascribed to the $\Sigma_g^+$ mode of the Br$_3{}^-$ anions. We were not able to determine the anion composition of single micro-crystals since their dimensions are below 2 μm.

We have also shown that Raman spectroscopy is very efficient in the characterisation of the I$_3{}^-$ anions in polycrystalline layers of the BRDP composites containing BEDT-TTF triiodides. Bands originating from the I$_3{}^-$ anions in the well-formed micro-crystals and some disordered phase(s) have been detected.

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