



# Structural, thermal and optical properties of Cu<sup>2+</sup> doped methacrylic acid–ethyl acrylate (MAA:EA) copolymer films

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**Abstract.** Pure and Cu<sup>2+</sup> doped methacrylic acid–ethyl acrylate (MAA:EA) copolymer films were prepared using the solution cast technique. The amorphous feature of the copolymer was depicted using X-ray diffraction scans and degree of crystallinity was found to vary with increasing doping content. UV–Vis absorption spectra in the wavelength region 200–900 nm were used to evaluate the optical properties like direct band gap, indirect band gap and absorption edge. The optical band gap decreased with the increase of mol% of Cu<sup>2+</sup> ions. Fourier transform infrared spectral studies on pure MAA:EA and Cu<sup>2+</sup> ions-doped films revealed the vibrational changes that occurred due to the effect of dopant salt in the copolymer. Thermal properties of these films were investigated by employing differential scanning calorimetry and thermogravimetric analysis. The variation in film morphology was examined by scanning electron microscopy. Electron paramagnetic resonance (EPR) spectra of all the doped samples exhibited signals due to Cu<sup>2+</sup> ions with the effective *g*-values  $g_{\parallel} = 2.177$  and  $g_{\perp} = 2.058$ . The observed variation in the EPR signal intensity is due to the isolated and aggregated copper ions. The photoluminescence spectra of Cu<sup>2+</sup> ions-doped MAA:EA copolymer exhibited four emission peaks at 480 (blue), 579 (yellow), 604 (red) and 671 nm (red).

**Keywords.** MAA:EA copolymer; XRD; DSC; TGA; UV–Vis spectroscopy; EPR.

## 1. Introduction

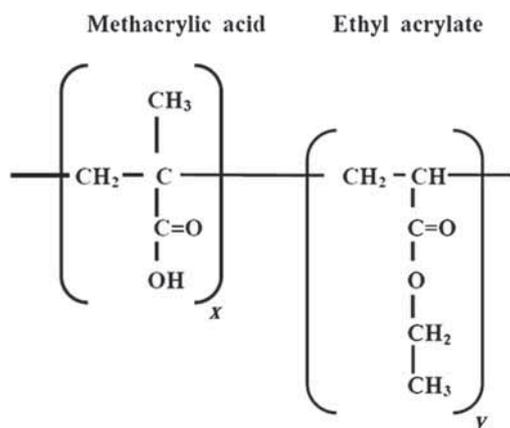
Copolymers are hybrid macromolecules that have captured the attention of scientists and technologists over the last several decades. Copolymer films are used for a number of technological and scientific applications due to their optical, thermal, mechanical, electronic and electrical properties. In recent years, there has been considerable interest in the preparation and characterization of copolymer films for their possible use as light stable colour filters [1], solar cells and optical sensors [2]. If the properties of the copolymer are modified in right direction by adding suitable dopants, these copolymers could be the best candidates for space applications [3].

The interaction of copolymer with oppositely charged dopants has been extensively studied because of its complex behaviour. The interaction between oppositely charged polymers and dopants is usually stronger because of the coulombic attractive force. The binding is generally considered as an electrostatic binding via an ion exchange interaction. Typically, the electrostatic interaction is reinforced by a dopant or the cooperative aggregation between alkyl chains of the dopant and the hydrophobic segment of copolymer chains

[4,5]. On the other hand, the complexation of copolymer with weak cationic dopant such as partially neutralized or non-neutralized polycarboxylic acid is extensively studied because of their industrial applications [6,7]. This system has a potential utility in the control of chemical reactivity, drug delivery and nano-specific binding of DNA [8].

Methacrylic acid–ethyl acrylate (MAA:EA) copolymer has drawn special attention amongst the copolymers because of its good environmental stability, easy process and transparency. MAA:EA copolymer is a potential material with good charge capacity and dopant-dependent electrical and optical properties. The chemical structure of MAA:EA copolymer is shown in figure 1.

Bajaj *et al* [9] studied the thermal behaviour of MAA:EA copolymers. Wang *et al* [4] studied the interaction between MAA:EA copolymer and bromide dopant. There are many methods to improve the ionic conductivity, optical properties, mechanical and electrical properties of the polymer films viz., polymer blending, addition of plasticizer, doping of ionic liquid, filler and mixed salt systems [10,11]. Based on the importance and relevance of the MAA:EA copolymer as a suitable matrix, transition metal ions can be used as a filler to modify the electric conduction and optical absorption of



**Figure 1.** Chemical structure of MAA:EA copolymer.

the polymer matrix. It should be noted that the formation of transition metal particles inside the polymer system is also of interest for potential applications, such as storage of optical data, shielding of electromagnetic radiation flexible elements for resistive heating, laser systems, optical lenses and integrated waveguides. In this context,  $\text{Cu}^{2+}$  doped polymer films are particularly attractive because of copper's high natural abundance and low cost and the practical and straight forward multiple ways of preparing  $\text{Cu}^{2+}$  based polymer thin films. The  $\text{Cu}^{2+}$  ion introduces more packing efficiency to the host, which successively influences the thermal properties of the polymer [12]. Moreover, so far, no work is reported on  $\text{Cu}^{2+}$  ions-doped MAA:EA films. Hence, the authors have aimed at the present investigation.

## 2. Experimental

Methacrylic acid–ethyl acrylate (1:1) dispersion with 30% copolymer with molecular weight of 2,50,000 was purchased from Merck Millipore India Ltd. MAA:EA copolymer (14  $\mu\text{m}$  thickness) films doped with  $\text{Cu}^{2+}$  ions at various concentrations were prepared at room temperature by solution casting method. The desired concentrations of  $\text{CuSO}_4$  solution (1.5, 3.5, 5, 7.5 and 10 mol%) were prepared by using distilled water. Five milli litres of MAA:EA copolymer was dissolved in distilled water separately. Different amounts of (1.5, 3.5, 5, 7.5 and 10 mol%)  $\text{Cu}^{2+}$  ions were added into the copolymer solution. The solution was magnetically stirred for 10–12 hours to get a homogeneous mixture and then cast into polypropylene dishes. The film was slowly evaporated at room temperature to obtain free standing copolymer film at the bottom of the dishes.

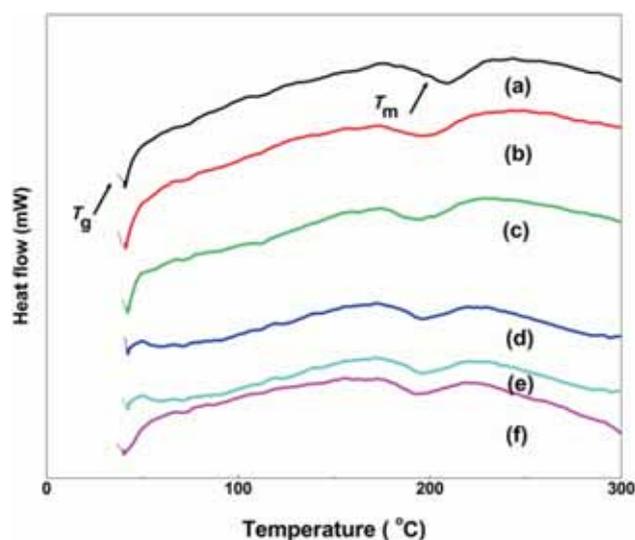
To investigate the nature of the copolymer films, differential scanning calorimetry (DSC) measurement was carried out by an SEIKO calorimeter (DSC-220) at a continuous heat rate of  $10^\circ\text{C min}^{-1}$  under nitrogen atmosphere from 40 to  $600^\circ\text{C}$ . The thermogravimetric data was recorded using the SEIKO

thermal analysis system (TGA-20) in the presence of nitrogen flow from 40 to  $600^\circ\text{C}$  at the heating rate of  $10^\circ\text{C min}^{-1}$ . X-ray diffraction (XRD) measurements were carried out using a Siemens D5000 diffractometer with  $\text{CuK}\alpha$  radiation (1.5406  $\text{\AA}$ ). The films were scanned at  $2\theta$  angles between 10 and  $80^\circ$  with a step size of  $0.02^\circ$ . Fourier transform infrared (FTIR) spectra of these electrofilms were recorded using a Perkin-Elmer FTIR spectrophotometer. The spectra were taken over a wavenumber range of  $1000\text{--}4000\text{ cm}^{-1}$ . Electron paramagnetic resonance (EPR) spectra were recorded at room temperature on a JEOL FEIX ESR Spectrometer operating in X-band frequency of 9.205 GHz with field modulation of 100 kHz. The magnetic field was scanned from 0 to 5000 G. UV–Vis absorption spectra of prepared samples were recorded in the range of 200–800 nm at room temperature using JASCO UV–VIS–NIR spectrophotometer (model V.700). The thickness of the film was determined from capacitance measurements at 1 kHz using LCR bridge, taking the dielectric constant ( $\epsilon$ ) of MAA:EA copolymer as 2.8. From these data, the optical constants such as band edge and optical band gap (both direct and indirect) were calculated. The morphology of the copolymer films was characterized by the Hitachi (TM-3000 and H-8100) electron microscope with scanning attachment. The photoluminescence (PL) measurements were performed on Horiba Fluro Log-3.

## 3. Results and discussion

### 3.1 Thermal studies

3.1a DSC: DSC is used to measure the changes that occur in a sample as a function of temperature. Using this technique, the glass transition temperature ( $T_g$ ) as well as melting temperature ( $T_m$ ) of the material can be identified [13]. Figure 2



**Figure 2.** DSC curves of MAA:EA copolymer films containing  $\text{Cu}^{2+}$ : (a) pure, (b) 1.5, (c) 3.5, (d) 5, (e) 7.5 and (f) 10 mol%.

shows the DSC curves of pure MAA:EA copolymer and MAA:EA doped with Cu<sup>2+</sup> ions in different concentrations (1.5, 3.5, 5 and 7.5 mol%). From the figure,  $T_m$  and  $T_g$  of pure MAA:EA copolymer films are observed to be 210 and 41°C, respectively. DSC analysis made on the pure and Cu<sup>2+</sup> ions-doped MAA:EA copolymer samples with only one  $T_g$  indicates homogeneous behaviour of the copolymer films.

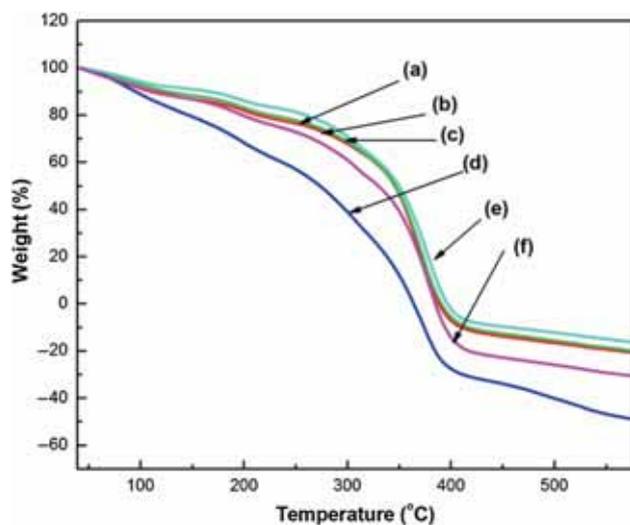
An endothermic peak is observed at around 210°C, which corresponds to the melting point of MAA:EA copolymer. A slight shift of  $T_m$  towards lower temperature upon the addition of Cu<sup>2+</sup> to the host polymer reveals the transition from semi-crystalline to an amorphous phase. The lowering of  $T_m$  upon dopant addition is quite common [14] and is related to the decrease in spherulite sizes [15] and their surface free energy. This clearly indicates the suppression of crystallites, thereby increasing the amorphous content in the polymer. As a result of more flexible amorphous environment getting trapped in or adjacent to the crystalline matrix, the suppressed crystalline portion of the Cu<sup>2+</sup> doped MAA:EA copolymer melts probably at lower temperatures. The smaller crystallites, due to the presence of Cu<sup>2+</sup> are less stiff to give a low  $T_m$  and consequently, the amorphous phase becomes more flexible. The increase of Cu<sup>2+</sup> ions content in copolymer matrix results in greater disordering of crystalline structure and disordering of polymer chains which successively enhance the amorphous nature of the doped MAA:EA film. This observation is in consistence with that from SEM and XRD studies.

**3.1b TGA:** Figure 3 shows the TGA curves of pure and Cu<sup>2+</sup> ions-doped MAA:EA copolymer films at different concentrations (1.5, 3.5, 5, 7.5 and 10 mol%). It can be clearly seen that the samples complete decomposition process at around 400°C. This indicates that the samples are stable up to

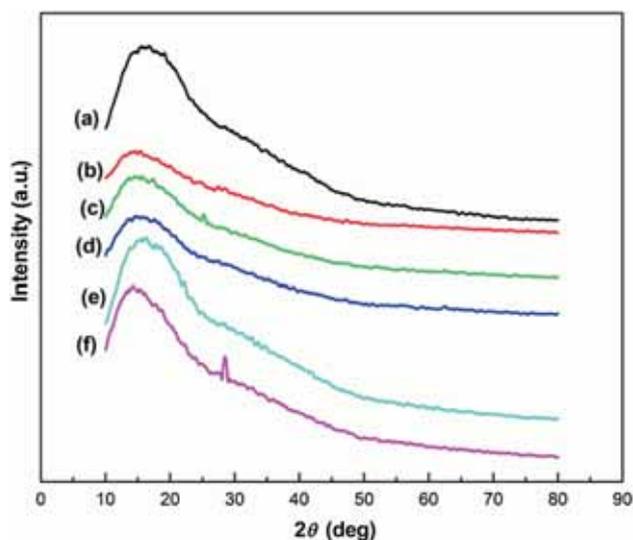
that temperature. Analysis of TGA curves of pure and Cu<sup>2+</sup> ions-doped copolymers reveals that there are three distinct steps of weight loss. The first step of weight loss in the range of 50–210°C may be attributed to the elimination of side products in the process of anhydride formation as indicated by an endothermic transition in the same temperature range as noticed from DSC scans. The 4–5% weight loss below 170°C is attributed to the loss of absorbed water [15,16]. The second and third steps observed in the temperature range 210–400°C and above 400°C are the regions of major weight loss, which are due to the extensive degradation of the polymer backbone. According to Zain *et al* [14], the decomposition at 210°C is attributed to the elimination of evaporated molecules in the side groups of MAA:EA copolymer and the decomposition above 400°C is due to quantized graft chain degradation.

### 3.2 XRD analysis

XRD patterns of pure and Cu<sup>2+</sup> ions (1.5, 3.5, 5, 7.5 and 10 mol%) doped MAA:EA copolymer films are shown in figure 4. The diffraction peak of pure MAA:EA was observed at 16.39°, whereas the peak observed for doped MAA:EA copolymer films has shifted for  $2\theta$  values varied from 13.91 to 15.87°, revealing the change in the crystallographic organization [17]. The changes in XRD are a clear indication of the complete insertion of the Cu<sup>2+</sup> ions in the copolymer matrix. The intensity of these characteristic peaks decreased on addition of Cu<sup>2+</sup> ions. This implies that the addition of Cu<sup>2+</sup> ions disrupted the arrangement in the MAA:EA copolymer. In the present XRD patterns, the intensity of diffraction patterns decreases as the amorphous nature increases with the addition of the dopant, no sharp peaks were found at higher concentrations of Cu<sup>2+</sup> ions in the copolymer thus, indicating the



**Figure 3.** TGA curves of pure and Cu<sup>2+</sup>-doped MAA:EA copolymer films: (a) pure, (b) 1.5, (c) 3.5, (d) 5, (e) 7.5 and (f) 10 mol%.



**Figure 4.** XRD patterns of MAA:EA copolymer films containing Cu<sup>2+</sup>: (a) pure, (b) 1.5, (c) 3.5, (d) 5, (e) 7.5 and (f) 10 mol%.

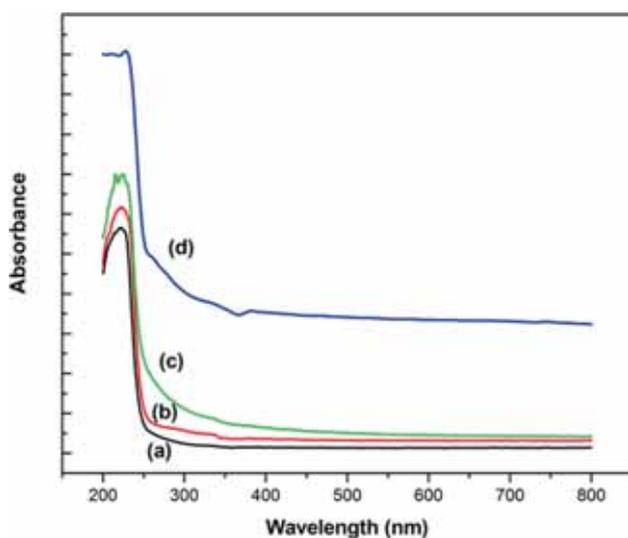
presence of dominant amorphous phase. This is in agreement with the results reported by Uma *et al* [18] and Janaki Rami Reddy *et al* [19], and indicates that the polymeric films are composed of semi-crystalline amorphous phases [20]. This is due to the interaction between the copolymer and  $\text{Cu}^{2+}$  ions dopant that leads to decrease in the intermolecular interaction between copolymer chains and  $\text{Cu}^{2+}$  ions dopant and  $\text{CH}_3\text{-O}$ ,  $\text{C=O}$  groups of copolymer [21].

The XRD analysis is used to determine the complexation and crystallization of the polymer matrix. The degree of crystallinity ( $\alpha$ ) of pure and  $\text{Cu}^{2+}$  doped MAA:EA copolymer films were estimated [17] by making use of the area under the diffraction peak and by using the following formula:

$$\alpha = \left( \frac{A_C}{A_T} \right) * 100, \quad (1)$$

where  $A_C$  is the area under crystalline region and  $A_T$  the total area of amorphous and crystalline regions. The degree of crystallinity for pure copolymer film is 23.9%, whereas for doped films, it is 14.8, 12.7, 11.8, 10.1 and 8.11%, respectively, at 1.5, 3.5, 5.0, 7.5 and 10.0 mol%  $\text{Cu}^{2+}$  ions.

Most of the literature reported the continual raise in conductivity of polymer films with incorporation of dopant [22,23], which indicates the decrease in the degree of crystallinity and simultaneous increase in the amorphous nature with the addition of the dopant. However, there are also reports where decrease in conductivity values was observed after reaching a maximum conductivity at a certain dopant content [24,25]. In the present work, the decrease in the crystallinity with increasing dopant concentration may be due to the interaction of  $\text{Cu}^{2+}$  cations with the end chain of the polymer [26].



**Figure 5.** UV-Vis absorption spectra of MAA:EA copolymer films containing  $\text{Cu}^{2+}$ : (a) pure, (b) 1.5, (c) 3.5 and (d) 7.5 mol%.

### 3.3 Optical absorption studies

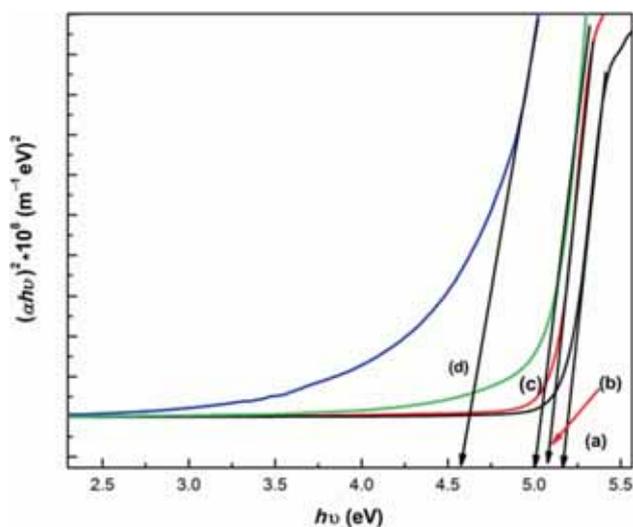
The study of the fundamental absorption edge in the UV region helps in the investigation of optical transitions and electronic band structure in crystalline and noncrystalline materials. In figure 5, the UV-Vis absorption spectra of pure MAA:EA copolymer and MAA:EA doped with  $\text{Cu}^{2+}$  ions at different concentrations (1.5, 3.5 and 7.5 mol%) are shown. The spectrum of undoped MAA:EA copolymer film shows a shoulder-like peak at about 221 nm, which is assigned to the carbonyl group of MAA:EA. In the doped films, the shoulder peak is observed to shift towards the higher wavelengths and the absorption coefficient increases as doping level increases. This may be due to the increase in the number of carbonyl groups and strong interaction between MAA:EA copolymer and  $\text{Cu}^{2+}$  ions [11].

Optical absorption studies on MAA:EA and various concentrations of  $\text{Cu}^{2+}$  ions-doped MAA:EA films are used to determine the optical constants such as optical band gap ( $E_g$ ) and the position of the fundamental band edge. The main feature of the absorption edge is an exponential increase of the absorption coefficient ( $\alpha$ ) with photon energy ( $h\nu$ ). The absorption coefficient  $\alpha$  can be determined from the spectra using the formula:

$$\alpha = \left( \frac{A}{d} \right) * 2.303, \quad (2)$$

where  $A$  is the absorbance and  $d$  the thickness of the sample. When a direct band gap exists, the absorption coefficient has the following dependence on the energy of the incident photon [13,27,28].

$$\alpha h\nu = c (h\nu - E_g)^{1/2}, \quad (3)$$



**Figure 6.**  $(\alpha h\nu)^2$  vs  $h\nu$  plots of MAA:EA copolymer films containing  $\text{Cu}^{2+}$ : (a) pure, (b) 1.5, (c) 3.5 and (d) 7.5 mol%.

**Table 1.** Absorption edge and optical band gap values of pure and Cu<sup>2+</sup> ions-doped (MAA:EA) copolymer films.

Concentration mol% Cu <sup>2+</sup> :MAA:EA	Absorption edge (eV)	Optical band gap energy (eV)	
		Direct	Indirect
Pure MAA:EA	5.04	5.16	4.82
1.5	4.94	5.10	4.81
3.5	4.86	4.99	4.67
7.5	4.83	4.57	4.57

where  $E_g$  is the band gap,  $c$  a constant,  $\nu$  the frequency of light and  $h$  the Planck's constant. A plot of  $(\alpha h\nu)^2$  vs.  $h\nu$  (photon energy) is shown in figure 6. The intercept on the energy axis on extrapolating the linear portion of the curve to zero absorption value may be interpreted as the value of the band gap. For pure (MAA:EA) film, the direct band gap lies at 5.16 eV, while for doped films, it varies from 5.16 to 4.57 eV (table 1). For indirect transition, which requires phonon assistance, absorption coefficient has the following dependence on the photon energy [13,27,28].

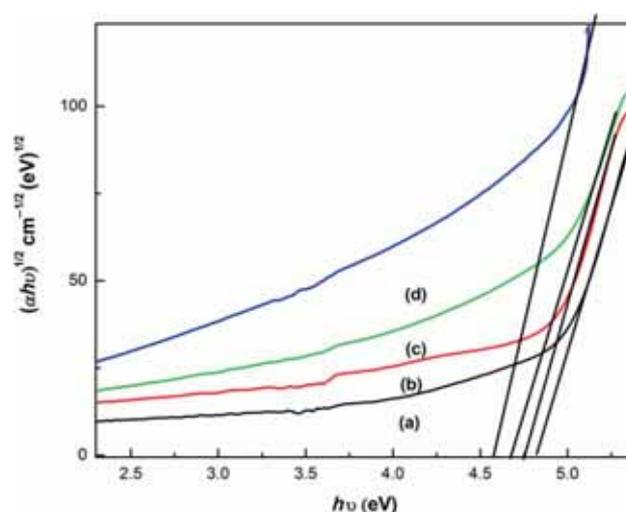
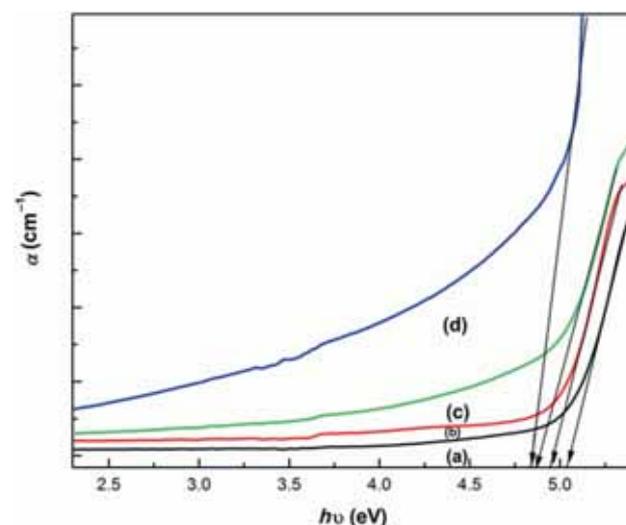
$$\alpha h\nu = A (h\nu - E_g + E_p)^2 + B (h\nu - E_g - E_p)^2, \quad (4)$$

where  $E_p$  is the energy of phonons associated with transition and  $A$  and  $B$  are the constants depending on the band structure. The indirect band gaps were obtained from the plots of  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  as shown in figure 7.

For pure (MAA:EA) copolymer film, the indirect band gap lies at 4.82 eV, while for doped films, the values varies from 4.82 to 4.57 eV. The position of the absorption edge was determined by extrapolating the linear portion of  $\alpha$  vs  $h\nu$  plot (figure 8) to zero absorption value. For pure (MAA:EA) film, absorption edge lies at 5.04 eV and for doped films, the values decrease from 5.04 to 4.83 eV (table 1).

From table 1, it can be found that the values of direct and indirect band gaps decrease with increase in the doping level. This decrease may be attributed to the formation of defects in the polymeric matrix. These defects produce the localized states in the optical band gap, which overlaps with band system and are responsible for decrease in band gap energy. This indicates that with increase in the concentration of Cu<sup>2+</sup> ions, MAA:EA films become more semiconducting in nature [29,30]. In other words, the decrease in the optical band gap results in the enhancement of the degree of the disordered film [31]. In comparison, the band gap energy lies between 5.16 and 4.57 eV for direct band gap and between 4.82 and 4.57 eV for indirect band gap. This decrease is attributed to the presence of -CH<sub>3</sub> group in MAA:EA copolymer [32].

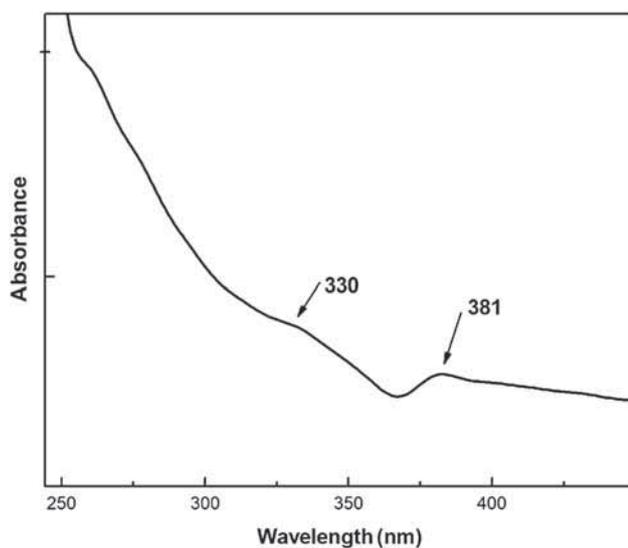
Figure 9 shows the optical absorption spectrum of 7.5 mol% Cu<sup>2+</sup> ions doped in MAA:EA copolymer recorded in the

**Figure 7.**  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  plots of MAA:EA copolymer films containing Cu<sup>2+</sup>: (a) pure, (b) 1.5, (c) 3.5 and (d) 7.5 mol%.**Figure 8.**  $\alpha$  vs.  $h\nu$  plots of MAA:EA copolymer films containing Cu<sup>2+</sup>: (a) pure, (b) 1.5, (c) 3.5 and (d) 7.5 mol%.

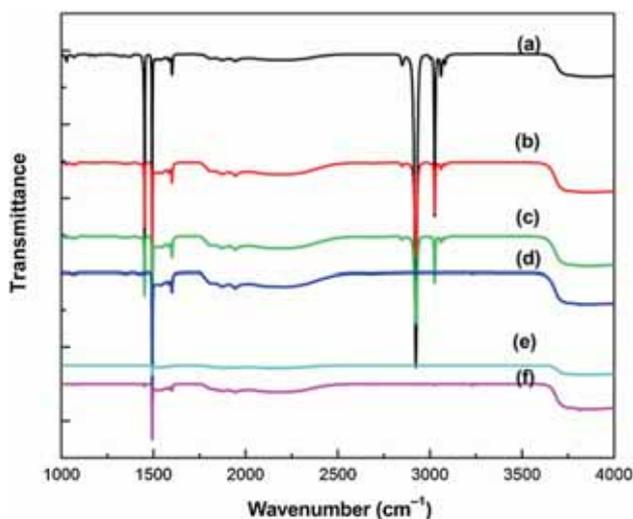
visible region at room temperature. In the UV region, two bands have been observed at 330 and 381 nm. These bands were attributed to charge transfer bands. The decrease in optical band gap on doping may be explained on the basis of the fact that the incorporation of small amount of dopant forms charge transfer complexes (CTCs) in the host lattice [22].

### 3.4 FTIR spectroscopy

FTIR spectra for pure and Cu<sup>2+</sup> ions (1.5, 3.5, 5, 7.5 and 10 mol%) doped MAA:EA copolymer are shown in figure 10. The spectra exhibit band characteristics of stretching, bending vibrations of O-H, C-H, C=O, CH<sub>3</sub>-O and CH<sub>2</sub> +  $\alpha$ -CH<sub>3</sub> groups. The observed FTIR band positions and their assignments are presented in table 2. In the pure film, a strong



**Figure 9.** UV-Vis absorption spectrum of MAA:EA copolymer film containing  $\text{Cu}^{2+}$  (7.5 mol%).



**Figure 10.** FTIR patterns of MAA:EA copolymer films containing  $\text{Cu}^{2+}$  ions: (a) pure, (b) 1.5, (c) 3.5, (d) 5, (e) 7.5 and (f) 10 mol%.

band observed at  $1452\text{ cm}^{-1}$  was assigned to bending mode of vibration corresponding to  $\text{CH}_3$  group, while another strong band observed at  $1492\text{ cm}^{-1}$  was attributed to C–H bending of  $\text{CH}_2$  [33,34]. The FTIR absorption bands are attributed to carbonyl stretching of the acid and ester units and have appeared as weak bands at  $1601\text{ cm}^{-1}$  [30]. A broad and very strong band observed at  $2923\text{ cm}^{-1}$ , which arises from C–H stretching frequency indicates the presence of methylene group [35]. Asymmetric C–H stretching of methyl group gives a peak at  $3026\text{ cm}^{-1}$  and C–H stretching of the methylene group yields peaks at  $3059$  and  $3082\text{ cm}^{-1}$ .

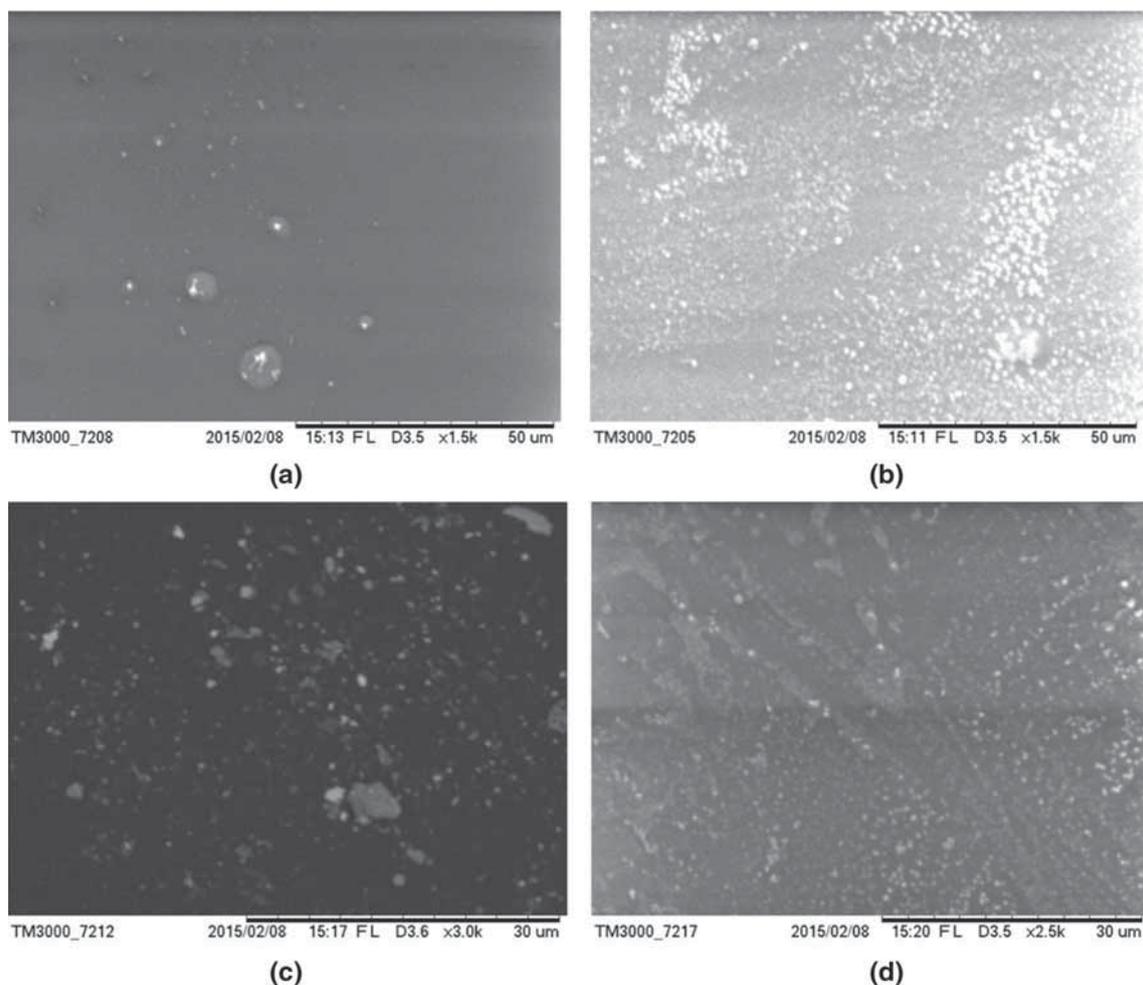
**Table 2.** FTIR peak assignment of pure and  $\text{Cu}^{2+}$  doped MAA:EA copolymer.

Wavenumber ( $\text{cm}^{-1}$ )	Band assignment
1452	$\text{CH}_3$ –O bending
1492	C–H bending of $\text{CH}_3$
1583	C=C stretching
1867	C–H stretching
1937	C–O stretching
1942	C–O stretching
1601	C=O stretching
2923	C–H stretching of methylene group
3026	C–H stretching methyl group
3059	C–H stretching methylene group
3082	C–H stretching methylene group

Compared to pure film,  $\text{Cu}^{2+}$  ions-doped films do not exhibit any change in their band position, whereas the intensity of the band varies considerably with varying  $\text{Cu}^{2+}$  ions concentration. The intensity of the band corresponding to C=O stretching of carboxylic acid observed at  $1601\text{ cm}^{-1}$  has increased with increasing  $\text{Cu}^{2+}$  content. The effect of dopant on the modes of vibration is observed in terms of increase in the intensity, broadening of the band and appearance of the new band, which results from the formation of crosslinks between the  $\text{Cu}^{2+}$  cations and oxygen atoms of carbonyl groups. This indicates the increase in the basicity of C=O groups with the increased  $\text{Cu}^{2+}$  ion concentration, implying that the carbonyl group is able to act as a strong electron donor to interact with  $\text{Cu}^{2+}$  cations. This leads to decrease in crystallinity and increase in amorphous content [33]. In addition, weak bands are observed at  $1583$  and  $1937\text{ cm}^{-1}$  in 5.0 mol%,  $1942$  and  $1867\text{ cm}^{-1}$  in 7.5 mol%  $\text{Cu}^{2+}$  doped MAA:EA copolymer. This indicates the transformation of crystalline regions of MAA:EA copolymer into amorphous regions due to the addition of  $\text{Cu}^{2+}$  ions [33]. As observed in the figure, for 5–10 mol% the disappearance of peaks from  $3000$  to  $3100\text{ cm}^{-1}$  may be due to the dense molecular packing in the crystal and stronger interaction of C–H bonds at higher concentration of  $\text{Cu}^{2+}$  in MAA:EA copolymer films [36]. All these changes in the FTIR spectra are a clear indication for the complexation of copolymer [21].

### 3.5 SEM analysis

SEM is often used to assess the compatibility between various phases through the detection of phase separations and interfaces. The compatibility between the polymer matrix and the inorganic dopants has great influence on the properties (mechanical, thermal and ionic conductivities) of the copolymer films. The morphology of the pure and  $\text{Cu}^{2+}$  ions-doped (1.5, 3.5 and 7.5 mol%) copolymer films studied by SEM technique are shown in figure 11a–d. A uniform type, but with different degrees of roughness is observed. This suggests that

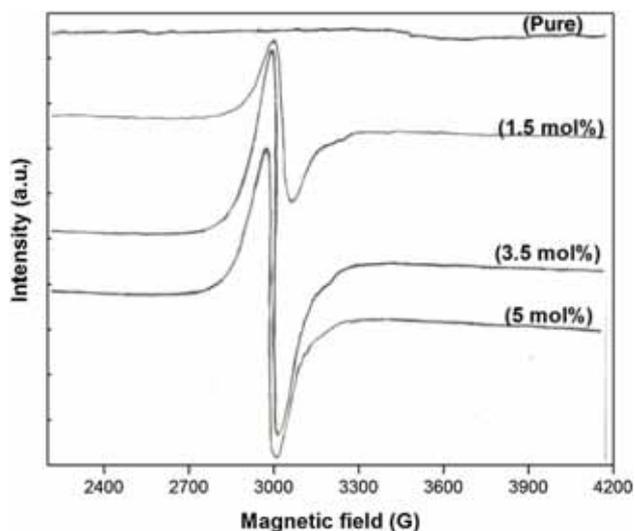


**Figure 11.** SEM photographs of MAA:EA copolymer films containing  $\text{Cu}^{2+}$ : (a) pure, (b) 1.5, (c) 3.5 and (d) 7.5 mol%.

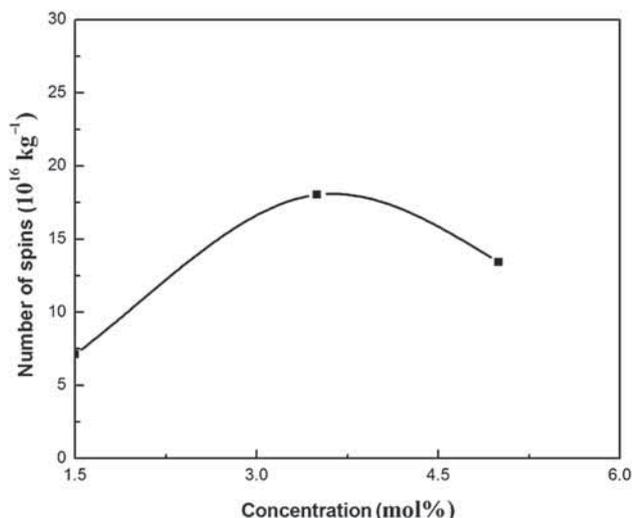
MAA and EA molecules may disperse in the soft-segment phase with little influence on the micro phase separation and mix of the hard and soft segments. The increase in the degree of roughness with increased  $\text{Cu}^{2+}$  ions concentration indicates a segregation of the dopant in MAA:EA copolymer. The lower degree of crystallinity and uniform morphology, which are also confirmed by XRD studies, may be suitable for better conductivity of the copolymer film [10].

### 3.6 EPR studies

EPR spectra of pure and different concentrations (1.5, 3.5 and 5 mol%) of  $\text{Cu}^{2+}$  ions-doped MAA:EA copolymer film are shown in figure 12. No signal was observed in the spectra of undoped MAA:EA copolymer film indicating that no paramagnetic impurities were present in the starting materials. When various mol% of  $\text{Cu}^{2+}$  ions were added to MAA:EA copolymer, the EPR spectra of all the investigated samples exhibit resonance signal due to  $\text{Cu}^{2+}$  ions with effective



**Figure 12.** EPR spectra of pure and various concentrations of  $\text{Cu}^{2+}$  doped MAA:EA copolymer at room temperature.



**Figure 13.** A plot of concentration of  $\text{Cu}^{2+}$  ions in MAA:EA copolymer vs. number of spins at room temperature.

$g$  values,  $g_{\perp} = 2.058$  and  $g_{\parallel} = 2.177$ . The observed EPR signals do not show variation in their linewidth and  $g$  values, whereas the intensity of the signal shows considerable variation with increasing dopant concentration. Compared to EPR spectrum of 1.5 mol%  $\text{Cu}^{2+}$  ions-doped film, the intensity of the signal for 3.5 mol%-doped sample has increased, which may be due to increased number of isolated  $\text{Cu}^{2+}$  ions resulting from enhanced doping content. The intensity of the signal for 5 mol%  $\text{Cu}^{2+}$  ions-doped film has been decreased compared to 3.5 mol%  $\text{Cu}^{2+}$  ions-doped film. The decrease in signal intensity may be due to the formation of  $\text{Cu}^{2+}$  ion clusters, which results from the aggregation of  $\text{Cu}^{2+}$  ions because of the more number of  $\text{Cu}^{2+}$  ions.

The number of spins ( $N$ ) participating in the resonance was roughly estimated by the equation given here [37]:

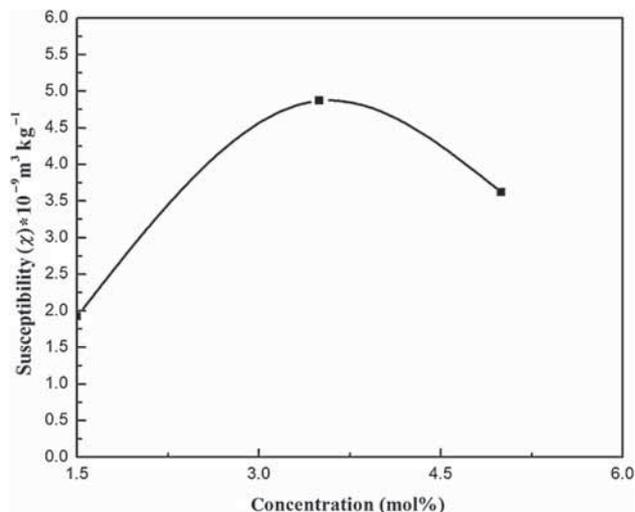
$$N = I (\Delta H_{pp})^2, \quad (5)$$

The intensity and linewidth were estimated by relative peak-to-peak height ( $I$ ) and width ( $\Delta H_{pp}$ ) in each first derivative resonance curve.

The number of spins participating in resonance in this polymer system was calculated for different concentrations. Figure 13 shows the variation of the number of spins with doping level. It is clear that the spin concentration reveals a minimum spin content at doping level of 1.5 mol% and maximum spin content at 3.5 mol%.

### 3.7 Calculation of paramagnetic susceptibility from EPR data

The paramagnetic susceptibility ( $\chi$ ) of the sample can be calculated from the EPR data using the formula [38]:



**Figure 14.** A plot of susceptibility as a function of dopant concentrations for  $\text{Cu}^{2+}$  doped MAA:EA copolymer films.

$$\chi = \frac{N_g^2 \beta^2 J(J+1)}{3k_B T}, \quad (6)$$

Where  $N$  is the number of spins per kg and rest of the symbols have their usual meaning. Figure 14 shows the plot of susceptibility ( $\chi$ ) as a function of dopant concentration.

### 3.8 PL studies

Generally, the densities of defects and oxygen vacancies affect significantly the optical properties of oxide copolymers. The correlation between structure and property is investigated by PL spectra [39]. The discovery of visible PL in polymers has enormous potential applications in polymer-based optoelectronics. Doping is the most widely used method for imparting the required properties to polymer materials, and materials doped with deep-level impurities are used extensively in modern electronics. For example, copper, the best known activator of efficient luminescence in polymers introduces a series of broad luminescence bands throughout the visible region. Among the impurities used for doping, a special place is occupied by transition metals. Therefore, we summarize that the optical properties of transition metal-doped polymer may possibly contain much more information to understand the basic physical mechanics involved in carrier recombination [40].

The emission spectrum of pure MAA:EA copolymer sample studied at room temperature (excitation at 320 nm) is shown in figure 15. The emission spectrum of pure MAA:EA sample exhibits six bands centered at 426, 454, 462, 479, 512 and 529 nm. The emission spectrum of pure MAA:EA copolymer film exhibits a strong band at 426 nm and the remaining bands are weak bands. These bands can be attributed to the recombination of free charge carriers at the defects, possibly at the surface of MAA:EA [30].

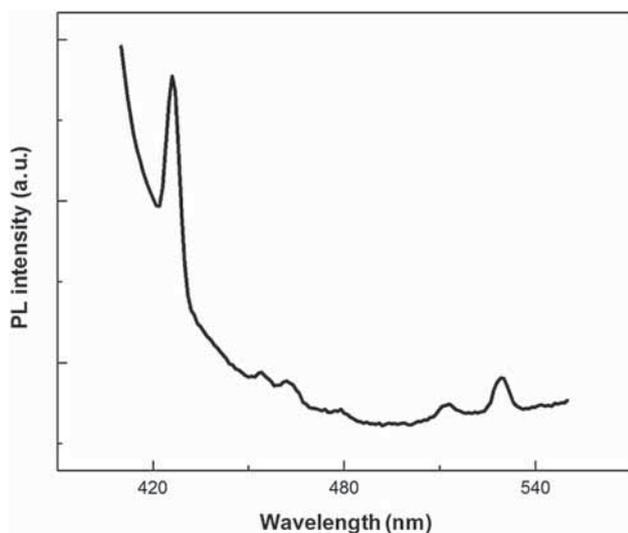


Figure 15. PL spectra of pure MAA:EA copolymer.

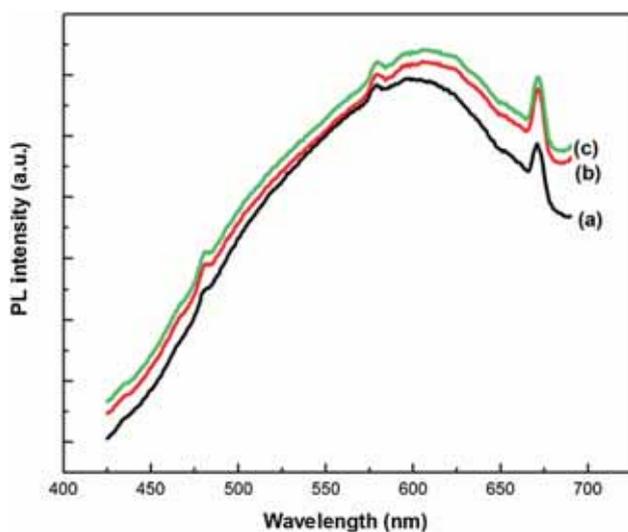


Figure 16. PL spectra of Cu<sup>2+</sup> doped MAA:EA copolymer: (a) 1.5, (b) 3.5 and (c) 5 mol%.

The room temperature PL spectra of Cu<sup>2+</sup> ions-doped MAA:EA copolymer at different concentrations (1.5, 3.5 and 7.5 mol%) are shown in figure 16. After excitation at 320 nm, four emission peaks are observed at 480 nm (blue), 579 nm (yellow), 604 nm (red) and 671 nm (red). It is noticed that the PL peak at 604 nm is quite broad. The central factor in this discussion is the nature of the characterized samples. The peak at 671 nm is more intense than 480 and 579 nm peaks. The peak at 480 nm corresponds to the band edge emission or artifact [41]. The peak at 579 nm arises from the singly ionized oxygen vacancy resulting in the yellow emission of Cu<sup>2+</sup> ions materials because of recombination of a photogenerated hole with a singly ionized electron in valance band [42]. The peak at 604 nm, i.e., the red luminescence band

is assigned to a band–band transition [40]. The peak at 671 nm arises due to band–acceptor transition [40]. Our experimental results indicate that the peak at 671 nm is caused by the copper impurity in the copolymer. We believe that the present result will contribute to the fundamental understanding of complicated properties of the copolymer.

#### 4. Conclusions

Pure and Cu<sup>2+</sup> ions-doped methacrylic acid–ethyl acrylate (MAA:EA) copolymer films were prepared using the solution cast technique. The DSC measurements of Cu<sup>2+</sup> ions-doped MAA:EA copolymer films show that the melting temperature shifted towards the lower temperature with increasing dopant concentration. The TGA curves in the pure and Cu<sup>2+</sup> doped copolymers reveal that there are three distinct steps of weight loss. This is due to loss of absorbed water, elimination of side chains and main chain decomposition. The first step of weight loss in TGA supports an endothermic transition in DSC. In XRD patterns, the intensity of diffraction pattern decreases as the amorphous nature increases with the addition of the dopant. The lower degree of crystallinity and uniform morphology, which is also confirmed from XRD studies, may be suitable for better conductivity of the copolymer film. The FTIR spectrum exhibits few bands which are attributed to stretching and bending vibrations of C=C, C–H, CH<sub>3</sub>–O and C=O groups. Optical absorption edge and optical band gap showed a decreasing trend with increasing dopant concentration. EPR spectra of all the doped samples exhibit signals due to Cu<sup>2+</sup> ions with elongated tetragonal symmetry. The observed variation in the EPR signal intensity with dopant concentration is due to the isolated and aggregated copper ions. The PL spectra of Cu<sup>2+</sup> doped MAA:EA copolymer exhibit four emission peaks corresponding to band–edge emission, ionized electron in valance band, band–band transition and band–acceptor transition.

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