Synthesis and characterization of polyaniline-nickel chloride composites

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Abstract. NiCl2/ polyaniline composites with varying NiCl2 concentration have been synthesized and characterized for structural and optical modifications in polyaniline with the addition of NiCl2, and to explore the effect of addition of NiCl2 on the electrical properties of polyaniline. FTIR spectral peaks attributed to various entities present in polyaniline have been shifted towards longer wavelengths with the addition of NiCl2. The d-spacing for the two x- ray diffraction peaks at 20.30° and 26.22° has been determined by using the Bragg’s relation and found to decrease with the addition of NiCl2. The SEM images of the composites indicate the uniform dispersal of the salt in the polymeric conformation. The band edge of UV -VIS spectra of the composites has been found to blue shift indicating increase in the band gaps with the increased NiCl2 concentration except for a concentration of 5%. The capacitance has been found to decrease with increase in frequency and the increase in the NiCl2 content. The resistance has been found to increase with the addition of NiCl2 thus establishing a positive correlation between the optical band gap and variations of resistance with the addition of NiCl2 to the polyaniline.

Keywords: NiCl2/ polyaniline composites, electrical properties, inductance, UV-Vis Spectra, Urbach’s tail, DTA.

1. Introduction

The potential applications of inorganic salt-conducting polymer hybrid composites in the field of colloidal ink [1-3], energy storage devices [4-7], optoelectronic devices [8-10] and anti-corrosion applications [11-14] have substantially attracted many researchers. Wherever conducting polymers owe the structural flexibility [15-16], controllable conductivities [17] and easy processability, metal harvest the potential for high charge carrier mobility and a range of electromagnetic properties [18]. Thus, during the last few decades various successful strategies have been developed to accumulate the properties of dissimilar materials through the fabrication of composites to overcome their inherent limitations. Successful preparation of composites with high mechanical stabilities has proven that these composites could be utilized in photovoltaic cells, transistors [19-20] and diodes. The most critical feature for the progress in such fields is attaining control over electrical and electrochemical properties of the composites.
Polyaniline offers a unique and optimal preference amongst the prime conducting Polymers due to its reversible electrochemical properties and easy processability. The present work reports the synthesis of polyaniline/ NiCl₂ composites through chemical route and the variations in structural, optical and thermal properties of the composites with increasing content of NiCl₂. The variations in electrical properties have been correlated to the modifications in structural and thermal properties.

2. Experimental section
Polyaniline has been synthesized by oxidizing 0.2M solution of aniline hydrochloride with 0.25M solution of ammonium peroxy disulphate under continuous stirring at room temperature. The solution is then divided into four equal parts and nickel chloride with varying concentrations ranging from 0 to 7.5% has been added to the solutions under continuous stirring and left over for a day to polymerize. The precipitates of the composites have been filtered and washed with distilled water for a number of times and then dried in a hot air oven at a constant temperature of 70°C, powdered and weighted. The filtered solutions have been analysed for Nickel concentration by gravimetric analysis technique to detect the amount of Nickel in the precipitates. The composites obtained have been characterized for Fourier transform infrared (FTIR) transmission spectra in the wavenumber range of 4000 – 400 cm⁻¹ at a spectral resolution of 4 cm⁻¹ using IR Affinity-1(Shimadzu Japan) spectrophotometer with diffused reflectance spectroscopy (DRS) attachment. The crystalline nature of composites has been analysed using BRUKER D8 FOCUS X-rays Diffractometer with a step size of 0.020 degrees. Surface structure of pristine and NiCl₂/ polyaniline composites has been photographed using Field effect scanning microscopy (FESEM) at an excitation potential of 9kV. Optical properties of composites have been explored by using a double beam UV-VIS spectrometer (UV-1800, Shimadzu, Japan) in the wavelength range of 250-800 nm.

The electrical properties have been examined using HIOKI 3532-50 LCR Hi Tester instrument in the frequency range 0.1 – 3.5 MHz. The thermal properties of the composites have been analysed through Differential Thermal Analysis (DTA) (NETZSCH STA449F1 Jupiter, Germany) in nitrogen atmosphere at the purge rate of 5 K/min in temperature range of 305 – 1370 K with a known amount of composites in alumina crucible.

3. Results and Discussion
The variations in structural, morphological, optical, electrical and thermal properties of NiCl₂/ polyaniline composites with the increased concentrations of NiCl₂ have been studied and have been reported in the following sections.

3.1. Structural and Morphological Properties
The variations in chemical properties of polyaniline with the addition of NiCl₂ have been analyzed by studying the variations in FTIR spectra and the results obtained are shown in figure 1.

![Figure 1. FTIR of pristine and NiCl₂/ Polyaniline Composites with varying NiCl₂ Concentrations](image-url)
A prominent peak at 1141 cm\(^{-1}\) with a shoulder at 1093 cm\(^{-1}\) has been observed corresponding to asymmetric (-NH\(^{\equiv}\)) structure associated with the N=O=N functional group present in the polymer unit and the C-N stretch of the saturated primary amines, respectively. A few more peaks attributed to C-N vibrations of secondary aromatic amines linked with para-aniline units and consecutive benzenoid units have been noticed at 1296 cm\(^{-1}\) and 1240 cm\(^{-1}\) [21], respectively. Weak intensity peaks at 2926 and 3217 cm\(^{-1}\) attributed to asymmetric N-H stretch vibrations associated with hydrogen bonded amino groups indicate the presence of inert imines in the polymeric matrix. The peak at 3217 cm\(^{-1}\) has been observed to shift towards lower wavenumber demonstrating the decrease in the intensity of inert amino groups that may be attributed to the formation of polymer NiCl\(_2\) composites. Another peaks corresponding at 877 cm\(^{-1}\) and 794 cm\(^{-1}\) corresponding to out of plane bending vibrations of para-di-substituted benzene have also been recognized. A peak at 702 cm\(^{-1}\) attributed to aniline oligomers bearing mono-substituted phenyl rings as terminal units signify the presence of free radicals in the polymer [22]. The peaks at 1465 cm\(^{-1}\) and 1550 cm\(^{-1}\) corresponds to C=C stretching vibrations of aromatic rings and quinoid structure respectively [23-24]. The former peak has been found to shift towards lower wavenumber with addition of NiCl\(_2\) specifying the interaction of benzenoid and quinoid unit of the polymer with the salt. Two successive weak intensity peaks at 592 and 619 cm\(^{-1}\) attributed to hydrogen sulphate counter-ions indicates the presence of remnants of ammonium peroxisulphate in the polymer and have been observed to blue shift with the increase of NiCl\(_2\) concentration. A very little variation in the peak corresponding to C-H stretches at 2854 cm\(^{-1}\) has been observed indicating that the salt interacts with the amine group of the polymer without influencing the benzene ring. A band at around 3500 cm\(^{-1}\) [25] due to the presence of N-H asymmetric stretches has been found to shift towards lower wavenumber with increased NiCl\(_2\) concentration affirming the interaction of the salt with the N-H linkage of the polymeric conformation. The narrowing of the band for 5% concentration of NiCl\(_2\) may be attributed to the strongest interaction of NiCl\(_2\) to the polymeric chains at this concentration, whereas the FTIR of 7.5% concentrations resembles more to the pristine polyaniline indicating weak interactions between salt and polyaniline molecules.

The XRD patterns of pristine and NiCl\(_2\) doped polyaniline have been recorded by measuring the intensity distribution as a function of varying angle between 10° to 70°. Polyaniline basically possesses partially monoclinic crystalline structure with cell parameters of \(a=8.34\ \text{Å}, b=5.21\ \text{Å},\) and \(c= 9.52\ \text{Å},\) respectively [26]. The peaks at 20=20.30° and 26.22° (Figure 2) correspond to periodicity parallel and perpendicular to polymeric chains, respectively [27].

The Bragg’s peak at 20.30° represents the characteristic close contact interchain distance [28-29], whereas the intense, well defined and sharp peak at 26.22° is associated with paracrystalline disorder in the polymer [30]. The d-spacing corresponding to the principal peaks at 20.30° has been determined by
using the Bragg’s relation and found to decrease with the addition of NiCl\textsubscript{2} that may be attributed to the decrease in the distance between the ring planes in adjacent chains. The d-spacing for the other peak at 26.22° has been found to increase with increased concentration of NiCl\textsubscript{2} indicating the increase in the paracrystalline disorders in the composites. The crystallite size (L) corresponding to the peak has also been determined from the Scherrer relation [31].

\[
L = \frac{K\lambda}{w \cos \theta}
\]

Here K is a dimensionless shape factor with a typical value of 0.9 and ‘w’ is the full width at half maximum of the crystalline peaks in radians. The interchain separation length (R) for the two peaks has been calculated using the relation

\[
R = \frac{5\lambda}{8 \sin \theta}
\]

And the results are reported in table 1.

### Table 1. The variations of d-spacing, crystallite size (L), interchain separation (R) and micro strain (ε) with respect to NiCl\textsubscript{2} concentration in polyaniline

| Percentage concentration of NiCl\textsubscript{2} in polyaniline | d-spacing (Å) | Crystallite size L (nm) | Inter-chain separation R (Å) | Microstrain ε |
|---------------------------------------------------------------|--------------|-------------------------|-------------------------------|--------------|
| 0                                                             | 4.37         | 3.86                    | 5.46                          | 0.051        |
|                                                               | 3.39         | 1.79                    | 4.24                          | 0.085        |
| 2.5                                                           | 4.16         | 17.95                   | 5.21                          | 0.010        |
|                                                               | 3.39         | 4.01                    | 4.24                          | 0.038        |
| 5                                                             | 4.18         | 12.62                   | 5.22                          | 0.015        |
|                                                               | 3.48         | 4.42                    | 4.34                          | 0.035        |
| 7.5                                                           | 3.03         | 4.12                    | 5.06                          | 0.044        |
|                                                               | 4.05         | 0.89                    | 4.28                          | 0.172        |

It has been found to decrease with the addition of the salt except at a concentration of 5% that may be attributed to the strong interaction between salt ions and polymeric moieties. Microstrain produced by dislocations and domain boundaries in pristine and NiCl\textsubscript{2}/ polyaniline composites have been calculated using the relation

\[
\varepsilon = \frac{w \cos \theta}{4 \sin \theta}
\]

and have been reported in the table 1 along with interchain separations and crystallite size.

The variations in microstrain correspond to anti-phase domain boundaries formed during the ordering of the material that goes through order disorder transformations. The other cause of variations in microstrain may be the presence of non-uniform lattice distortions induced due to variations in surface tension and morphology of the polymer. The variations in microstrain with the increases dopant concentration have also been reported by Bhardwaj et al [32]. The peak at 20.30° has been found to shift towards greater 2θ with the addition of NiCl\textsubscript{2} implying the modifications in the crystallite structure of the blends. The crystallite size has also been found to increase with the addition indicating the increase in the periodicity of the polymeric conformation due to the interstitial impurities. A few new peaks at around 23° and 29° have also been observed to originated with the increased concentration of NiCl\textsubscript{2} attributed to the crystallites planes of the metal halide itself.

SEM micrographs analysis has been used to assay the microstructure of the polymer and determining the particle size and the images obtained are shown in figure 3. The SEM image of pristine polyaniline seems to exhibit uniform morphology with flaky shaped structures dispersed. The metal salt has been found to disperse uniformly in the polymeric matrix with the formation of clusters that has been found to increase with the increased concentration of NiCl\textsubscript{2} as could be characterized by the upper range of
gray shades while the polymer is identified by the lower range of gray values. The particle size of pristine and NiCl₂ doped polyaniline have been calculated using average over a Gaussian distribution of particle diameters and are reported in table 2. The variations in particle size could be attributed to the different electrochemical graining conditions during the synthesis process [33].

| Percentage of NiCl₂ in Polyaniline | Granule size (μm) |
|-----------------------------------|-------------------|
| 0                                 | 0.17              |
| 2.5                               | 0.85              |
| 5                                 | 0.50              |
| 7.5                               | 0.90              |

The particle size has been found to increase with the addition of metal salt indicating the interaction between the polymeric matrix and the metallic salt. The SEM images also revealed the dispersion of NiCl₂ particles in the polymeric matrix and the phase separation could be observed from the intergranular boundaries revealed in the SEM images. These boundaries separate the region of same composition but different orientations. The interchain links through coupling modes have also been observed in the SEM images of the polymer indicating its lesser solubility in solvents. The presence of clusters may hinder the flow of current through the sample and hence increase the resistivity of the polymer with the addition of NiCl₂.

3.2. Optical Properties

The UV-Vis absorption spectra of pristine and NiCl₂/ polyaniline composites dissolved in NMP has been recorded and is presented in figure 4.

Two absorption edges at 282 and 410 nm have been observed for pristine polyaniline. The lower wavelength edge has been ascribed to polaron→π* transition in benzoid structure whereas a molecular exciton attributed to π→polaron transition associated with quinoid moieties present in the polymeric backbone is responsible for the presence of upper wavelength absorption edge [34-35]. Severe asymmetry of valence and conduction bands in polyaniline leads to broad band due to charge defects within the energy gap. The transfer integral of π electrons of carbon and nitrogen bond leads to the formation of valence band due to the arrangement of polaron in the polaron lattice [36] and the intensity of the transfer integral is influenced by the C-N bond length and the angle between π orbitals. Thus the oxidation level of the polymer plays an important role in the electronic structure and the optical spectrum.
of polyaniline. The addition of NiCl₂ to polyaniline results in the modification of oxidation state and thus variations in the UV-Vis spectra of the composites. The band edge has been found to blue shift except for a NiCl₂ concentration of 5%. The other band has also been found to reduce in intensity and shift toward lower wavelength. The exception of 5% concentration NiCl₂/Polyaniline could be understood on the basis of increase in the number of polarons, bipolarons and solitons, to act as charge storing sites and thus reduction in the chain length. The smaller particle sizes observed in SEM for the same concentrations also asserts the assumption. The UV-Vis spectra of the polymer have been utilized to calculate the direct and indirect band gaps as well as the Urbach’s tail. The results obtained have been reported in table 3. The direct band gap transitions occur without variations in the momentum of the interacting photons, whereas in case of indirect band gap transitions large deviations in momentum occur due to the emission or absorption of phonons.

### Table 3. The variations of Direct, indirect band gaps and Urbach’s tail energies with percentage concentration of NiCl₂ in polyaniline

| NiCl₂ Concentration (%) | Direct band gap (eV) | Indirect band gap (eV) | Urbach’s tail (eV) |
|-------------------------|----------------------|-----------------------|-------------------|
| 0                       | 4.26                 | 4.50                  | 0.18              |
| 2.5                     | 4.25                 | 4.42                  | 0.25              |
| 5                       | 2.84                 | 3.40                  | 0.42              |
| 7.5                     | 4.48                 | 4.45                  | 0.19              |

The band gap energies have been found to increase with the increase in the concentration of NiCl₂, which may be attributed to the strong attractive interactions between the salt and the polymeric moieties. The decrease in case of 5% may due to the increased intensities of polarons and bipolarons. The exceptions in the bandgaps of the 5% NiCl₂/Polyaniline composites may be interrelated to the structural changes as already discussed in the FTIR analysis of the composites. The higher values of indirect band gaps as compared to the direct band gaps indicate that polyaniline is better to be utilized in direct band gap applications. The creeping of band tail in to the forbidden gap due to the presence of impurities randomly distributed in the host crystal is known as the Urbach’s energy [37] and is considered as trap centres for conduction electrons, subsequently producing hindrance to the current flow. Thus the increase in Urbach’s energy with the increased concentration of NiCl₂ seem to cartel the resistivity of the polymer. However, an abrupt decrease in the Urbach’s energy for a 7.5% NiCl₂/Polyaniline composites may be due to the variations in chain lengths of the polymeric molecules due to the interactions with the inorganic salt.

### 3.3. Electrical Properties

The electrical properties of the polymer composites that have been studied include the variations of resistance, inductance, capacitance and dielectric losses with frequency in the range of 0.5 to 3.5 MHz. The variations of resistance in pristine and polyaniline/NiCl₂ composites with respect to frequency have been shown in figure 5. It has been observed that the resistance increase with increasing concentration of NiCl₂ except for a 7.5% doped sample, that may have been caused by the augmented inter chain distances and the interaction between NiCl₂ ions and the polymeric free radicals and unstable moieties. These interactions result in the reduction of the density of free charge carriers and hence aids in the increment of the resistivity of the composites. The band gap has also been found to increase of NiCl₂ concentrations asserting the results of resistance variations with the addition of salt. The decrease in the resistance for a composite with 7.5% concentration of NiCl₂ might be due to generation of extended states in composites or by changed defects with electronic structure. Also in heavy doping there is the formation of polarons and bipolarons that help in the enhancement of conducting properties of the composites. A very sharp peak in frequency range 1.75-1.80 MHz for 2.5% and 5% concentrations has also been observed, indicating an increase in resistance for these two concentrations at lower frequencies.
It is also obvious from the figure 5 that the resistance decreases with the increase in frequency. At lower frequencies the presence of clusters may hinder the flow of current through the composites and hence the resistance increases however the hopping frequency of the charge carriers increases with the increased frequencies and hence influences the conduction mechanism of the composites and hence the resistance decreases. However, a small bulge has been observed in frequency range of 1.8-2.4 MHz as shown in the inset zoom of figure 5. This might be attributed to the reduction in the resonance between the hopping frequencies of the charge carriers and the applied frequencies.

The variations of inductance in pristine and polyaniline/NiCl₂ composites with respect to frequency have been analysed and have been found to decrease exponentially with the increase in frequency (Figure 6). The inductance of the composites depends on the distribution of current within the conductor.

The cause of decrease in inductance at high frequencies is due to the reduction in the inner inductance; the current is focused in the peripheral of the composite pallet causing a decrease in the magnetic field intensity in the core and hence the internal resistance. The inductance is also influenced by the proximity effect; at high frequencies the effective area of the current loop reduces and thus the internal inductance [38]. The enhanced inductance at lower frequencies may be attributed to the distribution of return current over the available return paths and the spin rotations. The spin rotational component is of relaxation type and its dispersion is inversely proportional to frequency. The inductance has been found to enhance with the increase in NiCl₂ concentration. However 7.5% doped sample shows an absurd behaviour. This might be due to the fact that as the particle size of impurity changes in the vicinity of pristine solution, there is the variation in the conducting behaviour of the composite which changes the field in the surrounding and hence affect the inductance.

The variation of capacitance as a function of frequency at different NiCl₂ concentrations for Polyaniline/ NiCl₂ Composites has been shown in figure 7. The capacitance has been found to decrease with increased frequency followed by a plateau ranging from 23 to 2000 kHz. A sharp increase in the capacitance at higher frequencies with a peak at 2.47 MHz for pristine polymer has also been observed and has been found to sharpen with the increased NiCl₂ concentration with an exception at 7.5% content. The peak has been found to shift slightly towards higher frequency with the addition of NiCl₂. The spheroidal particles sparsely distributed, as also observable from SEM images of the composites, gives rise to Maxwell-Wagner polarization effect due to heterogeneous electrode electrolyte interphases and results in the formation of plateau at lower frequencies. The free charge carriers at the interphases of dissimilar materials cause charge build-up at the boundaries that gives rise to dielectric dispersion and does not contribute to the variations in capacitance with frequency [39]. The increase in capacitance at higher frequency beyond 2.2 MHz could be explained on the basis of dipole orientations with the applied
frequencies. The hindrance instigated to the orientation of dipole moments with applied field, by the thermal agitations, became submissive due to the effect of higher frequencies [40]. The capacitive reactance gets reduced with the increased frequency due to the availability of more space for the easy rotation of dipoles and hence assists in the increase of capacitance. A further decrease beyond 2.5MHz could be illustrated by Cole-Cole plot [41].

The capacitance has been found to decrease with the increase in the NiCl2 content except for a composite with 7.5% concentration of the salt. Similar fashion has been observed in the structural and optical properties of the composites.

Dielectric losses originate due to the movement of molecular dipoles, direct current conduction and Debye loss factors due to dipole orientations. The variations of dielectric losses with frequency for pristine and Polyaniline/ NiCl2 composites have also been studied and found to decrease with frequency in the low frequency range (Figure 8), indicating the existence of conduction losses in this range. The losses have been found to increase with further increase in the frequencies and attain a maximum at 2.1MHz and decreases thereafter. The peak has been found to red shift with the increased concentration of NiCl2. The peaks are comparatively sharp for the composites with NiCl2 concentrations of 2.5% and 5%, respectively, the moisture which get absorbed at the fibre-resin interface acts as a plasticizing agent [42], enhances the mobility of the polymer chain resulting in the formation of peaks at high frequency.

![Figure 7. Frequency Variation of Capacitance with varying NiCl2 concentrations in polyaniline](image1)

![Figure 8. Frequency Variation of dielectric losses with varying NiCl2 concentrations in polyaniline](image2)

At higher frequencies the orientations of the polymeric molecules may not succeed to resonate with the applied field and acquires a component out of phase to the applied field, resulting in thermal dissipation of energy and hence an increase in the dielectric losses. At further higher frequencies the inertia of the molecules tends to keep the molecules in motion and hence make the basis of reduced losses at these frequencies. The losses have been found to increase with the increase in the NiCl2 concentrations that may be attributed to polarizability of the molecules. The chains in the amorphous phase are more flexible and hence the orient easily with the applied field, however the addition of the salt enhanced the crystallinity of the composites and hence cause an increase in the dielectric losses.

### 3.4. Differential Thermal Analysis

DTA is one of the useful techniques to determine the thermal stability of the polymers and to find the onset temperature of thermal degradations. The DTA curves of pristine and NiCl2 composites of polyaniline have been shown in figure 9, and three complex peaks could be observed indicating a three step decomposition of the composites. The first complex peak with an onset temperature of 73°C and a peak at 110°C could be attributed to the interlayer water volatilization [43], the peak has been found to shift towards higher temperatures with the addition of the inorganic salt indicating the enhancement in the stability of the composites. However an exception for a composite with 7.5% concentration of NiCl2 has been observed. A continuous decrease in the heat flow with temperature could be attributed to the complete evaporation of the water from the polymer interlayers and the formation of stable structure of
the composites. The second complex peak has been detected at 259 °C for pristine polyaniline and seems to blue shifted with the increase in the concentration of salt.

![Figure 9. Differential Thermal Analysis of Polyaniline composites with Varying NiCl₂ composites](image)

Being partly crystalline in nature, the occurrence of this peak signifies the melting point of the sample [44]. Last peak has been observed at 547°C with an onset at 535°C and ends at 600°C, the peak could be attributed to the degradation of the polymeric composites [45]. The peak has been shifted towards lower temperature indicating that the composites could not withstand at higher temperatures.

4. Conclusions

The variations in electrical, optical and thermal properties have been interpreted in terms of the structural and morphological modifications and it has been concluded that the addition of NiCl₂ to polyaniline aided in enhancing its properties, but the best results have obtained for the composites with 5% concentration of NiCl₂. SEM, XRD and Optical properties specify the strong chemical interaction between polyaniline molecules and the salt. The present studies suggest that NiCl₂/ Polyaniline may be deployed as conductive electrodes in the development of electrochemical devices.

References

[1] Han MG, Sperry J, Gupta A, Huebner CF, Ingram ST and Foulger SH 2007 J. Mater. Chem. 17 1347.
[2] Hebner TR, Wu CC, Marcy D, Lu MH and Sturm JC 1998 Applied Physics Letters 72 519.
[3] de Gans BJ, Duineveld PC and Schubert US 2004 Advanced Materials 16 203.
[4] Wang ZL, Guo R, Li GR, Lu HL, Liu ZQ, Xiao FM, Zhang M and Tong YX 2012 J. Mater. chem. 22 2401.
[5] Conway BE, Birss V, Wojtowicz J 1997 J. Power Sources 66 1.
[6] Wang X, Lu X, Liu B, Chen D, Tong Y and Shen G 2014 Adv. Mater. 26 4763.
[7] Dubal DP, Ayyad O, Ruiz V and Gómez-Romero P 2015 Chem. Soc. Rev. 44 1777.
[8] Gündüz B 2015 Optik – Int. J. for Light & Electron Optics 126 4566.
[9] Facchetti A, Seger M, Mohebbi A 2017 US patent: US20170104160 A1, Filing date: Jul 13, 2016, Publication date: Apr 13, 2017.
[10] Magdassi S, Grouchko M, Layani M 2015 US patent: US 20150357511 A1, Filing date: Jul 6, 2015, Publication date: Dec 10, 2015.
[11] Caldona EB, de Leon ACC, Pajarito BB, Advincula RC 2017 Appl. Surface Sci. 422 162.
[12] Cai K, Zuo S, Luo S, Yao C, Liu W, Ma J, Mao H, Li Z 2016 RSC Adv. 6 95965.
[13] Bagherzadeh M, Ghasemi M 2015 J. Polym. Sci. Tech. 5 1.
[14] Grgur BN, Elkais AR, Gvozdenović MM, Drmanić SŽ, Trišović TL, Jugović BZ 2015 Prog. Org. Coat. 79 17.
[15] Shi Y, Pan L, Liu B, Wang Y, Cui Y, Bao Z, Yu G 2014 J. Mater. Chem. A. 2 6086.
[16] Hao GP, Hippauf F, Oschatz F.M, Leifert A, Nickel W, Noriega NM, Zheng Z and Kaskel S 2014 ACS Nano 8 7138.
[17] Brenner TM, Egger DA, Kronik L, Hodes G and Cainen D 2016 Nature Rev. Mater. 15007 1.
[18] Amer K, Ebrahimm S, FetehaM, Soliman M and El-Shaer A 2017 34th National Radio Science Conference (NRSC), Alexandria, 440.
[19] Bhadra J & Sarkar D 2010 Indian J Phys 84 693.
[20] Boyer ML, Quillard S, Louarn G, Froyer G, Lefrant S 2000 J. Phys. Chem. B 104 8952.
[21] Stejskal J, Hajna M, Kasparkova V, Humpolicek P, Zhigunov A, Trchova M 2014 Synthetic Metals 195 286.
[22] Furukawa Y, Ueda F, Hyodo Y, Harada I, Nakajima T, Kawagoe T 1988 Macromolecules 21 1297.
[23] Ping Z 1996 J. Chem. Soc. Faraday Trans. 92 3063.
[24] Trchova M, Sedenkova I, Konyushenko EN, Stejskal J, Holler P and Marjanovic GCÄ 2006 J. Phys. Chem. B 110 9461.
[25] Nicolau YF, Djurado D 1993 Synth. Met., 55 394.
[26] Moon YB, Cao Y, Smith P, Heeger AJ 1989 Polym. Commun. 30 196.
[27] Hsu CH, MacDiarmid AG, Epstein AJ 1995 Synth. Met. 69 119.
[28] Pouget JP, Jozefowicz ME, Epstein AJ, Tang X, MacDiarmid AG 1991 Macromolecules, 24 779.
[29] Chaudhari HK, Kelkar DS 1997 Polym. Int., 42 380.
[30] Scherrer P 1918 Nachr. Ges. Wiss. Göttingen 26 98.
[31] Bhardwaj E, Prasher S, Kumar M, Kaur U & Sahni M 2017 J. Elec. Materi. 46 1261.
[32] Cho MS, Cho YH, Choi HJ and Jhon MS 2003 Langmuir 19 5875.
[33] Rahy A, Sakrou M, Manohar S, Cho SJ, Ferraris J and Yang DJ 2008 Chem. Mater. 20 4808.
[34] Khow J, Akhtar A and Nabi SA 2015 New J. Chem. 39 3728.
[35] Ginder JM, Epstein AJ 1990 Phys. Rev. B 41 10674.
[36] Mahr H 1963 Phys. Rev. 132 1880.
[37] Mezhiba AV, Friedman EG Proc. 15th Annual IEEE International ASIC/SOC Conference, IEEE Circuits and Systems Society, 421.
[38] Bhardwaj E, Prasher S, Kumar M, Singh S 2009 Asian. J. Chem. 21 S043-S046.
[39] Cole KS and Cole RH 1941 J. Chem. Phys. 9 341.
[40] Prasher S, Kumar M, Singh S 2014 Internat. J. polym. anal. Charact. 19 204.
[41] Elyashevich GK, Terlemezyan L, Kuryndin IS, Lavrentyev VK, Mokreva P, Rosova E Yu, Sazanov Yu N 2001 Thermochimica Acta 374 23.
[42] Bershtien VA, Egorov VM, Kemp TJ 1994 Differential scanning calorimetry of polymers: Physics, Chemistry, Analysis, Technology, Ellis Horwood, Chichester.
[43] Wei Y, Hsueh KF 1989 J. Polym. Sci. A Polym. Chem. 27 4351.