



Temperature Dependence of AC Electrical Conduction in Plasma Polymerized Pyrrole-N,N,3,5 Tetramethylaniline Bilayer Composite Thin Films

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Abstract: The temperature dependence of alternating current (ac) electrical conduction in Plasma Polymerized Pyrrole-N,N,3,5 tetramethylaniline (PPPy-PPTMA) bilayer composite thin films have been discussed in this article. The thin films were deposited by using a parallel plate capacitively coupled glow discharge reactor. To study the temperature dependence of ac electrical conduction the variation of dielectric constant (ϵ'), the dielectric loss factor (ϵ''), and the ac conductivity (σ_{ac}) of the thin films were investigated in the frequency range 100 Hz to 10 MHz and in the temperature range 298K to 398K. The decrease of dielectric constant ϵ' with increasing frequency was observed and was attributed to the dielectric relaxation process. The dielectric constant, however, is observed to be increased with temperature in all frequency regions which is due to greater freedom of movement of dipole molecular chain in polymer films at high temperature. The variation of dielectric loss factor ϵ'' with frequency showed a loss minimum then rises to a sharp peak which was also attributed to the relaxation phenomena of polymer. It is, however, observed that the loss peaks have shifted towards the higher frequency side with the increase of temperature which is usually attributed to dipolar orientation. The dielectric loss factor is also observed to be increased with temperature in all frequency regions. At lower frequencies the increase of loss factor with temperature was attributed to the effective chain motion of polymer and at high frequencies this increase might indicate the orientational polarization due to chain motion in bilayer film. The linear behavior of the ac conductivity σ_{ac} with the frequency and the observed weak temperature dependence of σ_{ac} led to interpret the ac conduction mechanism as the hopping between localized states at the Fermi level.

Keywords: Plasma Polymerization, Bilayer Thin Films, AC Conduction, Temperature Dependence, Dielectric Properties

1. Introduction

Plasma polymerized thin films is found to be suitable dielectrics in integrated microelectronics and insulating layers for semiconductors as they have permanent dipole moment and hence exhibit dielectric dispersion. The frequency and temperature dependence of dielectric constant and the dielectric loss in this type of thin films is also remarkable. The analysis of dielectric data over a wide temperature and frequency range provides deep insight into

the nature of dominant polarization mechanism in polymer films, and therefore a dielectric study throws light on the molecular structure and relaxation behaviors of the polymers.

The dielectric constant, ϵ' , which is used to characterize the dielectric properties, is an essential piece of information when designing capacitors and in other circumstances where a material might be expected to introduce capacitance into a circuit. In an alternating (ac) field, the dielectric constant is a complex quantity, ϵ^* , and is the combination of a real component, called the relative permittivity or dielectric

constant, ϵ' , and an imaginary component, called the dielectric loss or dissipation factor, ϵ'' . This form, also called the complex dielectric permittivity, is defined as,

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (1)$$

It is to be noted that ϵ' is a measurement of energy stored per cycle and ϵ'' is the energy dissipated per cycle. Therefore, the variation of both ϵ' and ϵ'' with respect to frequency and temperature is a key issue for the ac measurements in plasma polymerized thin films, which would be presented in this article.

Many reports on the investigation of the structural, optical, direct current (DC) and alternating current (AC) electrical properties of plasma polymerized thin films are available in the literature but most of them dealt with single-layer thin films. Reports on the properties of bilayer thin films are relatively less abundant. Chowdhury and Bhuiyan [1] investigated the dielectric relaxation behavior of the plasma polymerized Diphenyl (PPDP) thin films over a wide frequency and temperature range and observed that the ac conductivity was more dependent on temperature in the low frequency region than in the high frequency region and dielectric constant was found to be dependent on frequency above 343K. Sakthi Kumar and Yoshida [2] studied the dielectric properties of rf plasma polymerized pyrrole (PPPy) thin film in the frequency range from 1 kHz to 1 MHz at various temperatures and reported that the PPPy thin films have high dielectric constant with small variations against frequency and temperature. The dielectric properties from a set of molybdenum (Mo) containing diamond like carbon (DLC) films were investigated by Huang et al [3] and a drastic reduction in the permittivity at frequencies up to 10 kHz was observed. Saravanan et al. [4] investigated on the dielectric constant and ac conductivity of plasma polymerized aniline thin films in a wide frequency range and found that the dielectric constant is considerably low in the high frequency. Akram et al. [5] studied on the frequency and temperature dependence of dielectric constant ϵ' in pure polyester resin and polymer composites in a wide frequency and temperature range. The value of ϵ' was found to be decreased with increasing frequency but was found to be increased with increasing temperature, which was an indication of the orientation polarization and greater freedom of movement of the dipole molecular chain at high temperature. Polyaniline thin films were characterized by Joseph Mathai et al. [6] and dielectric properties were investigated in the frequency range from 100 Hz to 1MHz and in the temperature range from 300 to 373 K. Capacitance and dielectric loss were observed to be decreased with frequency and increased with temperature. The ac conductivity $\sigma(\omega)$ was found to vary as ω^{-1} . The optical characterization and direct current electrical characterization of the plasma polymerized pyrrole-N,N,3,5 tetramethylaniline (PPPy-PPTMA) bilayer thin films were studied by Kamal and Bhuiyan [7, 8]. The optical characterization and thickness dependent direct current electrical characterization of the PPPy monolayer thin films were also reported by

Kamal and Bhuiyan [9, 10]. They further investigated the direct current electrical conduction mechanism of the PPPy monolayer thin films [11] and temperature dependence of DC electrical conduction in PPPy thin films [12]. The ac electrical characterization [13] and Dielectric properties [14] of PPPy monolayer thin films was also studied by Kamal and Bhuiyan.

The temperature dependence ac electrical conduction and the dielectric properties of PPPy-PPTMA bilayer composite thin films have been discussed in this article. The variation of dielectric constant, dielectric loss factor and ac electrical conductivity of PPPy-PPTMA bilayer thin were investigated at different temperatures. The experimental results were discussed thoroughly considering existing theory.

2. Experimental Details

In this study two types of monomers were employed to prepare plasma polymerized single-layer and bilayer thin films, namely, Pyrrole (Py) and N,N,3,5 Tetramethylaniline (TMA). The monomer pyrrole was collected from Aldrich-Chemie D-7924, Steinheim, Germany and the monomer N,N,3,5 Tetramethylaniline (TMA) was collected from BDH chemical limited, Germany.

The PPPy-PPTMA composite bilayer thin films were deposited on to chemically cleaned glass substrates at room temperature by using a capacitively coupled glow discharge plasma reactor. The vapor of the monomers was introduced into the glow discharge reactor through a flowmeter (Glass Precision Engineering, Meterate, England, UK) at the flow rate of about 20 cm³ (STP) / min. The glow discharge system consists of two parallel plate electrodes of stainless steel of diameter and thickness 0.09 and 0.001 m respectively placed 0.035 m apart. The glow discharge chamber was evacuated by a rotary pump (Vacuubrand GMBH & Co, 97877 Wertheim, Germany) and plasma was generated around the substrates with a power of about 30 W. To deposit the PPPy-PPTMA bilayer composite thin films, pyrrole-monomer has been used as the mother-material and TMA monomer has been deposited in different deposition time ratio after the pyrrole thin films were grown. The deposition time-ratios of PPPy: PPTMA were (50min: 10min), (45min: 15min), (40min: 20min), (35min: 25min) and (30min: 30min). Different time-ratios of the monomer have produced the bilayer thin films with different thicknesses. In this study, only one composition of PPPy: PPTMA (30min: 30min) of film thickness 400 nm has been discussed.

For electrical measurements the Al/PPPy/Al sandwich configuration were formed by using an Edward vacuum coating unit E-306A (Edward, UK) at a pressure of about 1.33×10⁻³ Pa with an effective electrode area of about 10⁻⁴ m². The ac measurement of PPPy-PPTMA bilayer thin films of different thicknesses was performed in the frequency range from 100 Hz to 3 MHz and temperature range 298K - 423K, by a low frequency (LF) Impedance analyzer, Agilent 4192A, 5 Hz -13 MHz (Agilent Technologies Japan, Ltd. Tokyo, Japan).

The temperature was recorded by a Cr-Al thermocouple placed very close to the sample which was connected to a Keithley 197A digital microvoltmeter (DMV). To avoid oxidation, all measurements were performed in a vacuum of about 1.33 Pa.

3. Results and Discussion

3.1. Variation of Dielectric Constant with Frequency and Temperature

Figure 1 shows the variation of the dielectric constant ϵ' of PPPy-PPTMA bilayer composite thin films of thicknesses about 400 nm at different temperatures 298K, 323K, 348K, 373K and 398K in the frequency range 100 Hz to 10 MHz.

From figure 1, a general trend of decreasing ϵ' with increasing frequency is observed; and the decrease in ϵ' is very prominent at both high frequencies and high temperature. This is a similar behavior of ϵ' -f curves for PPPy thin films [13]. The decrease of ϵ' with increasing frequency, however, is an expected behavior in most dielectric materials and is usually attributed to the dielectric relaxation process. In a system of inhomogeneous structure, ϵ' may arise due to interfacial and space charge polarization at frequencies from 100 Hz to few MHz. At lower frequency the dipole can respond rapidly to follow the field and dipole polarization has its maximum value and therefore higher values of dielectric constant and dielectric loss are usually observed in low frequency region. At higher frequencies dipole polarization has minimum values, since the field cannot induce the dipole moment, and values of ϵ' attain minimum values.

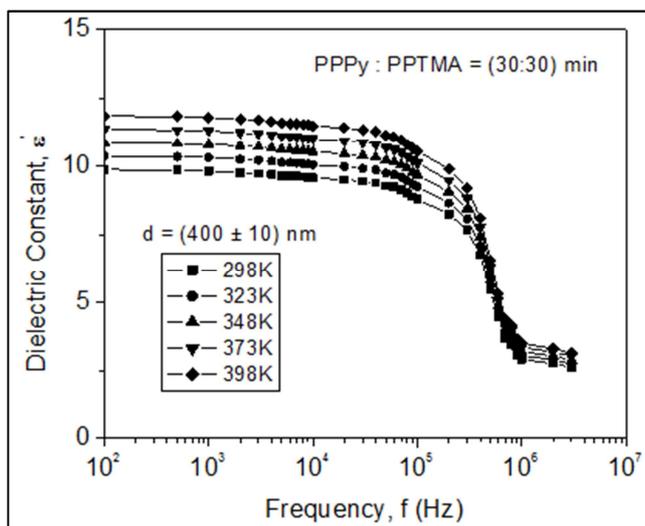


Figure 1. Dielectric constant, ϵ' , as a function of frequency of the PPPy-PPTMA composite thin films of thickness 400 nm at different temperatures.

The variation of ϵ' with temperature at different frequencies for the PPPy-PPTMA bilayer thin films of thicknesses 400 nm is presented in Figure 2.

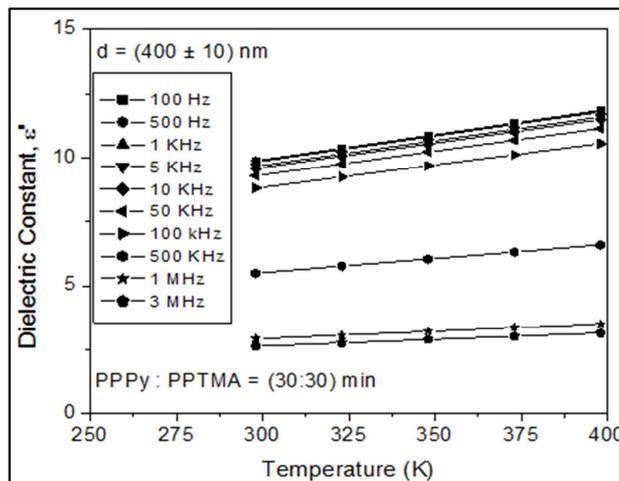


Figure 2. Variation of dielectric constant, ϵ' , with temperature of the PPPy-PPTMA composite thin films at different frequencies.

This figure shows a slightly different behavior to that of the PPPy thin films. The values of ϵ' in PPPy-PPTMA bilayer thin films were increased with temperature in all frequency region, whereas in PPPy thin films the values of ϵ' were found to be increased with temperature at lower frequency but remained constant at higher frequency at all temperature [14]. However, the increase in ϵ' with temperature is due to greater freedom of movement of dipole molecular chain in polymer films at high temperature. Since the dipoles are usually fixed in the dielectric rigidly, therefore the orientation of dipoles cannot be changed even by the applied electric field at lower temperature. As the temperature increases, the dipoles comparatively become free, and they respond to the applied electric field which causes an increase of polarization and consequently increase of ϵ' with the rise of temperature is observed [15].

3.2. Variation of Dielectric Loss Factor with Frequency and Temperature

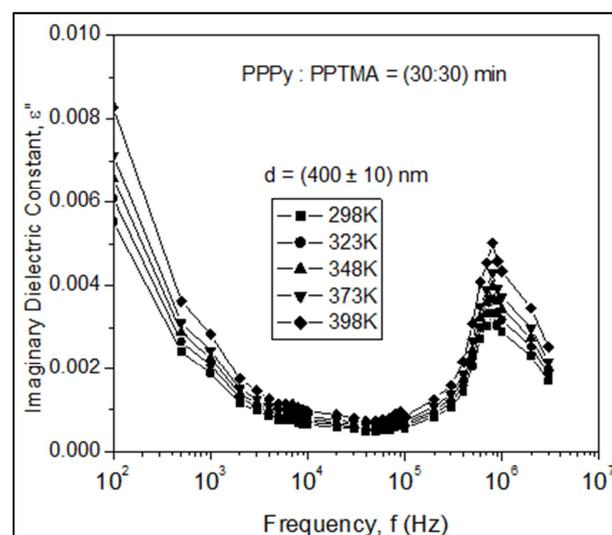


Figure 3. Variation of dielectric loss factor, ϵ'' , as a function of frequency of the PPPy-PPTMA composite thin films of thickness 400 nm at different temperatures.

The variation of dielectric loss factor ϵ'' with frequency for the samples of PPPy-PPTMA bilayer thin films of thicknesses 400 nm at different temperatures is presented in Figure 3.

From the figure, it is observed that at all temperatures, ϵ'' initially decreases with increasing frequency until a loss minimum is observed and then rises with frequency up to a sharp peak in the loss spectra, and thereafter decreases sharply with the increase of frequency. Since the appearance of peak in the loss factor is attributed to the relaxation phenomena of polymer, therefore there seem to be two relaxations exist in the lower and higher frequencies. The lower one seems to be out of the range of the measurement frequency.

It is already known that an increase in ϵ'' with increasing applied frequency is dominated by resistive losses since the mobile charges contained in the film cannot follow high-frequency electric fields. This loss of energy is associated with the degree of orientation of molecules in addition to the degree of internal friction of the films [16]. At higher frequencies, the very fast periodic reversal of the electric field occurs, and no excess ion diffusion would become possible in the direction of the field. Above f_{max} the polar ionization decreases due to the charge accumulation results to a decrease in the value of the loss factor.

It is, however, observed that the loss peaks have shifted towards the higher frequency side with the increase of temperature. The dielectric data is characterized by superposition of two processes: (a) conductivity contribution that produces an increase of both ϵ' and ϵ'' with the decreasing frequency which is not observed in these data; and (b) due to relaxation process exhibiting a maximum in ϵ'' that shifts higher frequency side with increase in temperature, which is usually attributed to dipolar orientation and these results are in agreement to this phenomenon.

Figure 4 shows the variation of dielectric loss factor ϵ'' with temperature for the samples of PPPy-PPTMA bilayer thin films of thickness 400 nm at different frequency.

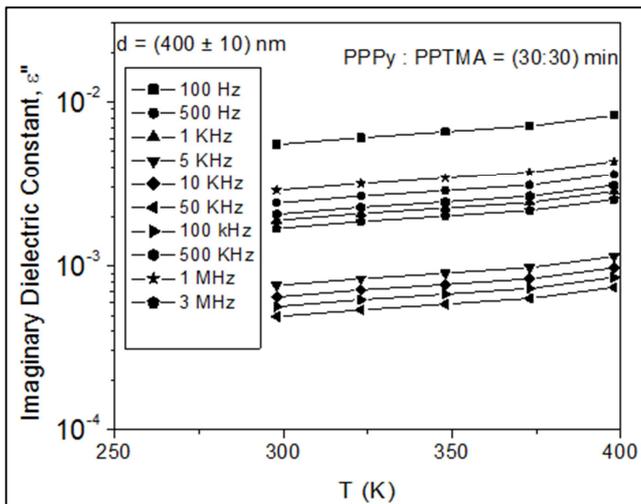


Figure 4. Variation of dielectric loss factor, ϵ'' , with temperature of the PPPy-PPTMA composite thin films at different frequency.

An overall trend of increasing ϵ'' with temperature in all frequency range is observed from the Figure 4. This result is slightly different than those of the component films, i.e., PPPy and PPTMA, since at very high frequency, the loss factor was found to be almost independent of temperature in those films [14]. However, at lower frequencies the increase of loss factor with temperature can be attributed to the effective chain motion of polymer and the increasing of loss factor with increasing temperature at high frequencies might indicate the orientational polarization due to chain motion of bilayer films.

3.3. Variation of ac Conductivity with Frequency and Temperature

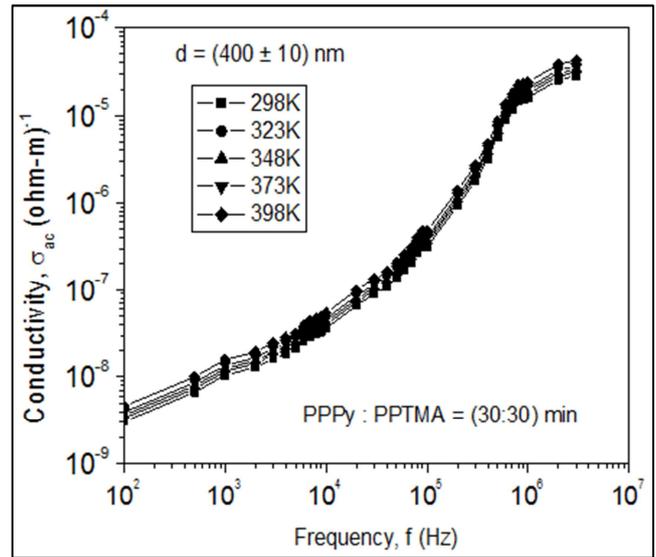


Figure 5. Plots of ac conductivity σ_{ac} as a function of the frequency for the PPPy-PPTMA composite thin films of thicknesses 400 nm at different temperatures.

Figure 5 shows the variation of σ_{ac} with the frequency for the PPPy-PPTMA composite thin films of thicknesses about 400 nm at different temperatures 298K, 323K, 348K, 373K and 398K.

From figure 5, a common pattern is seen that the ac conductivity σ_{ac} is linear function of the frequency; and like PPPy and PPTMA thin films [13], an increase of σ_{ac} is observed with increasing frequency. The dependence of ac conductivity, σ_{ac} on frequency may be described by the power law [17]:

$$\sigma_{ac}(\omega) = A\omega^n \quad (2)$$

where A is a proportionality constant and ω ($=2\pi f$, f is the linear frequency) is the angular frequency and n is the exponent, which generally takes the value less than or equal to unity for Debye type mechanism and is used to understand the conduction/relaxation mechanism in amorphous materials.

For physical convenience, the values of n are usually between 0.4 and 0.8 [17]. The values of n, however, for the sample for all temperature and frequency ranges have been found to lie in between 0.726 to 0.938, which is close to the

values of physical convenience. This type of result is usually attributed to the dielectric relaxations caused by the motion of charges or atoms. Such motion can involve hopping or tunneling between equilibrium sites [18]. By analyzing the observed behavior of the σ_{ac} -frequency relationship it can therefore be concluded that, the ac conduction mechanism may be due to the hopping of electrons between pairs of localized states at the Fermi level.

The variation of the ac conductivity σ_{ac} with the temperature at different frequency of the sample of thickness at about 400 nm is presented in Figure 6 and a weak dependence of σ_{ac} on temperature in both (high and low) frequency range is observed.

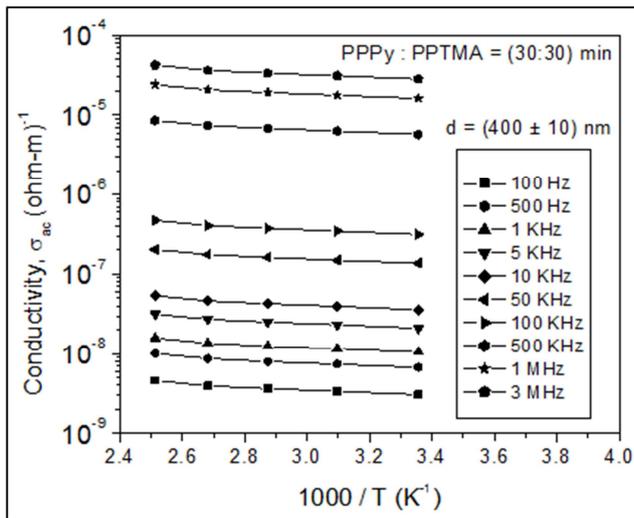


Figure 6. Variation of ac conductivity σ_{ac} with temperature of the PPPy-PPTMA composite thin films at different frequency.

The ac conductivity σ_{ac} can be explained in terms of the hopping of electrons between pairs of localized states at the Fermi level. The frequency-dependent σ_{ac} can usually be expressed as the sum of two different conduction mechanisms [19]:

$$\sigma_{ac} = \sigma_{ac}(f) + \sigma_{ac}(s) \quad (3)$$

where $\sigma_{ac}(f)$ represents the relatively weak temperature dependence mechanism which has been interpreted as being due to hopping between localized states at the Fermi level, and $\sigma_{ac}(s)$ represents the stronger temperature dependence component of ac conductivity. Since, in our study, the σ_{ac} is found to be weakly dependent on temperature, therefore $\sigma_{ac}(s)$ can be neglected and only $\sigma_{ac}(f)$ is activated which allow us to interpret the ac conduction mechanism as the hopping between localized states at the Fermi level.

However, the activation energy calculated from the curves are found to lie between 0.052 to 0.093 eV, which is very low. The strong dependence of conductivity on frequency and the low activation energies of the carriers are also an indication of a hopping conduction mechanism at low temperatures, and at high temperatures it may be due to the movements of thermally excited carriers from energy levels within the band gap [1].

4. Conclusions

The characteristics of the dielectric constant ϵ' as a function of frequency for PPPy-PPTMA bilayer composite thin films at different temperatures show a general trend of decreasing ϵ' with increasing frequency. The decrease in ϵ' is very prominent at both high frequencies and high temperature and it is an expected behavior in most dielectric materials which is usually attributed to the dielectric relaxation process and interfacial & space charge polarization. However, the ϵ' shows temperature dependence and it is seen that the value of ϵ' in PPPy-PPTMA bilayer thin films increases with temperature in all frequency region which may be due to greater freedom of movement of dipole molecular chain in polymer films at high temperature.

From the variation of dielectric loss factor ϵ'' with frequency at different temperatures, it is observed that at all temperatures ϵ'' initially decreases with increasing frequency until a loss minimum is observed and then rises with frequency up to a sharp peak in the loss spectra. The appearance of peak in the loss factor is attributed to the relaxation phenomena of polymer. It is also observed that the loss peaks have shifted towards the higher frequency side with the increase of temperature which is usually attributed to dipolar orientation. The temperature dependence of the ϵ'' at different frequencies has shown an increasing trend of the ϵ'' with temperature. At lower frequencies the increase of loss factor with temperature can be attributed to the effective chain motion of polymer and the increasing of ϵ'' with the rise of temperature at high frequencies might indicate the orientational polarization due to chain motion of bilayer films.

It is seen that the ac conductivity σ_{ac} is linear function of the frequency. The results have been attributed to the relaxations caused by the motion of electrons or atoms, which could involve hopping or tunneling between equilibrium sites. The observed weak temperature dependence of σ_{ac} also allowed us to interpret the ac conduction mechanism as the hopping between localized states at the Fermi level.

5. Suggestions for Further Research

In this paper and in our other communications [7-14] attempts were made to investigate the structural, optical and the electrical properties of PPPy, PPTMA and PPPy-PPTMA bilayer composite thin films. It was observed that both the optical and electrical properties are thickness dependent. An intimately arising question from this observation is: how to describe the thickness dependence of these physical processes in thin polymer films? Our result was explained by using existing theories, but the reports on thickness-dependent optical and electrical properties were found to be less abundant in literature. To study the thickness dependence more precisely the FTIR spectra could be taken and analyzed for the films of different thickness separately to know the

probable structural change due to the change of the thickness. The x-ray diffraction (XRD) analysis could also be done for each thickness to get information about the chemical structure of the materials. The XPS investigation which provides quantitative information of the element present could be carried on studying the bonding of different functionalities found present chemical states in the thin films of different thickness. The SEM analysis could provide information about the morphological change with the change of the thickness. The electron spin resonance (ESR) study may also be carried out to see the nature and source of radicals in this material. All the results of the above analyses could then be correlated with the thickness dependent optical and electrical properties of the thin films of different thickness.

Another important result was found from the study of this work is that the PPPy-PPTMA bilayer composite thin films have higher band gaps and consequently the lower electrical conductivity than that of its component thin films. The results were explained by assuming a complex polymer-polymer interface effect which might be inhomogeneous and irregular by nature. But we did not have any precise information about the structural change in the interface of the bilayer thin films for the different composition. To get a very important interpretation about the behavior of the polymer-polymer interface which is almost absent in the literature, the FTIR, XRD, XPS, SEM and ESR analyses could be carried on to know the change in the structural and elemental properties for each of the composition of the bilayer thin films and then these results could be correlated with the optical and electrical properties of the bilayer thin films in terms of the mysterious polymer-polymer complex interfacial character.

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