

Dip and spin coated nanoscale transparent PMMA thin films for field effect thin film transistors and optoelectronic devices

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Polymethylmethacrylate (PMMA) is one of the promising and useful polymer material and there are numerous proposals for its application in field effect thin films transistors and opto-electronic devices. Nanoscale PMMA films are prepared by dip and spin coating techniques. The FTIR analysis indicated the absence of any impurity in the dip and spin coated films. The XRD analysis of as grown and annealed films indicated amorphous nature. The SEM analysis revealed the phenomenon of self assembly on the mesoscopic scale without pits and pin holes on the surface. The optical band gap determined from Tauc's plot has been found to be 3.79 eV and 3.78 eV for as grown and annealed dip coating, 3.79 eV and 3.76 eV for as grown and annealed films prepared by spin coating. The dielectric behaviour of Al/PMMA/Al sandwich structure was carried out by using LCR meter. The observed amorphous structure, smooth surface, high transmittance and dielectric properties indicated that the prepared nanoscale transparent PMMA films could be used as opto-electronic devices and high k dielectric in organic field effect thin film transistors.

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1. Introduction

Polymers have emerged in recent years as promising materials for advanced electronic and optoelectronic devices. Polymer films attract much attention because of their unique properties, resistivity, electrical properties etc. The main advantage of polymer thin films is that they can be prepared easily and at low cost. Poly methyl methacrylate (PMMA) is one of the promising representatives of polymeric materials and there are numerous proposals for its application as dielectric layer in organic thin film transistors (OTFTs) [1-3], as optical lenses in cameras and optical fibers [4,5]. As a dielectric layer in OTFT structure along with high dielectric constant value it needs to satisfy various constraints concerning band offsets, limits on charge traps, process ability, reproducibility, stability against degradation, small leakage current, high breakdown potential and amorphous nature. Extensive work has been carried out on synthesis, preparation and various properties such as morphology, dielectric, optical and aging behavior of PMMA films [6-13]. Nanoscale PMMA thin films can be prepared by various methods like dip coating, solution coating, chemical bath deposition, organic vapour phase deposition, spin coating, screen printing etc. Our intention is to prepare good quality nanoscale thin films of PMMA through cost effective and easiest method, which could be used as an effective dielectric layer in field effect thin film transistor and in optoelectronic devices. Of the various methods mentioned, dip coating and spin coating are very simple and cost effective. The present study involved the preparation of nanoscale transparent PMMA thin films by

dip and spin coating techniques and characterized by using FTIR, XRD, SEM, UV-Vis-NIR Spectrophotometer and LCR meter. Dielectric and optical properties were studied with a view to use nanoscale transparent PMMA film as an efficient dielectric layer in OTFTs and optoelectronic devices.

2. Experimental procedure

Conventional PMMA obtained from Sigma-Aldrich was used without further purification to form the insulator layer. To prepare thin films by dip coating method, cleaned micro slides were held vertically above the PMMA solution (with a concentration of 2% with benzene as a solvent) by means of mechanical arrangement capable of slow and steady vertical movement. After bringing the solution to the room temperature, the substrates were immersed in the solution for different time periods ranging from 60 sec. to 1 hour. After withdrawal from the solution, the coated films were dried for 20 minutes and then kept inside an oven at 383K for one hour to evaporate the solvent remained in the film. In spin coating method, Then PMMA solution was spun on pre cleaned glass substrate at room temperature to prepare PMMA thin films. After that the coated films were dried for 20 minutes and then kept inside an oven at 383K for one hour to evaporate the solvent remained in the film. Both the dip and spin coated films were prepared in the same time interval and similar thickness samples were taken for characterization.

The metal-insulator-metal (Al/PMMA/Al) sandwich structure was fabricated to study the dielectric behavior. Initially, the bottom metal contact was formed by

evaporating aluminum (Al) on precleaned glass substrate. The middle insulator layer is deposited by dip and spin coating methods. Then the top metal contact was formed by evaporating Al over the PMMA film surface by using a suitable metal mask. The thickness of the coated films was measured by using an electronic thickness measuring instrument (Tesatronic-TTD-20), gravimetric method and cross checked by optical spectrophotometer. The coated PMMA films coated were identified by using FTIR spectrometer. The structure of the as grown and annealed PMMA films was studied by using XRD. The surface morphology of the as grown and annealed PMMA films was investigated by means of scanning electron microscope (SEM) and the optical property was studied by

using UV-Vis-NIR Spectrophotometer. The dielectric behavior was studied by using LCR meter.

3. Results and discussion

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy has proved to be valuable tool to provide information on the functional groups present in the polymer film [14]. Fig 1a-d shows the IR spectrum of dip and spin coated as grown and annealed PMMA films.

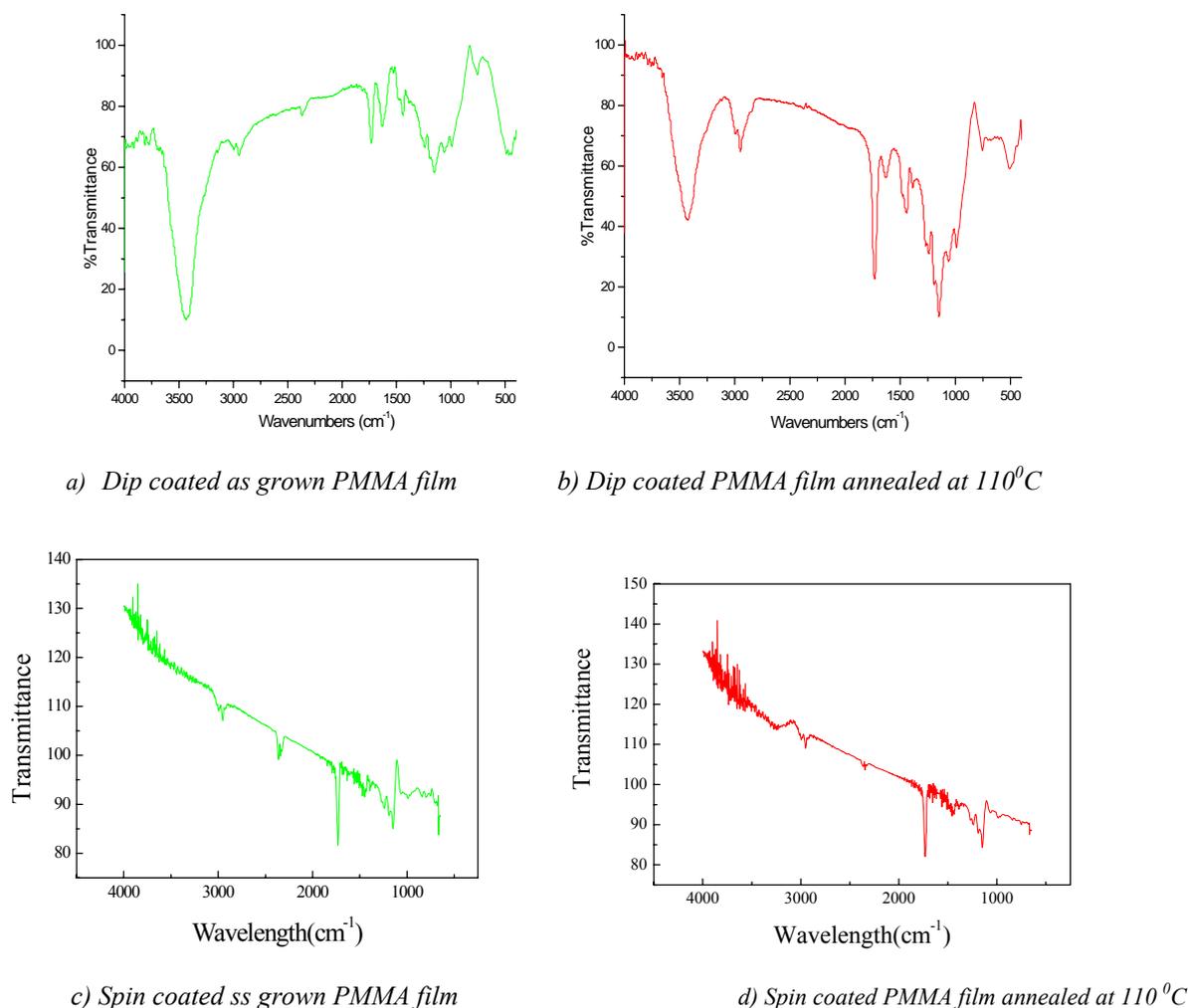


Fig.1(a-d) FTIR spectrum of dip and spin coated as grown and annealed PMMA film for various thicknesses a) 80 nm b) 75 nm c) 68 nm d) 61 nm.

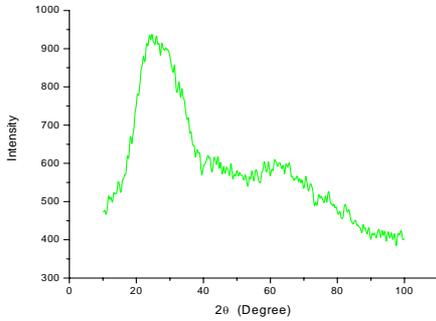
For dip coated films, the bands at about 677 cm^{-1} and 750 cm^{-1} are assigned to be out of plane OH bending. The band at around 960 cm^{-1} is the characteristic absorption vibration of PMMA. The bands at about 1060 cm^{-1} , 1245 cm^{-1} and 1730 cm^{-1} assigned to $\nu(\text{C-O})$ stretching vibration, wagging vibration of C-H and C=O stretching respectively for dip coated films whereas the peak observed at 1150 cm^{-1} , 1450 cm^{-1} and at 1740 cm^{-1} are

assigned to be C-O stretching, O - CH₃ bending and C = O stretching respectively for spin coated films. Broad and multi-banded small peaks observed near 3000 cm^{-1} may be due to symmetrical and asymmetrical C-H stretching for both dip and spin coated films. Films subjected to annealing shows no changes in the spectrum except a small decrease in the intensity of the peaks. The observed spectrum eliminated the possibility of solvent

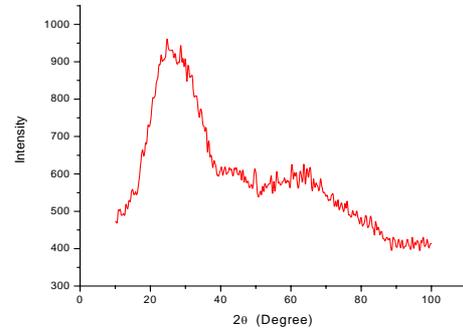
(Benzene) molecules in the deposited film. It was also found that both as grown and annealed dip and spin coated films showed similar FTIR spectrum which eliminated the probability of the presence of any impurity in the PMMA thin films.

3.2 X-Ray Diffraction (XRD)

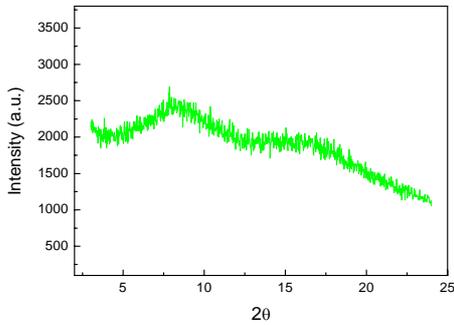
The X-ray diffractograms of the as grown and annealed PMMA film of thickness ranging from 80 nm to 61 nm for both dip and spin coated films are presented in the Fig. 2a-d.



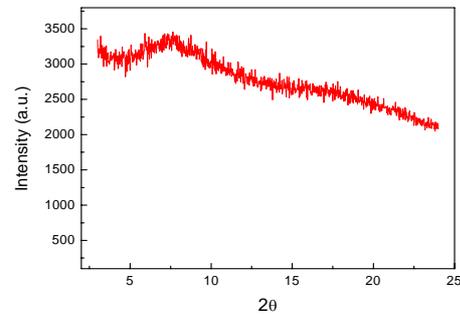
a) Dip coated as grown PMMA film



b) Dip coated PMMA film annealed at 110 °C



c) Spin coated as grown PMMA film



d) Spin coated PMMA film annealed at 110 °C

Fig.2(a-d) XRD pattern of Dip & Spin coated as grown and annealed PMMA films for various thicknesses a) 80 nm b) 75 nm c) 68 nm and d) 61 nm.

The x-ray diffraction pattern of both dip and spin coated films indicates the amorphous nature with large diffraction maximum that decreases at large diffraction angles. The shape of the first main maximum indicates the ordered packing of the polymer chains. The intensity and shape of the second maxima are related to the effect of ordering inside the main chains [15,16]. The observed broad humps in the XRD spectrum indicate the presence of crystallites of very low dimensions. The absence of any prominent peaks in the PMMA thin films indicates the amorphous nature of the films [17].

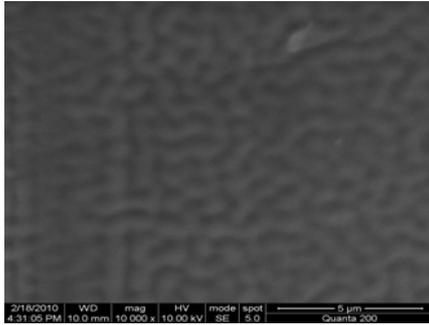
3.3 Scanning electron microscope (SEM)

Fig. 3a-d shows the SEM image of dip and spin coated as grown and annealed PMMA films of various thicknesses ranging from 80 nm to 61 nm.

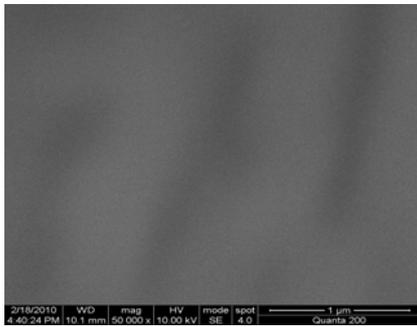
The SEM study of deposited films led to the conclusion that PMMA produced self assembled mesoscopic structured films as presented in the figure, when deposited under dip coating process [18].

Closer SEM inspection reveals various structures of mesoscopic cells for both as grown and annealed PMMA films [19]. The formation of the mesoscopic structures may be described with the help of the considerations presented below. Due to fast external drying, all solvents which leave the solution is immediately removed from the system. Then at an early stage of the evaporation process, a polymer rich layer is formed. The thickness of such layers may be of the order of mesoscopic scale range. The mesoscopic structures obtained for the thin film of PMMA could be used as an AFM-based data storage which is promising alternative to conventional magnetic data storage because it offers great potential for considerable storage density improvements. The dip coating process presented in this work is simple, highly reproducible and permits fabrication of large areas of mesoscopic structured films, which have a potential as membranes, long period gratings and photonic molecules. No pits and pinholes were found on as grown and annealed films. Surface morphology of dielectric layer is very important because it

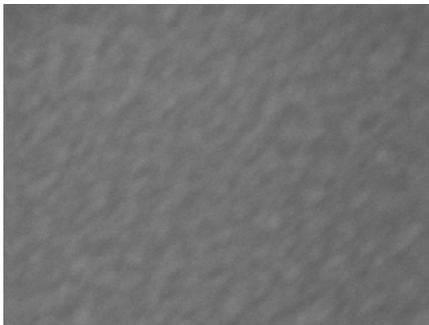
affects the property of the semiconductor layer coated over it.



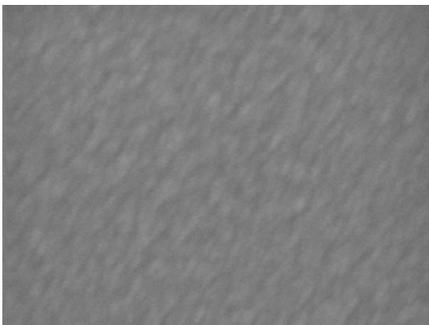
a) Dip coated as grown PMMA film ($d=80$ nm)



b) Dip coated PMMA film annealed at 110°C ($d=75$ nm)



c) Spin coated as grown PMMA film ($d=68$ nm).



d) Spin coated PMMA film annealed at 110°C ($d=61$ nm)

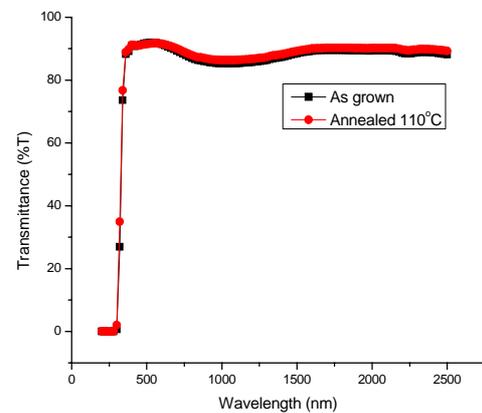
Fig.3 (a-d). SEM Micrographs of dip and spin coated as grown and annealed PMMA films for various thickness.

In the case of spin coated films, the film surface of as grown and annealed films are compact. No pits, pinholes and dendritic features are found in the surface. Macroscopic granular chains appear at the surface in the stretching direction of PMMA film. The granular structures (grooves) vary in size from few nanometers to hundreds of nanometers. Improved surface smoothness and greater grooves are found for films annealed at 110°C .

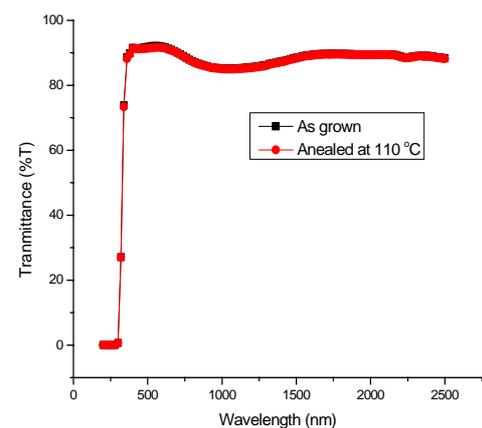
The surface morphology is quite homogenous and amorphous in nature for both dip and spin coated films. It is observed from the SEM analysis that both as grown and annealed films showed smooth surface, which is one of the most important requirements of a dielectric layer in organic thin film transistors.

3.4 UV-Vis-NIR Spectroscopy

The UV-Vis-NIR Spectra of as grown and annealed dip and spin coated films in the wavelength range of 400-2500 nm are presented in fig.4(a-d).



a) Dip coated PMMA films



b) Spin coated PMMA films

Fig.4(a,b) UV-Vis-NIR Transmission Spectra of dip and spin coated as grown and annealed nano scale PMMA thin films.

The transmittance increases uniformly with annealing temperature throughout the UV-Vis-NIR region of the

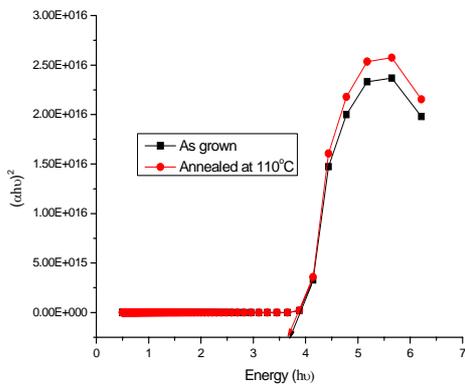
transmission curve. The transmission curves show that for high energies (lower wavelengths) there is no transmittance because all the light is absorbed. For low energies (higher wavelengths) however there are no appropriate electronic transitions possible so transmission is very high in this range. All the prepared films showed nearly 90% of transmittance. The observed transmittance for dip coated film is about 90% and 91 % respectively for as grown and annealed PMMA thin films, whereas, spin coated films showed a transmittance of 91% and 93% respectively for as grown and annealed PMMA films [5, 17]. The thin films with high transmittance in the entire wavelength region are good in material for antireflections coatings of optical devices and use in the construction of poultry roofs and walls.

annealing temperature for the prepared films. The obtained higher transmittance with wide band gap value of films prepared by both dip and spin coating methods could be used for opto-electronic devices.

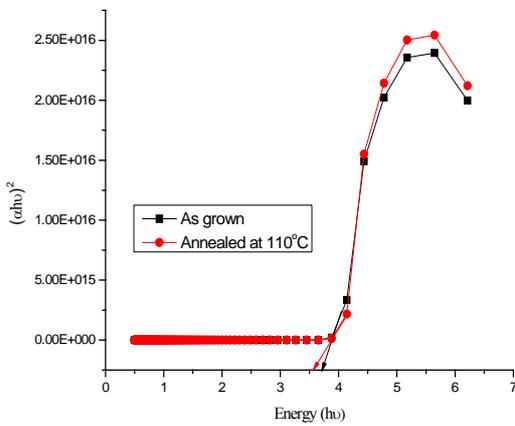
3.5 Dielectric behavior with annealing temperature

The dielectric behavior of PMMA films was studied for both dip and spin coated PMMA films subjected to various annealing temperatures ranging from 70⁰C to 200⁰C. Annealing is a process related with stress relief and local structural rearrangement of polymer chains.

Fig.6(a,b) shows the variation of dielectric constant with different annealing temperature for a frequency of 1 MHz.



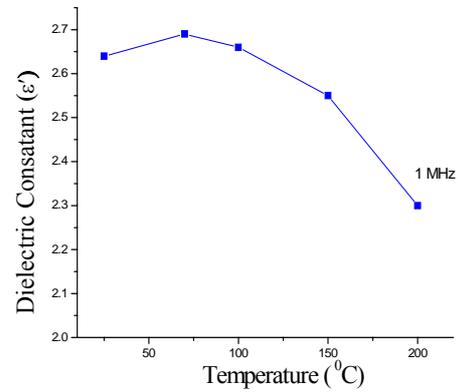
a) Dip coated PMMA



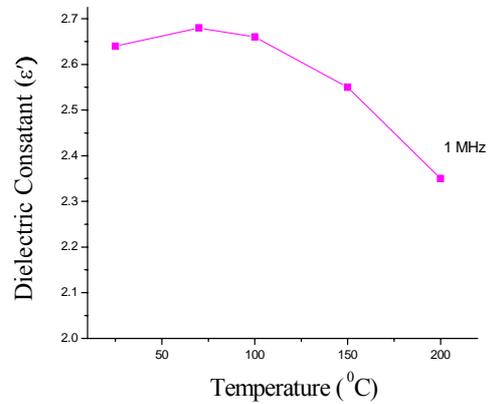
b) Spin coated PMMA films

Fig.5(a,b) Tauc's plot of $(\alpha hv)^2$ versus hv for dip and Spin coated PMMA films

The optical band gaps of PMMA films were estimated by extrapolating the linear portion of curves resulting from Tauc plot of $(\alpha hv)^2$ and hv is shown in fig.5(a-b). Where α , h , and ν are the absorption coefficient, Planck's constant and photon frequency respectively [20-23]. The band gap of the films were determined from the plots to be 3.79 eV and 3.78 eV for as grown and annealed dip coated films and 3.79 eV and 3.76 eV for as grown and annealed spin coated films[24]. The band gap decreases a little with the



a) Dip coated PMMA film



b) Spin coated PMMA film

Fig.6 (a-b) Variation of dielectric constant with various annealing temperatures.

The dielectric constant value increases initially and attains a maximum value at 70⁰C, where as films subjected to annealing above 70⁰C showed a decrease in dielectric constant value with the increase of annealing temperature. As the annealing temperature increases, the rate of decrease of the dielectric constant increases. The increase in the value of the dielectric constant with annealing temperature up to 70⁰C is due to an increase of total polarization arising from dipoles and trapped charge

carriers [19]. The observed decrease of dielectric constant with increase of annealing temperature above 70°C may be assigned to the reasons such as intensified thermal oscillations of molecules at higher temperatures leading to the diminished order of their orientation, the improved stoichiometry, reduction of defects and faster structural relaxation leading to a decrease in the effective thickness of the PMMA film with increase in annealing temperature. The observed dielectric constant values of the prepared nanoscale PMMA films are well matched with the previously reported values by different authors [20, 25-27].

4. Conclusions

The nanoscale transparent PMMA thin films were successfully prepared through dip and spin coating techniques. The FTIR analysis indicated the absence of any impurity in the dip and spin coated as grown and annealed PMMA thin films. The X-ray diffractogram revealed the amorphous nature of the films studied. The SEM studies indicated the phenomenon of self assembly on the mesoscopic scale obtained from dip coating and smooth and compact films obtained by spin coating. SEM studies revealed that no pits and pin holes were found on the surface. Both as grown and annealed films showed smooth and compact surface. The observed morphological features of the as grown and annealed films indicated the amorphous nature of the films studied. The dip and spin coating process presented in this work is simple, highly reproducible and permits fabrication of large areas of self assembly mesoscopically smooth structured films. The mesoscopic structured films have the potential as membranes, long period gratings, photonic molecules and AFM based data storage system. The prepared films showed nearly 90% of transmittance in the UV-Vis-NIR region. The prepared nanoscale films showed a good dielectric constant value. The observed amorphous nature without having any pin holes, higher transmittance, wide band gap and the dielectric behavior indicated that these dip and spin coated nanoscale transparent PMMA films could be used in opto-electronic devices and as an efficient dielectric layer in organic thin film transistors.

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