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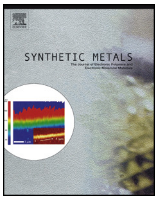

Role of solvents on the electrical conductivity of solution-processed poly (methyl methacrylate) thin films

Bipul Biswas, Avijit Chowdhury, Biswanath Mallik*

Department of Spectroscopy, Indian Association for the Cultivation of Science, 2A & 2B, Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India

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ABSTRACT

The role of solvents on the current–voltage characteristics of solution-processed poly(methyl methacrylate) (PMMA) thin films prepared by drop casting method, using solvents of different boiling points, has been studied under different experimental conditions. Hysteresis in current–voltage characteristics, area within the hysteresis loops, short-circuit current, open-circuit voltage and surface morphology of the PMMA films have been observed to depend on the boiling point of the solvents from which the films were prepared. Dependence of various parameters on the solvent boiling points in the present experiment is related to the amount of solvent vapour absorbed (or adsorbed) in the PMMA films. The results have been explained on the basis of molecular reorganization in PMMA and creation of different conduction paths during forward and reverse bias.

1. Introduction

The research interest on various problems related to polymers as well as doped-polymers has gained momentum in the recent years [1–8] following utilization of polymeric materials in technology. In fact, research on the electrical properties of polymers/doped-polymer films has become a subject of much interest due to flexibility in use of polymers/doped polymers in various fields like electronic [3,5,8] as well as optoelectronic devices [1]. Poly(methyl methacrylate) (PMMA) is an important polymer which has been widely used for making variety of optical devices, such as optical lenses and polymer optical fiber [9] and also in spectroscopic [10–12] as well as optoelectronic investigations [6,13,14]. Recent studies in our laboratory, related to the electrical properties of PMMA [14]/PMMA-doped with metallocenes [4] and also PMMA dispersed with silver nanoparticles [6] have shown some interesting results. The results include indication of formation of charge density waves in silver nanoparticles dispersed PMMA thin films [15], significant modifications in the electrical properties of PMMA thin films upon dispersion of silver nanoparticles [6], unusual photoinduced changes in the electrical conductivity of ferrocene doped PMMA thin film under different relative humidity conditions [4], observation of switching in the surface electrical conductivity of PMMA [14], etc. In the course of further studies on the surface electrical conductivity of solution-processed PMMA thin films, we have noticed that hysteresis behavior in the current–voltage (I–V) characteristics depends significantly on the boiling point of solvent used for the preparation of the film. Research on solution-processed organic semiconductors has become a subject of interest [8,16–18] and electrical properties of organic films prepared from solvents of different boiling points have shown solvent-dependent electrical characteristics [8,17,18]. Solution-processed organic semiconductors are of interest because they allow the fabrication of flexible electronic devices by low-cost manufacturing approaches [18]. Kim et al. [18] has demonstrated that the solvent from which the active layer is drop cast dramatically influences the electrical characteristics. Film casting from high boiling point solvents allows slower crystallization and exhibit stable characteristics, whereas devices made from lower boiling point solvents show hysteresis. In the study of the electrical properties of organic thin film transistors based on the film/layer prepared from various solvents, Choi et al. [17] mentioned that solvents with higher boiling points resulted in larger grain sizes and improved crystallanity of the film, showing the higher electrical performance. The effects of solvents on the electrical characteristics in regioregular poly(3-hexylthiophene) organic thin film transistors have been reported recently by Cheng et al. [8] and it has been mentioned that devices made by lower boiling point solvents have shown greater hysteresis effects. These authors interpreted the films coated by high boiling point solvents as superior in crystalline quality, homogeneity and low vacancies. The hysteresis was dominated by the vacancy related charge traps in the semiconductor created during film solidification and subsequent solvent evaporation. In contrast, in the present experiment PMMA films made by higher boiling

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* Corresponding author. Tel.: +91 33 2473 4971; fax: +91 33 2473 2805.
E-mail addresses: spbm@iacs.res.in, spbm07@gmail.com (B. Mallik).

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point solvents have shown greater hysteresis effects. In the past, hysteresis behavior has been studied in doped polymers [3,5,19,20]. The observation of changes in hysteresis behavior in a pure PMMA polymer film (without doping), depending on the nature of solvent used for the preparation of PMMA film is novel and the results are reported in this article.

2. Experimental

PMMA having average molecular weight 120,000, obtained from Aldrich (USA), was used for this experiment. PMMA was dissolved (concentration: 75 mg/ml) in four solvents (acetone, chloroform, benzene and toluene) having different boiling points and stirred ultrasonically for 30 min to make homogeneous solutions. Using each solution several almost identical thin films were cast on cleaned glass plates in ambient air with a relative humidity of 65–70%. To allow the evaporation of solvent from the films, the films were kept at room temperature for about 24 h. For electrical measurements, the films were placed in a specially designed brass conductivity chamber fashioned with Teflon [4,13,15]. Silver paste was used for electrical contact. The area of each electrode was $2 \times 9\,\text{mm}^2$, and the separation gap between two electrodes was 4 mm, respectively. The current–voltage characteristics were studied for different sweeping voltage amplitudes. The sweeping direction of the applied bias was −ve → +ve → −ve with a scan speed of 250 mV/s. The temperature was controlled by a temperature controller. The rate of heating and cooling was 4 °C/min and 2.5 °C/min, respectively. The current was recorded by a programmable electrometer Keithley (model 6517 A). Before measuring the conductivity the heating cooling treatments were applied upto 50 °C. All the measurements were performed under vacuum. Between two successive measurements the sample was allowed to relax for at least 30 min. The instrument was interfaced with a computer.

3. Results and discussion

Fig. 1 shows the current–voltage (*I*–*V*) characteristics at room temperature, under dark condition, of PMMA thin films prepared from different solvents. This figure shows a clock-wise hysteresis in *I*–*V* characteristics, which depends on the nature of solvents from which the PMMA films were prepared. Observed sudden changes in current (i.e. current transients) at end positions (Fig. 1) could be due to release of voltage stress during the reversal of the direction of bias potential. Inset of Fig. 1 shows the chemical structure of a PMMA molecule. Fig. 2 demonstrates the effect of solvent on the change in area within the hysteresis loop versus sweeping voltage, measured in PMMA films prepared from different solvents. It is interesting to note that for a particular sweeping voltage the area within the loop increases with the boiling point of the solvents used. Fig. 2 shows that the area within the hysteresis loop increases almost linearly with the increasing extent of bias voltage in the case of solvents acetone and chloroform. But in the case of benzene and toluene, the plots of area versus sweeping voltage are not linear. Fig. 1 shows that at zero bias voltage the value of current is not zero which can be termed as short circuit current, I_{sc}. Again, from Fig. 1 it is noted that the voltage, where the current passes through zero is not zero bias (called as open circuit voltage, V_{oc}) and the value of V_{oc} depends on the value of bias voltage as well as its sweep direction. Variation of both I_{sc} and V_{oc} with the magnitude of sweeping bias voltage is represented in Fig. 3a and b, respectively for PMMA films prepared from different solvents. The magnitude of I_{sc} increases with increasing extent (V_{max}) of sweeping voltage, which indicates that more charges can be stored by applying higher voltage amplitude. The higher I_{sc} indicates that charges are more mobile that increase the conductivity. Interestingly, the variation of I_{sc} and V_{oc} with sweeping voltage depends significantly on the nature of solvent used (Fig. 3).

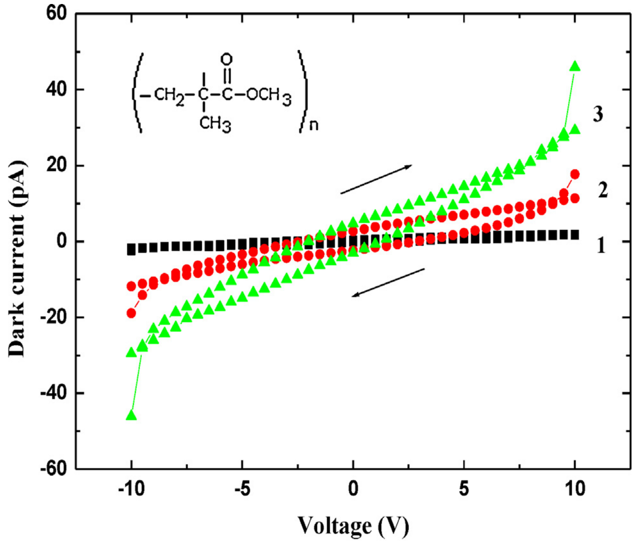

Fig. 1. Current–voltage characteristic curves of PMMA thin films measured at room temperature (303 K) under dark condition: films prepared from different solvents; (1) acetone, (2) benzene, (3) toluene, respectively. The arrows indicate the direction of voltage sweeps. Inset of Fig. 1 shows the chemical structure of a PMMA molecule.

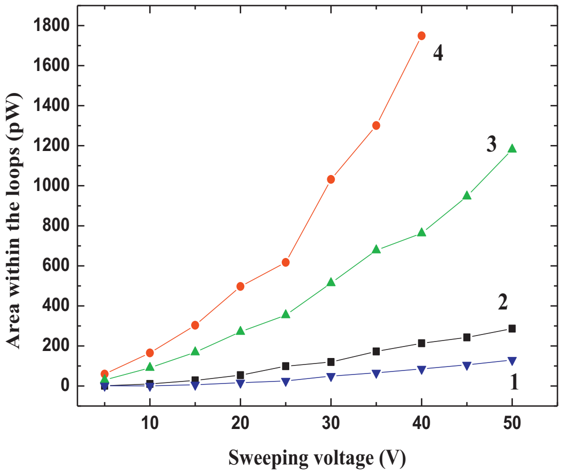

Fig. 2. Plots of areas within the hysteresis loops as a function of sweeping voltage, measured at room temperature (303 K), under dark condition, in PMMA films prepared from different solvents: (1) acetone, (2) chloroform, (3) benzene, (4) toluene, respectively.

Fig. 4a shows the *I*–*V* characteristics at two different temperatures, in the case of PMMA thin films prepared from toluene. With increasing temperature, the characteristic curves are seen to be shifted upward and downward at higher voltage range (with respect to voltage axis) depending on the polarity of the applied bias voltage. Fig. 4b shows the area within the hysteresis loop versus sample temperature for PMMA thin films prepared from different solvents and this Fig. 4b shows that charge storage in such films increases with sample cell temperature. At a fixed sample cell temperature, the storage of charge in the PMMA film increases with the boiling point of the solvents from which the films were prepared.

The temperature-dependence of the steady-state dark current (I_d) in the sample cells of organic and organometallic materials can be expressed by the relation [4,14]

$$I_d = I_0 \exp\left(\frac{-E_d}{2kT}\right) \tag{1}$$