Photocarrier Mobility in Poly(2-methoxyaniline)

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ABSTRACT: In the current study the mobility of photogenerated charge carriers in PMA [poly(2-methoxyaniline)] and their transport were investigated using time-of-flight (TOF) techniques. Also studied was the effect on hole mobility of film thickness and of the method of polymer processing during device fabrication. The highest value of hole mobility found was $4.5 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$ at an applied field of 1.3×10^6 V/cm and 293 K in solution-cast film of PMA. The hole mobility of solution-cast films was about 2 orders of magnitude higher compared to spin-coated films, for which the ordering of the polymer chains may be the reason. To our knowledge, this is the first time the TOF mobility of this material has been presented. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1506–1512, 2001

Key words: time of flight; poly(2-methoxyaniline); mobility; photoconduction; disorder; photocarrier

INTRODUCTION

Conducting polymers have recently attracted a good deal of attention in the scientific community because of their applications in electro-optic devices (light-emitting diodes (LED)[1] and photoelectric conversion[2] and solid-state electronics.[3] Recent developments in material processing and device architecture have generated a new impetus for the use of organic LEDs, which are waiting at the main gate of commercialization, while the use of organic photovoltaics is at the stage of rapid development. One of the most important stumbling blocks to the development of organic solar cells is their low photoconversion efficiency, which is the result of their low photocarrier mobility.[4] In addition to their use in the fabrication of efficient organic solar cells, materials with high carrier mobility are also required to make efficient organic LEDs that are highly bright but operate at low voltage and in the construction of electrically pumped laser diodes.[5–6]

A number of methods have been reported in the literature for estimating mobility—time-of-flight (TOF) method,[7] steady-state photoconductivity measurement,[8] field effect mobility,[9] space-charge limited-current method,[10] Hall conductivity measurement,[11] and dielectric studies.[12] The first two methods are commonly used to evaluate photocarrier mobility in conjugated polymers and oligomers. Recently, the time-resolved microwave-conductivity method has been applied to conducting polymers to estimate the photocarrier mobility; however, this method only estimates the intrachain carrier mobility in a solution state.[13] Up to now, PPV [poly(phenylenevinylene)] and poly(alkylthiophene), which belong to a class of intrinsically conducting polymers, have been the main conducting polymers used in the attempt to
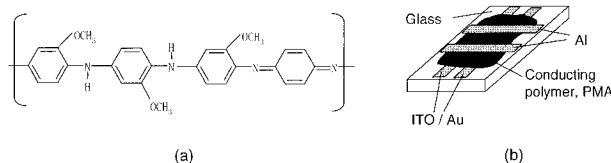
Figure 1 Schematic of (a) device structure and (b) chemical structure of PMA [poly(2-methoxyaniline)].

fabricate organic photovoltaics.[14–15] For organic photovoltaics, measuring photocarrier mobility is quite important compared to other mobility-measurement methods. Ample TOF mobility data are available for organic conducting polymers such as PPV,[16] polyfluorene (PFO),[17] polythiophene,[18–19] polyacetylene,[20] and polycarbazole[21] along with their derivatives, but such studies on polyaniline and its derivatives are not currently available. Very recently, field-effect mobility on one of the processible polyaniline-derivative sulfonated polyanilines has been reported by Narasimhan et al.,[22] indicating the possible attainment of high mobility in the polyaniline family of conducting polymers. The ease of synthesis, low cost, and environmental stability of polyaniline encouraged us to explore the photocarrier mobility in this interesting class of conjugated polymeric materials. The present article reports on the investigation of photocarrier mobility in the processible polyaniline derivative PMA [poly(2-methoxyaniline], using the TOF method for estimation, as shown in Figure 1(a). To our knowledge, this is probably the first report on TOF mobility in a polyaniline derivative.

EXPERIMENTAL

PMA used in the present study was chemically synthesized by oxidative polymerization using ammonium persulfate as the oxidant. The chemically synthesized powder was dedoped with an aqueous ammonia solution for a total of 6 days in 3 repetitive steps, each step repeated after 2 days, to ensure sufficient dedoping.[23–24] The dedoped polymer was washed with ample distilled water and then with acetone to remove oligomeric impurities. Subsequently, the polymer was dried at 60°C under a dynamic vacuum for 48 h. This was the polymer used for device fabrication. The UV-visible absorption spectra of PMA and polyaniline in N-methylpyrrolidone (NMP) solvent were measured to characterize the electronic structure. The

FTIR spectrum of the PMA was taken for the freestanding film cast from the NMP solution. For the preparation of the TOF sample, the PMA powder was dissolved in dichloromethane, followed by filtration with a 0.2-μm poly(tetrafluoroethylene) membrane filter.

The TOF samples were fabricated in a sandwich-cell configuration, as shown in the schematic drawing in Figure 1(b). The bottom electrode was either patterned indium tin oxide (ITO) or thermally evaporated Au, followed by a polymer coating. A patterned ITO–coated glass plate was subjected first to mechanical polishing, followed by chemical polishing and washing in distilled water for 5 min under sonication. It was then dried under a stream of N_2 gas, followed by sonication in ethanol, acetone, and 2-propanol in that order. Then the ITO was dried at 80°C for 24 h under a dynamic vacuum. The PMA was coated to Au or ITO electrodes using either spin coating (5 wt %) or solution casting (1 wt %) under a slow solvent evaporation. This semicompleted device was subjected to drying under a dynamic vacuum at 60°C for 48 h. After polymer coating and drying, the top electrode was made by the thermal deposition of 40-nm-thick aluminum. The aluminum electrode was 25% transparent at 337 nm with a N_2 laser light, which was sufficient to obtain a detectable photocurrent signal. PMA used for device fabrication was kept between 0.6 and 1.5 μm thick, and the active device area was 0.02 cm^2. The PMA was intentionally thin relative to the usual thickness (5–30 μm) in molecularly doped polymers used with the TOF method because of the high absorption coefficient of PMA, on the order of 10^5/cm[7]. The TOF technique requires that the pulsed laser light be strongly absorbed. Borsenberger et al.[25] defined this strong absorption as 90% of the radiation being absorbed in the first 10% of the sample thickness.

TOF measurements were performed on sandwich-cell devices using a conventional experimental setup. Photocarriers were generated by illuminating the device with a pulsed N_2 laser (wavelength of 337 nm, pulse width of 0.6 ns, and output laser power of 70 μJ/pulse) through a semitransparent Al electrode. The measurement was done under a vacuum at a pressure of 10^{-3} torr and at a constant temperature. The drift of the photogenerated carriers under an external bias applied for 50–100 ms resulted in a time-dependent photocurrent. This was monitored across an external 50 Ω load resistor. At each applied bias, 8–16 N_2 laser pulses were triggered,

and the data were averaged and analyzed by a computer. The dark current–voltage characteristic was measured at room temperature in air by a Keithley Model 6517 programmable Electrometer/Source.

RESULTS AND DISCUSSION

In PMA the methoxy substituent in the parent polyaniline backbone provides this polymer with processability as well as donor like behavior. Structural elucidation by electronic absorption and FTIR spectroscopy are in accordance with the structure shown in Figure 1(a). A slight blue shift of both $\pi-\pi^*$ (300 nm) and $n-\pi^*$ (610 nm) absorption in the UV-visible spectrum [Fig. 2(a)] in PMA was observed compared with those of polyaniline. This suggests a shorter conjugation length because of the lower molecular weight in PMA as compared to polyaniline. As shown by the FTIR spectrum in Figure 2(b), the presence of new vibration bands at 1020, 1257, 2840, and 2950 cm^{-1} associated with the methoxy substituent, along with all the other peaks characteristic of a polyaniline main chain, fully corroborates the structure shown in Figure 1(a).

Curves in Figure 3 show the dark current–voltage (I–V) characteristics of the ITO–PMA (spin-coated)–Al devices, which indicate the formation of a Schottky barrier at the Al–PMA interface very similar to our earlier report on polyaniline-based diodes.[3] Careful observation of the two different devices reveals that they exhibit similar characteristics in diode performance, indicating homogeneity in spin-coated films. The inset of Figure 3 shows the I–V characteristics of the glass–Au–PMA–Al device and of spin-coated PMA. It shows similar rectifying behavior; at the same applied bias voltage, the magnitude of current is one-third that for the ITO–PMA–Al device.

This experimental investigation was undertaken to study the effect of the nature of materials making ohmic contact with PMA, along with impurities. Based on an elemental analysis, recently it has been suggested that it takes a long time to achieve sufficient dedoping. For instance, the doping level was found to still be 0.09% after 4.6 days dedoping in polyaniline.[24] The ITO surface is susceptible to chlorine, and a decrease in LED performance has been observed in ITO/PPV–based LEDs and attributed to InCl$_3$ formation.[26] In the case of the ITO–PMA interface, if the PMA still contains some chloride ions and reacts with ITO,
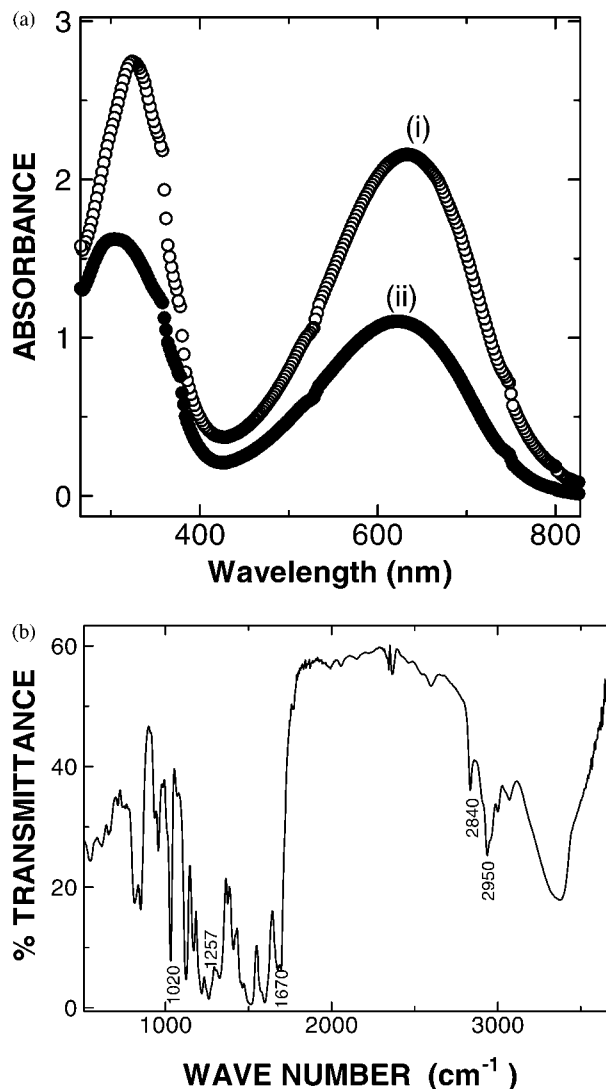

Figure 2 (a) Electronic absorption spectra of (i) polyaniline and (ii) poly(2-methoxyaniline) in NMP solution; (b) FTIR spectrum of freestanding film of poly(2-methoxyaniline).

the ITO–PMA–Al diode should perform more poorly in magnitude of current compared to the Au–PMA–Al diode. The present results of measurements of the Au–PMA and ITO–PMA junctions suggest that PMA at least did not contain sufficient chloride ions to form an insulating layer at the ITO–PMA junction.

The inset of Figure 4 shows a typical transient photocurrent obtained for an Au–PMA (spin-coated)–Al device after laser irradiation from the Al electrode, which was positively biased at a field (E) of 1.5×10^6 V/cm. It was found that the photocarriers are the holes by reversing the polarity of bias. No decrease in the subsequent pho-
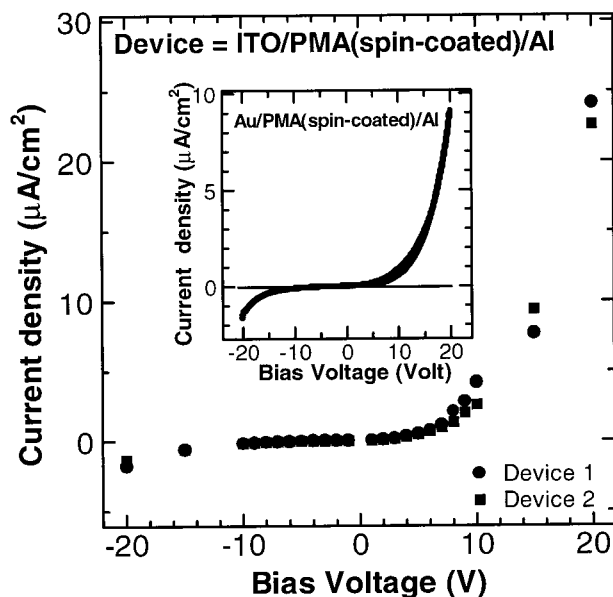
Figure 3 Current-voltage characteristics of ITO–PMA (spin-coated)–Al device. I-V characteristics of Au–PMA–Al device is shown as inset. PMA thickness is 0.6 μm.

tocurrent has been observed even after repeated pulses. This rules out the possibility of space-charge buildups in the film and degradation of the device by laser irradiation. The nature of the transient photocurrents was dispersive, which is characteristic of carrier trapping in amorphous polymers. The transient photocurrents have been analyzed using Scher-Montroll formalism to estimate the photocarrier mobility for the dispersive photocurrents.[27] The analysis suggests that in the double logarithmic plot of log I versus log t, there is a change of slope originating from passage of the carriers through the sample. The point of intersection gives the transit time (Tr), which is shown in Figure 4 at 3 applied electric fields. This figure clearly shows that Tr decreases with increasing applied bias voltage, indicating that it is a characteristic of real carrier transport. The drift mobility of the photocarrier can be calculated by the relation $\mu = L\,Tr^{-1}\,E^{-1}$, where μ is carrier mobility and L is sample thickness. The hole mobility has been determined to be 1.5×10^{-5} cm^2 V^{-1} s^{-1} at 293 K and at an applied field of 1.5×10^6 V/cm.

We also tried to calculate the quantum efficiency of photogeneration per pulse by considering the number of 337-nm laser photons on the active device area and the transmittance of 40 nm of aluminum. The quantum efficiency obtained

was 2×10^{-2} %, which is somewhat higher than that reported in polyfluorene and comparable to that of PMA–Si under monochromatic light irradiation.[5,28] In polyfluorene the dc photocurrent yield is approximately similar to that obtained in PMA, but it is lower under laser-light irradiation. The lower photocurrent yield per pulse has been explained as sublinear intensity dependence at higher intensities.[5]

Figure 5 shows the transient photocurrent signal after laser irradiation to the positively biased Al electrode for the ITO–PMA (spin-coated)–Al device. The transient photocurrents exhibit a dispersive nature, as shown in the inset of Figure 5; however, the double logarithmic plot clearly exhibits identical behavior as that obtained in Au–PMA–Al devices. The room temperature mobility was 1.4×10^{-5} cm^2 V^{-1} s^{-1} at an applied field of 1.5×10^6 V/cm. The similar values of hole mobility for Au–PMA and ITO–PMA devices suggest that mobility depends mainly on the bulk property of PMA, not on the interface.

To check the bulk properties of PMA film, ITO–PMA (spin-coated)–Al devices with thicker PMA films (1.0–1.2 μm) were fabricated. The photocurrent transient and double logarithmic plot are shown in Figure 6. We observed dispersive photocurrents with a mobility value of 8.7×10^{-6} cm^2
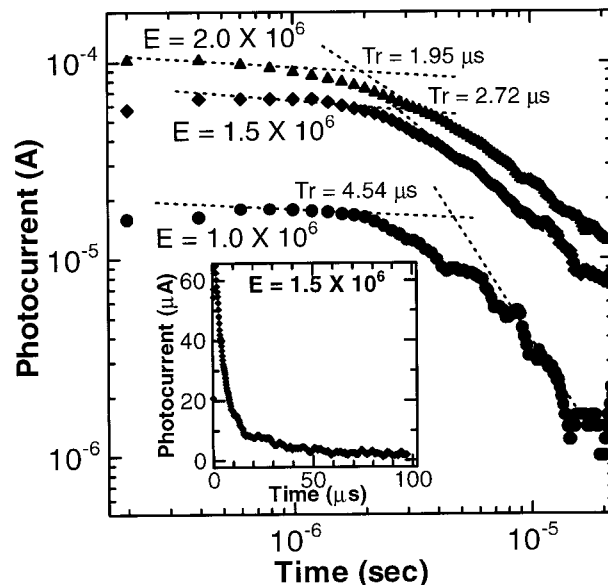

Figure 4 Double logarithmic plot for Au–PMA (spin-coated)–Al device at different applied fields and at 293 K. Inset is a typical photocurrent transient (linear plot) of PMA at 293 K and at an applied field of 1.5×10^6 V/cm. Film thickness is 0.6 μm.
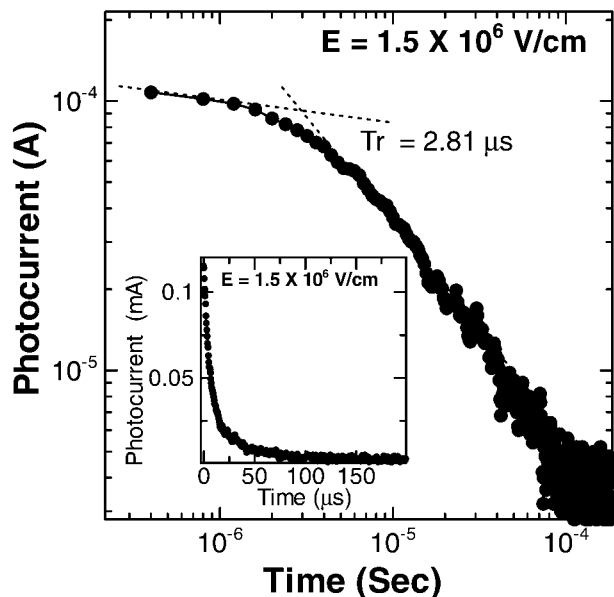
Figure 5 A typical transient photocurrent of ITO–PMA–Al device at 293 K and 1.5×10^6 V/cm applied field in a linear plot (inset) and in a double logarithmic plot. Film thickness is 0.6 μm.

V^{-1} s^{-1} at an applied field of 1.5×10^6 V/cm, which is a bit lower than thin-film devices.

It is well known that organic conducting polymers are amorphous, containing some short-range ordered fractions, and the degree of crystallinity is less than 30% even in regioregular poly(alkylthiophene).[29] Although the thickness difference between thicker and thinner films of PMA is not very large, mobility in the former is about half of the latter. The exact reason is not yet clear; however, the smaller value of hole mobility in thicker films may be explained by the heterogeneous structure of the polymer film, where polymer chains near the substrate are more aligned by the influence of the substrate as compared to the top surface.

The charge transport in conjugated polymers is not as clear as that in molecularly doped polymers (MDPs) and is still a subject of detailed investigation. At the same time, it is governed by the availability of effective conjugation and by finite molecular disorder. Charge transport occurs by migration along the conjugated backbone in the same polymeric chain (intrachain transport) and by hopping between adjacent chains (interchain transport). In intrachain transport carriers get kinetic energy from the externally applied electric field, depending on the direction of chain in relation to the field direction. According to Hartel et al.,[30] interchain charge transport is more important and a rate-limiting condition for macroscopic mobility; otherwise mobility would be 1 cm^2 V^{-1} s^{-1} or even higher. Irrespective of the conjugation length in thicker film, the relative extent of interchain transport is larger than that of thinner films, which perhaps could be responsible for its decreased mobility.

The inset of Figure 7 shows the transient photocurrent obtained for the ITO–PMA–Al device where the thin film of PMA has been cast with a thickness of 1.5 μm. The nature of the transient photocurrents are again dispersive. The double logarithmic plot shows a transit time of 0.25 μs, which produces a hole mobility of 4.6×10^{-4} cm^2 V^{-1} s^{-1}. It should be noted that the hole mobility of cast film is about 2 orders of magnitude higher than that of spin-coated film. This can be attributed to better ordering of polymeric chains under slow solvent evaporation. Better chain ordering leads to the formation of more planarized and ordered segments with stronger π-orbital overlapping, which seems to facilitate the interchain charge transfer and results in enhanced macroscopic mobility. Better chain ordering in poly(3-hexylthiophene) cast film has also been confirmed by X-ray crystallographic and electronic absorption spectroscopic analysis.[31] Apart from this, higher field-effect (FET) mobility has also been
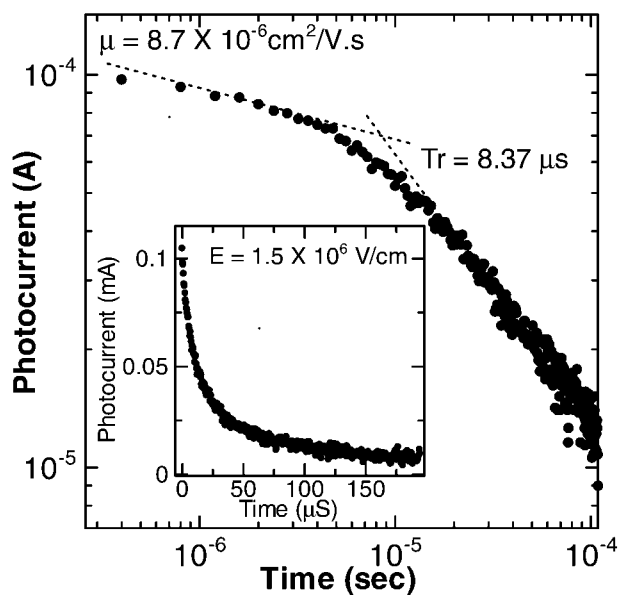

Figure 6 A typical transient photocurrent for ITO–PMA–Al device at applied field $\times 10^6$ V/cm and 293 K in a double logarithmic plot and in a linear plot (inset). Film thickness is 1.1 μm.
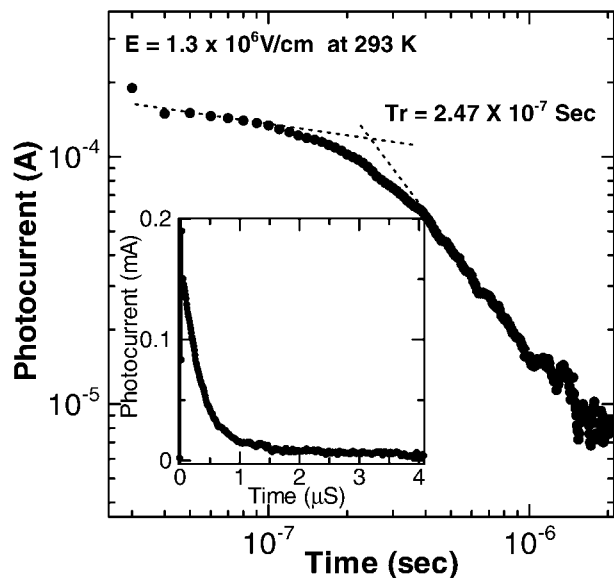
Figure 7 Photocurrent transient of ITO–PMA–Al device in double logarithmic plot at applied field of 1.3 $\times 10^6$ V/cm and 293 K. Its linear plot is shown in inset. PMA is solution cast with a thickness of 1.5 μm.

Figure 8 Field dependence of transit time for ITO–PMA–Al device at 293 K. PMA is spin-coated and has a thickness of 1.0–1.2 μm.

observed in cast regioregular poly(3-hexylthiophene)[32] as compared to that with the spin-coated device. Using a different solvent for film preparation, authors have shown that in each case the FET mobility of cast film was about 1 order of magnitude higher than that of spin-coated film. The high FET mobility in cast film can be explained by better chain ordering and molecular packing during slow solvent evaporation.

One important requirement for realizing real carrier transport is inverse dependence of transit time as a function of applied electric field, which is exhibited in Figure 8. It shows that transit time decreases with an increasing electric field. Field dependence of hole mobility at 293 K for spin-coated and cast films is shown in Figure 9. Spin-coated film shows linear-positive field dependence, which becomes weaker in a high field region. A similar positive-field dependence at room temperature has also been observed in conjugated polymers such as PPV[7] and PFO.[5]

It has been reported that hole drift mobility follows variable trends, such as increasing, decreasing, or remaining constant, as a function of applied electric fields in molecularly doped polymers. This depends on the nature of the dispersed material and the host polymer as well as the temperature.[33–34] To explain this field dependence in molecularly doped polymers, Bassler's disorder formalism[35] has been successfully ap-
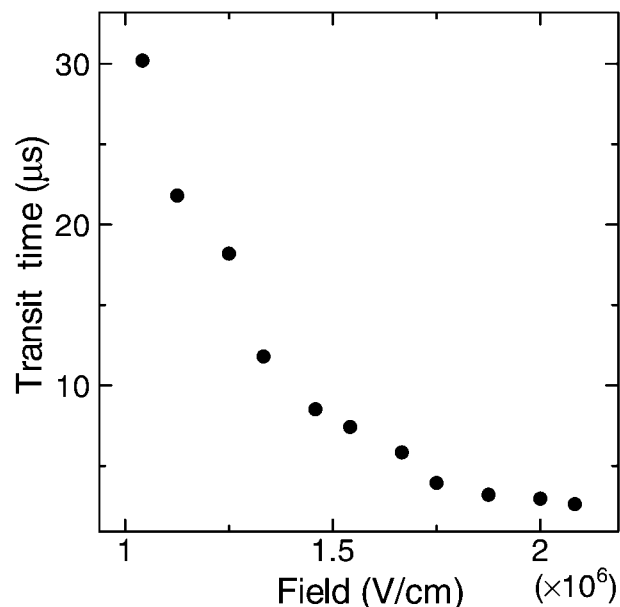
plied, which suggests that the nature of field dependence is governed by the interplay of energetic (σ) and positional (Σ) disorders.

Applying disorder formalism, it seems that in spin-coated films the extent of energetic disorder is contributing more than that of positional disorder, which might be responsible for its positive-
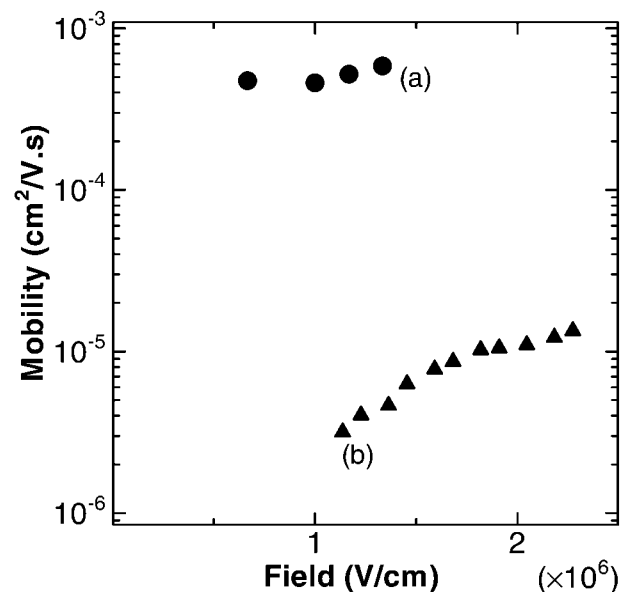

Figure 9 Field dependence of hole mobility of PMA (a) solution-cast film and (b) spin-coated film at 293 K.

field dependence.[36] On the other hand, very weak positive-field dependence in cast film indicates that energetic disorder perhaps make a slightly greater contribution than positional disorder.

CONCLUSIONS

Poly(2-methoxyaniline) has been found to have dispersive transient photocurrents, and an estimation of hole mobility was performed by TOF measurement. Room-temperature hole mobility on the order of 10^{-5} cm^2 V^{-1} s^{-1} was estimated, which is comparable to the highest TOF mobility reported for other conjugated polymers. The processing of the polymer has a marked influence on carrier mobility, and an increase of about 2 orders of magnitude in hole mobility of solution-cast film was observed as compared to that of spin-coated film. This high carrier mobility has been attributed to the better ordering of the polymeric chains leading to smooth carrier transport.

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