Terahertz mobility measurements on poly-3-hexylthiophene films: Device comparison, molecular weight, and film processing effects

Okan Esenturk,[1] Joseph S. Melinger,[2] and Edwin J. Heilweil[1,a]

[1]*Optical Technology Division, Physics Laboratory, NIST, Gaithersburg, Maryland 20899-8443, USA*
[2]*Electronics Science and Technology Division, Code 6812, Naval Research Laboratory, Washington, DC 20375, USA*

We directly compare relative carrier mobilities in semiconducting organic polymer films measured using noncontact optical pump terahertz (THz) probe spectroscopy to those reported in electrical device studies. Relative transient signal amplitude measurements of photoinjected carrier mobility as a function of poly-3-hexylthiophene (P3HT) molecular weight correlate directly with electrical device test values, indicating that the THz method shows promise as a rapid material screening approach. We also present measurements on P3HT conducting films as a function of structural regularity, dispersing solvent, addition of C_{60} electron traps, sample temperature, and other growth parameters relevant to device manufacture. © *2008 American Institute of Physics*.
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I. INTRODUCTION

Semiconducting polymers attract great scientific and industrial interest because of their potential applications in flexible conducting or emitting flat panel devices, light-emitting diodes, solar cells, field effect transistors (FETs), and many other fields. Since their discovery in the early 1980s (e.g., polyacetylenes),[1] organic semiconductor materials were found to attain charge carrier mobilities[2,3] approaching those of inorganic, amorphous silicon based FETs. One of the more recently synthesized and characterized high mobility organic semiconductor materials is poly-3-hexylthiophene (P3HT). Several recent studies have shown that many factors contribute to the observed mobility of devices employing P3HT such as stereoregularity of the polymer structure, casting solvent, postcasting processing such as annealing, and molecular weight distribution of the polymers employed.[1,4–6]

P3HT based solar cells[7] and FETs[4,8,9] have been found to exhibit increased efficiency or carrier mobility with increasing molecular weight. However, the origin of the observed increase in the conductive properties of these electronic devices is still unclear. Kline *et al.* suggested that domain boundaries play an important role in determining the observed mobilities for FETs made from P3HT using various molecular weights.[4] Zen *et al.* suggested that the main-chain conformation instead of domain boundaries plays the strongest role in determining the mobility in P3HT based FETs.[9] Both studies relied on direct electrical measurement of the mobility in an actual device where many other device-related (nonintrinsic) factors such as film growth conditions, impurity traps, and electrical contact-film surface interactions may also play significant roles and affect the characteristic mobility of the device. For example, observing an increase in mobility of these devices with increasing molecular weight could also simply be explained by varying contact resistance

at metal-polythiophene interfaces with change in molecular weight of the polymers.[10] For these reasons, directly determining the origin and mechanisms responsible for the intrinsic conduction properties of semiconducting polymer films have not been clearly identified and need to be explored.

Time resolved terahertz spectroscopy (TRTS) has a potentially unique advantage for directly measuring the device independent intrinsic photoconductive properties of semiconductor polymer films. With its noncontact optical measurement approach and previously proven capability of measuring carrier mobilities in inorganic semiconductors,[11,12] we and other groups[13–21] have recently endeavored to apply this technology to directly ascertain carrier mobilities in organic conducting polymers. Time resolved THz spectroscopy and direct device electrical measurements differ by orders of magnitude in carrier lifetime and structural sensitivity. Ultrafast THz spectroscopy, which focuses on short-time dynamics [(up to a few nanoseconds (ns)], measures "local" carrier migration phenomena whereas ac electrical measurements probe "long-time" (microseconds or longer) conduction processes occurring over tens to hundreds of micrometers length-scale of a device. Electrical measurements are therefore more sensitive to grain size, boundaries, and interfacial effects due to the inherent carrier migration over these large dimensions.[22] Therefore, for some observables that are sensitive to structural effects (i.e., molecular weight dependence), both measurements may correlate well upon measuring the mobility of the film when all other variables remain constant. However, for some observables (such as temperature dependent mobility), ultrafast THz measurements may provide complementary or even unique information when compared to electrical measurements. Therefore, comparative measurement studies need to be carried out to potentially observe complementary behavior and better characterize the unique contributions of the THz technique.

In this paper, we present a systematic correlation study of the molecular weight dependence of the conductivity of

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a)Electronic mail: edwin.heilweil@nist.gov.

TABLE I. MW, PDI, and supplier of P3HT polymers used in this study.

MW	PDI	Co.
17.6	1.1[a]	Aldrich
~55	1.7[b]	Aldrich
72.8	2.1[a]	EMD
153.8	2.5[a]	EMD

[a]PDI values are calculated from manufacturing company reported MW and Mn.
[b]Taken from Ref. 27.

P3HT films using a similar polymer molecular weight range as used previously for P3HT-based transistors, which exhibited relatively high mobilities ($10^{-3}-10^{-1}$ cm^2/V s).[4,8,9] In addition, we investigate film processing effects such as the solvent employed for film deposition and postfilm growth annealing on the photoconductivity of P3HT. The results reported from our TRTS studies are highly correlated with previously reported device measurements, suggesting this rapidly employed optical technique is a potentially useful means to assess or predict the conductive properties of newly designed, synthesized, or grown films for future device applications.

II. EXPERIMENTAL

P3HT polymers were purchased from the Sigma-Aldrich Co. and EMD Chemicals, Inc. and used as received without further purification.[23] The manufacturing company's reported weight average (MW) and number-average (Mn) molecular weights with their polydispersity indexes (PDI) are found in Table I.[24] This molecular weight range (17.5–150 kD) is assumed to be a high molecular weight range and the cast film morphologies from these samples is expected to be similar.[4] Spin or drop cast samples were prepared on THz-transparent fused quartz slides (GM-7525, GM Associates, Inc.)[23] from saturated solutions (unless otherwise specified) of P3HT dispersed in chloroform, xylene, or toluene. Optical density measurements and ultraviolet (UV)-visible ellipsometry indicated the spin cast films were ~50–100 nm thick while the drop cast films were >10 μm thick. An amorphous quartz substrate (instead of commonly used z-cut quartz) was chosen because oriented z-cut quartz generates weak UV pump pulse-induced THz interference signals of similar magnitude to the measured film transient response.[25] All THz measurements were carried out from freshly prepared materials stored in the dark. We did not observe any effects on our measurements from significant photo-oxidation or photobleaching of the films over the course of the experiments. Temperature dependent measurements were carried out under vacuum conditions ($<10^{-2}$ Pa or 10^{-4} Torr) in a helium cryostat fitted with an input quartz window and high-density polyethylene output window.

Charge carrier time-dependent dynamics of the polymer films were measured by following UV excitation/pump-pulse induced modulation of THz probe pulses transmitted through the sample after photoexcitation as a function of time delay. The apparatus is based on a kilohertz Ti:sapphire amplifier optical pump-THz probe spectrometer with slight modifi-
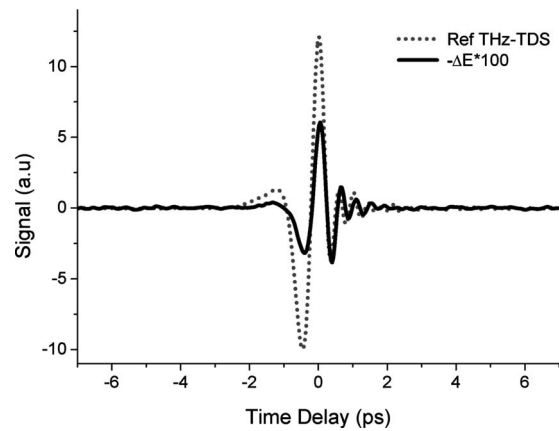

FIG. 1. Measured representative THz field amplitude (dotted line) transmitted through a P3HT sample film and the pump-induced decreased transmission of the reference field (solid line, inverted and multiplied by 100) with 400 nm excitation indicating insignificant frequency effects.

cations.[26] The THz probe pulse is photogenerated and electro-optically detected using 1 mm thick ZnTe crystals. A representative THz field strength signal transmitted through a sample as a function of time for a typical single cycle THz pulse (dotted line) is shown in Fig. 1 along with a differential transmitted THz field envelope after passing through an excited semiconductor film (solid line). Polymer films were optically excited above their absorption band gaps (~2.2 eV) with 400 nm (3 eV, fluence of $5.7\pm0.2 \times 10^{18}$ photons/m^2), 60 fs pulses, and interrogated with optically gated and synchronized time-delayed ultrafast THz probe pulses. The strongest observed pump-induced decrease in the THz probe transmission $|\Delta T/T_o|$ is less than 3% of the peak THz field amplitude. Typical signal-to-noise levels of our spectrometer is ~10^6-10^7 for the measured THz probe field amplitude, but due to the un-normalized pump pulse amplitude noise, the detectable change in probe transmission ($|\Delta T/T_o|$) is limited to ~10^{-4} or larger. Transient time-resolved data were obtained by averaging 20 time-delay scans over the course of 20 min. Analysis of averaged spectra (20 scans) yielded an uncertainty from the baseline of less than $\pm0.03\%$ ($k=1$; type B analysis). The reported decay dynamics were recorded by measuring the pump-induced modulation of the THz peak field strength as a function of delay time of the incident UV excitation pulse (time zero at $t=0$) with respect to the THz pulse. The longest accessible time delay of ~250 ps was limited by the length of an optical delay line employed in our apparatus. Time zero was measured using a double side polished silicon wafer as a reference sample (in dry-air or inside the cryostat) and is defined as the half-rise of the observed modulation. The THz spectrometer was contained inside a Plexiglas® housing purged with dry, CO_2-free air to avoid water vapor interference effects. All samples were preconditioned inside the dry spectrometer or held under vacuum in the cryostat for 1 h before measurements were conducted.

III. RESULTS AND DISCUSSION

A. Molecular weight dependence

Figure 2 shows the time-dependent pump-induced decrease of the THz transmission for four different molecular
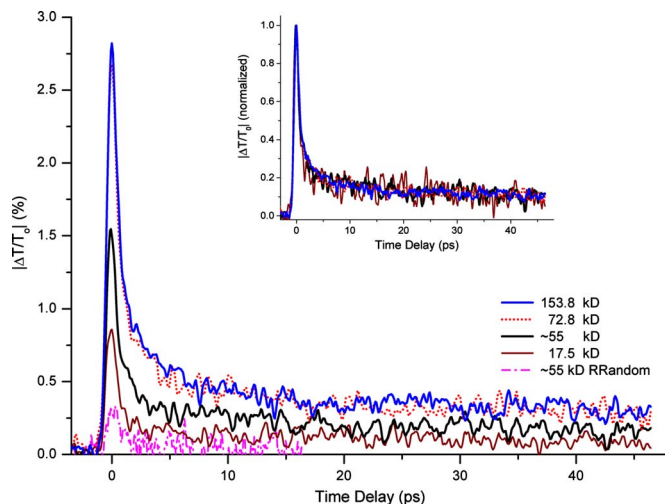
FIG. 2. (Color online) UV (400 nm) pump induced modulation of the transmitted peak THz field of P3HT films varying with molecular weight measured as a function of pump-probe delay time. The inset shows the peak-normalized modulation to emphasize the comparison between the dynamics of the observed carrier time decays.
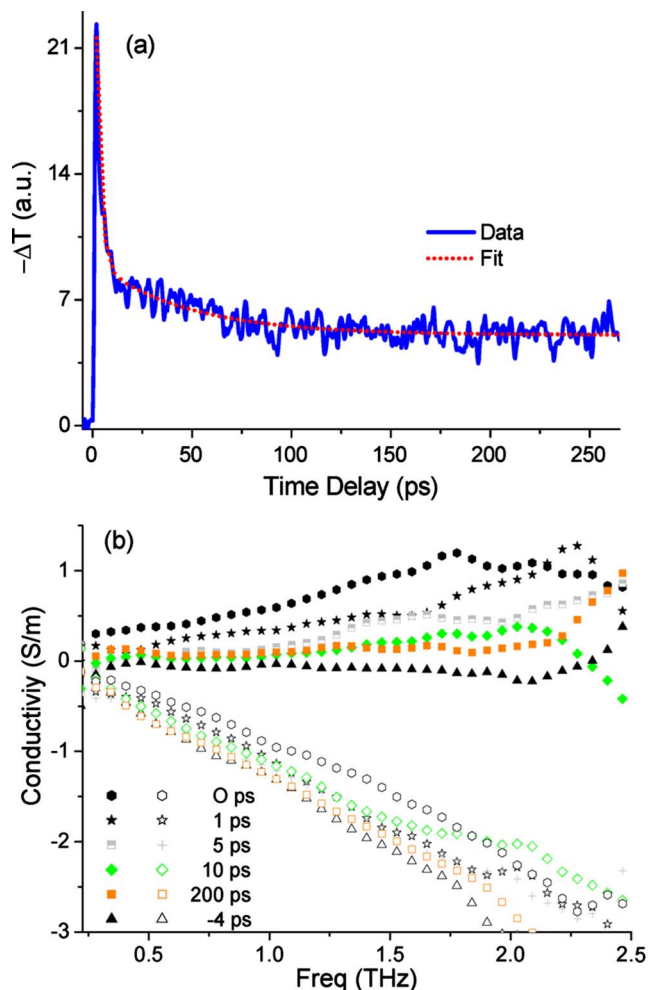

FIG. 3. (Color online) Transient photoconductivity dynamics (a) and frequency dependent complex conductivity (b) at various selected pump-probe delay times of 72.8 kD P3HT drop cast film from saturated chloroform solution. The nonzero imaginary conductivity at −4 ps is a result of an inexact estimate for the dielectric constant of the unexcited polymer.

weight P3HT polymer films (Table I). Again, the amplitude decrease in THz probe transmission ratio against the peak probe transmission ($\Delta T/T_0$), originating from absorption or reflection from free carriers, is measured as a function of pump-probe time delay. These transients were recorded at the peak of the THz probe pulse field as a function of UV pump-THz probe delay time with 400 nm photoexcitation of the sample. The absolute value of the differential transmission clearly increases with increasing molecular weight of the P3HT polymers. All TRTS molecular weight dependence measurements were carried out on thick (>10 μm, optical density OD>3 at 400 nm) drop cast samples made from saturated (∼10 mg/ml) P3HT/xylene solutions. The estimated optical penetration depth, $1/\alpha$, at 400 nm is ∼220 nm. Having films with an OD>3 at the pump wavelength ensures absorption of all the pump light by the polymer film. Excluding the structurally regiorandom 55 kD sample (magenta, dash-dot-dash line), the lowest molecular weight (17.5 kD) P3HT film (brown, thin solid line) showed the lowest differential change in the THz transmission. Both 153.8 kD (blue, medium solid line) and 72.8 kD (red, dotted line) P3HT films generated very similar differential THz transmission changes with the highest MW P3HT sample (153.8 kD) yielding a ∼5% increase in signal over the 72.8 kD sample. The inset of Fig. 2 shows the peak normalized differential transmission change (excluding the weak regiorandom response for clarity) so that the decay dynamics can be compared relative to the molecular weights of the polymers. The results exhibit no significant difference in the signal decay dynamics arising from the transiently THz absorbing carriers. After peak response normalization and despite having the lowest signal level, the 17.5 kD P3HT transient signal appears noisier than the others but still exhibits the same time dependence as the higher molecular weight samples. In all cases, and as has been observed both in P3HT and MEH-PPV film systems,[16] the time-dependent THz response shows complex ultrafast decay components followed

by a very slow (∼ns time scale) component. The relative changes in signal intensity are in good agreement with the device mobility measurements and this important relative measurement and decay dynamics of carrier mobilities using THz methods will be discussed in detail later.

B. Decay dynamics

The room temperature carrier absorption decay dynamics observed in our experiments [Figs. 3(a) and 3(b)] are similar to ones reported elsewhere.[13,16] The decay in photoconductivity of all examined regioregular P3HT films exhibits multiexponential relaxation behavior [Fig. 3(a)]. A best multiexponential fit [red line in Fig. 3(a)] results in four exponential decay constants: an ultrafast decay ($t_1 < 1$ ps), two intermediate time scale decays ($t_2 \cong 10$ ps and $t_3 \cong 50$ ps), and a long-lived decay (t_4 estimated to be ∼1 ns). The ultrafast component is most likely the result of a very fast electron-hole geminate recombination process. The time resolution is limited by the rise-time response of our instrument (∼1 ps base line to peak) as measured from the silicon time zero single-sided reflection transient. The intermediate decay

contributions most likely originate from local carrier recombination processes that are expected to be most sensitive to the amorphous material structure. The longest, nearly flat decay constant estimated to be ~1 ns, is expected to be carrier diffusion limited. These results suggest that the photogenerated carriers may live longer than several ns in these polymer films. Figure 3(b) shows the real and imaginary parts of the measured conductivity of 72.8 kD P3HT spin cast from saturated chloroform solution. The structure displayed in the real and imaginary conductivity curves at various pump-probe delay times [Fig. 3(b)] are mainly due to the low signal levels at higher frequency giving rise to oscillations rather than actual frequency dependent features, especially for frequencies >2 THz. Therefore, the real component of the conductivity is assumed to be frequency independent. The real and imaginary conductivity for the unexcited system (−4 ps before UV excitation) are displayed as empty and full triangles, respectively. The nonzero sloping imaginary conductivity derived for $t=-4$ ps arises from using an estimated dielectric constant for the undoped film since the actual value is not known. By iterative calculations one may obtain a better estimate for the dielectric value but the important point for the imaginary part is that the conductivity change (relative to the $t=-4$ ps offset, open triangles) follows the real conductivity, shows the strongest change at 0 ps, and nearly recovers back to its initial value similar to the extracted real conductivity time dependence. The near linear frequency dependence in conductivity, and the existence of nonzero (real) conductivity out to 200 ps shows that even at the longest measurable time delay, conductivity is still dominated by free carriers.[16]

C. Stereo regularity effect

One of the most striking results that we observed was the comparison between the transient response of regiorandom and regioregular 55 kD P3HT films. The results shown in Fig. 2 (magenta dash-dot-dash versus black solid lines, respectively) demonstrate the importance of local structural regularity and how it potentially affects and enhances the carrier mobility. The measured peak transmission signal change is almost an order of magnitude smaller for the regiorandom sample than for the regioregular P3HT film and decays to nearly zero signal (to within the experimental noise) on a very short time scale [within a few picoseconds (ps)]. The difference between the two films becomes increasingly large with time and suggests that many orders of magnitude difference in conductivity (or mobility) exists for long time scale measurements, as is the case for device measurements.[27] These simple relative THz signal measurements demonstrate the strength of using THz methods to directly distinguish between highly conductive versus near-insulator behavior of polymeric materials.

D. Comparison to device mobility measurements

The change in THz transmission is directly proportional to the mobility (μ) times carrier photogeneration efficiency (η),

$$\mu \eta = C|\Delta T/T_0|, \tag{1}$$

where C is a constant that is composed of Planck's constant, pump frequency, incident fluence, substrate index, optical density of the film, the electric charge, and free space impedance (see Ref. 21, and references therein, for more detail).

Without the availability of any knowledge about the carrier generation efficiencies for these samples, absolute mobilities cannot be directly extracted from our measurements. Two reported photogeneration efficiency values for P3HT polymer films are inconsistent. Bonn and co-workers reported less than 1% photogeneration efficiency for an Aldrich sample,[16] whereas a much higher carrier generation efficiency (>25%) was reported by Ai *et al.* for 20 kD P3HT samples.[13] Our comparison of absolute THz differential transmission signal levels (or conductivities) to a Si wafer (with mobility of 300 cm^2/V s and assumed 100% photon to carrier generation within an absorption skin depth <1 μm) and P3HT polymers suggests <1% carrier generation in P3HT films when excited with 400 nm light. These measurements also suggest a lower limit of the mobility (by assuming 100% efficiency in P3HT) of 1 cm^2/V s at zero time delay.

Even though absolute mobility values for the film samples could not be calculated to compare with the device mobilities measured for the same polymer systems, the ratios of the lower molecular weight polymer mobilities to the saturation mobility for both types of measurements can be compared to evaluate the correlation between the THz and device measurements. If one assumes that the carrier generation efficiencies for all of these molecular species are the same, then differences observed in the signal levels (at the same time delay but especially at $t=0$) should directly correlate with the intrinsic mobility of the highly regioregular (>90%) P3HT polymers. The assumption that the carrier generation efficiency for these polymers is the same is reasonable because of their similar regioregularity and that they are built from long chains of the same monomeric unit. In addition, Hendry *et al.* demonstrated similar weak carrier generation efficiencies for two significantly different polymers, MEH-PPV and P3HT, by photoexcitation using 400 nm light.[16] Following these arguments, the ratio of mobilities of two P3HT films with different molecular weights is equal to the ratio of their differential transmissions

$$\frac{\mu_1 \eta = C(\Delta T/T_0)_1}{\mu_2 \eta = C(\Delta T/T_0)_2}. \tag{2}$$

The normalized ratios of THz mobility measurements and relative ratios calculated from previously reported FET device measurements[8] are summarized in Table II. Since the highest molecular weights of the two experiments are significantly different, we can only estimate the maximum differential transmission value for 270 kD as the saturation limit for $\Delta T/T_0$. The saturation value is estimated by extending a straight line passing through the differential transmission values of 72.8 and 153.8 kD P3HT films reaching 270 kD MW. Using the estimated differential transmission value for the 270 kD polymer instead of the 150 kD measurement only changes the observed results by a few percent. In addition,

TABLE II. Unity normalized ratios of the THz and FET device mobilities. The THz and device mobilites are calculated from the ratio of the relative mobilities divided by the value derived from the highest molecular weight (270 kD) P3HT mobility, μ_{sat}.

THz		FET device by Chang et al.[a]	
MW_n/MW_{sat}	μ_1/μ_{sat}	MW_n/MW_{sat}	μ_1/μ_{sat}[b]
17.5/270[c]	0.27	22/270	0.22
55/270	0.5	52/270	0.75
72.8/270	0.87	76/270	0.87
153.8/270	0.92	270/270	1

[a]Reference 8.
[b]Estimated from the FET mobility values reported for P3HT spin cast films from trichlorobenzene solutions.
[c]In this comparison, the 270 kD P3HT mobility is assumed to be the saturation mobility and is given a maximum value of 1. The $\Delta T/T_0$ value of 270 is estimated with an assumption of a linear increase of signal level with molecular weight since the molecular weight dependence in this range is very weak.

this approach is expected to be more accurate than assuming a saturation value for 150 kD MW P3HT and should not affect the accuracy of the comparison since the change in ΔT from 73 to 150 kD polymer films is only ~5%.

The increase in differential THz transmission of P3HT films with respect to P3HT molecular weight is similar to the reported increase in P3HT mobility in FET device measurements over a similar range of P3HT molecular weights.[8] We find there is a significant increase in differential signal with increasing molecular weight when comparing the 17.5 kD sample to the 72.8 kD sample. Our results suggest that $\Delta T/T_0$ saturation occurs for molecular weights larger than 70 kD. The difference in peak signal amplitude between 73 and 150 kD is ~5% and is nearly within the noise level of the experiment. FET mobility measurements also exhibited mobility saturation for P3HT based devices when the polymer molecular weight exceeded ~70 kD for drop or spin cast films grown from low volatile solvents.[4,8]

Figure 4 demonstrates there is a qualitative correlation between our THz relative mobility measurements and FET electrical device measurements. An approximate fourfold in-
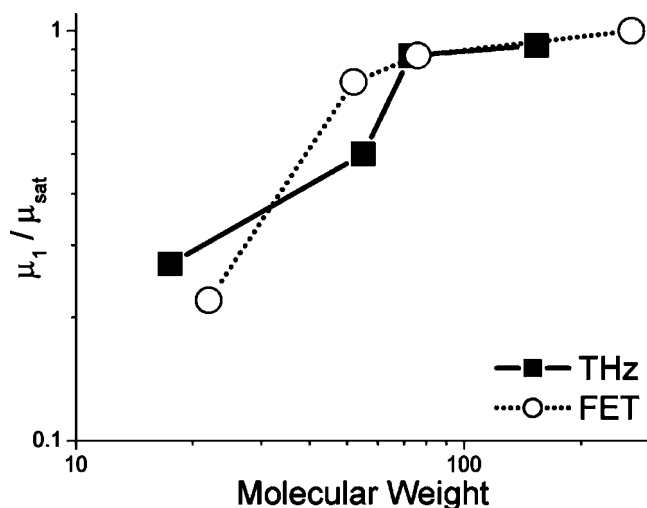

FIG. 4. μ/μ_{sat} ratio of mobilities measured by noncontact THz spectroscopy and FET device measurements (Ref. 8). The data are given in Table II.

crease from the lowest molecular weight polymer mobility to that of the highest molecular weight polymer film is apparent in both cases. Such qualitative agreement may be expected if the mobility of the P3HT based devices is dominated mainly by the intrinsic mobility of the films for these molecular weights. However, we note that there is ~40% lower (relative) mobility measured using the THz method near a molecular weight of 55 kD and ~15% higher mobility measured using the THz method near a molecular weight of 20 kD.

The deviation from an exact 1:1 correspondence between the THz and device measurements may be related to several factors, such as material produced by different vendors, differences in polydispersion indices, film processing conditions, polymer purity, and the possibility that the device measurement may also include effects due to film-metal contact interfaces which may vary as a function of polymer molecular weight. For example, the THz measurements were conducted using drop cast films prepared from low volatility xylene solutions, whereas the films for device measurements were spin cast from trichlorobenzene. Drop versus spin cast preparation methods and the use of different solvents might account for some of the differences exhibited in Fig. 4.

The 55 kD P3HT polymer is synthesized by a different vendor and the purchased batch was not characterized for both molecular weight and polydispersity.[28] We have used a reported literature value[29] as the average molecular weight and polydispersity index even though the batches were different. Assuming the observed THz mobility trend shows the true molecular weight dependence from the intrinsic properties of P3HT polymers, our data suggest that the average molecular weight of the 55 kD polymer may actually be ~40 kD. Unfortunately, we do not have any means to independently measure the average molecular weight and polydispersity of the polymer sample we employed.

We again point out that film morphology may also play a role leading to differences in THz and device related measurements of the film mobility. For example, morphology studies conducted using atomic force microscopy reported slightly higher crystallinity and more domain boundaries for material composed of 15 kD molecular weight compared to higher molecular weight range materials.[4] THz measurements (especially near $t=0$ ps when carriers have experienced minimal diffusion) are less sensitive to these domain boundaries or domain size effects compared to the device measurements. Therefore, the mobility differences when comparing the highest molecular weight P3HT to lowest molecular weight is expected to be smaller than that of the device measurements, as seems to be the case. Further study with lower molecular weight P3HT would be necessary to substantiate this argument.

The inset of Fig. 2 compares the decay dynamics of all the available molecular weight samples and helps us to assess effects due to impurity or end group density effects. The result indicates there is no dependence on the end group density. The shorter chains have more end groups in a given area than the longer ones. Higher end group density is expected to alter and/or shorten the observed decay dynamics of the carriers for the shorter chain length samples. The 17.5
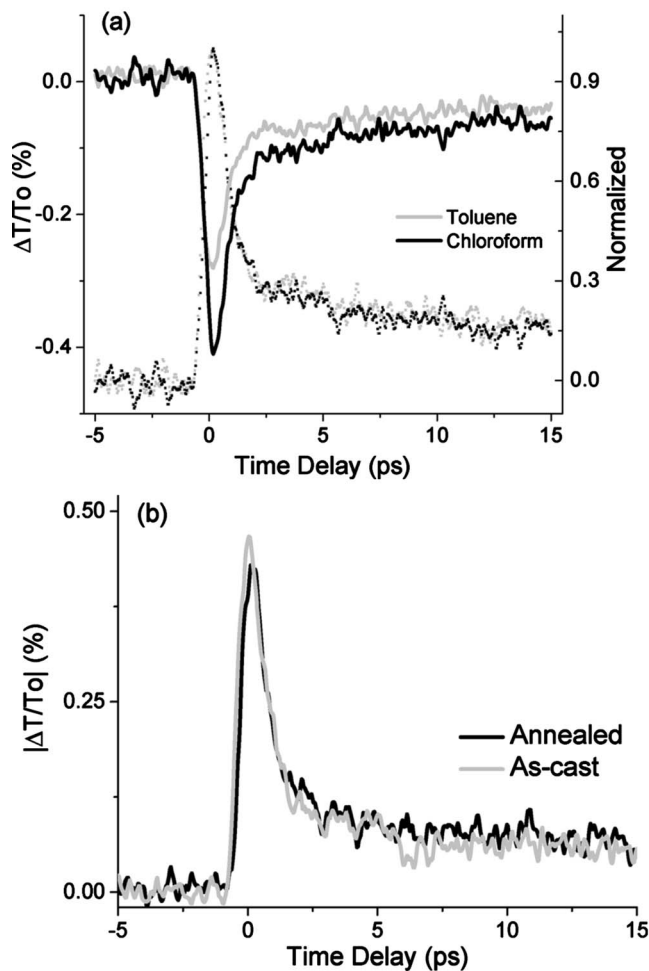
FIG. 5. (a) Dispersing solvent effect on drop cast P3HT films and their peak normalized comparisons (dotted same color lines, but inverted and normalized to 1.0 using the right-hand vertical axis for clarity). (b) Postannealing effect on a spin cast film from ~5 mg/ml xylene solution.

FIG. 6. (Color online) Temperature effect of the photoconductivity of 55 kD P3HT film spin cast from chloroform solution.

kD data are noisy compared to the other data but clearly show that the carrier decay dynamics is very similar to that of the longest P3HT 150 kD polymer. Even though we have not observed significant differences, we do not rule out the possibility of such effects for very short polymers since the shortest polymer length studied (17.5 kD) corresponds to a chain length of ~100 nm, which is still reasonably long.

E. Film processing conditions—Solvent and postannealing

We also studied the effect of film processing conditions including solvent and postfilm growth annealing on the photoconductivity of the P3HT polymer films. Figure 5(a) compares the response of two drop cast films from toluene and chloroform solutions of 55 kD regioregular P3HT polymer as an example to show the importance of the solvent choice. Different molecular weight materials also showed similar behavior. Films cast from chloroform solution always produced ~25% larger differential transmission signals than those cast from toluene, presumably arising from a higher $\mu\eta$ product but exhibiting indistinguishable decay dynamics [see Fig. 5(a) normalized decay response]. Assuming similar carrier generation efficiencies for both samples cast using the same
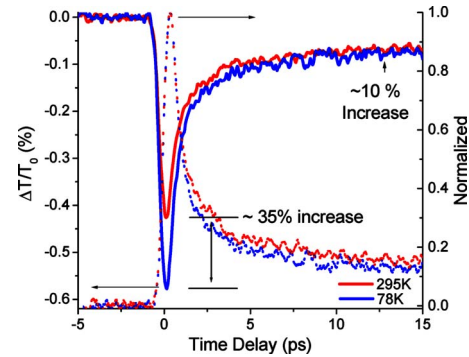
P3HT polymer source, these results suggest slightly higher mobility values for chloroform solution cast P3HT films compared to toluene cast films. Having higher solubility in chloroform, the ability to incorporate higher molecular weight fractions of P3HT conducting chains is expected to produce films with longer, more regular conjugation lengths and increased π stacking in the film. Hence, as was observed for higher molecular weight films, this yields improved mobility and conductivity. Our results support this expected behavior. Even though using chloroform during drop-cast film growth is reasonable, chloroform is not the best solvent for spin-cast processing of P3HT polymers due to its high volatility and vapor pressure. Chloroform dries too quickly unless one searches for a favorable spin speed. Instead, low volatility solvents such as xylene, dichlorobenzene, and their mixtures with chloroform are preferred for generating spin-cast conductive films. Previous electrical device measurement studies also showed the importance of the choice of solvent on the observed mobility of devices.[4,8,9]

Figure 5(b) shows the effect of post-annealing of films on the photoconductivity of a spin-cast xylene-dispersed 55 kD regioregular P3HT film. The film was cast at 4000 rpm from ~5 mg/ml solution and measured (labeled as-cast in the figure) with our THz apparatus. The sample was then annealed under nitrogen at 523 K (above T_m) for 5 min and slowly cooled to 453 K (above T_g). The film temperature was kept constant at 453 K for ~20 min and slowly cooled to room temperature (293 K), then measured again [labeled as annealed in Fig. 5(b)]. The data suggest there is a slight improvement in conductivity and possible increase in π-stacking orientation of the chains for the annealed versus as-cast films. This effect is expected to increase the carrier mobility slightly for high molecular weight polymers as was also seen in device measurements.[4]

F. Temperature effect on the mobility

Figure 6 shows two representative differential THz transmission measurements (monitored at the peak transmitted THz field amplitude) at 293 K (red lines, upper traces) and 78 K (blue lines, lower traces) of a chloroform spin-cast 55 kD regioregular P3HT polymer film. Measured absorption spectra at 293 and 78 K did not show a significant o.d. change at 400 nm. Both measurements were carried out under vacuum ($<10^{-2}$ Pa). The absolute differential transmis-

sion signal level increases as the temperature was decreased to 78 K and fully recovered to its original value when warmed to room temperature. The temperature dependence of the peak signal appears to be linear between 78 and 293 K (data not shown) and the signal recovery suggests that the film structure did not significantly change during temperature cycling. FET device measurements exhibited a decrease in mobility with decrease in temperature, which was attributed to a thermally activated hopping mechanism.[30]

At first glance, the observation of increased mobility at low temperature in the THz measurement would seem to be in conflict with the device results. However, as described in Sec. I, short-time THz measurements are more likely to be very sensitive to local environmental or structural changes including chain conformational changes and torsions. The conjugation length is determined by the chain's torsional constraints; therefore, as the film temperature is decreased, the conjugation length is expected to increase since the chain becomes more rigid (and adopts more trans density configurations).[31,32] An increase in conjugation length results in a more polarizable excited state which in turn would result in increased differential THz transmission at early times following optical excitation. If all other polymer film properties remain the same, then the decay dynamics at 78 K are expected to be the same as the room temperature decay dynamics. However, for the 78 K transient, we observed ~35% signal increase at the peak and ~10% increase at 12 ps in differential transmission signal (see Fig. 6). These results clearly indicate that the decay dynamics are different at these two temperature extremes. The morphology of the film is not expected to significantly change by cooling. Therefore, the faster decay of the 78 K film may be attributed to an increase in recombination rate of the carriers. This can only be achieved if the pathways for interchain hopping are reduced or hindered with respect to the room temperature situation. These results are consistent with a thermally activated hopping mechanism, where the activation energy can be obtained from a detailed study of the temperature dependence of the photoconductivity. The activation energy for the hopping mechanism is estimated to be ~15–30 meV from device measurements.[1] A detailed temperature-dependent THz study exploring conductivity at much longer delay times needs to be performed to obtain a quantitative activation energy comparison.

G. Effect of adding C_{60} electron traps to the mobility

Figure 7 shows the effect of changing [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM) (a soluble C_{60} derivative) concentration in P3HT:PCBM blend films' relative THz transmission signals. In all cases, adding PCBM significantly increases the differential peak signal and lifetime of generated carriers by trapping electrons and hindering the electron-hole recombination process. However, the initial carrier concentration appears to be lower for the 1:1 P3HT:PCBM blend compared to bare (1:0) and 4:1 P3HT:PCBM blends. The highest response is observed from
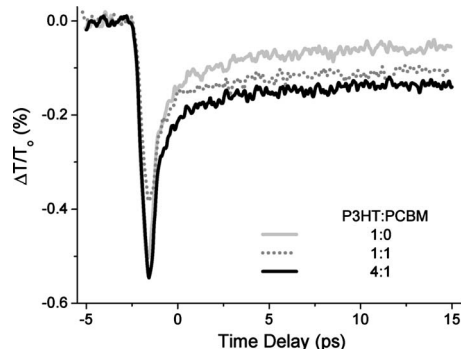

FIG. 7. Comparing transient decay dynamics of 72.8 kD P3HT and PCBM blended films at three different blend ratios.

the 4:1 mixture blend both in peak and long time response. These results are consistent with recently published TRTS study of P3HT:PCBM blends.[13]

IV. CONCLUSIONS

In this study we characterized the effects of molecular weight, casting solvent, adding PCBM electron traps, post-annealing, and temperature on the photoconductivity of four P3HT polymers with weight-averaged molecular weight of 17.5, ~55, 72.8, and 153.8 kD. Our TRTS measurements were compared with results reported from electrical measurements on P3HT-based FET devices. We observe qualitative agreement between the THz and device-based measurements on the dependence of the carrier mobility on polymer molecular weight and on film processing conditions. An approximately fourfold increase in mobility occurs by increasing the molecular weight from 17.5 to 153.8 kD which is comparable to published FET device measurements. Annealing experiments showed a slight increase in mobility of the polymer film as was also observed in the device measurements. The temperature dependence study showed an increase in THz transmission (higher mobility) at lower temperatures possibly due to an increase in torsional constraints and, hence, on the conjugation lengths of the polymer. The faster decay in differential transmission at 78 K compared to 295 K supports a thermally activated hopping mechanism, as previously reported in papers describing device measurements. Measurements as a function of temperature are underway to better understand carrier mobility effects and to extract activation energies for these and related polymer systems.

With its all optical approach, noncontact application, and relatively quick measurement technique, THz spectroscopy appears to be very effective in measuring photoconductivity of high-mobility polymeric materials. In addition, potential industrial application of the technique would be very beneficial through its cost cutting approach of measuring the property of a candidate material without the need to manufacture a test device. THz measurements will simplify the testing of the solution processed devices prior to designing or fabricating an actual device and we think this would be a very beneficial process for both the device manufacturing community and the electronics industry. Understanding carrier decay mechanisms and the origin of THz transient response contin-

ues to be of keen interest, and we are currently designing experimental methods to explore sources of carrier recombination, measuring nanosecond and longer carrier lifetimes and means to further increase carrier mobilities by molecular design.

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[24]The 55kD molecular weight P3HT polymer purchased from Sigma-Aldrich was not characterized for molecular weight or dispersity by the vendor.

[25]The strength of the observed *z*-cut signal contribution depends on the plane angle of the *z*-cut quartz with respect to the incoming pump beam orientation and polarization. These effects were eliminated by using amorphous quartz material.

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