Thermal stability of P3HT and P3HT:PCBM blends in the molten state

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Rheometry

Abstract

The thermal stability of poly(3-hexylthiophene) (P3HT) in its molten state was investigated in air and nitrogen atmospheres under no illumination conditions, with the aim of testing the feasibility of processing it using polymer melt techniques. A large set of different experimental characterization techniques was used including thermogravimetric analysis (TGA), rotational rheometry, infrared spectroscopy (FTIR-ATR), proton nuclear magnetic resonance spectroscopy (^{1}H-NMR), gel permeation chromatography (GPC), UVVis and fluorescence spectroscopy. The results obtained strongly suggest that the processing of P3HT in its molten state is possible, without noticeable degradation, if carried out under nitrogen atmosphere and if the processing (residence) times are relatively short. Conversely, as expected, in a normal air atmosphere P3HT degrades rapidly at temperatures above its melting point. The effect of PCBM on the thermal stability of P3HT:PCBM blends in the molten state was also studied using TGA, and in air atmosphere PCBM is shown to delay oxidation.

Introduction

Poly(3-hexylthiophene) (P3HT) is a semiconducting polymer which, in the last decade, has found widespread use in the general area of organic electronics and photonics in diverse applications such as polymer light emitting diodes [1], electro-chromic windows [2], nonlinear optical devices [3], batteries [4], artificial muscles [5], capacitors [6], organic field effect transistors (OFETs) [7] and organic photovoltaics (OPVs) [8]. Among these numerous applications, its use in OPVs has most contributed to its popularity.

In OPV applications, P3HT (electron donor) is usually blended with the fullerene derivative [6,6]-phenyl-C61-

butyric acid methyl ester (PCBM) (electron acceptor). P3HT is a semi-crystalline polymer with a melting temperature of ca. 240°C, depending on the molecular weight and regioregularity [9-11]. Pure PCBM nanoparticles have two melting temperatures at ca. 268 and 288°C [9-11], which are associated with different crystallographic orientations.

Despite the fact that the P3HT used in devices has been until now mostly processed from solution, there are significant societal drivers to either find environmentally benign solvents for these polymers, or alternative processes that do not require solvents at all [12-14]. In the search for more eco-friendly alternatives, conventional polymer melt processing methods have recently started to be exploited to produce fibers [13] and thin films [15] of polythiophenes. Fanous et al [13] have demonstrated the production of pure poly(3-hexylthiophene) (P3HT) fibers by melt spinning at 260°C followed by drawing at 150°C.

However, the authors made no considerations about the possible degradation of P3HT at 260°C.

Although previous degradation studies have clearly identified that P3HT has a limited resistance to a simultaneous combination of oxygen, light, moisture and high temperatures, the vast majority of those studies have focused mainly on conditions relevant to OPVs device operation, namely presence of light, temperatures well below the melting point of P3HT, either air or N_2 atmospheres and long exposure times to these conditions [1626]. Studies of thermal degradation of P3HT or other polythiophenes focusing on conditions more relevant to conventional polymer melt processing techniques (absence of light, temperatures above melting point, N_2 or air atmospheres and short exposure times to these conditions) are still very rare in the literature [27,28].

Ljungqvist et al [27] studied the thermal and photooxidation of poly(3-octylthiophene) thin films. Samples were heated in air or nitrogen atmospheres at temperatures ranging from 180 to 220°C with heating times from 10 to 30 min . Gel permeation chromatography (GPC) showed that at high temperatures an increase of molecular mass occurs. ^{13}C-NMR and infrared spectroscopy (FTIR) showed that thermo-oxidation and photo-oxidation occur through different mechanisms. The mechanism of thermal oxidation at processing temperatures occurs mainly via degradation of the alkyl side chain through hydrogen abstraction from the α-carbon. This position then becomes the site for the oxidation products.

Ramani et al [28] studied the thermal degradation kinetics of P3HT in nitrogen and air. Based on derivative thermo-gravimetry results, they concluded that, while in nitrogen P3HT decomposition starts at ca. 460°C and occurs through a single stage decomposition, in air P3HT decomposition starts at ca. 285°C and a triple stage decomposition was

observed. The authors attributed the degradation in nitrogen to be mainly due to the cleavage of the hexyl chains attached to the aromatic thiophene backbone.

Previous differential scanning calorimetry (DSC) studies [9-11] of pure P3HT and P3HT:PCBM blends, under N_2 atmosphere, and up to the temperature of 300°C have shown no apparent signs of chemical degradation.

Fullerenes have been shown to enhance the stability of some polymers due to their action as excited state quenchers and radical scavengers [29,30]. However, as far as we know, the impact of PCBM on the thermal stability of P3HT:PCBM blends at temperatures above the melting point of P3HT and under no illumination conditions, has still not been reported.

In the present work, a systematic study on the thermal stability of P3HT and P3HT:PCBM blends, in conditions relevant to polymer melt processing techniques, was performed. Our goal was to access the time and temperature windows in which P3HT and P3HT:PCBM blends can be processed in the dark, either in air or N_2 atmospheres, without noticeable degradation and, therefore, to verify the feasibility of processing these polymer systems using melt techniques.

The dependence of P3HT degradation, both on temperature and time, was investigated using a combination of Thermo-Gravimetric (TGA) analysis, Rotational Rheometry, Infrared Spectroscopy (FTIR-ATR), solubility tests, Nuclear Magnetic Resonance (^{1}H-NMR) in solution, Gel Permeation Chromatography (GPC), UV-Vis and Fluorescence Spectroscopy. The dependence of the degradation of P3HT:PCBM bulk samples on temperature was investigated by TGA.

Experimental

Materials

Two different poly(3-hexyl thiophenes) (P3HTs) were purchased from Ossila, with the following characteristics: (a) Mw = 65,500 and Mn = 32,000 (batch # M101) and (b) Mw = 31,300 and Mn = 15,600 (batch # M107). Carbon nanoparticles of phenyl-C61-butyric acid methyl ester (PCBM) with > 99% purity were acquired from Solenne BV. Chloroform and 1,2-dichlorobenzene (both ACS reagents, ≥ 99.8%) were purchased from Sigma-Aldrich. All these materials were used as received, without any further purification. The chemical structures of P3HT and PCBM are shown in Fig. 1.

Sample preparation

Pure P3HT fibers were compacted into circular shaped flat samples on a SPECAC hydraulic press at room

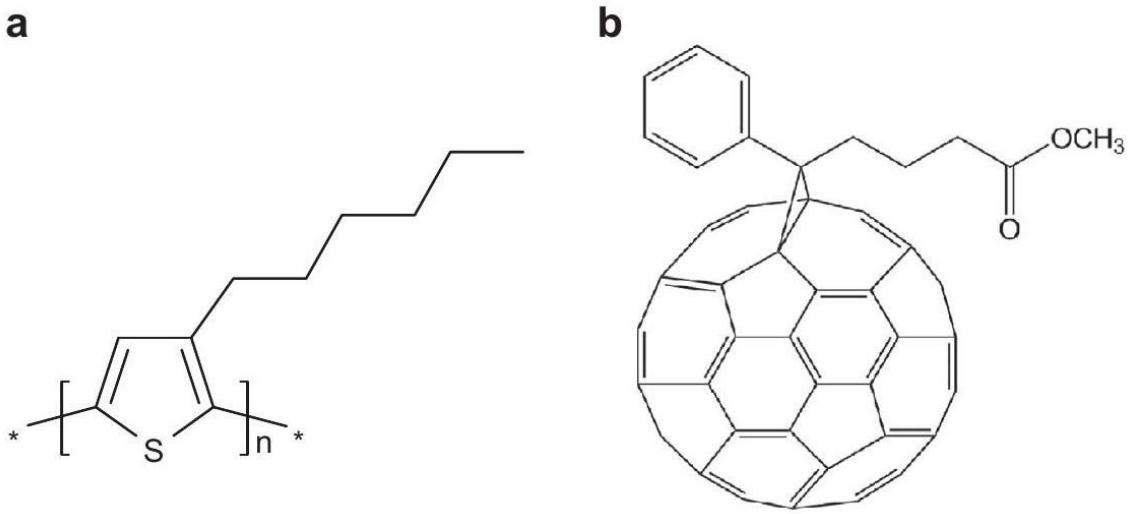


Fig. 1. Chemical structure of the materials used in this work: (a) P3HT and (b) PCBM. temperature with a pressure of ~ 10MPa. P3HT samples were subjected to isothermal treatments in the TGA, in air and nitrogen atmospheres at temperatures of 150, 250 and 350°C, and for 10 and 60 minutes. The 12 different samples (2 different atmospheres * 3 different temperatures * 2 different times) were stored, in the dark, for subsequent detailed study using a large set of experimental techniques.

P3HT:PCBM blends, with relative weight % compositions of 80: 20,60: 40,40: 60 and 20:80 respectively, were prepared by solvent casting. In this preparation, appropriate quantities of P3HT and PCBM were placed separately inside small glass bottles containing chloroform ($CHCl_3$), and sonicated in a water bath until complete solubilization has been achieved. Then, both solutions were mixed and sonicated in order to achieve full mixing. Later, the mixtures were drop cast into glass Petri dishes and left drying overnight. Then, the Petri dishes were placed inside a vacuum oven at 60°C for 5 hours in order to remove completely the solvent. Finally, the well dried solvent cast films were peeled off the Petri dishes and stored, in the dark, for subsequent TGA characterization.

Sample characterization

Two different types of experimental characterization techniques were used: (i) techniques in which the sample subject to analysis was on its solid or molten state; (ii) techniques in solution which required the dissolution of previously annealed samples. The first category of techniques used includes: DSC, TGA, rotational rheometry and FTIR-ATR. The second category of techniques includes: solubility tests, GPC, ^{1}H-NMR and UV-Vis and fluorescence spectroscopies. GPC, ^{1}H-NMR, UV-Vis and fluorescence spectroscopies were used mainly to characterize the pristine P 3 HT and those samples which, after thermal treatment, still exhibited full solubility in $CHCl_3$ and in 1,2 – dichlorobenzene.

Differential Scanning Calorimetry measurements of pure P3HT and pure PCBM were performed on a Perkin Elmer Diamond calorimeter at $10\,°C.min^{-1}$ from 30 to 300°C, under nitrogen. Two heating-cooling cycles were run. Melting temperatures were taken as peak maxima.

Thermogravimetric measurements were carried out using a TA Q500 thermobalance. The instrument was calibrated with respect to indium and aluminum standards. Samples (~

20mg) were placed in platinum crucibles and both dynamic and isothermal tests were performed. In the dynamic tests, samples were heated from 30°C to 600°C using a conventional heating ramp with a slope of $10\ ^{\circ}C.min^{-1}$, under nitrogen and air flow (50 mL/min). Isothermal tests were run at 150,250 and 350°C for 10 and 60 minutes, under nitrogen and air flow. After the isothermal tests, the samples were removed from the TGA crucibles and stored in the dark for subsequent characterization.

Rotational rheometry tests were performed using disks of P3HT (diameter = 25 mm; thickness ~ 0.5 mm) prepared by compression molding pristine P3HT in its powder state in a SPECAC hydraulic press at room temperature and with a pressure of ~ 10MPa. The disks were loaded between the parallel plates (diameter 25 mm) of a stress-controlled rotational rheometer (ARG2, TA Instruments) at a temperature of 150°C under nitrogen and air (two separate experiments performed with the environmental test chamber fed with air or nitrogen flux of 10 L/min). The gap between plates was set to nearly 500 microns, which is the thickness of the molded disks. Time was left for the sample to mechanically stabilize, as inferred from the on-line reading of the normal force applied by the sample on the sandwiching plates, which reached a steady state value of the order of 1 N . This residual normal force ensured satisfactory strain and stress transmissions between the shearing geometry and the sample. A temperature ramp with heating rate of 10°C/min was performed and Small Amplitude Oscillatory Strain (SAOS) testing was carried out with a strain of 0.1% at 1 Hz in the linear viscoelastic regime (a sinusoidal stress response was measured on-line). Then, a SAOS time sweep was carried out at 250°C using 2.5% strain to follow the effect of curing on the viscoelastic properties.

Infrared spectra of pristine P3HT and isothermally treated P3HT samples, were recorded in ATR mode between 400 and 4000 cm^{-1} using a Jasco 4100 spectrophotometer. Spectra were obtained from 32 scan summations at $4\ cm^{-1}$ resolution. The flat samples for FTIRATR analysis were prepared by compression molding the previously isothermally treated P3HT samples in a SPECAC hydraulic press at room temperature and with a pressure of ~ 10MPa.

Solubility tests were performed by placing P3HT samples, previously subjected to several different isothermal treatments (10 and 60 minutes; air and nitrogen atmospheres; temperatures of 150,250 and 350°C), inside small glass bottles containing 1,2-dichlorobenzene and chloroform and sonicating in a water bath until completely or partially dissolved. Depending on the difficulty of dissolving samples, the water bath temperature was varied from ca. 25°C up to ca. 85°C and the sonication times were varied from a few minutes up to several hours.

Gel permeation chromatography was used to determine the molecular weight distribution of the thermally treated P3HT samples. Solutions were prepared in chloroform (99.9%) and prefiltered on filter plate (hydrophobic polytetrafluoroethylene, 0.45μ m pore size) before injection. A Waters Alliance GPC Model 2695, equipped with 3 PLgel MIXED-B columns (inner diameter = 7.5 mm, length = 30 mm and particle size = 10μ m) and a Waters 2410 Differential Refractometer as detector, were used for the determination. Chloroform was used as eluent with a flow rate of 1 mL/min and the temperatures were 25 and 35°C at the injector and detector, respectively.

Solution state ^{1}H-NMR studies of the completely soluble samples were performed in order to detect eventual P3HT degradation. Samples were placed inside NMR tubes containing deuterated chloroform and sonicated for 15 min in an ultrasonic bath. Proton NMR

spectra were recorded on a Bruker Avance-300 spectrometer at 300.13 MHz using tetramethylsilane as internal reference.

Fluorescence spectra of the completely soluble samples were recorded, at room temperature, using a FluoroMax-4 spectrofluorometer. UV-visible absorption spectra (200 700 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. Solutions for analysis were prepared by dissolving pure P3HT as well as previously thermally treated P3HT samples in 1,2-dichlorobenzene and then placing on a quartz cell having path length of 10 mm .

Results and discussion

P3HT pure

Differential scanning calorimetry

Pure P3HT (both molecular weights) and pure PCBM, were analyzed by DSC in order to determine their melting temperatures. P3HT with Mw = 65500 and Mn = 32000 $g.mol^{-1}$ displays a melting peak at 241°C with an enthalpy of 22.2 J/g on its 1st heating scan. P3HT with Mw = 31300 and Mn = 15600 $g.mol^{-1}$ displays a melting peak at 232°C with an enthalpy of 22.1 J/g on its 1st heating scan. PCBM displays, on its 2nd heating scan, two melting peaks: a smaller one at ca. 267.2 °C with an enthalpy of 3.67 J/g and a larger one at 286.3°C with an enthalpy of 15.48 J/g. These results are in excellent agreement with previous published data [9-11].

Thermogravimetry

Fig. 2 shows the TGA curves of normalized mass and derivative TGA (DTGA) data of the derivative mass of two different P3HTs, with different Mw and Mn, in (a) nitrogen and (b) air media, respectively. As clearly illustrated by the DTGA curves, the decomposition of P3HT in nitrogen occurs through a single-step mechanism, while in air it occurs through a multiple-step mechanism.

According to Fig. 2(a), the thermal decomposition reaction of P3HT in nitrogen starts at ca. 440°C and ends at ca. 530 °C, the maximum rates of degradation observed being at ca. 498°C and 503°C for the P3HTs with molecular weights of 65500 and 31300 $g.mol^{-1}$, respectively. Finally, when the maximum temperature of 600°C is reached, the residual mass of both polymers is ca. 30% of the initial mass.

The decomposition behavior of P3HT in air is different and more complex than that in nitrogen, as clearly shown in Fig. 2(b). The first stage of decomposition in air is mild and starts at ca. 400°C. As the temperature increases, the rates of thermal degradation increase until a maximum is reached at ca. 476 °C. When the maximum temperature of 600°C is reached, the residual masses of both polymers with Mw = 65500 and 31300 are ca. 20% and 11%, respectively.

These results are in excellent agreement with previous studies, which have shown that P3HT displays a singlestage decomposition in nitrogen and displays a multiplestage decomposition in air [28].

The results shown in Fig. 2(a) and (b) also clearly demonstrate that the molecular weight (Mw) of P3HT has a negligible effect on the corresponding degradation mechanism as well as on the thermal degradation temperatures.

As previously mentioned, the results shown in Fig. 2 were obtained at a heating rate of $10\ ^{\circ}\mathrm{C.min^{-1}}$, in accordance with the common practice in the literature. Although the temperatures obtained at which the thermal decomposition reactions start, are in excellent agreement with previous reports in the literature, it should be emphasized that such temperatures are dependent on the heating rates

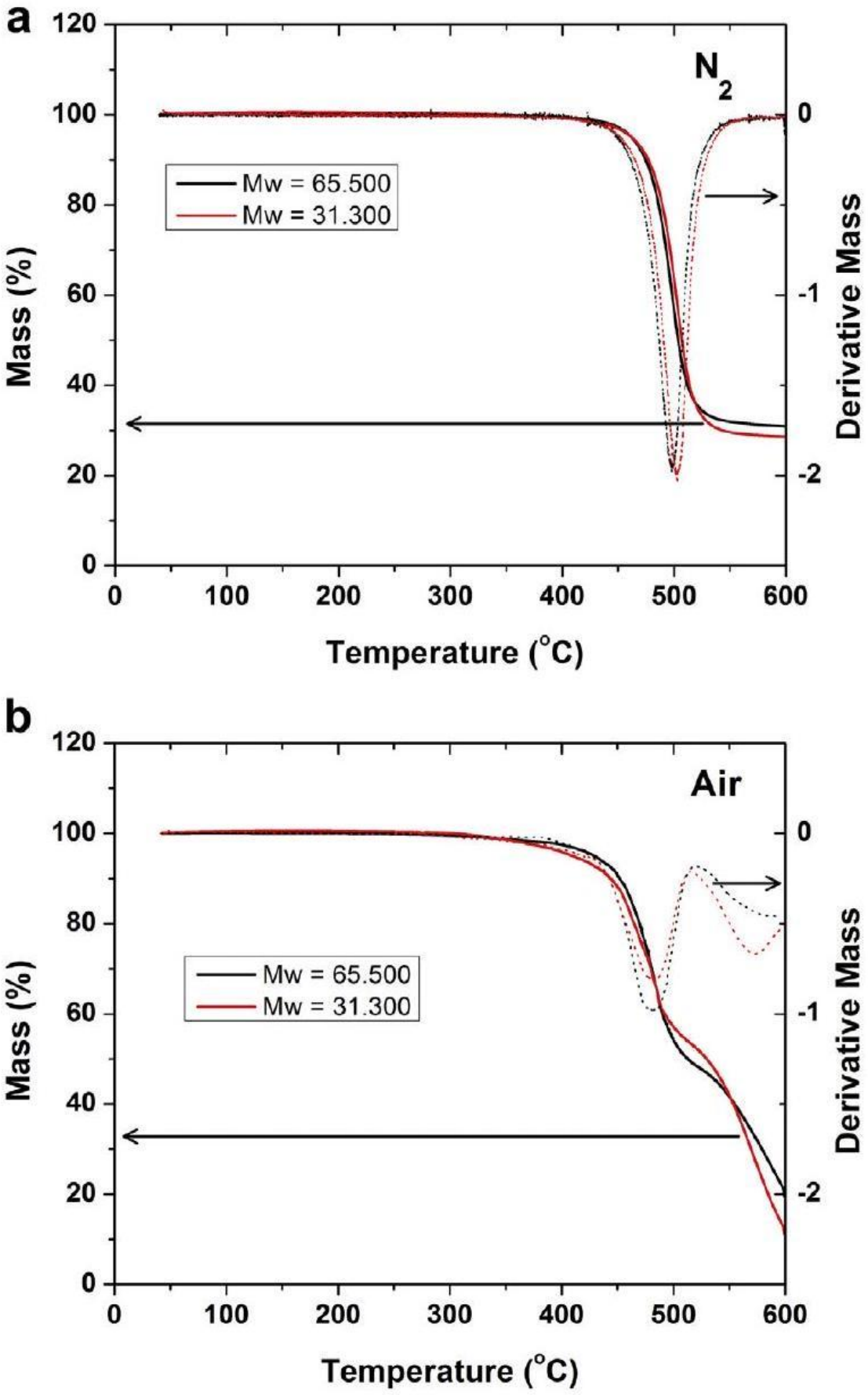

a
N2
Mw = 65.500
Mw = 31.300
Mass (%)
Derivative Mass
Temperature (°C)
b
Air
Mw = 65.500
Mw = 31.300
Mass (%)
Derivative Mass
Temperature (°C)

Fig. 2. Thermogravimetric results, with a heating rate of 10°C/min, for pure P3HT with two different molecular weights in (a) nitrogen and (b) air medium. used. In order to remove this heating rate dependence, we have also performed isothermal treatments of 10 and 60 minutes at the temperatures of 150,250 and 350°C, both in air and nitrogen atmospheres, and the corresponding curves of mass loss (%) as a function of time are shown in Fig. 3. As shown in Fig. 3, after 1 hour of thermal treatment under N_2 atmosphere the total mass losses are $\sim 0, \sim 0.3$ and 1.6% at 150,250 and 350 °C, respectively. Under a normal air atmosphere the total mass losses after 1 hour of annealing are $\sim 0, \sim 0.7$ and $\sim 3.8\%$ at 150,250 and 350°C, respectively.

Rotational rheometry

The rotational rheometry results are shown in Fig. 4. Fig. 4(a) shows the evolution of the viscoelastic properties of P3HT during heating from 150 to 250°C, in a normal air atmosphere and in N_2 atmosphere. Right after sample loading and relaxation between plates, P3HT shows the expected elastic behaviour (G'' is smaller than G') of a solid. In addition, testing in air or N_2 gives essentially the same result at short times and at 150°C, which is also expected since both disks were loaded under similar normal force

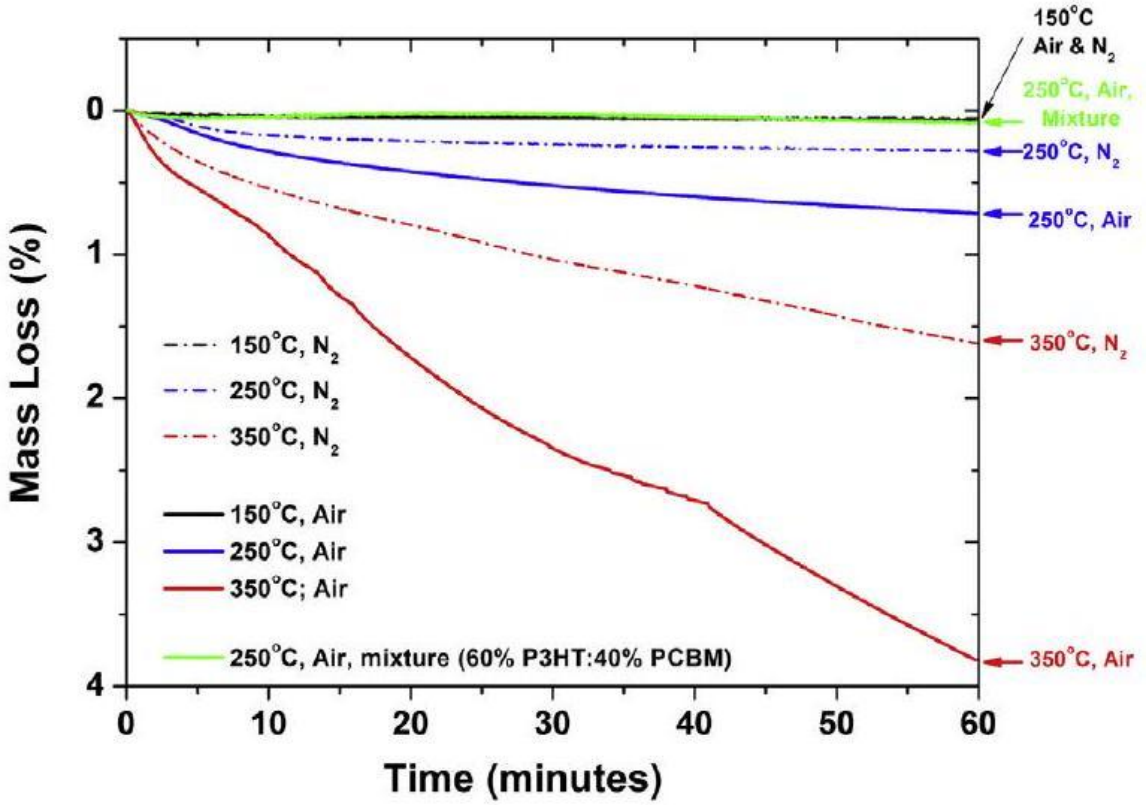
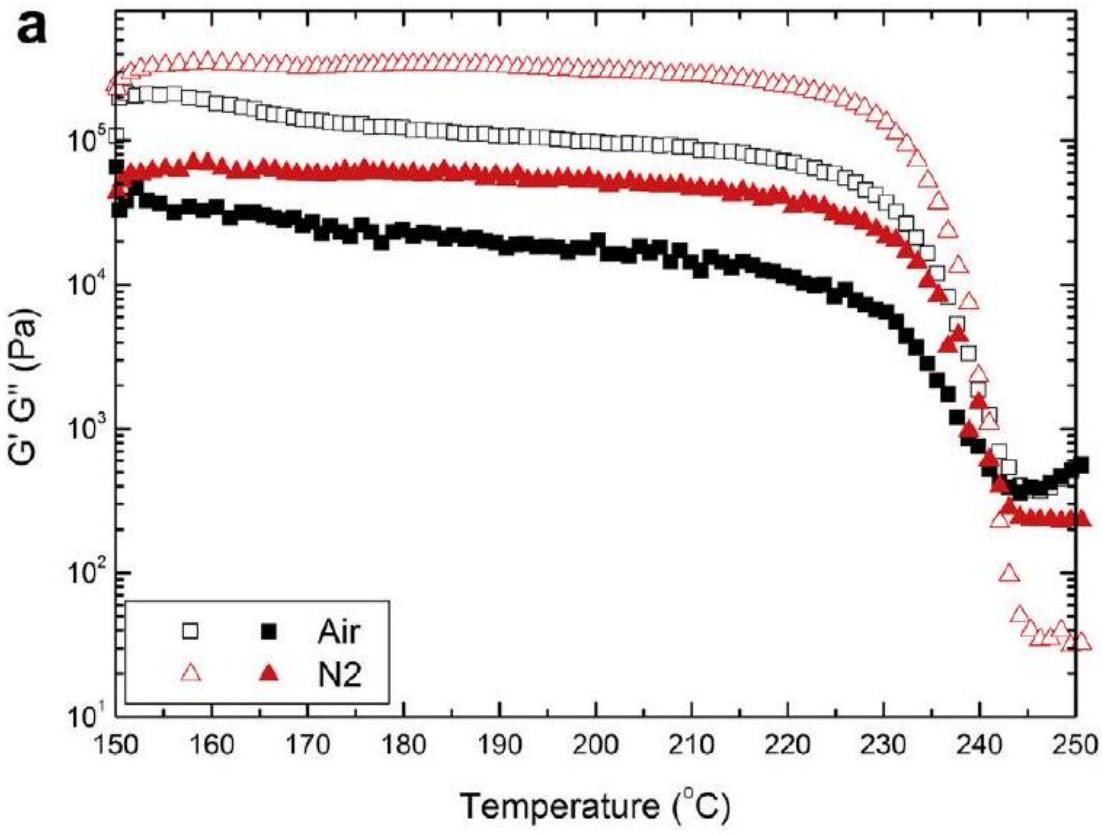


Fig. 3. Isothermal treatments for 60 minutes of P3HT at 150,250 and 350°C in nitrogen and air atmospheres and of a mixture of 60% P3HT:40% PCBM at 250°C in air.


a
G' G'' (Pa)
Temperature (°C)
Air
N2

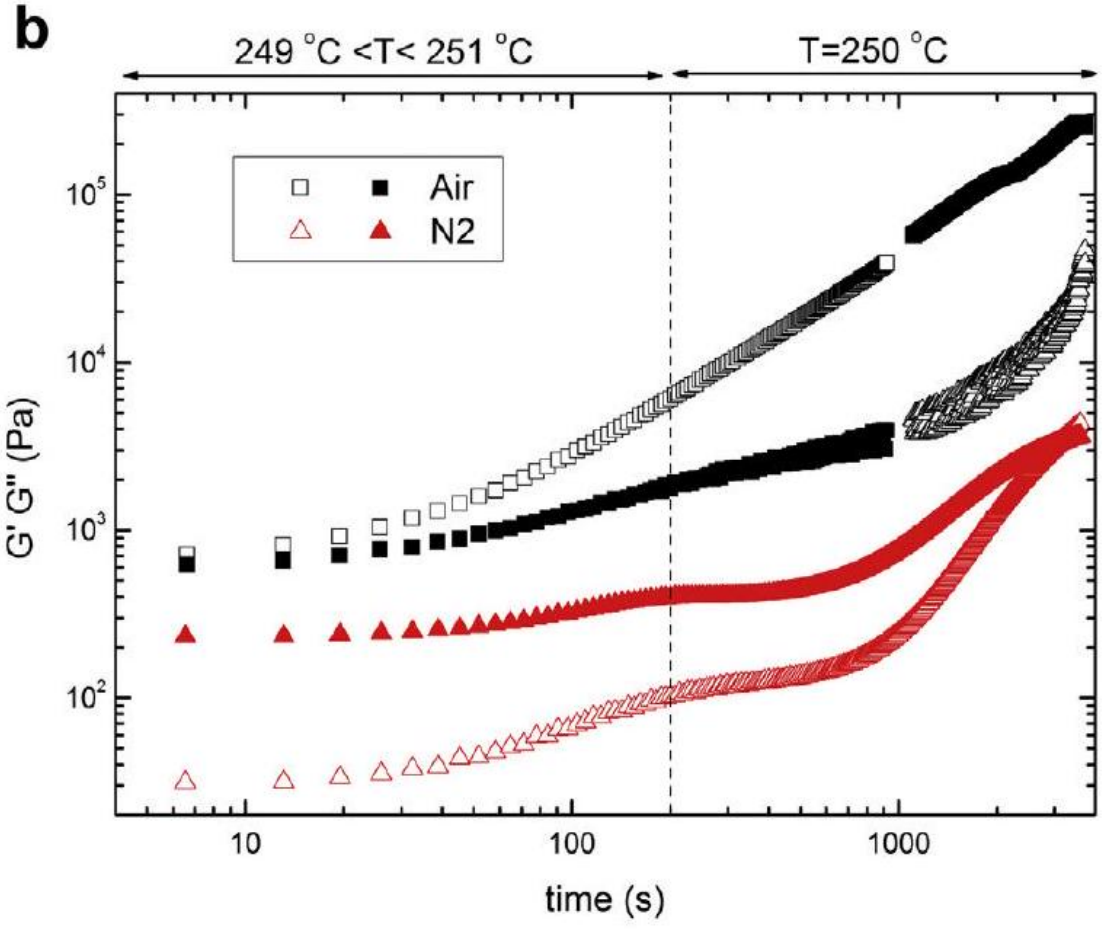
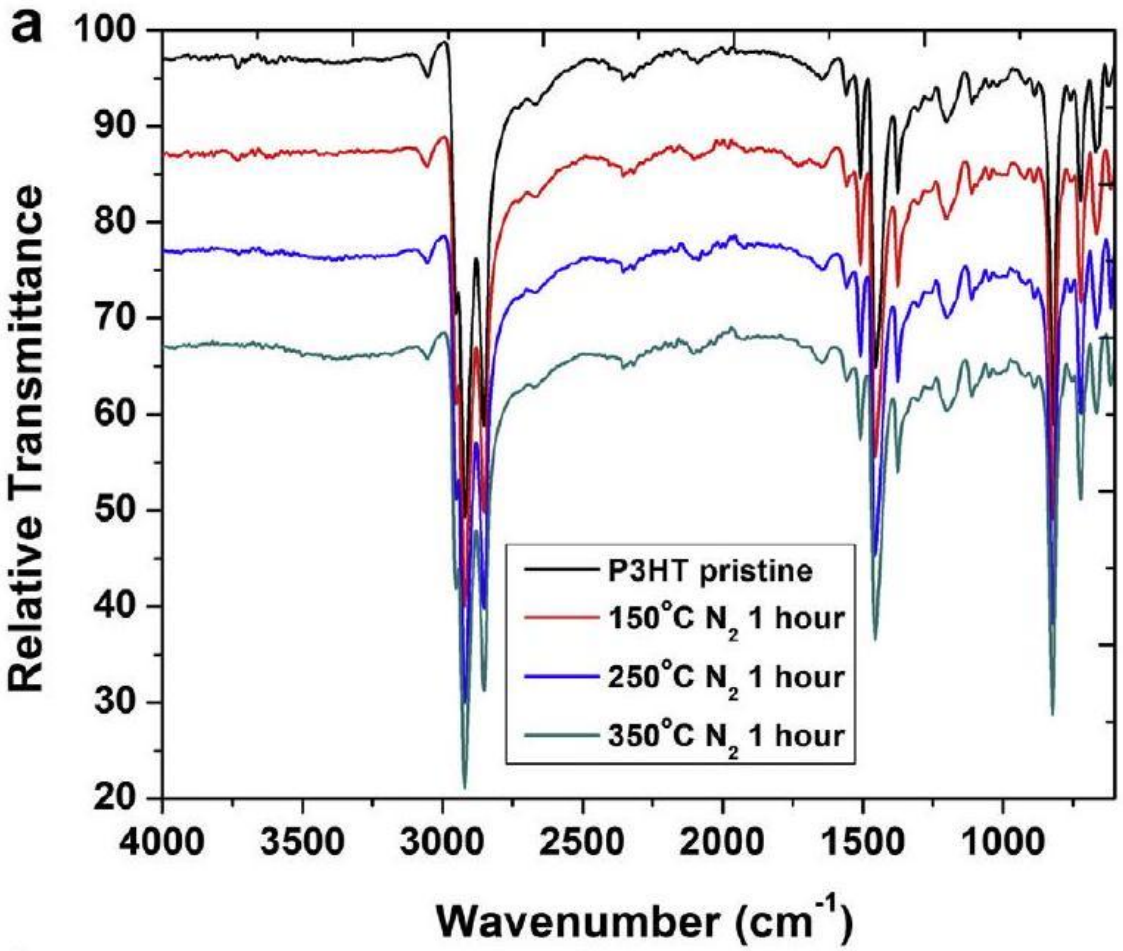

b
249 °C <T< 251 °C
T=250 °C
G' G'' (Pa)
time (s)
Air
N2

Fig. 4. (a) Temperature dependence of the storage (G', empty symbols) and loss (G'', solid symbols) moduli recorded during the heating of P3HT in a normal air atmosphere (squares) or in N_2 atmosphere (triangles); (b) Time evolution of the storage (G', empty symbols) and loss (G'', solid symbols) moduli recorded at $250°C$ right after completing the heating displayed in Figure 3(a): P3HT in a normal air atmosphere (squares) or in N_2 atmosphere (triangles).

conditions. However, during heating in air, the moduli significantly decrease whereas moduli recorded in N_2 show much less temperature dependence up to $220°C$. A melting process characterized by an abrupt drop in both G' and G'' is observed between $220°C$ and $240°C$, where $G' = G''$. Above $240°C$, the behaviour under air significantly contrasts with the behaviour observed in N_2. Both moduli increase with air temperature, whereas G' and G" are independent of the temperature up to $250°C$, with the viscous component remaining larger than the elastic component, thus suggesting that P 3 HT is a liquid at this temperature and frequency. The time sweeps performed at $250°C$ are displayed in Fig. 4(b). Immediately after reaching $250°C$, G' and G" steadily increase with time in air. In contrast to this, the moduli recorded in N_2 atmosphere show a plateau after 200 seconds, the time needed for the temperature to stabilize at $250°C$. Note that the P3HT in N_2 still shows viscous behaviour at that time (G'' is larger than G'), whereas in air,


a
Relative Transmittance
100
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
P3HT pristine
150°C N2 1 hour
250°C N2 1 hour
350°C N2 1 hour

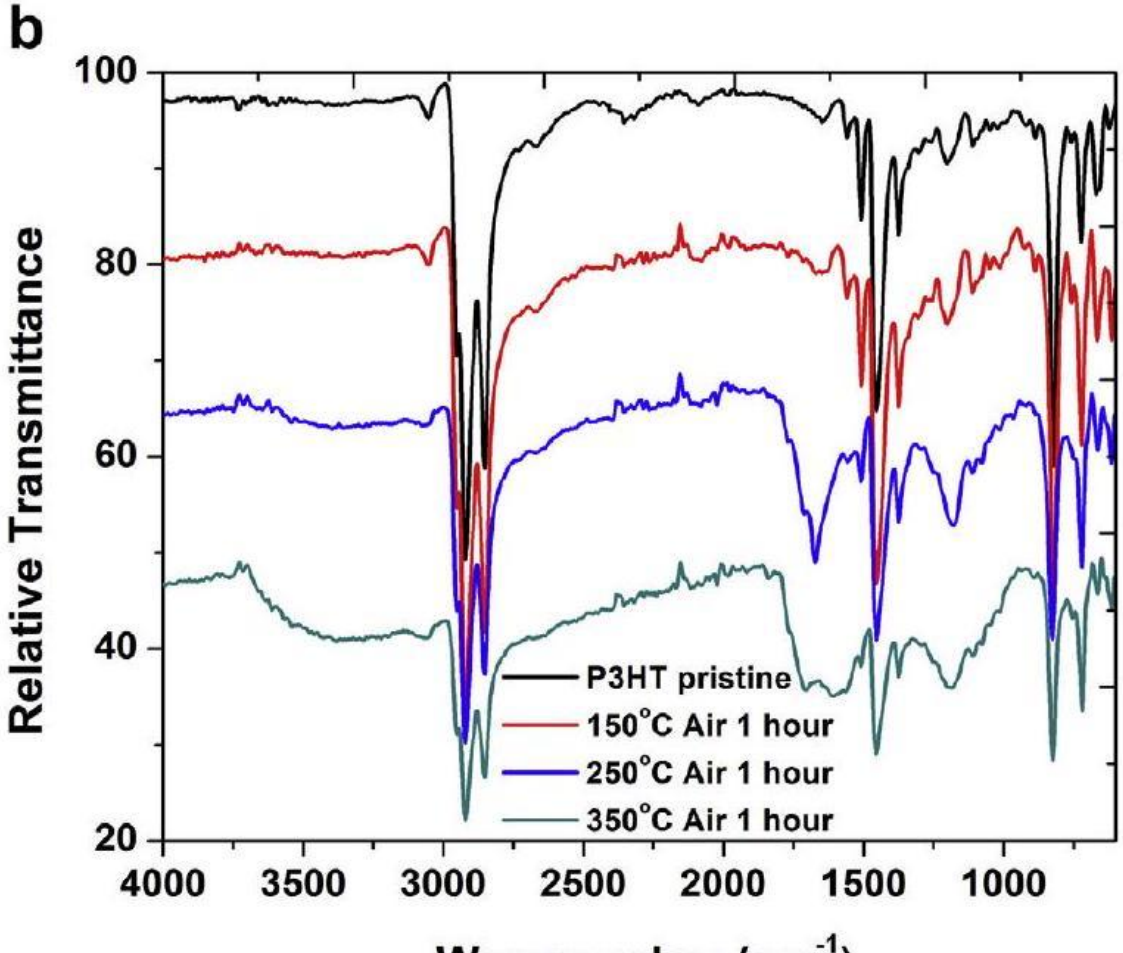

b
Relative Transmittance
100
80
60
40
20
4000
3500
3000
2500
2000
1500
1000
P3HT pristine
150°C Air 1 hour
250°C Air 1 hour
350°C Air 1 hour

Fig. 5. FTIR-ATR spectra of samples thermally annealed in the following conditions: (a) N_2 atmosphere for 1 hour; (b) Air atmosphere for 1 hour. Spectra have been shifted vertically for clarity. Only the spectra of the top sides of the samples are shown.

Table 1
Main infrared spectral bands of our pristine P3HT compared with previous reports: (a) from Ref. [19]; (b) from Ref. [28].

	Previous reports	Current work
Assignment	$\nu(\ cm^{-1})$	$\nu(cm^{-1})$
$=C-H$ stretching	3055 [a,b]	3054
CH_3 asymmetric stretching	2954 [a]	2952
CH_2 asymmetric stretching	2924 [a,b]	2921
CH_2 symmetric stretching	2852b, 2855 [a]	2852
$C=C$ stretching	1510 [a], 1511 [b]	1509
CH_2 bending (scissoring mode)	1454 [a]	1454
CH_3 symmetric bending	1377 [a], 1378 [b]	1375
$=C-H$ bending	820 [a], 822[b]	822
$(CH_2)_n$ in-phase rocking	725 [a]	723

P3HT turned into a more elastic solid at a short time. Beyond 10 minutes, P3HT moduli start to increase in N_2 atmosphere with time, which suggests that some thermal degradation might also be occurring. Thus, these results suggest that P3HT degradation under N_2 at $250\ ^{\circ}C$ is delayed by nearly 10 minutes and that degradation relates to an increase in P3HT elasticity. Chemical crosslinking between P3HT chains could eventually explain the change from viscous to elastic behaviour.

FTIR-ATR

Fig. 5 shows the FTIR-ATR spectra of P3HT after thermal treatments of 1 hour in nitrogen (a) and in air atmosphere (b). For comparison, the FTIR-ATR spectrum of pristine P3HT is also included in both Figures and all the FTIR spectra were shifted vertically for clarity. In Table 1, the main infrared spectral features of our pristine P3HT are identified and compared with other spectral assignments previously reported [19]. There is an excellent agreement between our results and previous reports with the FTIR spectrum of our pristine P3HT showing the main essential spectral features of P3HT.

From the results shown in Fig. 5(a) it can be observed that after 1 hour at $350^{\circ}C$ under nitrogen no noticeable changes in the FTIR spectra of the samples are observed, the same obviously happening for lower temperatures.

As shown in Fig. 5(b), under a normal air atmosphere, the spectra of a P 3 HT sample annealed at 150°C for 1 hour has no noticeable differences from the spectra of pristine P3HT. However, when the annealing in air is performed at temperatures of 250°C and 350°C very significant changes, indicative of substantial chemical degradation, can be observed after 1 hour. Annealing in air at 250°C and 350°C leads to a substantial decrease in the intensity of the absorption bands at 2921,2852 and also at 1454 cm^{-1}, characteristic of the hexyl side chains, which strongly suggests that under such experimental conditions hexyl side chains start to detach from the thiophene rings and eventually volatilize. This explanation is consistent with the substantial mass losses observed at 250°C and 350°C in air (as illustrated in Fig. 3). At the same time, the spectra of samples annealed at 250 and 350°C show a progressive decrease in the intensity of the bands characteristic of the thiophene rings (namely the bands at 820, 1510 and 3054 cm^{-1}), and also the appearance of new large intense bands in the carbonyl region ($\sim 1700 - 1800\ cm^{-1}$). In the FTIR spectra of samples thermally treated for 1 hour at 350°C in air the appearance of a very characteristic broad band is also clearly visible at $\sim 3400\ cm^{-1}$, due to $O - H$ stretching, which can be attributed to the formation of -OH groups as a result of oxidation.

In the case of samples annealed in air at 250 and 350°C, i.e. above the melting temperature of P 3 HT , it is worth mentioning that considerable differences are usually observed between the FTIR spectra of the two sides of a sample: the bottom side being much less degraded then the top side. This occurs because, above its melting temperature, the P3HT flows and accommodates to the TGA metallic pan with the top side staying in direct contact with the oxidizing air atmosphere and the bottom side staying in direct contact with the inert metallic pan, therefore remaining to some extent protected from the direct contact with air. For this reason, in Fig. 5(b) we have just included the spectra of the most degraded sides (the top side).

In the case of samples annealed in nitrogen, no differences can be observed between the top and bottom sides as all the FTIR spectra are similar to the spectra of pristine P3HT.

The FTIR-ATR spectra of samples after annealing just for 10 minutes in air (not shown) reveal that after just 10 minutes in air at 250 and 350 °C, the extent of chemical degradation is already comparable to the degradation observed under the same conditions after 1 hour. This observation is not surprising considering that FTIR-ATR just analyzes the surface of the sample. Therefore, these results show that at 250 and 350°C in air atmosphere the degradation of the polymer that is in direct contact with the air is relatively rapid.

Solubility tests

The results obtained in the solubility tests are summarized in Table 2. P3HT samples subjected to thermal

Table 2
Solubility behavior of pre-annealed P3HT samples in 1,2-dichlorobenzene and in chloroform.

Temperature (°C)	Time (minutes)	Air	N_2

150°C	10 60	Dissolves completely, in chloroform and 1,2-dichlorobenzene, after a few minutes of sonication at room temperature	
250°C	10 60	Remains partially insoluble, in chloroform and 1,2-dichlorobenzene, after several hours of sonication at high temperature (> 80°C)	Dissolves completely, in chloroform and 1,2-dichlorobenzene, after a few minutes of sonication at room temperature
350°C	10	Remains partially insoluble, in chloroform and 1,2-dichlorobenzene, after several hours of sonication at high temperature (> 80°C)	

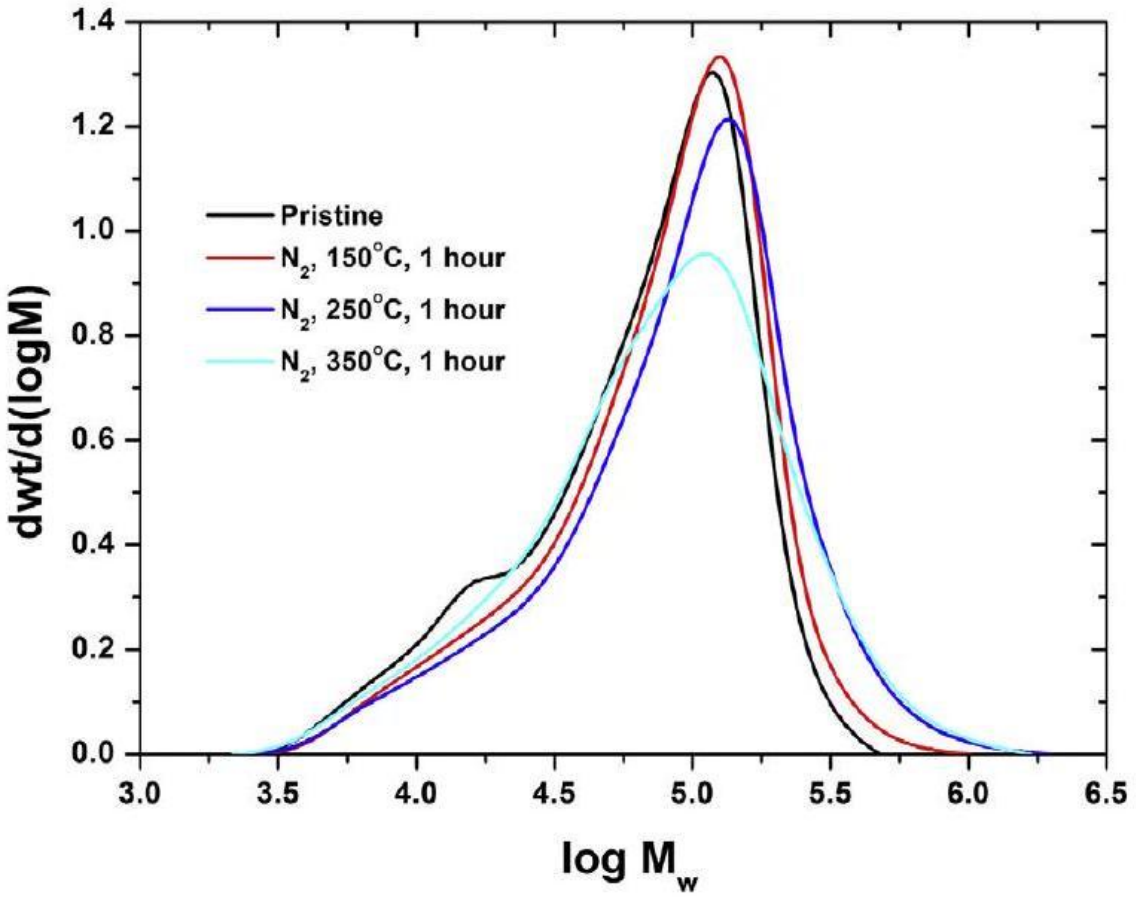


Fig. 6. Gel Permeation Chromatography (GPC) of pristine P3HT and of P3HT previously annealed for 1 hour in N_2 atmosphere at 150,250 and 350 °C. All these samples were fully soluble in chloroform.

treatments in an N_2 atmosphere for up to 350°C for 1 hour, always remain completely soluble both in 1,2dichlorobenzene and in chloroform. However, when the P3HT samples are heated under identical conditions but in the presence of a normal air atmosphere, a different solubility behavior is observed. In this case, although the samples annealed for 10 and 60 minutes at 150°C still remain fully soluble (both in 1,2-dichlorobenzene and in chloroform),
those samples annealed for 10 or more minutes at temperatures of 250°C or higher in air were rendered partially insoluble in both solvents. However, and contrary to previous reports [16] on the crosslinking of P3HT upon oxidation, we find that in our samples the insoluble part does not swell or jellify when immersed in the solvent.

Gel permeation chromatography

GPC experiments were performed to detect the eventual occurrence of chain scission or branching/cross-linking upon annealing. Fig. 6 presents the GPC results of pristine P3HT (Mw = 65500) and of P3HT previously annealed for 1 hour in nitrogen at 150,250 and 350°C. Based on these results, and on the fact that P 3 HT annealed in nitrogen remains completely soluble, the broadening of the molecular mass distribution to higher molar mass can be attributed to branching.

GPC results of the soluble fraction of the samples annealed in air (not shown), evidence a reduction in the polymer molecular mass only for the sample treated in the most extreme conditions (1 hour at 350°C in air atmosphere), which can be associated with chain scission.

Solution ^1H-NMR

The ^{1}H-NMR spectra of the samples subjected to 60 minutes of isothermal treatments at 150,250 and 350°C in N_2 atmosphere are shown in Fig. 7. The spectrum of P3HT pristine is also shown for comparison and is in excellent agreement with previous reports [31]. In agreement with

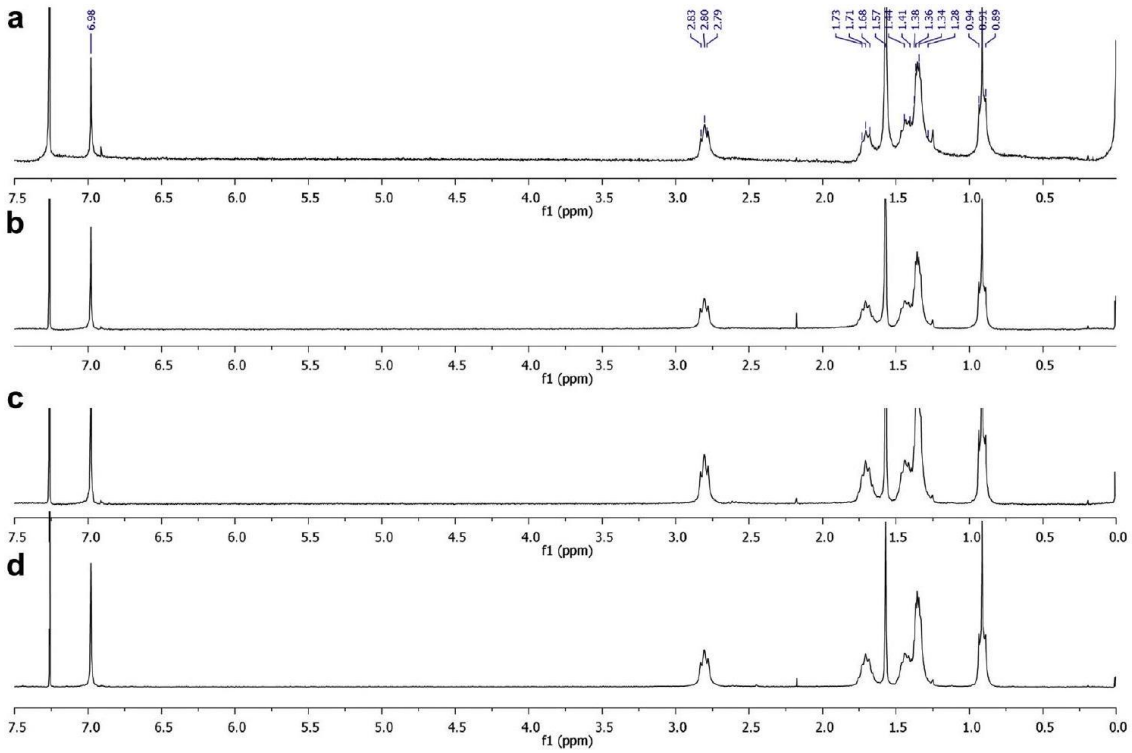


Fig. 7. ^{1}H-NMR spectra of P 3 HT in $CDCl_3$ after 1 hour of thermal treatment under N_2 atmosphere at: a) rt ; b) 150°C; c) 250°C; d) 350°C. All these P 3 HT samples were fully soluble in chloroform (as shown in Table 2).
the FTIR-ATR results, the ^{1}H-NMR spectra in CDCl 3 of the samples treated under nitrogen did not show any differences compared to the pristine P3HT. Looking at the integral of the signal at δ6.98ppm, corresponding to the proton resonance of the thiophene ring, and for example the one at δ0.91ppm, corresponding to resonance of the CH_3 group of the hexyl chains, no differences are observed between samples.

UV-Vis and Fluorescence spectroscopy

UV-vis absorption and emission spectra of pure P3HT as well as P3HT samples subjected to 60 minutes of isothermal treatments at 250°C and 350°C in N_2 atmosphere were recorded in 1,2-dichlorobenzene solution. The results are presented in Fig. 8. As can be seen from the UV-vis absorption and emission spectra, all the samples have the peak absorption and emission maxima at the same wavelengths, which are respectively 462 (absorption) and 583 nm (emission). This is a clear indication that the solubilized samples are essentially the same. These results are in accordance with previously reported data for the pure P3HT using the same solvent [31,32].

P3HT:PCBM blends

Fig. 9 displays the thermogravimetric results, with heating rate 10°C/min, both in nitrogen (Fig. 9(a)) and in air (Fig. 9(b)) obtained for mixtures of P3HT (Mw = 65.500) and PCBM prepared by solvent casting and with weight ratios 80:20; 60:40; 40:60 and 20:80.

The derivative thermogravimetry (DTG) data of the derivative mass of P3HT:PCBM mixtures in both nitrogen and air are shown in Fig. 10.

As shown in Figs. 9(a) and 10(a), in a nitrogen atmosphere pure P3HT starts decomposing at ca. 440°C and the P3HT:PCBM blends with compositions 20:80, 40:60, 60:40

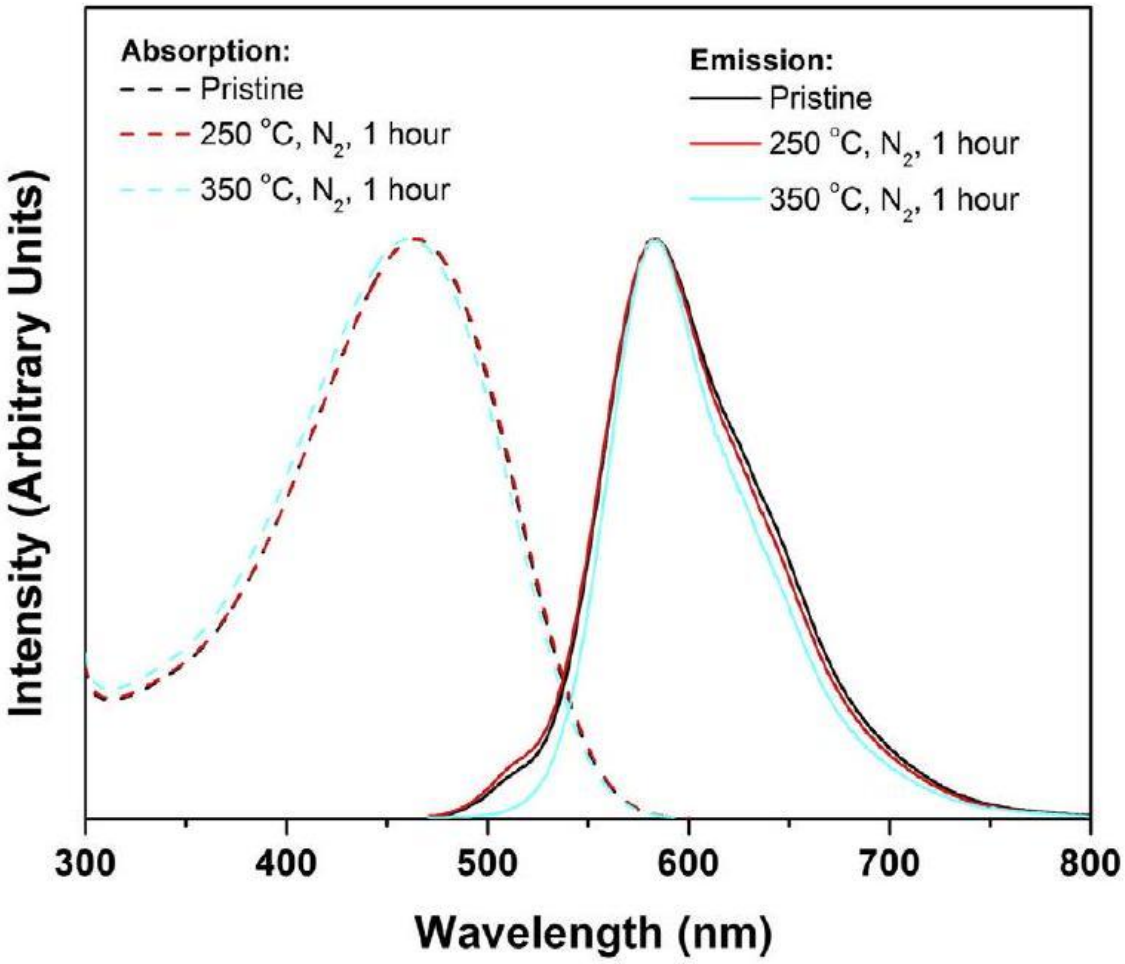
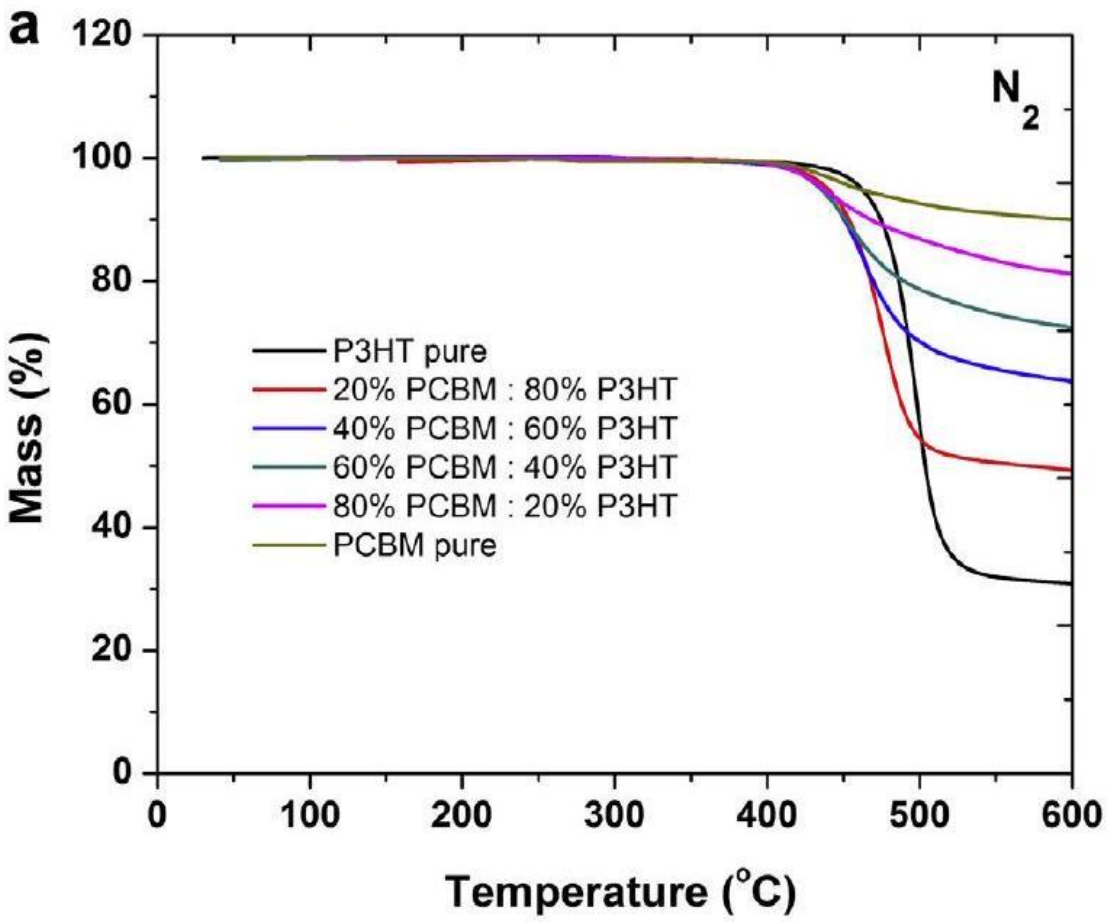


Fig. 8. UV-Vis (absorption) and fluorescence (emission) spectra, in 1,2dichlorobenzene, of samples previously annealed for 60 minutes in nitrogen atmosphere. The spectra of pristine P3HT are shown for comparison. All these P3HT samples were fully soluble in 1,2-dichlorobenzene (as shown in Table 2).
and 80:20 start decomposing sooner at the temperature of ca. 410 °C, i.e. 30 °C lower than the pure P3HT. The maximum rates of degradation for the P3HT:PCBM blends with weight ratios 80: 20,60: 40,40: 60 and 20: 80 are observed respectively at the following approximate temperatures: 476 °C, 462°C, 453°C and 440°C. All these values are lower than the temperature of 498°C observed for the maximum rate of degradation of pure P3HT.

As shown in Figs. 9(b) and 10(b), in air atmosphere the thermal decomposition reactions start in all the systems at a very similar temperature (~ 400°C) suggesting that, in the presence of air and at temperatures ≥ 400°C, PCBM has a negligible effect on the thermal stability of the P3HT:PCBM blends. In order to test the effect of PCBM on the thermal stability of P3HT:PCBM mixtures at temperatures more relevant to polymer melt processing techniques, we have also performed isothermal treatments at 250°C in air atmosphere of a mixture of 60-wt%-P3HT:40-wt %-PCBM being the corresponding curve

of mass loss (%) as a function of time displayed in Fig. 3. As this


a
N2
Mass (%)
Temperature (°C)
P3HT pure
20% PCBM : 80% P3HT
40% PCBM : 60% P3HT
60% PCBM : 40% P3HT
80% PCBM : 20% P3HT
PCBM pure
0
20
40
60
80
100
120
0
100
200
300
400
500
600

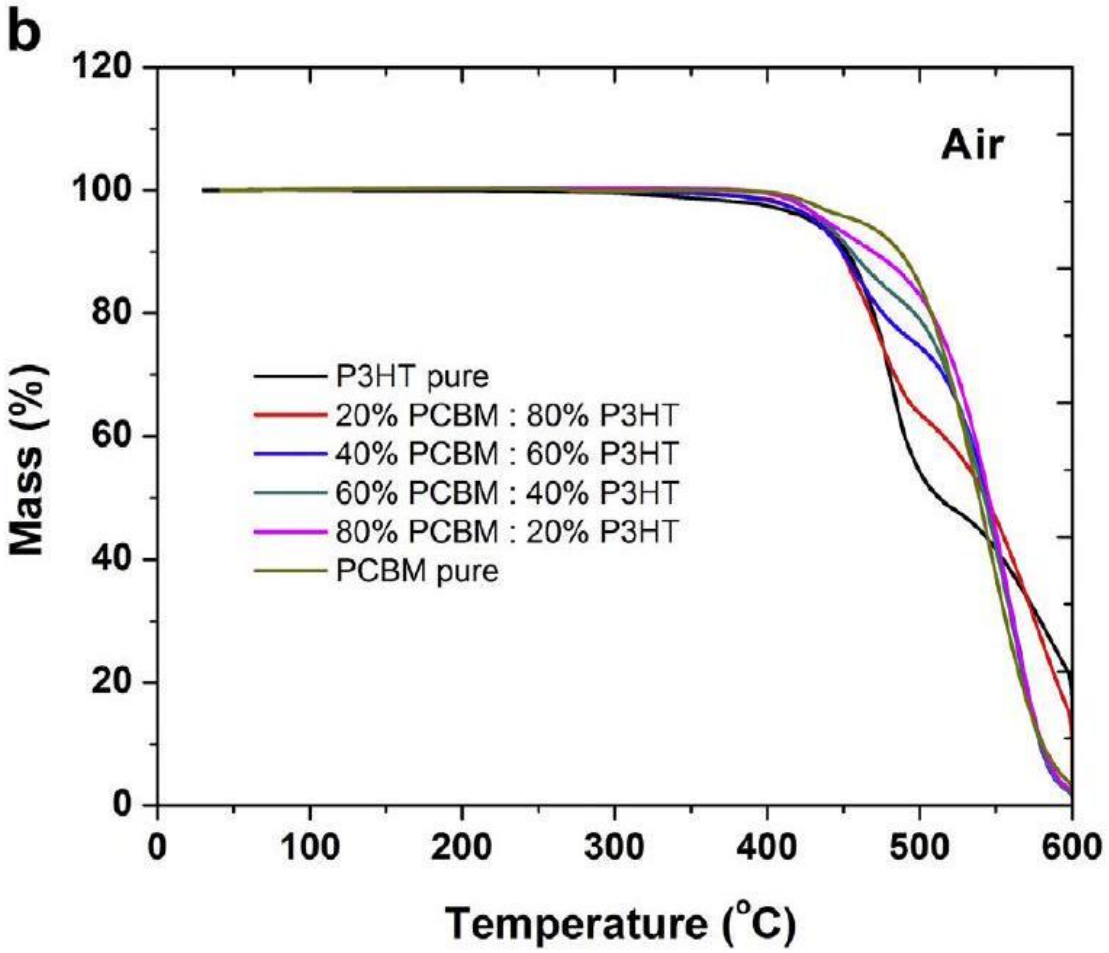
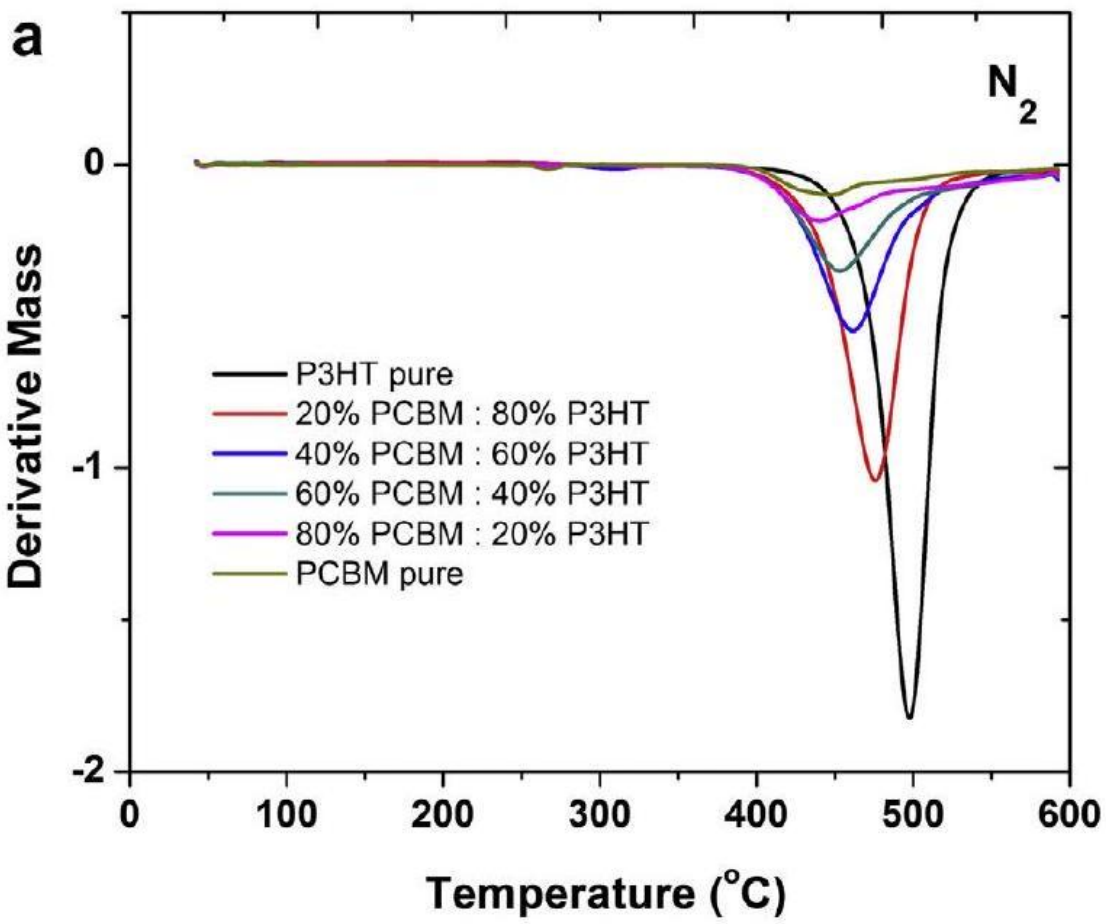

b
Air
Mass (%)
Temperature (°C)
P3HT pure
20% PCBM : 80% P3HT
40% PCBM : 60% P3HT
60% PCBM : 40% P3HT
80% PCBM : 20% P3HT
PCBM pure
0
20
40
60
80
100
120
0
100
200
300
400
500
600

Fig. 9. Thermogravimetric results, with heating rate 10°C/min, for mixtures of P3HT (Mw = 65.500) and PCBM with different weight ratios, prepared by solvent casting, in (a) nitrogen and (b) air medium.


a
N2
0
-1
-2
Derivative Mass
P3HT pure
20% PCBM : 80% P3HT
40% PCBM : 60% P3HT
60% PCBM : 40% P3HT
80% PCBM : 20% P3HT
PCBM pure
0
100
200
300
400
500
600
Temperature (°C)

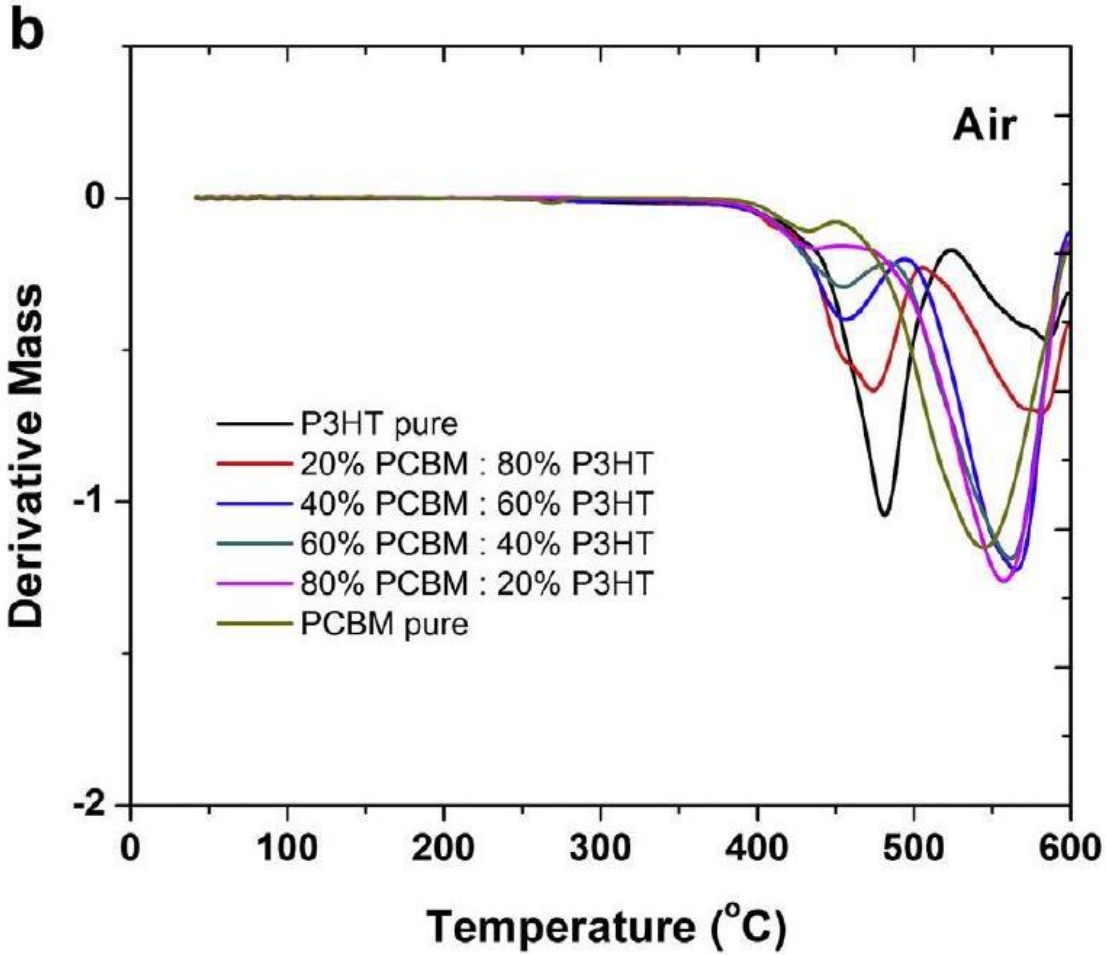

b
Air
0
-1
-2
Derivative Mass
P3HT pure
20% PCBM : 80% P3HT
40% PCBM : 60% P3HT
60% PCBM : 40% P3HT
80% PCBM : 20% P3HT
PCBM pure
0
100
200
300
400
500
600
Temperature (°C)

Fig. 10. Derivative thermogravimetry (DTG) data of the derivative mass of P3HT:PCBM mixtures in: (a) N_2; (b) air.

Figure clearly shows, in air atmosphere at 250°C the total mass loss observed after 1 hour treatment for the mixture is < 0.1% which contrasts with the value of ~ 0.7% observed for the pure P3HT under identical conditions. This clearly shows that, in air atmosphere, PCBM enhances the thermal stability of P3HT.

Conclusions

The thermal stability of P3HT on its molten state has been studied with the aim of assessing the possibility of processing P3HT using polymer melt techniques.

At 150°C, no signs of degradation have been found after 1 hour of annealing in both nitrogen and air atmospheres. However, at 250 and 350°C the behavior observed in nitrogen and air differ completely.

In nitrogen, despite the observation of some minor mass loss after 1 hour of annealing (~ 0.3% at 250°C and 1.6% at 350 °C) no significant differences could be detected through FTIR-ATR, solubility tests, solution ^{1}H-NMR, GPC, UV-Vis and Fluorescence spectroscopy. These results suggest that if some minor degradation really occurs at high temperatures it should be very small and below the detection limits of those techniques.

Conversely, annealing at 250 and 350°C in a normal air atmosphere leads to a rapid degradation of the P3HT, rendering it partially insoluble in chloroform and 1,2dichlorobenzene, after just 10 minutes of annealing. This extensive degradation is clearly visible in FTIR-ATR.

In the present work we have also studied the impact of PCBM on the thermal stability of P3HT:PCBM mixtures at high temperatures, using thermogravimetric analysis. In a nitrogen atmosphere, our results show that, although PCBM seems to have some detrimental effect on the thermal stability of the corresponding P3HT:PCBM blends, this effect occurs only at temperatures > 400°C, i.e. well above the temperatures required for polymer melt processing. On the other hand, in air, although conventional heating ramps suggest that PCBM has a negligible effect on the thermal stability of the corresponding blends, as all of them start degrading at approximately the same temperature as the pure P3HT, isothermal tests at 250 °C clearly show that PCBM enhances the thermal stability of P3HT.

In general, the results obtained in this work suggest that it should be possible to process P3HT at 250°C, i.e. in the molten state, without noticeable degradation as long as the processing is performed in a nitrogen atmosphere and if the residence times are relatively short (preferably < 10 minutes). This will eventually require some re-adaptation of conventional polymer melt processing techniques as these are usually performed in normal air atmosphere.

A more detailed investigation of the effect of PCBM on the thermal stability of P3HT:PCBM mixtures at temperatures relevant to melt processing (~ 250°C), as well as the effect of melting P3HT on the corresponding electrical properties (conductivity and mobility) is currently being undertaken in our group.

As a final observation, it should be mentioned that environments completely depleted from oxygen (oxygen concentrations on the order of a few ppm) can usually only be achieved using the Ultra-High-Vacuum (UHV) techniques normally used in electronics. Therefore, it is very likely that the nitrogen atmospheres used in the present work (either in the TGA or in the rheometer) still contained some traces of oxygen.

Acknowledgements

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