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Thermal analysis of $FeCl_3$-doped poly(3-butylthiophene) and poly(3-dodecylthiophene)

Show-An Chen* and Jui-Ming Ni

Chemical Engineering Department, National Tsing-Hua University, Hsinchu, Taiwan 30043, China

Summary

For neutral and $FeCl_3$-doped poly(3-butylthiophene) (P3BT) and poly(3-dodecylthiophene) (P3DDT), conductivity measurement and thermal analysis are performed. Before doping, the glass transition temperatures (T_g) of the P3BT and P3DDT are 75.4 °C and 5.6 °C respectively. No melting transition of an ordered phase for P3BT is observed. But for P3DDT, the melting temperatures of ordered side chains and main chains are 56.1 °C and 116.3 °C respectively. Upon doping, the T_g's shift upward to 150.5 °C and 51.2 °C for P3BT and P3DDT respectively and the two melting peaks of the ordered phases of P3DDT disappear. The dopant anions decompose in the range of about 150 to 230 °C. The conductivities increase with increasing temperature and reach maxima at 135 °C and 28 °C and drop sharply in the range of 160-200 °C and 130-170 °C for P3BT and P3DDT respectively. This indicates that the thermal motion of the main chains would lead to a drop of conductivity due to thermal undoping, while the dopant decomposition would lead to a rapid loss of conductivity and an occurrence of crosslinking reaction.

Introduction

Polythiophene (PT) is an enviromentally stable conjugated polymer in both neutral form and doped form having conductivity as high as 500 S/cm (1). Introducing a flexible side chain such as alkyl group with carbon number of or more than four on the 3-position of the thiophene ring allows the polymer to become soluble in common organic solvents, fusible and melt processable, yet retains rather high conductivity about 10 to 100 S/cm (2-4). However the doped poly(3-alkylthiophenes) (P3ATs) will be subject to thermal undoping at elevated temperatures. Thus the phenomenon of thermal undoping and characterization of doped P3ATs have been subject to considerably detailed investigations (4-10). Thermal analysis on the doped P3AT that has been reported so far is reviewed below.

The conductivity drop of doped P3AT containing halogenated anions due to standing at elevated temperatures is primarily due to dopant degradation (4-6). For the $FeCl_3$-doped Poly(3-hexylthiophene) (P3HT), Poly(3-decylthiophene) (P3DT) and Poly(3-methylthiophene) (P3MT), it was found that (7,8) after thermal undoping upon heating to 110 °C, the dopant anion $FeCl_4^-$ is converted to $FeCl_2$ and there is no major change of

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*To whom offprint requests should be sent the chemical structure of the polymers. In addition, the P3MT was found to undergo a much slower rate of thermal undoping. A model for explanation of such dependence of thermal undoping rate on alkyl side chain length was then proposed as that: the doped P3ATs undergo a planar to non-planar transformation at elevated temperatures as in the neutral state, which results in an increases of oxidation potential allowing the polymer to reduce to its neutral form and thus reduces the stability of the doped polymer (7). Further studies on the thermal undoping of the $FeCl_3$- and $NOPF_6$- doped P3ATs with the alkyl side chains of C_1, C_4, C_6 and C_8 through analysis of IR spectra and time scans on conductivity at various temperature levels showed that the thermal stability not only depends on the kind of dopant but also on the length of the alkyl side chains (10). It decreases with increasing the length of the side chain, which also supports the model of planar/non-planar transformation mentioned above. In addition, for the $FeCl_3$-doped P3ATs, a thermally activated additional doping was also observed.

In this work, we report the temperature scans of conductivity, thermogravimetric analysis, differential scanning calorimetry and dynamic flexual modulus on the $FeCl_3$-doped poly(3-butylthiophene) (P3BT) and poly(3-dodecylthiophene) (P3DDT) in order to provide better understanding on the structures of the doped polymers and the thermal undoping behavior. These measurements have not been reported in literatures.

Experimental

Neutral P3BT and P3DDT were prepared following the chemical method used by Sugimoto et al (11). 0.1 N 3-alkylthiophene monomer (i.e. butylthiophene and dodecylthiophene) was oxidation-polymerized in 0.4 N $FeCl_3$ solution in chloroform at room temperature under nitrogen atmosphere. The resulting mixture was then poured into methanol for precipitating out the polymer. This polymer was then washed several times with methanol and then extracted with methanol in a Soxhlet extractor in order to remove the residual oxidant and oligomers. The purified polymer was then dissolved in chloroform and subsequently cast in a Teflon mold to give a film, which has a thickness of about 70 microns. The P3AT film, after dynamic vacuum pumping until a constant weight was retained, was then doped in 0.1 M $FeCl_3$ in nitromethane solutions for 2 hr. The doped P3ATs were washed with dry nitromethane and then dried in dynamic vacuum until a constant weight was retained. The doping levels of the doped P3BT and P3DDT were 0.27 and 0.29 by mole respectively as determined by weight uptake.

Sandwich type four-probe method were used to measure the conductivities of the doped P3ATs in the temperature range of -150 °C to 200 °C with the heating rate of about 2 °C/min under a dry nitrogen atmosphere.

Thermogravimetric analyzer (Perkin Elmer Model TGS-2) was used to measure weight loss during the temperature scan from 30 °C to 450 °C with the heating rate of 10 °C/min in a flow of nitrogen purge.

Differential scanning calorimeter (Du Pont Model DSC10) was used to examine thermograms of polymer in the temperature range of -100 °C to 300 °C with the heating rate of 10 °C/min in a flow of nitrogen purge.

Dynamic mechanical analyzer (Du Pont Model DMA983) was used to measure elastic flexual modulus (E') and loss tangent ($\tan\delta$) of the polymer film in the temperature range of -150 °C to 300 °C with the heating rate of 2 °C/min and frequency of 1 Hz. The sample length subject to cyclic flexual motion was about 1 mm.

Results and Discussion

1.Thermogravimetric Analysis (TGA)

% weight loss versus temperature of the neutral and doped P3ATs are shown in Fig.1. As can be seen, the neutral P3ATs are highly thermally stable and the P3BT has a weight loss of 0.5 % higher than the P3DDT at 300 °C. The onsets of decomposition are 410 °C and 414 °C for the neutral P3BT and P3DDT respectively. For the doped P3ATs, a two-stage weight loss is observed. In the first stage, the weight losses of the doped P3BT and doped P3DDT start at 170 °C and 158 °C respectively, much earlier than those of their neutral forms, and have maximum rates at 212 °C and 198.8 °C, and the total weight losses of 10.8 % and 7.9 % counted at the end temperature 292 °C and 234 °C respectively. The onset temperatures of decomposition in the second stage are 403.8 °C and 398.2 °C close to that of their neutral forms (410 °C and 414 °C) respectively. Thus the weight loss in the first stage can be attributed to the decomposition of dopant anions. If all the dopant anions are assumed to be $FeCl_4^-$ and docomposed to become $FeCl_2$ completely in the first stage, the estimated weight uptakes are 30.2 % and 22.07 % by weight for the P3BT and P3DDT, rather close to the actual values of the weight

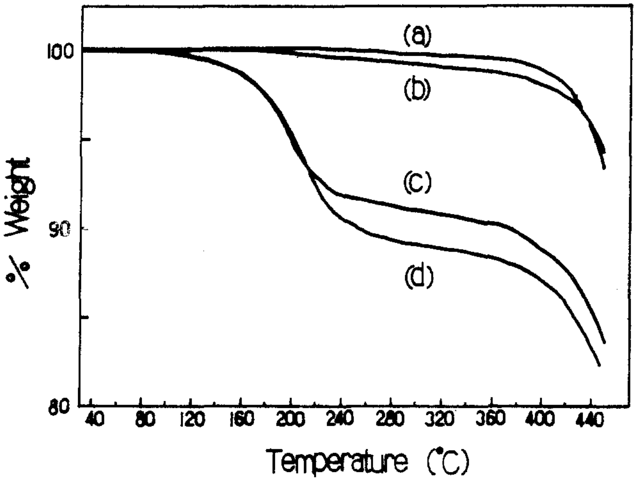

Figure 1. TGA curves of the polymers: (a) neutral P3DDT; (b) neutral P3BT; (c) doped P3DDT and (d) doped P3BT

uptake 27.6 % and 18.4 % respectively. These results are in agreement with the observation by use of XPS as that FeCl$_2$ is generated during this stage (7).

2.Differential Scanning Calorimetry (DSC)

The thermograms of DSC of the neutral and doped P3ATs are shown in Fig.2. As can be seen, the neutral P3BT (curve a) exhibits two endothermic peaks, one at 64.9 °C and the other at 229.2 °C; the former peak can also be characterized by the temperature of maximum rate of heat flow, 58.7 °C. Since the transition temperature at 58.7 °C from DSC is close to the glass transition temperature T$_g$ (75.4 °C) obtained from DMA result as will be stated in the next section, it can be assigned as T$_g$. While the second peak might be attributed to the decomposition of the trace of dopant anions remained in the polymer. The reason is that this peak disappears in the second run and there is about 0.5 % weight loss in this temperature range in the TGA curve. It is hardly to remove the trace impurities remained in the polymer, though the polymer was extracted consecutively with methanol and acetone in a Soxhlet extractor for two weeks. For the neutral P3DDT (curve b), in addition to the presence of T$_g$ (-18.5 °C) and Tm (116.3 °C), an endothermic peak (at 56.1 °C) in advance of the melting peak is observed. The thermogram of the second run also shows a presence of this peak in addition of the melting peak. In conjuntion with the presence of a transition centered at 57.4 °C, which is 51.8 °C higher than T$_g$ in the tanδ curve, and the presence of the second plateaus in the range of 50-70 °C in E' curve of DMA (see next section), this peak can be attributed to a melting of the ordered side chains. The phenomenon of separate meltings of ordered side chains and main chains also occurs in comb-like structure polymers, such as poly(1-alkyl ethylene)s (12), in which the side chains also participate in the formation of crystalline phases together with the main

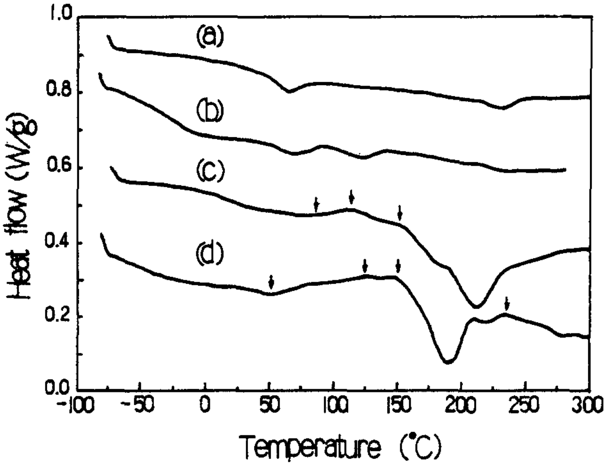

Figure 2. DSC thermograms of the polymers: (a) neutral P3BT; (b) neutral P3DDT; (c) doped P3BT and (d) doped P3DDT

chains when the length of the side chain reaches 10-12 carbons as in the case of the P3DDT. The small melting peak at 116.3 °C is present, even though no or very low crystallinity at and above the room temperature was observed from X-ray diffraction analysis (13). The melting peak might indicate a presence of ordered phase as in the case of ordered hard domains in the polyurethane elastomer in which no crystallinity was observed from X-ray diffraction analysis (14).

For the doped P3BT, an exothermic peak in the range 73 °C to 153 °C with a peak centered at 111.5 °C following with an endothermic peak ranging from 153 °C to 292.3 °C and centered at 212.5 °C are observed. It has been observed from the decrease in intensity of the C-H stretching band (3000-2800 cm^{-1}) that a thermally activated additional doping occurs in the vicinity of 50 °C for the $FeCl_3$-doped P3HT at a doping level of 0.20 (10). Although the additional doping is also an exothermic process, the exothermic peak centered at 111.5 °C is much higher than 50 °C and can not be assigned to an occurrence of the additional doping. A possible assignment for the exothermic peak is the aggregation of the dopant. While the temperature of the endothermic is rather close to the temperature of maximum rate of weight loss and thus this peak can be assigned to the conversion of $FeCl_4^-$ to $FeCl_2$ and chlorine gas. The evolution of chlorine gas could be responsible for the weight loss in the first stage. For the doped P3DDT, the melting peaks of side chains and main chains disappear, but an exothermic peak centered at 124.0 °C in the range 51 °C to 150 °C (due to the aggregation of the dopants), following with an endothermic peak ranging from 150 °C to 234.6 °C and centered at 190.4 °C (due to the decomposition of the dopants) are generated.

3.Dynamic Mechanical Analysis (DMA)

Elastic flexual modulus E' and loss tangent (Tanδ) from DMA of the neutral and doped P3ATs are shown in Fig.3. As can be seen, each neutral P3AT exhibits three transitions, being γ, β and α transitions of the disordered phase resulting from the relaxations of methylene linkages, side chains, and disordered subchains respectively as demonstrated below. The γ transitions of the P3ATs all have a peak with significant size at the temperature below -150 °C and can be assigned as a relaxation of methylene linkages of the side chains. The reason is that: relaxation of the methylene linkages in polyethers usually occurs at about -130 °C (14) and in comb-like structure polymers with alkyl side chain (e.g. poly(n-alkyl methacrylate)s) below -150 °C (15). For the α transition, E' drops by a factor of 10^2, same as that in the glass transition of conventional amorphous or partially crystalline polymers. Thus, the α relaxation can be regarded as the glass transition of the disordered phase. While the β transition lying in between the γ and α transitions must be due to a relaxation of the side chains.

For the neutral P3BT, the β transition seems occuring from about -75 °C to 20 °C and has no observable peak, indicating that thermal motion of the shorter side chain is coupled with thermal motion of the attached thiophene ring. The α transition peak is at 75.4 °C (T_g). In the glassy region, tanδ is lower than those of P3DDT, reflecting a lower extent of relaxation effect during this temperature range; while E' in this temperature period remains a rather constant level. These results imply that the β transition probably does not occur.

For the neutral P3DDT, the β relaxation peak presents as a shoulder at -37.4 °C and is followed immediately with the α relaxation peak, indicating that the α transition starts before the completion of the β transition. In other words, the effect of thermal motion of the side chains on the thermal motion of the disordered subchains is higher than that of P3BT due to the longer side chain. While the T_α (5.6 °C) is lower than that of P3BT (75.4 °C), which can be attributed to the higher free volume provided by a plasticization effect of the longer alkyl side chains in the disordered phase, since at that temperature the side chains are relaxed. As temperature further increases, tanδ curve shows a maximum at 57.4 °C, which can be assigned as the melting temperature of the ordered alkyl side chains in the ordered phase, since the E' in the vicinity of this temperature presents as a plateau.

Upon doping, the α transition of the doped P3BT shifts to 150.5 °C and the original α transition disappears. The

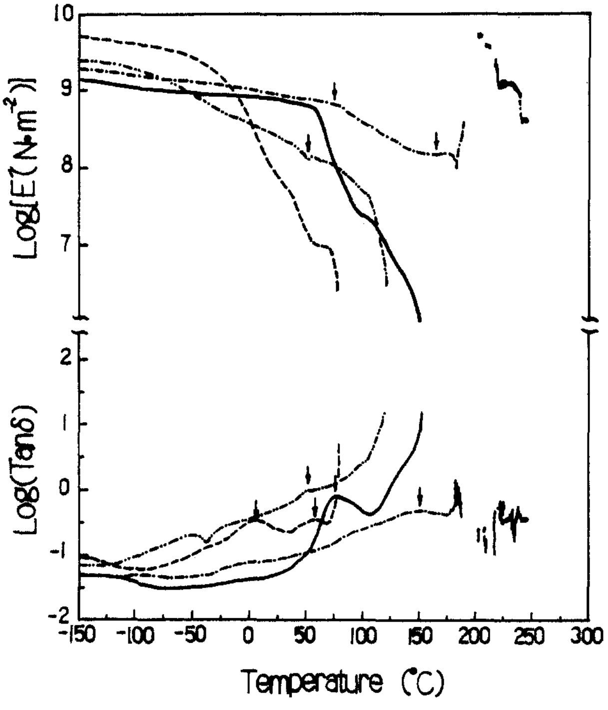

Figure 3. Dynamic mechanical measurements on the polymers: (——) neutral P3BT, (—·—) neutral P3DDT, (– – –) doped P3BT, (—··—) doped P3DDT

increase in T_g after doping is resulted from the conversion of aromatic rings to more rigid quinoid rings in the subchains and the coulombic interaction between two neighboring subchains with the counter anion as the bridge. As the temperature is higher than the T_g (150.5 °C), E' levels off in between 164 °C and 177 °C and then raises sharply. This result would strongly indicate that crosslinking reaction occurs mainly in the temperature range of dopant decomposition. Such crosslinking has also been observed by one of us (16) in the cis-trans polyacetylene when exposed to air at 90 °C as also detected by use of DMA. The drops of E' from 74 °C to the T_g (150.5 °C) might reflect an occurrence of the change in chain conformation from the more rigid subchain in quinoid form to the more flexible distorted subchain.

For the doped P3DDT, a broad and poor resolved transition around 51.2 °C and a significant transition at about -48.2 °C in the tanδ curve are observed. According to the drops of E', the transition around 51.2 °C in tanδ can be regarded as the T_g of the doped P3DDT. While the transition temperature at -48.2 °C is lower than the temperature of the β transition -37.4 °C before doping; this result would explain that the ordered side chains are disturbed upon doping. Unlike the doped P3BT, the E' value has no sharp increase as temperature raises above T_g, indicating that crosslinking reaction might not occur or occur only in an insignificant extent. This result also confirms that crosslinking reaction is resulted from the dopant decomposition, since dopant decomposition occurs insignificantly below 120 °C.

4. Conductivity

Conductivity versus temperature of the doped P3BT and P3DDT are shown in Fig.4. For the doped P3BT, the conductivity

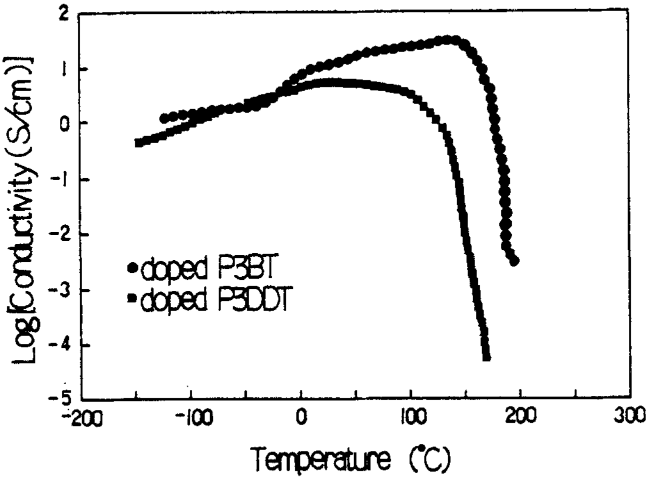

Figure 4. Logarithmic conductivity versus temperature of the doped P3BT and P3DDT

increases with temperature linearly up to about 135 °C except around -25 °C to 0 °C where the conductivity exhibit a jump of about one half of order, then decreases more rapidly down to 162.7 °C and finaly very sharply to 200 °C. While the conductivity of the doped P3DDT, however, increases almost linearly with temperature and reach a maximum at 28 °C much lower temperature than that of the doped P3BT (135 °C); after this maximum, it decreases slowly down to 99.9 °C and then more rapidly down to 132.9 °C and finaly very sharply to about 170 °C. The switching in conductivity from increase to decrease can be attributed to the α relaxation of the main chains. Such thermal motion of the main chain can lead to an irreversible thermal undoping as evidenced by the decrease in the absorption intensity related to mid-gap transition and the increase in the absorption intensity of π-π^* transition after heating at 80 °C and 120 °C from the UV-VIS spectroscopic observation for $FeCl_3$-doped P3HT (10). While the rapid drop in conductivity can be attributed to dopant decomposition.

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