Electrically conducting copolymers from 3-octylthiophene and 3-methylthiophene

Qibing Pei* and Olle Inganäs
Laboratory of Applied Physics, Department of Physics, Linköping University, S-581 83, Linköping, Sweden

and Jan-Eric Österholm and Jukka Laakso
Neste Oy Research Center, Kulloo, SF-06850, Finland

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Poly(3-octylthiophene-*co*-3-methylthiophene) (POTMT), with a molar ratio of 3-octylthiophene/3-methylthiophene (OT/MT) of 1/2.5, has been prepared by electrochemical polymerization and subsequent reduction. POTMT is soluble in chloroform and fusible. Upon doping, either chemically with $FeCl_3$ or electrochemically, this copolymer becomes conducting. Stability of doped POTMT has been significantly improved compared to poly(3-octylthiophene). Solvatochromism, thermochromism, thermal undoping, and charging–discharging degradation are appreciably suppressed in this copolymer. The effects of dopant size and OT/MT ratio have been investigated, and a free volume mechanism is highlighted to interpret these stability modifications. It is suggested that stable, processible conjugated polymers can be obtained by attaching flexible side chains to separated mers along the conjugated backbone.

(Keywords: 3-alkylthiophene copolymers; stable processible conducting polymers; thermal undoping)

INTRODUCTION

Polythiophene (PT) and poly(3-methylthiophene) (P3MT) are conducting polymers which have been the subject of extensive investigation due to their high conductivity and stability[1]. These polymers are, however, insoluble and infusible and therefore non-processible. It has been found that poly(3-alkylthiophene)s (P3ATs) with long flexible alkyl chains attached onto the 3-positions of the thiophene rings are soluble in common organic solvents and in some cases fusible[2–4]. This discovery caused a flurry of research activity as it opened the way to more complete characterization of conducting polymers and towards their commercial application. The addition of long alkyl side chains not only renders the conjugated polymer main chains soluble and fusible, but also results in such associated phenomena as thermochromism and solvatochromism occurring in the undoped polymers[5–7]. The driving force behind the chromism is believed to be the distortion or twist along the conjugated polymer main chains caused by the steric interaction between the bulky side chains during thermal excitation or in good solvents[5–12]. Conductivity in doped P3ATs can reach as high as $10\,S\,cm^{-1}$. Unfortunately, all P3ATs doped either chemically or electrochemically are unstable, especially at elevated temperatures[13–15], while doped PT and P3MT appear remarkably stable[13,16,17]. The instability of P3AT increases with increasing length of the side chains[15]. The conductivity of thin doped P3AT films decreases by several orders of magnitude in 1 h at 110°C in laboratory air[13]. *In situ* optical absorption, i.r. and X-ray photoemission spectra, etc., all indicate that the thermal treatment has an effect on the behaviour of doped P3ATs similar to chemical undoping. This 'thermal undoping' was suggested to be due to the side chain geometry and dynamics[13,18]. Distortion of the conjugated main chains and the ejection of the dopant anions by the thermally excited side groups causes thermal undoping, a mechanism similar to that driving the thermochromism in neutral P3ATs[15,18]. Other interpretations have also been advocated[19]. However, whatever happens during the thermal undoping, the instability of conducting P3ATs is an intrinsic property of the polymers themselves, limiting their attraction as processible conducting polymers of practical interest. Other processible conducting polymers have been prepared which usually contain long side groups in order to achieve processibility[20,21]. Some of them are inevitably unstable, probably due to the attached long side groups.

We believe that if the conformational change due to steric interactions between side chains (free volume mechanism) is the major driving force of thermal undoping, then it may be avoided or suppressed when the 3-alkylthiophene rings are diluted by inserting thiophene or other appropriate rings without bulky side groups. In such systems the interaction between long alkyl side chains will be much weaker and room can be left to accommodate the dopants. Thus copolymers of poly(3-octylthiophene) and 3-methylthiophene (POTMT) have been prepared to test this theory and to explore stable processible conducting polymers. Similar copolymers have been mentioned in the literature[3,4,22–24] without attention to stability improvement in the copolymers. We found[25] that POTMT with appropriate molar ratio retains the solubility and fusbility of pure P3ATs, but is much more stable in the doped states.

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* To whom correspondence should be addressed

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EXPERIMENTAL

Monomers 3-methylthiophene (MT, Aldrich) and 3-octylthiophene (OT, Neste Oy) were used as received. Polymerization was carried out electrochemically in a standard one-compartment three-electrode cell with a Pt foil working electrode (1 cm × 1 cm), Pt wire counter electrode and an Ag/AgCl reference electrode. The electrolyte solution contained 0.1 M OT, 0.2 M MT, and 0.1 M $LiClO_4$ in acetonitrile. It was purged with argon before electrolysis. Constant potential at 2.0 V was applied, with current density during polymerization typically from 2.0 to 5.0 mA cm^{-2}. A rather high voltage was employed to avoid the potential difference of the onset of polymerization between the two monomers. The same technique was employed to electropolymerize OT and was not significantly different to the technique of Hotta[23]. The resulting random copolymer was reduced electrochemically at -0.50 V *versus* Ag/AgCl in 0.1 M $LiClO_4$ solution in acetonitrile. Around 0.20 C charges were consumed for the reduction corresponding to 1.6 C of charges consumed during electropolymerization. Charge density (y) in the doped copolymer as-prepared can be estimated to be 0.3 charge per mer unit, assuming that $(2+y)$ charges were needed to polymerize and charge each mer. The neutral copolymer (POTMT) as-prepared was rinsed with acetonitrile and dried in laboratory air and then dissolved in chloroform. The insoluble residue was removed by filtering.

POTMT films ($\sim 0.2\,\mu m$ thick) were prepared for the following studies by solution casting from a chloroform solution onto a quartz or indium–tin oxide (ITO)-coated glass substrate. The films were doped chemically in 0.1 M $FeCl_3 \cdot 6H_2O$ in acetonitrile or electrochemically in 0.1 M $LiClO_4$, p-toluenesulphonic acid or dodecylbenzenesulphonic acid in acetonitrile at 1.2 V *versus* Ag/AgCl. They were then washed with acetonitrile and dried in vacuum at room temperature.

A BAS-1000 electroanalytical system with an electrochemical cell described above was used for sample preparation, electrochemical doping and cyclic voltammetry. Optical characterization of thermochromism and thermal undoping was done using a Perkin-Elmer Lambda 9 u.v./vis/near i.r. spectrophotometer. The sample films on either glass or ITO glass substrate were inserted into a copper block, the temperature of which was controllable. The block was then put in a small vacuum jar. This jar was connected to a dynamic pump and placed across the beam pathway of the spectrometer.

An Olympus BH-2 polarizing microscope was used to observe the colour change and melting of POTMT films during heating. A Mettler FP82 HT hot stage was mounted on the objective stage of the microscope for regular heating. The sample was inserted into the hot stage (exposed to laboratory air) and heated at a rate of 10°C min^{-1}. To obtain stability data of conductivity, POTMT films were cast onto a glass substrate with an evaporated four-probe gold pattern. After doping, the samples were mounted onto a sample holder, the temperature of which could be controlled. The conductivity decay at 110°C in laboratory air was taken by measuring the change of the four-probe resistance.

RESULTS AND DISCUSSION

Chemical structure of POTMT

The ^1H n.m.r. spectrum of neutral POTMT solution in $CDCl_3$ shows resonances at 0.9, 1.2–1.8, 2–2.6 and around 7 ppm (*Figure 1*). The peaks at 2–2.6 ppm (95.25) can be assigned to aryl methylene in OT units and the methyl group in MT units, and the 0.9 ppm (30.0) to the methyl group in OT units[26]. Then from the resonance intensities, indicated in parentheses, the molar ratio of the copolymer can be roughly estimated to be 1.0/2.5 OT/MT. This ratio is quite close to the monomer composition (1/2) of the solution for preparing the copolymer. It is reasonable to see slightly less OT units in the copolymer as quite a large amount of soluble product was formed during electropolymerization and diffused into the bulk solution, which was due mainly to OT.

Gel permeation chromatography (g.p.c.) with polystyrene standard has recently been shown to give an accurate estimate of the molecular weights of conjugated polymers[27]. G.p.c. analysis of POTMT indicated a number-average molecular weight of 4300 with polystyrene standard, corresponding to an average polymer chain of roughly 10 OT units and 25 MT units. As a

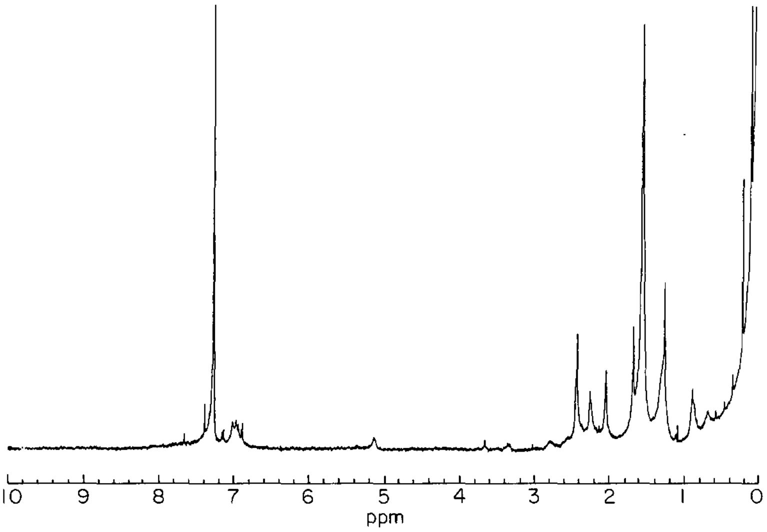

Figure 1 ^1H n.m.r. spectrum of POTMT in $CDCl_3$ solution

comparison, Hoeve *et al.*[28] reported the chemical synthesis of soluble, all α–α' linked undecithiophenes with long alkyl sidechains at the 2nd, 6th and 10th thiophene units, the longest thiophene oligomers ever reported. POTMT chains are much longer than those oligomers but shorter than 3-alkylthiophene homopolymers. It is likely that the higher molecular weight part of the copolymer is no longer soluble and is removed during sample preparation. Results on copolymers with various OT/MT ratios indicate that the higher the ratio, the less insoluble part is found.

Solubility and solvatochromism

Neutral POTMT is readily soluble in chloroform, tetrahydrofuran and toluene. Optical absorption spectra of POTMT solutions also show the presence of solvatochromism, though weaker than that of P3AT. In a chloroform solution, a sharp peak appears at 2.9 eV due to the band gap transition[25], indicative of a random copolymer rather than a block copolymer. For a block copolymer of MT and OT, the two kinds of segment would show different degrees of solvatochromism and result in two peaks or one broad peak on the spectrum. In the block copolymer the MT segments would be rather long considering the molecular composition of the copolymer, their band gap must be much smaller than 2.9 eV. The spectrum for POTMT in a poor solvent, methanol/chloroform (90/10 volume ratio), is close to that in the solid film with a broad peak at around 2.8 eV. In POTMT, the long octyl groups are sparsely separated from each other, and the interaction between those side chains attached to one single conjugated main chain is negligible. There are two possible reasons for the presence of the solvatochromism: one is the interaction between the octyl and methyl side groups, or between the octyl groups and the main chain; the other is the aggregation of the copolymer in a poor solvent and dissociation in a good solvent, since interaction between the conjugated main chains contributes quite a lot to the π-electron extension[29].

After doping either electrochemically or chemically with $FeCl_3$, the copolymer becomes insoluble in common organic solvents.

Fusibility and thermochromism

Figure 2 shows the optical absorption spectrum of a thin POTMT film at different tempertures. The band-gap absorption maximum at 2.65 eV at room temperature undergoes hypsochromic shift continuously with increasing temperature to 2.75 eV at 160°C and to 3.0 eV at 240°C. Significant shift occurs at 160–200°C, higher than the relevant temperatures for the thermochromism in poly(3-octylthiophene) (P3OT). Upon cooling down, the spectrum change reverses. Like the solvatochromism, the origin of the thermochromism in POTMT is probably two-fold: the breaking of the one-dimensional π-electron extension or distortion along the conjugated polythiophene mainchain and the breaking of the three-dimensional π-electron extension. Both processes occur at higher temperatures than in P3ATs as the flexible octyl groups which can be readily thermally excited have been sparsely diluted in the copolymer.

The thermochromism and fusibility of a neutral POTMT film were further studied on a polarizing microscope during regular heating in laboratory air. The pristine film before heating was red–brown (transmission mode), but gradually turned to yellow–brown as the temperature exceeded 130°C, in accordance with thermochromism. Noticeable softening occurred at around 140°C. The copolymer melted in the temperature range 150–160°C. By comparison, OT homopolymer[30] melts at 150°C, while P3MT does not melt at all before it begins to decompose at high temperature. No liquid crystalline phase could be observed under crossed polarizers during the melting process. For a solution-cast neutral P3AT, no liquid crystalline phase appeared either by the same technique. However, in an oligomer of thiophene, α-sexithienyl, a nematic phase appears during melting[31].

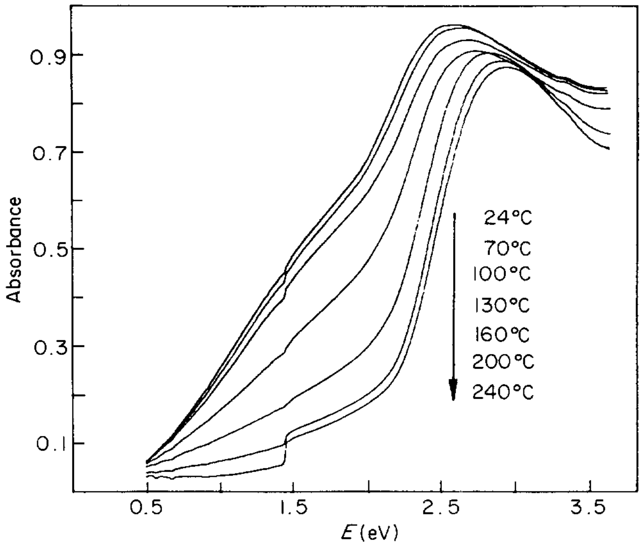

Figure 2 Optical absorption spectra of thin POTMT film at the temperatures indicated. The discontinuity at 1.5 eV is due to light scattering

Neutral POTMT can be melted, cooled and remelted for a few cycles without losing its fusibility. After doping either electrochemically or chemically with $FeCl_3$, however, the polymer ceases to be fusible.

Conductivity and stability of doped films

Chemical doping in 0.1 M $FeCl_3 \cdot 6H_2O$ solution turned a solution-cast POTMT film from red–brown to dark green. Four-probe conductivity of the doped film was 5–10 S cm^{-1}, comparable with doped P3AT films but lower than chemically prepared similar copolymers with higher feed ratio of 3-alkylthiophene to MT[22,32], and much lower than electrochemically as-synthesized P3MT films[3,4,23]. As the quality of the POTMT film was not so good, especially after doping when many small cracks were formed in the film, the real conductivity of the film may be higher than the measured value. The cracking of the film during doping probably indicates doping-induced shrinkage in the film[33]. Doped POTMT is quite stable in air, its conductivity decreased one order of magnitude in 1 h even at 110°C, while that of a doped P3OT film decreased by more than four orders of magnitude[25]. It is interesting to note that upon heating from room temperature to 110°C the conductivity first increased more than two-fold and then started to decrease. The initial conductivity increase with increasing temperature is characteristic of semiconductors.

The stability was also studied by *in situ* optical absorption spectra during heating in dynamic vacuum. At 80°C the spectrum changes little in 1 h. *Figure 3* shows the spectrum evolution at 110°C. Absorption in the near

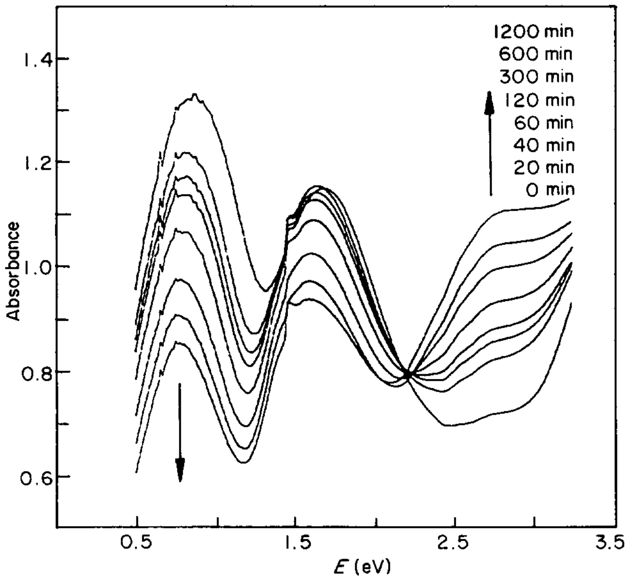

Figure 3 Evolution of the optical absorption spectrum of $FeCl_3$-doped POTMT film heated at 110°C, for the times indicated

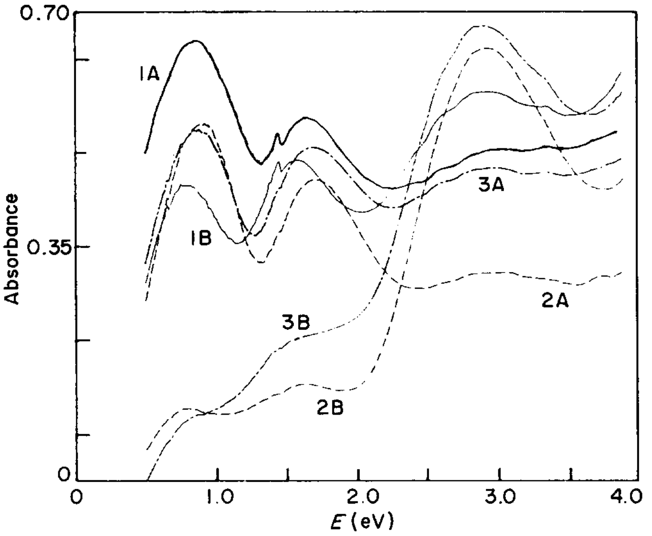

Figure 4 Optical absorption spectra of electrochemically doped POTMT films before heating (A) and after heating at 110°C for 1 h (B). Dopants: 1, ClO_4^-; 2, TsO^-; 3, DBS^-

i.r. region decreases very slowly and absorption in the u.v. region increases very slowly, so that after heating for 20 h the spectrum is still typical of that for a doped conducting polymer. Under such conditions all P3ATs would be completely undoped within 1 h. The stability of doped POTMT is comparable with P3MT[13,14]. This result may mean that the strong side-chain interaction behind the thermal undoping of P3ATs has been essentially suppressed in the copolymer system, supporting the free volume mechanism for interpreting the instability of conducting P3ATs[18].

Investigations were made of the stability of electrochemically doped POTMT films with perchlorate (ClO_4^-), *p*-toluenesulphonate (TsO^-), dodecylbenzenesulphonate (DBS^-) dopants of different sizes, in order to check the effectiveness of the free volume mechanism.

Figure 4 shows the optical spectra of ClO_4^-, TsO^- and DBS^- doped POTMT films before heating and during heating at 110°C in dynamic vacuum for 1 h. It is obvious that all these electrochemically doped films are not as stable as the $FeCl_3{\cdot}6H_2O$ doped film. POTMT(ClO_4^-) retains the general characteristics of conducting polymers after heating, while POTMT(TsO^-) and POTMT(DBS^-) are essentially undoped. *Figure 5* shows the intensity evolution of the near i.r. peak (0.8 eV) during the heating. Since this peak shifts only slightly and the half-peak width changes just a little, *Figure 5* should reflect the depletion of the doped states with heating time. It indicates a faster undoping with dopants of larger size, consistent with the free volume mechanism. A larger dopant is ejected more easily than the smaller one due to thermally induced disorder in the side chains. The effect of OT/MT ratios on the thermal stability of doped POTMT is discussed below.

Electrochemical properties of POTMT

Solution-cast POTMT films (0.2 μm thick) on Pt foil (0.8 cm²) were characterized by cyclic voltammetry between 0 and 1.4 V *versus* Ag/AgCl in an acetonitrile solution containing 0.1 M $LiClO_4$ (*Figure 6*). An anodic peak at ~1.0 V and a cathodic peak at ~0.8 V appear on the voltammograms, similar to the results of Leclerc *et al.*[26] with P3ATs. The very high redox potential indicates that the neutral undoped polymers are very stable and inert to ambient air. The instability of doped P3ATs has often been attributed to the high redox potential of the polymers as they are sensitive to reductants. Even hydrogen evolution from the aryl methylenes on the side chains has been suggested[19] to cause the undoping of P3ATs. The high stability of doped

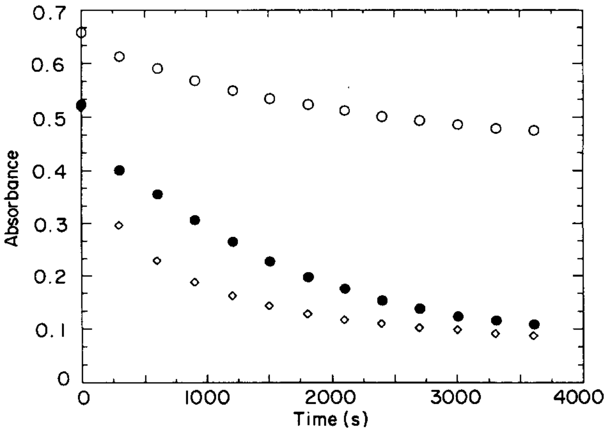

Figure 5 Intensity evolution of the near i.r. peak at 0.8 eV on the optical absorption spectra of electrochemically doped POTMT films during heating at 110°C. Dopants: ○, ClO_4^-; ●, TsO^-; ◇, DBS^-

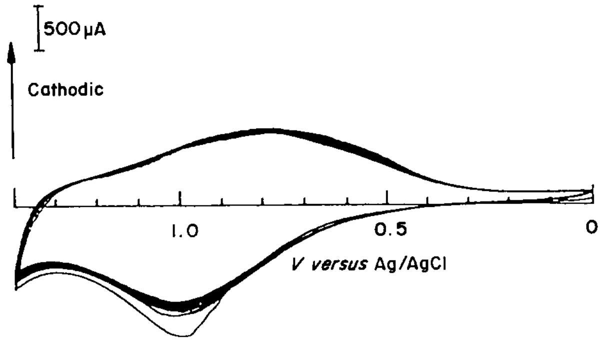

Figure 6 Cyclic voltammograms of POTMT film in 0.1 M $LiClO_4$ solution in acetonitrile. Scanning rate $100\,mV\,s^{-1}$

Table 1 Molar ratios of 3-octylthiophene to 3-methylthiophene units in POTMT copolymers

	Feed ratio of OT/MT	OT/MT ratio found in POTMT
Ot	1:0	1:0
2OT/1MT	2:1	2.31:1
1OT/MT	1:1	0.75:1
1OT/2MT	1:2	0.4:1
MT	0:1	0:1

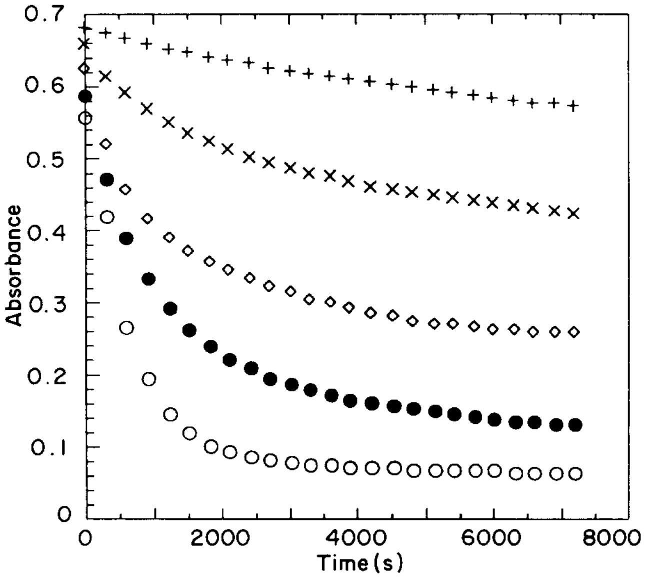

Figure 7 Intensity evolution of the near n.i.r. peak at 0.8 eV on the optical absorption spectra of electrochemically doped POTMT(ClO_4^-) films during heating at 110°C. OT/MT ratios in the copolymers are listed in *Table 1*. ○, OT; ●, 2OT/1MT; ◇, 1OT/1MT; ×, 1OT/2MT; +, MT

POTMT discussed in the preceding section is not, however, in favour of the attribution of undoping to high redox potential. At least it is not the major cause. Thus the free volume mechanism becomes more important.

The redox reversibility of this copolymer is fairly good. Combining the processibility and high stability in both the neutral and doped states, POTMT may find some practical applications which employ the chemical or electrochemical reduction and oxidation for the operation of devices[34].

POTMT films with various OT/MT ratios

POTMT films with various OT/MT ratios were prepared by the same technique described in the Experimental section, but with various feed ratios of the two thiophene monomers. Molar ratios of the two units found in POTMT as determined by ^1H n.m.r. are listed in *Table 1*. In all of the cases the ratios found are close to the feed ratios, indicative of the effectiveness of the present copolymerization technique. We have chosen MT instead of thiophene in preparing the copolymers, in order to avoid the difference in polymerization potentials between the monomers.

Neutral films (about 0.2 μm thickness) of these copolymers were prepared through solution casting except P3MT which was an electropolymerized film with subsequent reduction. Electrochemical doping in 0.1 M $LiClO_4$ solution in acetonitrile at 1.2 V *versus* Ag/AgCl rendered these films conductive. *Figure 7* shows the intensity evolution of the near i.r. peak (0.8 eV) on the optical absorption spectra of the doped films during heating at 110°C in dynamic vacuum. As OT/MT ratio increases, the stability of the doped copolymers decreases rather significantly, in accord with the free volume mechanism. Thus low OT/MT ratio is needed to improve the stability of doped alkylthiophene copolymers, whereas high OT/MT ratio means better processibility. The appropriate OT/MT ratio is in the range 1:2.5–1:1.

CONCLUSION

In conclusion, the conflict between obtaining processible conducting polymers by attaching long flexible side groups to the conjugated backbones, and the instability caused by the attached side groups, can be settled by diluting adjacent mers bearing long side chains with mers without long side chains. In other words, by attaching long flexible chains to some separated mers along the conjugated backbone, a processible conductive polymer which retains the stability of the parent polymer can be obtained. Interaction between the flexible side chains in this system can be effectively suppressed, and room can be found to accommodate the dopants. The free volume mechanism is highlighted which attributes the instability of doped P3ATs to thermally induced disorder of the long side chains and the main chain distortion[18], rather than the high redox potential of the polymers[13,14].

At present there are few commercial applications of conducting polymers due to their non-processibility, instability in the doped or neutral state, or/and sensitivity to ambient air or water. The processibility of the random copolymer POTMT, especially its melt processibility, the high stability in both neutral and doped states, and its fairly high redox reversibility, indicate that such copolymers may be of great practical importance. Development of an efficient synthesis of these copolymers is thus desirable.

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