Chemical synthesis and spectroscopic studies of soluble electrically conducting copolymers of 3-methylthiophene and methyl methacrylate

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Copolymerization of 3-methylthiophene and methyl methacrylate yielded solution-processible electrically conducting copolymers. The soluble copolymers were characterized by proton nuclear magnetic resonance, gel permeation chromatography, infra-red and ultra-violet/visible absorption spectroscopic techniques. The analytical results indicate the formation of low-molecular-weight random copolymers. One copolymer exhibited a maximum electrical conductivity of 6.5 S cm^{-1} after doping with iodine. The magnitude of the electrical conductivities of these copolymers depends on the extent of incorporated conjugated 3-methylthiophene blocks in the copolymer backbone. Thermogravimetric analysis showed high thermal stability of neutral and doped copolymers in an oxidative atmosphere. The electrical, optical and thermal properties of the soluble copolymers are discussed.

INTRODUCTION

Over a decade ago, electrically conducting polymers emerged as a new class of electronic materials. Polyacetylene, which possesses the simplest π-electron conjugated system, became the first example of organic conducting polymers[1]. The electrical conductivity of polyacetylene can be varied from an insulating to a metallic state with respect to the doping reactivity of the conjugated carbon backbone. For example, the electrical conductivity of polyacetylene in the doped state ranges from 10^3 to 10^5 S cm^{-1} depending on the synthetic conditions[2–4]. In addition to such interesting electroactive phenomena, polyacetylene also shows environmental instability and insolubility, thereby making its practical applications difficult[5]. Like polyacetylene, polyheterocycles such as polypyrrole and polythiophene are a class of electrically conducting polymers. Although these polyheterocycles exhibit good environmental stability, they also suffer from the processibility point of view[6,7]. In the early stages, processible conducting polymer composites were prepared by mixing insoluble polyheterocycle components with highly soluble conventional organic polymers (poly(vinyl alcohol), poly(vinyl chloride), poly(methyl methacrylate), polystyrene), still lacking the virtual solution processibility[8]. Recently attempts have been made to develop solution-processible polypyrrole[9] and polythiophene[10–12], which can have practical potentials at ambient conditions.

From the synthetic viewpoint, processible polythiophenes can be obtained either by substitution of appropriate side-groups on the β-positions of heterocycles or by copolymerization with conventional organic polymers. On a molecular level, soluble homopolymers having side-groups still retain a highly conjugated π-electron backbone whereas the interruption of π-conjugation takes place in a copolymer backbone because of the incorporated non-conjugated polymer segments. Poly(3-alkylthiophene) homopolymers almost maintain the initial conductivity of the polythiophene backbone. For example, poly(3-alkylthiophenes) having n-alkyl chain length from 2 to 20 exhibit electrical conductivities of $10–300 \text{ S cm}^{-1}$ (ref. 13). A copolymer system consists of at least two building blocks in the backbone. The copolymers of 3-methylthiophene and methyl methacrylate represent such an example. The non-conjugated methyl methacrylate segments are linked to the conjugated 3-methylthiophene segments through the 2- and 5-positions of the heterocycle. A considerable loss of electrical conductivity can be anticipated in such copolymers due to the interruption of π-electron conjugation. The electrical conductivities of iodine-doped copolymers range between 10^{-5} and 0.20 S cm^{-1} as reported by Huang and Park[14]. It has been suggested that the electrical conductivities of these copolymers are correlated to the incorporated conjugated segments in a polymer strand. Therefore, it was of considerable interest to the author to explore further the possibility of developing even more highly conducting processible copolymers of 3-methylthiophene and methyl methacrylate.

Keeping this in view, soluble copolymers of 3-methylthiophene and methyl methacrylate were prepared. These copolymers were characterized by proton nuclear magnetic resonance (^{1}H n.m.r.), gel permeation chromatography (g.p.c.) and infra-red (i.r.) absorption

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spectroscopy. The ultra-violet/visible (u.v./vis.) absorption studies of neutral and oxidized copolymers in solution and solid state are reported. The copolymers exhibit electrical conductivities as high as 6.5 S cm^{-1} on iodine doping[15]. The copolymers are stable up to about 300°C in an oxygen atmosphere. The electrical and optical properties of soluble and thermally stable copolymers are discussed in this paper.

EXPERIMENTAL

The copolymers of 3-methylthiophene (3-MeTH) and methyl methacrylate (MMA) were obtained via the synthetic approaches reported by Huang and Park[14]. Two kinds of copolymers can be obtained due to the fact that an intermediate Grignard reagent of 3-MeTH leads to the formation of poly(3-methylthiophene) as well as poly(methyl methacrylate) blocks. The degree of polymerization of each block and the method of copolymerization depend on the synthetic routes. The details of copolymerization routes are shown in *Figure 1*. The 2,5-diiodo-3-methylthiophene was prepared by iodinating 3-methylthiophene in dichloromethane using a 1:1 mixture of nitric acid and water according to a method developed by Barker *et al.*[16]. The intermediate Grignard reagent was obtained in a dry atmosphere with magnesium in highly purified tetrahydrofuran. The 3-methylthiophene blocks were polymerized by the cross-coupling reaction using a nickel–phosphine complex catalyst [NiBr$_2$(dppp) = 1,3-bis(diphenylphosphinopropane-nickel(II) bromide] in dry 2-methyltetrahydrofuran[17]. The copolymerization takes place via a Grignard reagent catalysed polymerization process of methyl methacrylate as reported in the literature[18,19]. The copolymer obtained via this route is a red powder and is referred to as co(3-MeTH/MMA)-red copolymer. In another approach, first the polymerization of methyl methacrylate is performed by using the intermediate 3-methylthiophene Grignard reagent and then it is allowed to polymerize itself using NiBr$_2$(dppp) catalyst. The yellow

powder obtained by this approach is referred to as co(3-MeTH/MMA)-yellow copolymer.

The chemical structure of the copolymers was confirmed by 300 MHz ^{1}H n.m.r. spectra recorded on a Varian-Gemini 300 spectrometer. The chemical shifts were calibrated using CDCl$_3$ (7.3 ppm). The i.r. spectra were recorded as KBr on a JEOL *FT*-i.r. spectrophotometer (model JIR-100, Japan). The x.p.s. spectral results were obtained by an X-ray photoelectron spectrometer (model 5100 ESCA System) using a Mg Kα source (1245.9 eV). For recording u.v./vis. absorption spectra, a Shimadzu spectrophotometer (model UV-260, Japan) was used. The u.v./vis. spectra were recorded both in solution form by dissolving the copolymers in tetrahydrofuran and in solid-state form by casting thin films on a glass slide. The thin films were thoroughly dried under vacuum at room temperature for a couple of hours to avoid solvent contamination. Thermogravimetric analysis (t.g.a.) and differential scanning calorimetry (d.s.c.) studies were carried out by a Rigaku system (Rigaku, Denki Co., Japan) at a scanning rate of 20°C min^{-1}. The electrical conductivities of pressed pellets were measured by the four-probe method. Doping of the copolymers was achieved by exposing the pellets to iodine vapour in a closed chamber.

RESULTS AND DISCUSSION

The co(3-MeTH/MMA) copolymers are soluble in chloroform, tetrahydrofuran and toluene[14]. The solubility of these copolymers originates due to the incorporated polar methyl methacrylate segments since poly(3-methylthiophene) homopolymers are insoluble materials. Therefore, solution characterization of these copolymers was possible. *Figure 2* shows the 300 MHz ^{1}H n.m.r. spectrum of co(3-MeTH/MMA)-yellow copolymer recorded in deuterated chloroform (CDCl$_3$) at room temperature. The lines are broad, indicating the presence of a high-molecular-weight compound. The low-field broad line at 6.9 ppm is due to the C(3) proton on the thiophene
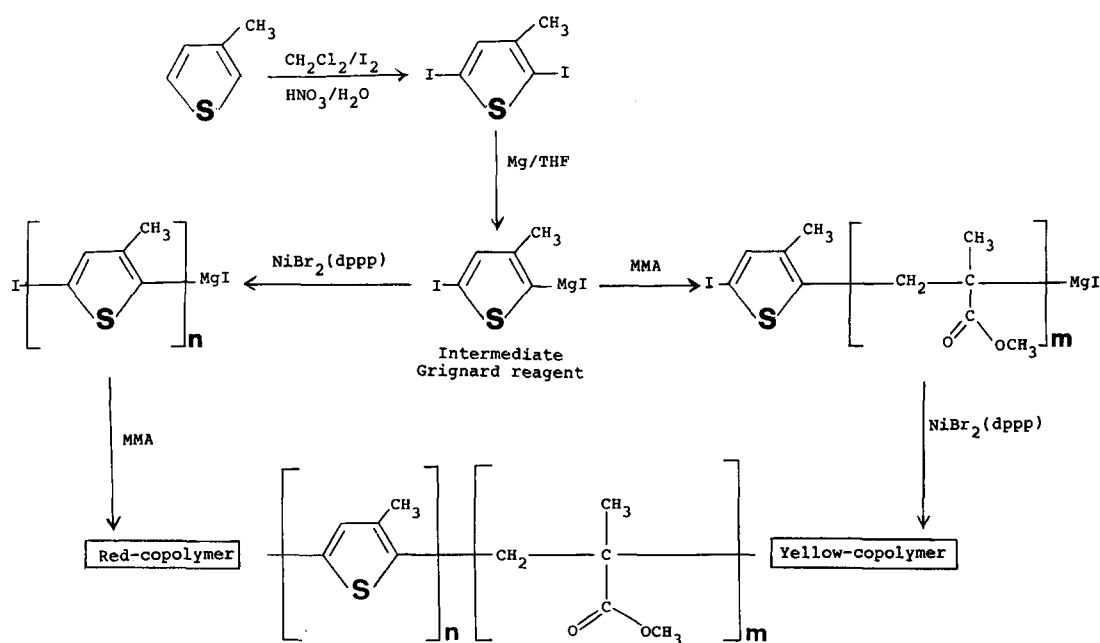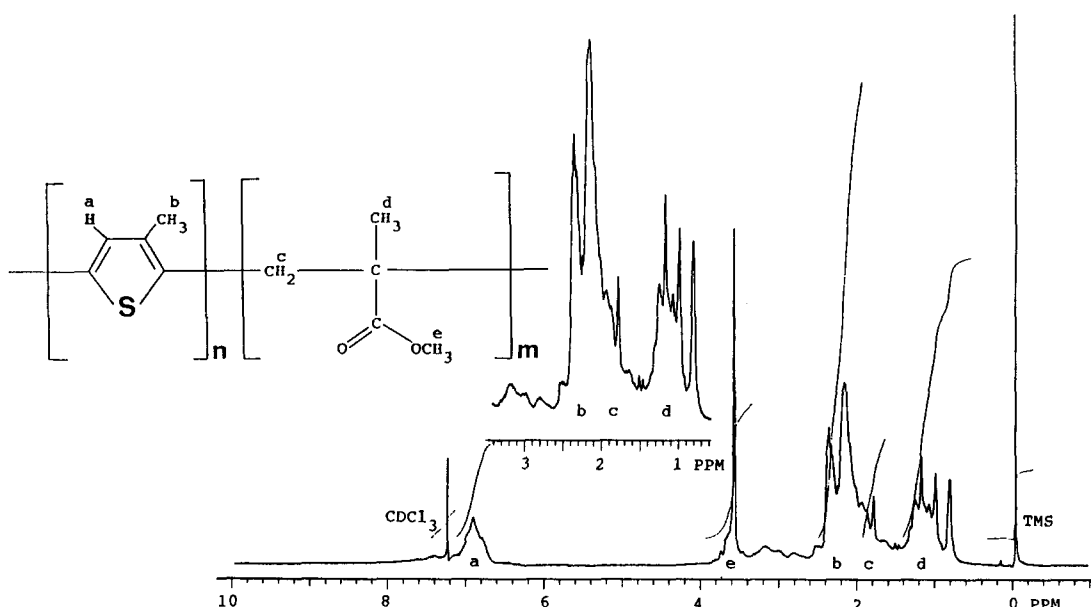

Figure 1 Synthetic routes for red and yellow copolymers of 3-methylthiophene and methyl methacrylate

Figure 2 Proton nuclear magnetic resonance spectrum of yellow copolymer recorded in deuterated chloroform at room temperature by a 300 MHz n.m.r. spectrometer

Table 1 Molecular-weight distribution, u.v./vis. peaks, thermal decomposition temperature and room-temperature electrical conductivities of 3-methylthiophene and methyl methacrylate copolymers

Co(3-MeTH/MMA) copolymers	Molecular weight evaluated by g.p.c. technique[a]	Electronic absorption peak (nm)		Initial decomposition temperature[b] (°C)	Electrical conductivity in doped state[c] (S cm⁻¹)
		Solution	Film		
Red copolymer	$M_n = 1900$ $M_w = 8400$ $M_w/M_n = 4.42$	400	425	290	6.5
Yellow copolymer	$M_n = 2046$ $M_w = 3346$ $M_w/M_n = 1.63$	360 (shoulder)	360 (shoulder)	200	7.2×10^{-5}

[a] M_n and M_w are number-average molecular weight and weight-average molecular weight respectively. M_w/M_n represents the polydispersity index of copolymers
[b] T.g. thermograms were recorded in an oxidative atmosphere
[c] Doping reaction was carried out by exposing the pressed pellets of copolymers to iodine vapour in a closed chamber

ring. The multiplicity may be due to the end units. The α-methyl (CH₃) proton peak appears in the range 0.9–1.3 ppm[20]. The proton signal at 3.8 ppm is associated with the methoxy (–OCH₃) groups[19]. The methylene (–CH₂–) protons appear in the range 1.8–2.1 ppm. The methyl proton on thiophene rings is observed in the resonance range 2.2–2.4 ppm. The presence of –CH₂ and –OCH₃ groups confirms that the copolymerization reaction occurred but the copolymer is not completely pure in terms of tacticity. From integration at 6.9 ppm (one proton) and 3.8 ppm (three protons), the ratio of 3-methylthiophene to methyl methacrylate is 2.33:1, indicating the formation of a random copolymer. The ¹H n.m.r. spectrum of red copolymer also confirms the copolymer skeleton. The elemental analysis obtained by X-ray photoelectron spectroscopy (x.p.s.) indicated that the number of 3-MeTH segments is much higher in the red copolymer than in the yellow copolymer. Both ¹H n.m.r. and x.p.s. techniques confirm that the copolymer backbone comprises 3-methylthiophene and methyl methacrylate segments as expected.

Molecular-weight distribution of red and yellow copolymers was evaluated in tetrahydrofuran solvent by

g.p.c. using polystyrene standards. The results for number-average molecular weight M_n and weight-average molecular weight M_w are listed in *Table 1*. The polydispersity index (M_w/M_n) estimated is 4.42 and 1.63 for red and yellow copolymers, respectively. The determined M_w of red copolymer is about 2.5 times higher than that of yellow copolymer. The molecular chain length calculated from M_w corresponds to approximately 43 and 17 comonomer units per copolymer chain for red and yellow copolymers, respectively. This suggests that these two copolymers have entirely different compositions of conjugated and non-conjugated segments. The high-molecular-weight red copolymer possesses the higher number of 3-methylthiophene units as evidenced by x.p.s. elemental analysis. Moreover, the colour change is also associated with the length of conjugation.

The i.r. absorption spectra of red and yellow copolymers are shown in *Figures 3a* and *3b* respectively. It is necessary to mention that some of the i.r. bands associated with 3-methylthiophene and methyl methacrylate blocks are superimposed. The bands arising due to 3-MeTH segments are apparently visible in red copolymer, whereas those originating due to MMA
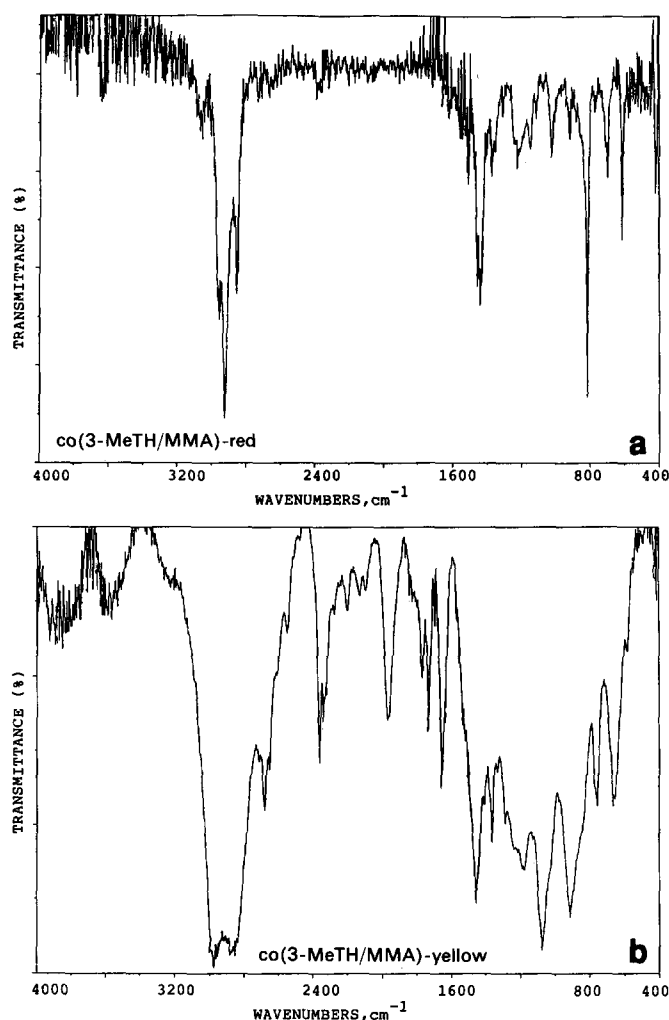
Figure 3 Infra-red spectra of red (a) and yellow (b) copolymers obtained as KBr in 400–4000 cm^{-1} region

segments are very dominant in yellow copolymer. The bands are not characteristically similar. They are either shifted or weak due to the different compositions of 3-MeTH and MMA blocks. The i.r. absorption bands appearing at 2968s, 2925vs, 2852s, 1514w, 1461m, 1440m, 1374w and 818s cm^{-1} in red copolymer correspond to 3-MeTH blocks*. The strong bands in the range of 2850–3000 cm^{-1} are attributed to the aliphatic carbon–hydrogen stretching vibrations[21]. The strong bands between 1440 and 1514 cm^{-1} are due to the ring stretching vibrations[22]. The deformation vibration of methyl group appears at 1378 cm^{-1}. A sharp and strong band at 818 cm^{-1} is associated with the out-of-plane carbon–hydrogen vibrations, showing the features of trisubstituted 3-methylthiophene rings[23]. These i.r. spectral results are in excellent agreement with that reported by Hotta *et al.*[21] for poly(3-methylthiophene) homopolymer. In yellow copolymer, the i.r. bands associated with 3-MeTH blocks appear at 2981bvs, 2854bvs, 1506vw, 1457ms, 1436w, 1363m and 839w cm^{-1}. The i.r. bands are shifted compared to red copolymer, probably due to the higher contents of MMA segments. The i.r. absorption bands occurring at about 3000w, 1733ms, 1182m, 1074bs, 916bs and 756m cm^{-1} are characteristic

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* m = medium, s = strong, b = broad, v = very, w = weak

of MMA blocks[20,24–26]. These bands are apparently visible in yellow copolymer but they are relatively weak in red copolymer. A medium-intensity band at 1734 cm^{-1} is associated with the ester –C=O stretching vibrations[25]. Another ester –C–O stretching vibration appears at 1074 cm^{-1}. The absorption band at 1182 cm^{-1} is attributed to the –OCH$_3$ groups. The bands at 1074 and 916 cm^{-1} indicate that the copolymer contains dominantly syndiotactic sequences of PMMA[19]. A sharp band at 756 cm^{-1} is characteristic of copolymers of PMMA[20]. Since yellow copolymer contains higher PMMA contents, related bands are therefore stronger than that of red copolymer. The present i.r. data support the existence of 3-MeTH and MMA segments in a copolymer strand[20,21]. It has been reported that MMA segments in a copolymeric system show deviant i.r. spectral characteristics and the syndiotactic sequence dominates the conformation featured by i.r. absorption bands[20]. In copolymers, the MMA sequences are usually short, indicated by low molecular weights.

The undoped copolymers show electrical conductivities in the range of 10^{-11} to 10^{-13} S cm^{-1} at room temperature. A significant increase in the conductivity (more than 11 orders of magnitude) of red copolymer is observed on doping with iodine. The oxidized red copolymer shows a maximum conductivity of 6.5 S cm^{-1}. On the other hand, iodine-doped yellow copolymer exhibits relatively much lower conductivity (7.2 × 10^{-5} S cm^{-1}) than that of iodine-doped red copolymer (*Table 1*). The higher electrical conductivity of doped red copolymer (five orders of magnitude higher than yellow copolymer) originates due to the existence of more conjugated 3-methylthiophene blocks. The colour and electronic absorption spectral studies support the idea that a higher degree of π-conjugation exists in red copolymer. In contrast, the broad and strong i.r. bands attributable to the methyl methacrylate blocks are very prominent in yellow copolymer (*Figure 3b*), which indicates the presence of higher numbers of non-conjugated MMA segments. Therefore the magnitude of electrical conductivity of these copolymers depends on the extent of incorporated conjugated segments in the copolymer backbone. Colaneri *et al.*[27] reported an electrical conductivity of 750 S cm^{-1} for poly(3-methylthiophene) homopolymers obtained by an electrochemical polymerization method. In another study, Roncali *et al.*[28] reported the conductivity of electrochemically synthesized poly(3-methylthiophene) as high as 2 × 10^3 S cm^{-1} for 200 nm thick films in optimal conditions. The extent of electrical conductivity in poly(3-methylthiophene) homopolymers depends on the extended conjugation length obtained by electropolymerization. Relatively lower conductivities in copolymers appear because of the interrupted π-conjugation by incorporated non-conjugated MMA segments, which localizes the mobility of charge carriers. Furthermore, the adjacent polar

$$\begin{array}{c} O \\ \parallel \\ -C-OCH_3 \end{array}$$
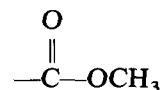
groups act as carrier traps and thus circumvent charge-carrier mobility. Although the copolymerization of 3-MeTH with MMA induces solubility, it also affects the electrical conductivity due to the hindrance of the π-electron delocalization process.

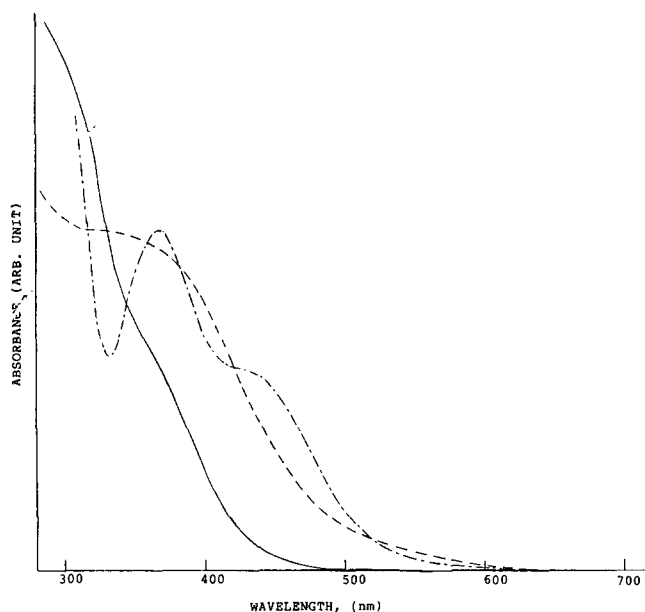*Figure 4* shows the electronic absorption spectra of
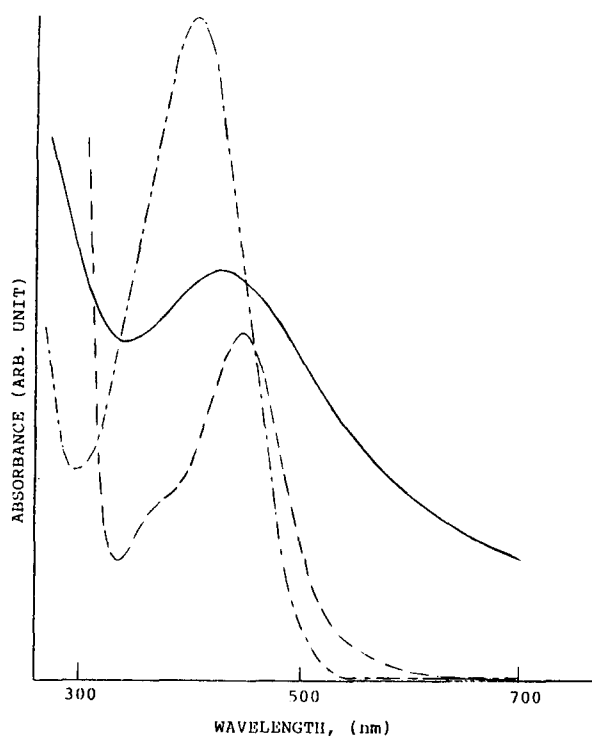
Figure 4 Electronic absorption spectra of red copolymer recorded in tetrahydrofuran (— · —), solution-cast films (————) and iodine-doped (oxidized) in tetrahydrofuran solution (— — —)
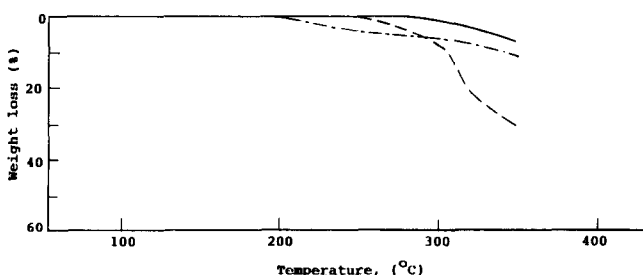
neutral and oxidized red copolymer. The neutral copolymer solution in tetrahydrofuran shows an absorption peak at 400 nm[15]. This peak is associated with the interband transition between the valence and conduction bands. In solution-cast films of neutral red copolymer, the absorption peak appears at 425 nm, thus indicating a spectral shift from the solution to the solid state. The iodine-doped (oxidized) red copolymer solution in tetrahydrofuran exhibits a peak at 450 nm and, in addition, a shoulder develops around 370 nm. The absorption edge in solid films and iodine-doped solution shifts to higher wavelength. The electronic absorption spectra of yellow copolymer in neutral and oxidized states are illustrated in *Figure 5*. Although no clear absorption peak appeared, a shoulder at about 360 nm is observed in both tetrahydrofuran solution as well as solution-cast solid films (*Table 1*). The iodine-doped yellow copolymer solution shows a clear peak at 370 nm and a shoulder develops at 440 nm. Similar to red copolymer, the absorption edge in solid films and iodine-doped samples shifts to higher wavelength. The absorption peaks are in good agreement with that reported by Huang and Park[14]. The absorption spectral results indicate that the number of conjugated 3-MeTH blocks is higher in red copolymer compared to yellow copolymer. Further, the colour of the copolymers is also related to the length of conjugated segments. The $\pi-\pi^*$ transition spectral changes noticed between solution and solid films of red copolymer are similar to those reported in soluble poly(diacetylene)[29,30] and poly(3-alkylthiophene) homopolymers[12,21,31]. The intermolecular interactions are less in the solution state and increase extensively in the solid state because the conjugated backbone restores an ordered conformation[32]. In poly(3-methylthiophene) homopolymer, the $\pi-\pi^*$ absorption band occurs at about 504 nm[13]. The difference in absorption maximum associ-

ated with $\pi-\pi^*$ transition of homopolymer and copolymer results due to the lower degree of polymerization and interruption of π-electron conjugation. Further the sequence of conjugated and non-conjugated blocks is unknown. Presumably, in these random copolymers these two segments are segregated from each other. Depending upon the copolymerization, once either a conjugated or a non-conjugated block is formed, it inhibits the polymerization process of the other segment. The spectral studies show that both 3-MeTH and MMA segments are present in the copolymer.

Figure 6 represents the t.g. thermogram of red and yellow copolymers recorded in an oxidative atmosphere. It is evident that the red copolymer is thermally more stable than the yellow copolymer. The red copolymer begins to decompose at 290°C and a 10% weight loss occurs at 350°C. The yellow copolymer is thermally stable up to 200°C and about 11% weight loss takes place at 300°C. The higher thermal stability of red copolymer is apparently related to the higher content of 3-MeTH blocks in a copolymer strand. In iodine-doped red copolymer, two weight loss processes are observed, one beginning from 250°C and another from 290°C. The first process corresponds to the desorption of the iodine from the copolymer. The second process is associated

Figure 5 Electronic absorption spectra of yellow copolymer obtained in tetrahydrofuran solution (————), solution-cast film (— — —) and iodine-doped (oxidized) in tetrahydrofuran solution (— · —)

Figure 6 T.g. thermograms of neutral red copolymer (————), iodine-doped (oxidized) red copolymer (— — —) and neutral yellow copolymer (— · —) recorded at a heating rate of 20°C min⁻¹ in an oxygenated atmosphere

with the decomposition of the copolymer backbone, since it is characteristically similar to neutral red copolymer. Considerably less thermal stability of iodine-doped red copolymer corresponds to the desorption of iodine counterions. The d.s.c. scans could not clearly show any glass transition temperature in either red or yellow copolymer. These soluble copolymers exhibit good thermal stability in oxygenated atmosphere.

CONCLUSIONS

In summary, using an intermediate Grignard reagent of 3-methylthiophene, two kinds of random copolymers of 3-methylthiophene and methyl methacrylate can be obtained. These copolymers are soluble. Since the homopolymer of 3-methylthiophene is an insoluble material, copolymerization with methyl methacrylate resolves the problems of insolubility and infusibility. The copolymers referred to as yellow and red copolymers are insulators in the neutral state; iodine doping raises their electrical conductivity to 7.2×10^{-5} and $6.5\,S\,cm^{-1}$, respectively. The magnitude of the conductivity is mainly governed by the extent of incorporated conjugated segments. Although red copolymers possessing even higher conductivities can be prepared, their solubility declines. The yellow and red copolymers are thermally stable up to about 200 and 290°C, respectively, in an oxidative atmosphere. The electronic absorption spectral data and thermogravimetric analysis indicate that both electrical conductivity as well as thermal stability are correlated with the conjugated 3-methylthiophene segments present in the copolymer backbone. These results suggest that electrically conducting copolymers exhibiting solubility and good environmental stability can be obtained. These conducting copolymers may find potential applications in the field of electrotechnology.

ACKNOWLEDGEMENTS

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Note added in proof

Third-order non-linear optical properties of co(3-MeTH/MMA) copolymers were investigated using a degenerate four-wave mixing technique. The yellow copolymer shows third-order non-linear optical susceptibility $\chi^{(3)}$ of 7.0×10^{-12} e.s.u. at 602 nm for a 1.30 μm thick film[33]. The $\chi^{(3)}$ value of the red copolymer is about an order of magnitude larger at the same wavelength. Like electrical conductivity, the magnitude of third-order non-linear optical properties also depends on the extent of incorporated conjugated 3-MeTH blocks in the copolymer backbone. These copolymers offer solution processability and, in particular, the yellow copolymer exhibits good optical transparency over various π-electron conjugated polymers. These processible and environmentally stable copolymers may have potential for applications in non-linear optical devices.

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