

# Chemical Synthesis, Characterization, and Properties of Conducting Copolymers of Imidazole and Carbazole

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**ABSTRACT:** Conducting copolymers of imidazole and carbazole were chemically synthesized in various molar ratios of the imidazole and carbazole by chemical oxidative polymerization in acetonitrile medium using ammonium persulphate as oxidant. The selection and composition of solvent, concentration of the monomer, polymerization time, and temperature were optimized to obtain better quality and yield of the copolymers. The synthesized conducting copolymers were characterized by various techniques such as UV-visible, Fourier transform infrared, <sup>1</sup>H-NMR, and X-ray diffraction spectroscopy. The solubility of the copolymers was

tested in various solvents. Their conductivity was tested at various temperatures. The thermodynamic stability of the copolymers was examined by differential scanning calorimetric and thermogravimetric analysis. The copolymers show comparatively higher conductivity, better solubility, and higher thermal stability than the homopolymer poly(carbazole) and lower than that of poly(imidazole). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2824–2833, 2011

**Key words:** conducting polymers; copolymers; differential scanning calorimetry; X-ray; FTIR

## INTRODUCTION

Many potential applications of conducting polymers become limited because of their general insolubility in common organic solvents, poor mechanical properties vis-à-vis their insufficient environmental stability. To improve these properties, one method was used to prepare copolymers with other monomers. New aromatic nitrogenous polymers are continuously emerging due to their versatility, easy preparation, and very attractive property-cost performance including much higher gas separation ability than any other polymer.<sup>1</sup>

The most widely studied conducting polymers are poly(aniline),<sup>2–12</sup> poly(pyrrole),<sup>13–20</sup> poly(thiophenes),<sup>21–26</sup> and poly(carbazole).<sup>27–33</sup> The carbazole (CZ) homopolymers have potential applications in the field of optoelectronics because of their interesting blue luminescence due to their limited  $\pi$ -conjugation. Recently, poly(2, 7 carbazole) has been synthesized and was found to exhibit a limited solubility and blue luminescence due to biphenilic type conjugation along the backbone.<sup>34–36</sup> However, electroluminescence performance and blue color purity can be obtained with poly(carbazole) molecules. Romero et al.<sup>37</sup> reported the synthesis and

luminescence properties of *N*-ethyl carbazole dimers. However, because of their limiting solubility in common organic solvents, their infusibility and photoluminescence properties of the aforementioned synthesized polymers, there is a constant search for a new class of polymers that fulfills all the requirements of optoelectronic devices.

There are some reports concerning the copolymerization of aniline and thiophene derivatives with pyrrole,<sup>38</sup> pyrrole and *o*-anisidine,<sup>39</sup> *m*-toluidine and *o*-nitroaniline, and pyrrole and *m*-toluidine.<sup>40</sup> However, the chemical oxidative copolymerization of CZ with imidazole (IMI) has not been reported. In the present investigation, copolymers of IMI and CZ with six monomer ratios were prepared for the first time. Their solubility in several organic solvents, macromolecular structure and thermal behavior of the copolymers are investigated systematically. Even though they possess multiple functionality, such as excellent conductivity, high gas separation ability, unique proton dopability, excellent redox recyclability and chemical stability, their applications have been very limited by their intractable nature since they are usually obtained chemically as brittle films.<sup>41</sup> Considerable progress has been made in the last few years in the processibility of conducting polymers by the synthesis of polymer blends, composites,<sup>42,43</sup> and copolymers.<sup>44,45</sup> The aim of this study is to obtain copolymers with improved solubility, to evaluate their conductivity, and to study their spectral, and thermal properties.

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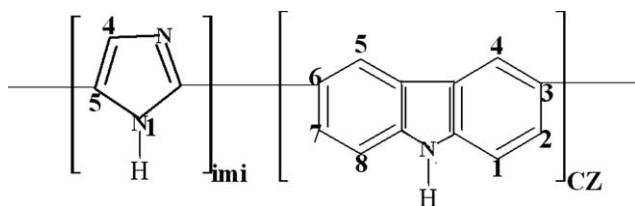


Figure 1 Structure of poly(IMI-co-CZ).

## EXPERIMENTAL

### Materials

CZ (Kemphasol) was recrystallized from hexane and obtained as light brownish needles. IMI analytical reagent grade (Himedia) and ammonium persulfate (Rankem) was used as procured. Acetonitrile (Merck) was freshly distilled prior to utilization. All other solvents were of Analytical reagent grade and used after necessary purification.

Monomer, i.e., CZ  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz,  $\delta$  ppm): 7.1 (2 H,  $\text{H}_{3,6}$ ), 7.3 (2H,  $\text{H}_{1,8}$ ), 7.4 (2H,  $\text{H}_{2,7}$ ), 8.0 N–H proton of the pyrrole nuclei.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50 MHz,  $\delta$  ppm): 139 ( $\text{C}_{9a}$ ), 130 ( $\text{C}_2$ ), 125 ( $\text{C}_{3,6}$ ), 123 ( $\text{C}_{4a,4b}$ ), 121 ( $\text{C}_5$ ), 120 ( $\text{C}_{4,7}$ ), 110 ( $\text{C}_{18}$ ).

### Copolymerization

IMI/CZ copolymers (structure and quinoid form of IMI unit are given in Figures 1 and 2, respectively) were prepared by an oxidative polymerization through a previously described method.<sup>46–49</sup> A representative procedure for the preparation of the IMI/CZ (50/50) copolymer is as follows: to 100 mL of the 95% acetonitrile solution added 0.3404 g (5 mmol) IMI and 0.8361 g (5 mmol) CZ in a 250-mL glass flask and stirred vigorously for an hour. Ammonium persulfate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ , 2.964 g (13 mmol), was dissolved separately in 30 mL of 95% acetonitrile to prepare an oxidant solution. The monomer solution was added with the oxidant solution dropwise at a rate of one drop for every 3 s at room temperature (the total molar ratio is monomer/oxidant = 1/1). Immediately after the first few drops, the reaction solution turned pale yellow. The reaction mixture was stirred for 24 h at ambient temperature. It was then added to 200 mL of methanol (as a nonsolvent) to precipitate out the copolymer. The grayish-white precipitate obtained was filtered and washed with excess of water to remove the oxidant and oligomers. Then it was dried under vacuum for 72 h. The copolymer of 0.907 g was obtained with a yield of 60%. The nominal structure of IMI/CZ copolymer is exhibited in Figures 1 and 2.

### Characterization

Solubility of the synthesized copolymers was evaluated using the following method: polymer powder

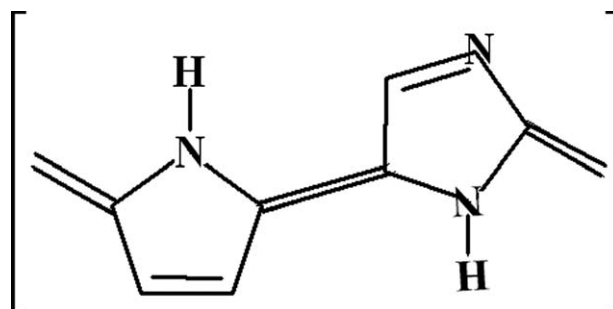


Figure 2 Quinoid form of IMI unit.

sample of 5 mg was added into the solvent of 0.5 mL and dispersed thoroughly. After the mixture was swayed continuously for 24 h at room temperature, the solubility of the copolymers was characterized. UV–visible absorption spectra of the copolymers were recorded using a Perkin–Elmer UV–visible Spectrometer using 0.5-cm path quartz cells in the range 190–1100 nm. Fourier transform infrared (FTIR) spectrum of the polymer was recorded on Perkin–Elmer FTIR spectrometer with KBr-pressed pellet.

NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ) spectra of the copolymer were recorded in  $\text{CDCl}_3$  solvent with a Bruker AC 200 spectrometer at 200 and 50 MHz. All the chemical shifts ( $\delta$  in ppm) were referenced to tetramethyl silane. Dry IMI/CZ powder was compressed into pellets of 13 mm in diameter and 1-mm thick and the conductance was measured by four-probe method (using four-probe resistivity setup) at various temperatures ranging from 308 to 368 K.

Thermal stability of the copolymer was determined using Mettler TA 3000 analyzer and TGA-DSC 910S differential scanning calorimeter. The measurement was performed at a heating rate of

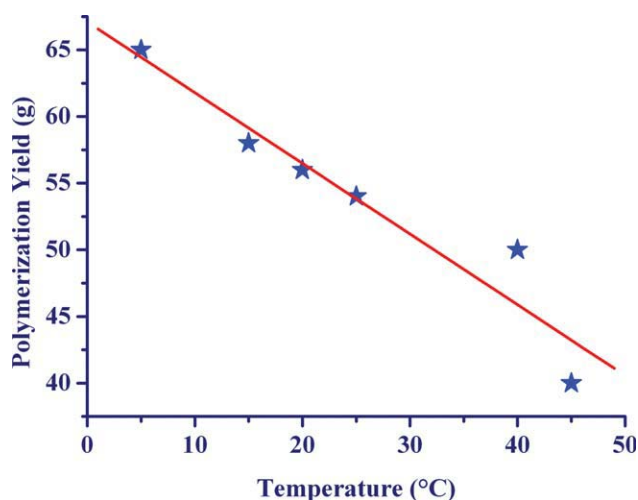


Figure 3 Influence of temperature on polymerization yield of the copolymer in acetonitrile for 24 h at room temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

**TABLE I**  
Solubility of IMI/CZ copolymers in organic solvents

IMI/CZ molar ratio		Yield	Solubility in solvents <sup>b</sup> and solution color <sup>c</sup>					
Feed	Calculated <sup>a</sup>		NMP	DMF	DMSO	THF	CHCl <sub>3</sub>	Benzene
100/0		37	MS(b)	MS(b)	MS(b)	PS(bv)	PS	IS
80/20	74/26	38	MS(b)	MS(b)	MS(b)	S(b)	PS(bv)	IS
60/40	57/43	31	MS(b)	MS(b)	MS(bb)	MS(b)	PS(bv)	IS
50/50	47/53	64	MS(b)	MS(b)	MS(bb)	S	PS(bv)	IS
20/80	14/86	36	MS(b)	MS(br)	MS(br)	SS	MS	IS
0/100		52	MS(b)	MS(br)	MS(br)	SS	MS	IS

<sup>a</sup> IMI/CZ molar ratio calculated based on the <sup>1</sup>H-NMR spectra.

<sup>b</sup> IS, insoluble; MS, major soluble; PS, partially soluble; S, soluble; SS, slightly soluble.

<sup>c</sup> The solution's color is indicated in the parenthesis with the following abbreviations: b, blue; bb, bluish black; br, brownish red; bv, bluish violet.

10°C/min with the sample size of 5–10 mg in nitrogen atmosphere. X-ray diffraction was performed on a Phillips X-ray diffractometer using Cu-k $\alpha$  radiation source operating at 50kV and 30 mA.

## RESULTS AND DISCUSSION

### Optimization of polymerization conditions

Oxidant/monomer ratio plays an important role on the polymerization yield of copolymer. With the increase of the oxidant content, the copolymerization yield increase monotonically from 6% to 80%. In general, more oxidant is beneficial to the formation of the cation radical with higher polymerizability promoting chain propagation reaction and the increasing the length of polymer chain and polymerization yield.

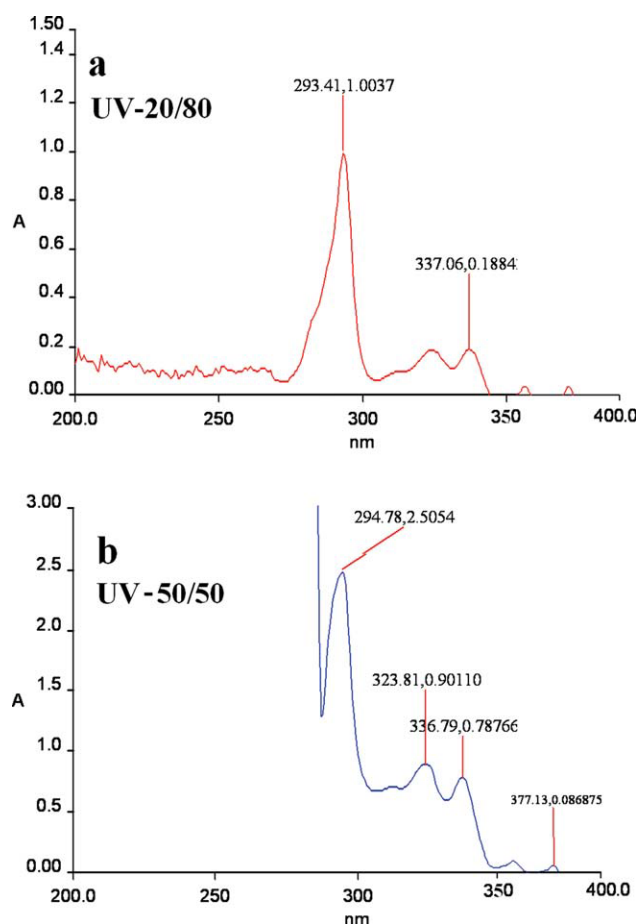
Polymerization temperature has a strong effect on the polymerization yield. The polymerization yield diminishes monotonically with elevating temperature. This may be due to the side reaction that occurs at the elevated temperature, leading to the depression of the polymerization yield. Note that in Figure 3, the highest yield but slightly low molecular weight at low temperature (5°C) could be attributed to slow diffusion rate of oxidant and monomers. To get more yield, polymerization was carried out at room temperature.

Polymerization was carried out using the different solvents like HCl, H<sub>2</sub>SO<sub>4</sub>, CHCl<sub>3</sub> oxalic acid, and methyl ethyl ketone. All these lead to poor yield. But, when the polymerization was carried out using acetonitrile we can able to get more yields.

### Synthesis of copolymers

The copolymerization of IMI and CZ (IMI/CZ) with ammonium persulphate as oxidant in 100 mL of 95% acetonitrile solution afforded grayish-white precipitate as products. The progress of the copolymer-

ization reaction was monitored by testing the solution temperature. It was found that, on dropping oxidant solution slowly and regularly, the polymerization solution temperature increases and finally reaches a nearly constant temperature. IMI/CZ (40/



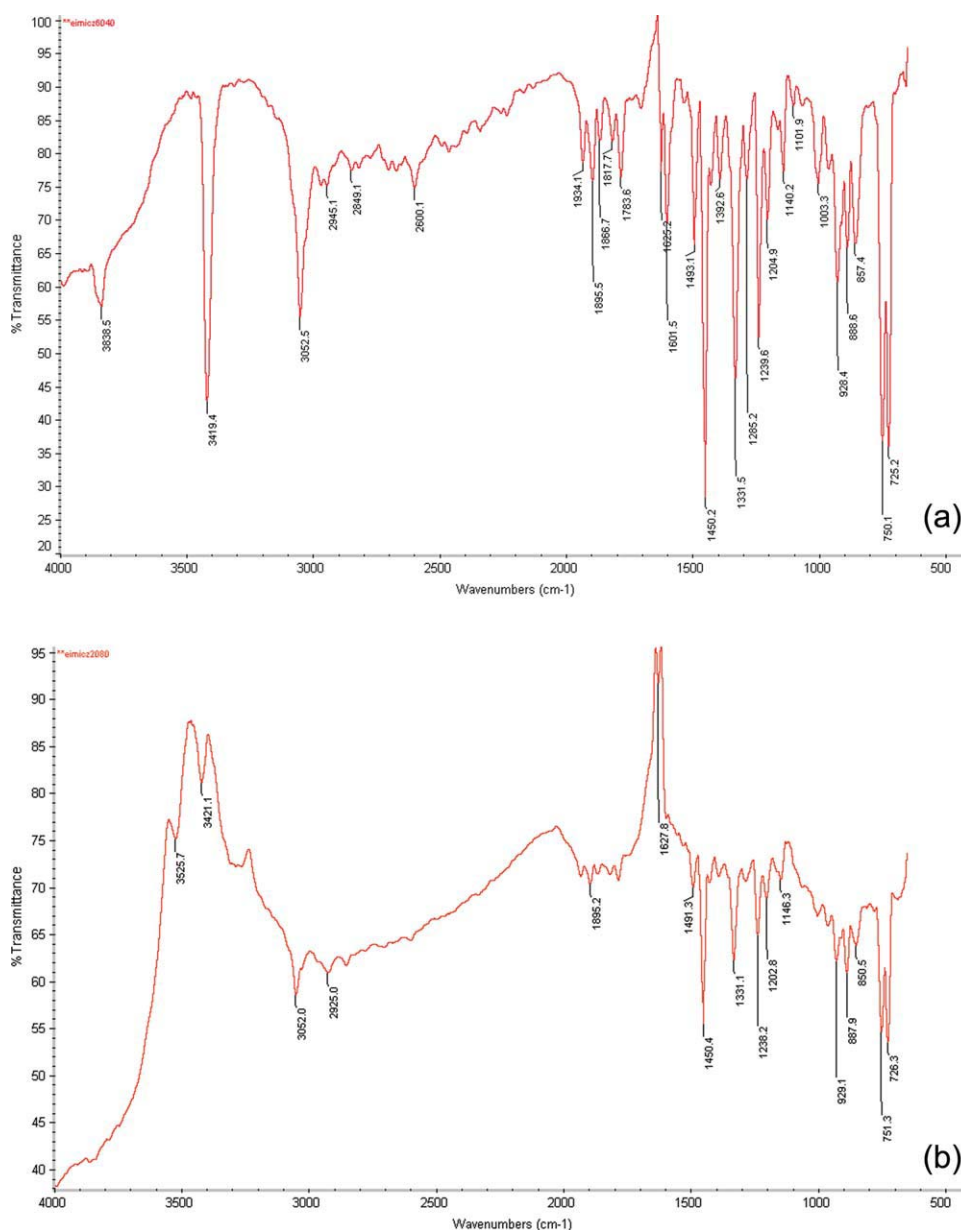
**Figure 4** UV-visible spectra of poly(IMI-co-CZ) of monomer ratios (a) 20/80 and (b) 50/50 in CHCl<sub>3</sub> solution (quartz cell) of concentration  $5 \times 10^{-4}$  M. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE II**  
The Variation of UV-Vis Spectra of IMI/CZ Copolymer in  $\text{CHCl}_3$  with IMI/CZ Molar Ratios

Feed IMI/CZ molar ratio	Wavelength (nm)			
	Strong band		Weak band	
0/100	302	317	247	372
20/80	293	–	337	–
40/60	292	323	336	–
50/50	291	323	335	–
100/0	282	–	–	–

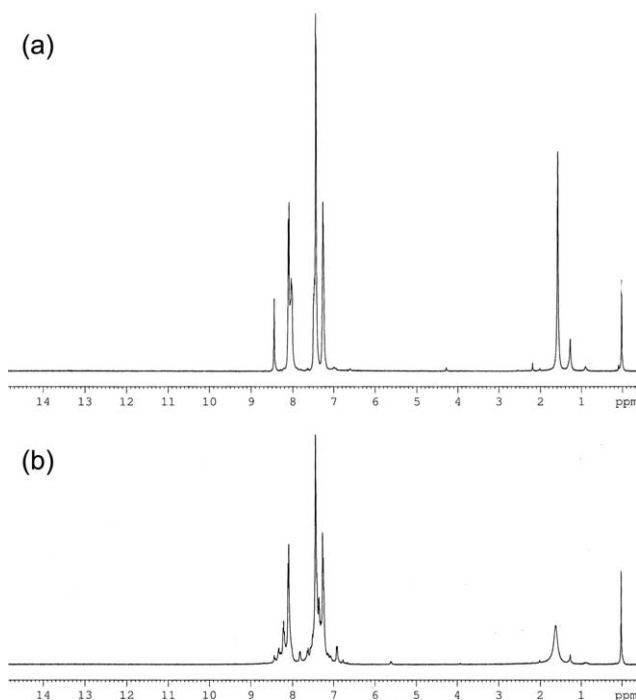
60) copolymerization exhibits the strongest exothermic capability among the five copolymerization systems. The enhancement of solution temperature is

4.5°C for this system. On the contrary, IMI/CZ (20/80) copolymerization exhibits the lowest exothermic effect with enhancement of the solution temperature of 2°C. These results may be due to the highest initial polymerization temperature for the IMI/CZ (20/80). That is the exothermic capacity of the copolymerization depends on the initial temperature of the reaction solution. In other words, initial solution temperature is an important parameter for the oxidative polymerization of IMI with CZ. The influence of temperature on polymerization yield is fitted linearly with the correlation coefficient of 0.95763, which is shown in Figure 3. It should be noted that the different enhancement in solution temperature may be due to the difference in dropping rate of



**Figure 5** FTIR spectral pattern of poly(IMI-co-CZ) of monomer ratios (a) 50/50 (b) 20/80. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 6**  $^1\text{H-NMR}$  spectra of the copolymers with IMI/CZ molar ratios of (a) 50/50 and (b) 80/20 in  $\text{CDCl}_3$  at 200 MHz.

oxidant solution. The copolymers were synthesized using five different molar ratios of IMI and CZ in the comonomer feed as given in Table I. The yield of the copolymers was found to be dependent on the monomer ratio. The yield was found to decrease with increasing IMI content in the feed.

### Solubility of IMI/CZ copolymer

The solubility of the newly prepared copolymers in various solvents was tested at room temperature. The polymers were easily soluble in polar aprotic solvents viz. chloroform, DMF, *N*-methyl-2-pyrrolidone and dimethyl acetamide, but insoluble in hydrocarbons (e.g., benzene, toluene, xylene) and hydroxyl group containing solvents such as methanol, ethanol, and 2-propanol. Table I shows the solubility of IMI/CZ copolymers in the six solvents.

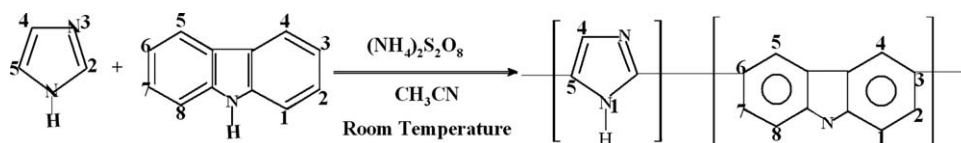
### UV-visible spectra of the copolymer of IMI and CZ

Figure 4(a,b) shows the UV-vis absorption spectra of two copolymer solutions with IMI/CZ ratios 20/80

and 50/50 in chloroform. The absorption bands of all the copolymers are listed in Table II. A strong band and a weak band are observed. The strong absorption bands appear in the wavelength range of 317–323 nm and weak band 247–335 nm are due to CZ moiety of the copolymer and a strong band at 282–302 nm was due to IMI moiety of the copolymer. It can be seen from Table II that the wavelength of both bands moves to lower values monotonically with increasing feed IMI content.<sup>50</sup> Additionally, the relative intensity of weak band becomes weaker further with increasing IMI content. The continuous variation of wavelength and intensity of UV-vis bands may result from copolymerization effect of IMI with CZ. In other words, the polymer formed by oxidative polymerization of IMI with CZ is the copolymer of two monomers rather than the mixture of two homopolymers. A similar variation of UV-vis spectral characteristics with pyrrole content was observed for the pyrrole/*m*-toluidine copolymer solution in DMSO.<sup>40</sup>

### FTIR spectra of the copolymers of IMI and CZ

Representative FTIR spectra for the copolymers with IMI/CZ molar ratios of 50/50 (a) and 20/80 (b) are shown in Figure 5. It is reported that poly(carbazole) exhibits  $-\text{NH}-$  stretching vibration<sup>51</sup> at  $3053\text{ cm}^{-1}$  and poly(imidazole) exhibits  $-\text{NH}-$  vibration weak peak at  $3077\text{ cm}^{-1}$ . Sharp band at  $3052\text{ cm}^{-1}$  due to characteristic  $\text{N-H}$  stretching vibration suggests the presence of  $-\text{NH}-$  groups in IMI and CZ units. The sharp band becomes weaker and broader and shifts to higher wave number with an increase in IMI feed content from 0% to 100%. Two weak peaks at  $2926$  and  $2852\text{ cm}^{-1}$  are due to aromatic  $\text{C-H}$  stretching vibrations. With increasing feed IMI content, these two peaks become weaker because CZ unit contain less  $\text{C-H}$  bond. Thus, the characteristics of IR absorption spectra of IMI/CZ copolymers above  $2000\text{ cm}^{-1}$  are dominated by the CZ unit. However, the absorption below  $2000\text{ cm}^{-1}$  is influenced by the IMI units. A comparison of the spectra of poly(imidazole), poly(carbazole),<sup>51</sup> and IMI/CZ copolymer shown in Figure 4 reveals some differences in the relative absorbance and wave number. With increasing feed IMI content, the relative absorption intensity at  $1625\text{--}1604\text{ cm}^{-1}$  and  $1492\text{--}1450\text{ cm}^{-1}$  gets stronger significantly. This should be attributable to IMI unit to some extent because the



**Figure 7** Schematic diagram of formation of copolymer IMI/CZ from its monomers.

TABLE III  
Conductivity and NMR Peak Positions for the Copolymer

Sample feed IMI/CZ	Conductivity	Peak Positions $\delta$ in ppm
100/0	$1.9 \times 10^{-3}$	7.3 (1H, C <sub>4</sub> of imidazole ring)
80/20	$5.48 \times 10^{-4}$	7.25 (1H, C <sub>4</sub> of IMI), 7.45 (2H, C <sub>1,8</sub> of CZ), 8.1 (2H, C <sub>2,7</sub> ), 8.3 (NH proton of the IMI and CZ)
60/40	$2.72 \times 10^{-4}$	7.3 (1H, C <sub>4</sub> of IMI), 7.5 (2H, C <sub>1,8</sub> of CZ), 8.0 (2H, C <sub>2,7</sub> ), 8.45 (NH proton of the IMI and CZ)
50/50	$2.1 \times 10^{-4}$	7.2 (1H, C <sub>4</sub> of IMI), 7.45 (2H, C <sub>1,8</sub> of CZ), 8.1 (2H, C <sub>2,7</sub> ), 8.45 (NH proton of the IMI and CZ)
20/80	$1.28 \times 10^{-4}$	7.3 (1H, C <sub>4</sub> of IMI), 7.5 (2H, C <sub>1,8</sub> of CZ) 7.9 (2H, C <sub>2,7</sub> ), 8.45 (NH proton of the IMI and CZ)
0/100	$2.68 \times 10^{-5}$	7.1 (2H, C <sub>3,6</sub> ), 7.3 (2H, C <sub>1,8</sub> ) 7.4 (2H, C <sub>2,7</sub> ), 8.0 (NH proton), 8.5 (2H, C <sub>3,6</sub> aromatic proton of the terminal ring)

bands<sup>52–54</sup> at 1625–1592 cm<sup>-1</sup> and 1454–1441 cm<sup>-1</sup> are characteristic of poly(imidazole). The absorption at 1592 cm<sup>-1</sup> increase significantly with increasing feed IMI content suggesting that the IMI unit in the polymer chains seems to exist mainly in the following quinoid form.<sup>39</sup> The difference of wave number might result from the copolymerization effect of IMI and CZ.

#### <sup>1</sup>H-NMR spectra of the copolymers of IMI and CZ

Figure 6(a,b) shows the <sup>1</sup>H-NMR spectra of the two copolymers IMI/CZ 50/50 (a) and 80/20 (b). The spectra of the copolymers exhibit peaks arising from both poly(imidazole) and poly(carbazole) units. The five-membered heteroaromatic proton of CZ (1, 8) appear at 7.4 ppm. The benzenic proton of the aromatic ring is appearing at 7.5 ppm (2, 7). The signal at 8.1 ppm is due to N–H proton of the pyrrole nuclei. The aromatic proton of the terminal ring was observed at 8.5 ppm (3, 6) and the signal at 7.3 ppm (C<sub>4</sub>) due to the proton of IMI ring.

<sup>1</sup>H-NMR analysis of IMI/CZ copolymer disclosed that oxidative coupling essentially occurred as anticipated in 3rd and 6th position of the CZ moieties and 2nd and 5th position of IMI moiety. It is consistent with the expected structure. As polymerization proceeds, 3, 6 proton peaks of the CZ at 7.1 ppm as well as the corresponding tertiary carbon at 125 ppm disappear and new signal ascribed to the quaternary carbon of the 3, 6 polymer linkages appears at 130.68 ppm. No abnormal linkages resulting from 2, 7 coupling (reaction is given in Fig. 7) were detected in the <sup>1</sup>H-NMR spectra of copolymers<sup>27</sup> and the yield with peak positions are given in Table III.

It can be seen that the aromatic protons of CZ are sifted slightly upfield in the spectra of the copolymers, whereas the protons of poly(imidazole) do not show much shift. The upfield shift of the aromatic protons of CZ could be attributed to an increase in the electron density of the ring. The <sup>1</sup>H-NMR spectra of IMI/CZ copolymers do not change systematically

with increasing feed IMI content. These spectra are not much informative on the calculation of sequence of distribution of the comonomers units.

#### The molar ratio of IMI over CZ = (imidazole proton area/1)/(carbazole proton area/7)

Based on the comparison of area of CZ proton peak and IMI proton peak, the ratios of IMI/CZ units on the copolymers have been calculated and listed in Table I. It seems that the actual IMI content is slightly lower than the feed IMI content for IMI/CZ copolymers. This difference in IMI content should be due to the lower solubility of poly(imidazole) in CHCl<sub>3</sub> as listed in Table I because the higher the IMI content, lower the solubility of the copolymer in CHCl<sub>3</sub>. A similar trend has been observed in the Py/MT copolymers.<sup>40</sup>

#### Thermal analysis

Representative thermogravimetric analysis (TGA) and Derivative thermogravimetric (DTG) curves of IMI/CZ copolymers 50/50 are shown in Figure 8, from which a series of thermal degradation parameters are obtained and listed in Table IV. The

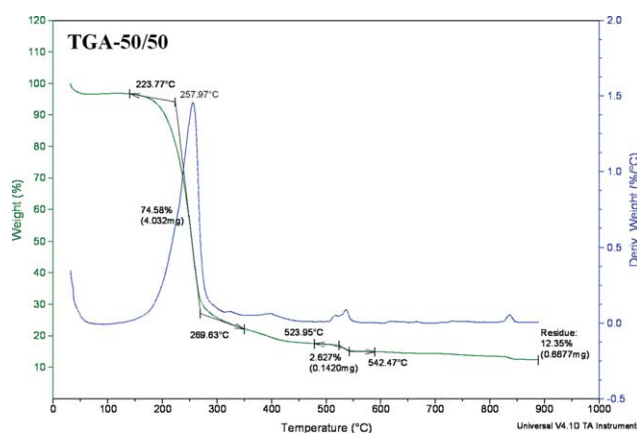


Figure 8 TGA/DTG curves of poly(IMI-co-CZ) of monomer ratio 50/50. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV  
Thermal Parameters of Copolymers

Poly(Imi-co-Cz)	Weight loss in %			Maximum decomposition temperature (°C)	Range of decomposition temperature (°C)
	200°C–300°C	400°C–500°C	500°C–600°C		
0/100	64	20	–	193, 300	100–400
20/80	58	10	5	224, 459, 665	100–690
50/50	62	18	–	223, 524	200–542
80/20	90	5	–	257, 368	200–400
100/0		53	–	373	300–420

copolymers lose weight rapidly between 200°C and 300°C and more slowly from 300°C to 500°C with increasing IMI content from 0 to 100 mol %. The temperature at the second maximum weight loss rate increases suggesting that the char yield at elevated temperature could be attributed to IMI unit in the copolymer. These results show that the thermo stability of the IMI/CZ copolymer increases with increasing IMI unit content.

The differential scanning calorimetric (DSC) analysis of poly(carbazole) and poly(imidazole) is shown in Figures 9 and 10, respectively. DSC scans of the IMI/CZ copolymers with ratios of 50/50 (a), 20/80 (b), and 60/40 (c) are shown in Figure 11. All the three scans show a sharp decomposition peaks at 234°C, 292°C, 329°C for IMI/CZ for (20/80), 240°C, 252°C, 333°C for (60/40), and 235°C, 305°C, 349°C for (50/50) copolymers respectively. The peaks appear at (234–240) and other peaks (292–349) are assigned to the inter chain crosslinking in the polymer.<sup>55</sup>

In TGA of poly(carbazole), the endothermic peaks present between 62°C and 150°C are due to the removal of water dopant molecules present in the polymer and other endothermic peaks between 201°C and 324°C (64%) arising due to morphological changes in the polymer. In DSC of poly(carbazole), exothermic peaks found between 231°C and 377°C

were assigned to the interchain crosslinking in the polymer.

The transitions for pure PIMI at 373°C with 53% weight loss are due to interchain crosslinking. In DSC of poly(imidazole), exothermic peak at 143°C was due to the removal of water dopant molecules present in the polymer and other exothermic peak at 412°C was assigned to interchain crosslinking in the polymer. Thermal analysis data also suggest that homopolymer poly(imidazole) is more stable compared with the copolymer IMI/CZ and poly(carbazole).

#### XRD measurements of the copolymers of IMI and CZ

The XRD pattern of the PCZ, PIMI, and copolymer IMI/CZ (50/50) are shown in Figures 12–14, respectively. There are four main peaks at about  $2\theta = 19.1^\circ, 19.6^\circ, 23.2^\circ, 28.0^\circ$  and five small peaks at  $18.6^\circ, 22.6^\circ, 23.5^\circ, 37.9^\circ, \text{ and } 48.2^\circ$ . The XRD pattern exhibit a sharp diffraction peaks at  $19.1^\circ$  (54.56%),  $19.6^\circ$  (100%),  $23.1^\circ$  (55.6%), and  $27.9^\circ$  (57.81%). The peak

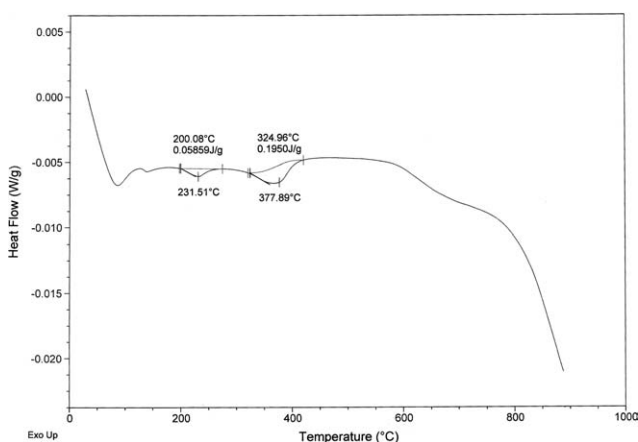


Figure 9 DSC analysis of poly(carbazole).

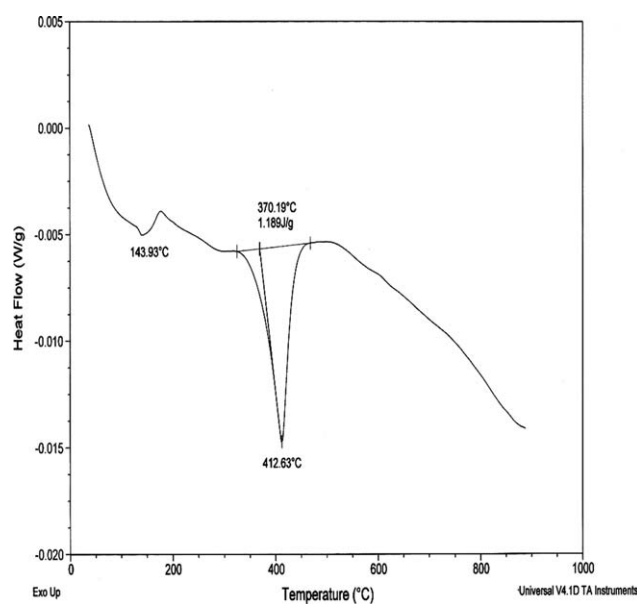
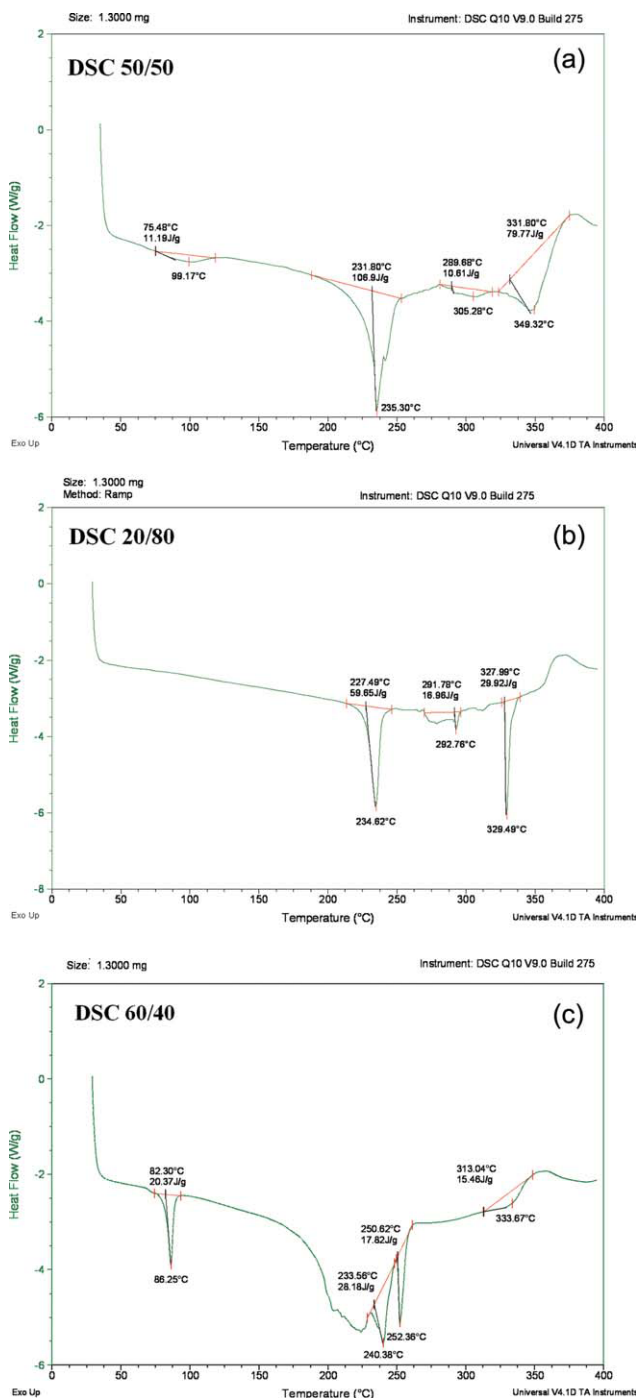
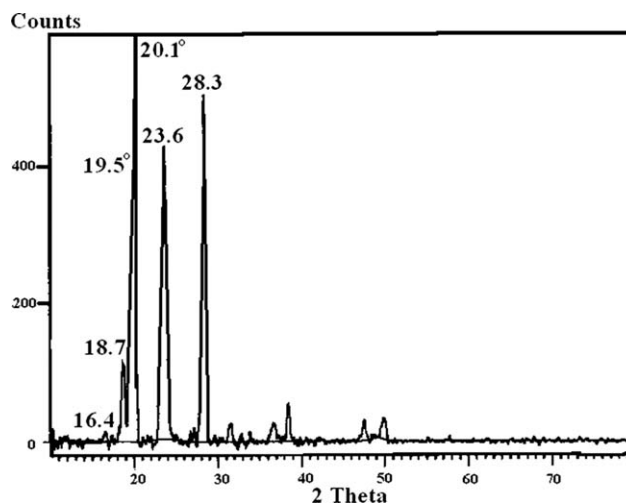


Figure 10 DSC analysis of poly(imidazole).



**Figure 11** DSC analysis of copolymers with IMI/CZ molar ratios of (a) 50/50 (b) 20/80 and (c) 60/40. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

centered at  $2\theta = 19.6^\circ$  may be ascribed to the periodicity parallel to the polymer chain, while the weak peaks at high angles may be caused by periodicity perpendicular to the polymer chain.<sup>56</sup> The diffraction pattern of PCZ have peak at about  $2\theta = 20.1^\circ$ , which is a characteristic peak of poly(carbazole).<sup>51</sup> The characteristic peak of PCZ has been shifted slightly to low angle in the copolymer. This shows the crys-

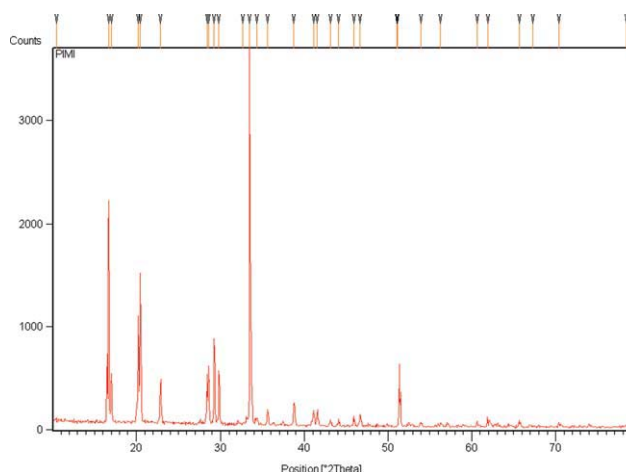


**Figure 12** Powder XRD pattern of poly(carbazole).

talline nature of the copolymer. This is also evidenced by our previous report.<sup>51</sup> Previously, the researchers reported that the amorphous and crystalline nature was exhibited in low angle and high angle ( $42.2^\circ$  and  $49.2^\circ$ ), respectively, for polyaniline powder.<sup>57</sup> But in our case, we observed sharp peaks at about ( $19.63^\circ$ ,  $19.08^\circ$ ,  $18.60^\circ$ ). The crystallite size of both homopolymer and copolymer was also calculated using Debye Scherer's formula (for copolymer =  $38.3046 \times 10^{-9}$  nm; poly(imidazole) =  $1.80 \times 10^{-9}$  nm; poly(carbazole) =  $70.9257 \times 10^{-9}$  nm).

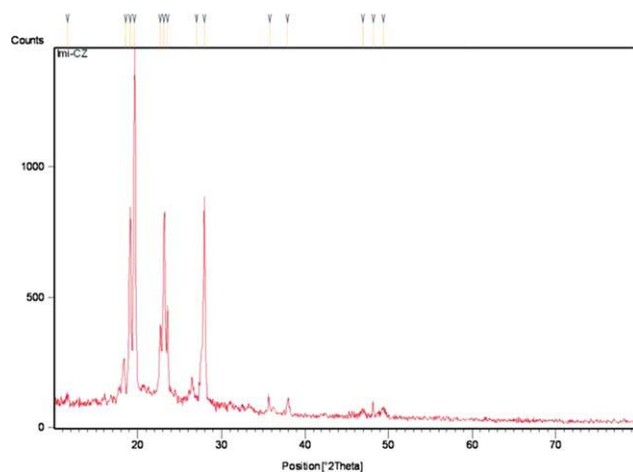
### Electrical conductivity

The electrical conductivity of the copolymer was measured on pellets at room temperature<sup>58</sup> by using the four probe method of Vander Pauw<sup>58</sup> pressed at  $2 \text{ T cm}^{-2}$  is close to  $10^{-4} \text{ S cm}^{-1}$ . The conductivity of the copolymers measured at various temperature



**Figure 13** Powder XRD pattern of poly(imidazole). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 14** Powder XRD pattern of copolymer 50/50 with IMI/CZ. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

are given in Table IV. The conductivity of various copolymers lies in the narrow region of  $2.7 \times 10^{-4}$  to  $5.48 \times 10^{-5} \text{ S cm}^{-1}$ . The conductivity of all the copolymers was found to be higher than that of poly(carbazole) ( $2.68 \times 10^{-5}$ ) and lower than that of poly(imidazole) ( $1.9 \times 10^{-3}$ )  $\text{S cm}^{-1}$ . The conductivity of copolymers increases with increase in IMI content. The higher conductivity of the copolymers compared with that of the poly(carbazole) homopolymer indicates lowering of the band gap in the copolymers formed with IMI. The trend of an increase in conductivity with lowering of CZ content in the comonomer feed suggest that the donor-acceptor type of interactions are dependent on the composition of the copolymer.<sup>38</sup> It is evident from the Table V that, conductivity increases steadily with increase in temperature showing semiconductor behavior.

## CONCLUSIONS

A series of the copolymers & varying monomer ratios from IMI and CZ have been synthesized successfully by oxidative polymerization in acetonitrile

**TABLE V**  
Electrical Conductivity of Copolymer (50/50) at Different Temperature

Temperature (°C)	Conductivity ( $10^{-4} \text{ S cm}^{-1}$ )
35	0.99
45	1.24
55	2.07
65	2.74
75	3.05
85	3.18
95	5.30

medium at ambient temperature for 24 h. UV-visible, FTIR,  $^1\text{H-NMR}$  measurements suggest that the polymers obtained are actual copolymers consisting of two monomer units but calculated IMI content is lower than feed content. XRD and DSC measurements indicate that the copolymers are crystalline. The copolymers exhibit higher conductivity and good solubility in various solvents than the homopolymer poly(carbazole).

## References

- Li, X. G.; Huang, M.-R. *J Appl Polym Sci* 1997.
- Mac Diarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L.; Wu, W.; Yaniger, S. I. *Mol Cryst Liq Cryst* 1985, 121, 173.
- Chiang, J. C.; Mac Diarmid, A. G. *Synth Met* 1986, 13, 193.
- Huang, W. S.; Humphery, B. D.; Mac Diarmid, A. G. *J Chem Soc Faraday Trans* 1986, 82, 2385.
- Genies, E. M.; Syed, A. A.; Tsintavis, C. *Mol Cryst Liq Cryst* 1985, 121, 181.
- Pron, A.; Genoud, F.; Menardo, C.; Nechtschein, M. *Synth Met* 1988, 24, 193.
- Armes, S. P.; Miller, J. F. *Synth Met* 1988, 22, 385.
- Asturias, G. E.; Mac Diarmid, A. G.; Epstein, A. J. *ICSM '88. Synth Met* 1989, 26, E157.
- Andreata, A.; Cao, Y.; Chiang, J. C.; Heeger, A. J.; Smith, P. *Synth Met* 1988, 26, 383.
- Cao, Y.; Li, S.; Xue, Z.; Guo, D. *Synth Met* 1986, 16, 305.
- Baird, D. G.; Smith, J. K. *J Polym Sci: Polym Chem Ed* 1978, 16, 61.
- Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J Chem Soc Chem Commun* 1979, 635.
- Diaz, A. F.; Bargon, J. In *Hand book of Conducting Polymers*, Vol. 1; Skotheim, T. A., Ed.; Marcel-Dekker: New York, 1986; p 82.
- Ouyang, J.; Li, Y. *Polymer* 1997, 38, 3997.
- Myers, R. E. *J Electron Mater* 1986, 15, 61.
- Armes, S. P. *Synth Met* 1987, 20, 365.
- Thieblemont, J. C.; Brun, A.; Marty, J.; Planche, M. F.; Calo, P. *Polymer* 1995, 36, 1605.
- Nishino, K.; Fuimoto, M.; Ando, O.; Ono, H.; Murayama, T. *J Appl Electrochem* 1996, 26, 425.
- Cassignol, C.; Oliver, P.; Ricard, A. *J Appl Polym Sci* 1998, 70, 1557.
- Oh, E. J.; Jang, K. S.; Mac Diarmid, A. G. *Synth Met* 2002, 125, 267.
- Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J Chem Soc Chem Commun* 1986, 1346.
- Elsenbaumer, R. L.; Jen, K. Y.; Obodi, R. *Synth Met* 1986, 15, 169.
- Kaeriyama, K.; Sato, M.; Tanaka, S. *Synth Met* 1987, 18, 229 and 233.
- Sato, M.; Tanaka, S.; Kaeriyama, K. J. *J Chem Soc Chem Commun* 1986, 873.
- Bryce, M. R.; Chissel, A.; Kathirgamanathan, P.; Parker, D.; Smith, N. R. M. *J Chem Soc Chem Commun* 1987, 873.
- Rughooputh, D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J Polym Sci Part B: Polym Phys* 1987, 25, 1071.
- Siove, A.; Ades, D. *Polymer* 2004, 45, 4045.
- Cloutex, E.; Olivero, C.; Ades, D.; Castex, M. C.; Siove, A. *Polymer* 2002, 43, 3489.
- Romero, D. B.; Schaer, M.; Leclerc, M.; Ades, D.; Siove, A.; Zuppiroli, L. *Synth Met* 1996, 80, 271.
- Stephan, O.; Vial, J. C. *Synth Met* 1999, 106, 115.

31. Jin, S. H.; Sun, Y. K.; Sohn, B. H.; Kim, W. *Eur Polym Mater* 2000, 36, 957.
32. Bai, F.; Zheng, M.; Yu, G.; Zhu, D. *Thin Solid Films* 2000, 363, 118.
33. Ahn, T.; Song, Y. S.; Shim, H. K. *Macromolecules* 2000, 33, 6764.
34. Moshusiki, H.; Hasui, T.; Kawamoto, M.; Ikeda, T.; Adachi, C.; Taniguchi, Y.; Shirota, Y. *Macromolecules* 2003, 36, 3457.
35. Morin, J. F.; Leclerc, M. *Macromolecules* 2001, 34, 4680.
36. Morin, J. F.; Beaupre, S.; Leclerc, M.; Levesque, I.; D'loro, M. *Appl Phys Lett* 2002, 80, 341.
37. Romero, D. B.; Niesh, F.; Benazzi, T.; Ades, D.; Siove, A.; Zuppiroli, L. *Adv Mater* 1997, 9, 1158.
38. Savitha, P.; Sathyanarayann, D. N. *Synth Met* 2004, 145, 113.
39. Xin-Gui, L.; Lin, X. W.; Mei-Rong, H. *Polymer* 2001, 42, 6095.
40. Xin-Gui, L.; Lin, X. W.; Mei-Rong, H. *Synth Met* 2001, 123, 435.
41. Chan, H. S. O.; Ng, S. C.; Sim, W. S.; Tan, K. L.; Tan, B. T. G. *Macromolecules* 1992, 25, 6029.
42. Anand, J.; Palaniappan, S.; Sathyanarayanan, D. N. *Prog Polym Sci* 1998, 23, 993.
43. Pud, A.; Ogurtsov, N.; Korzhenko, A.; Shapoval, G. *Prog Polym Sci* 2003, 28, 1701.
44. Zheng, W.-Y.; Levon, K.; Laakso, J.; Osterholm, J.-E. *Macromolecules* 1994, 27, 7754.
45. Nguyen, M. T.; Kasai, P.; Miller, J.; Diaz, A. F. *Macromolecules* 1994, 27, 3625.
46. Li, X.-G.; Huang, M.-R.; Li, F.; Cai, W.-J.; Jim, A.; Yang, Y.-L. *J Polym Sci Part A: Polym Chem* 2000, 38, 4407.
47. Li, X.-G.; Huang, M.-R.; Yang, Y.-L. *Polym J* 2000, 32, 348.
48. Li, X.-G.; Huang, M.-R.; Yang, Y.-L. *Polymer* 2001, 42, 4099.
49. Huang, M.-R.; Li, X.-G.; Yang, Y.-L. *Polym Degrad Stabil* 2000, 71, 31.
50. Anand, J.; Palaniappan, S.; Sathyanarayanan, D. N. *Polymer* 1998, 39, 6819.
51. Raj, V.; Madheswri, D.; Mubarak Ali, M. *J Appl Polym Sci* 2009, 116, 147.
52. Varma, I.-K.; Veena, J. *J Polym Sci: Polym Chem Ed* 1976, 14, 973.
53. Socrates, G. *Infrared Characteristics Group Frequencies*; Wiley: Chichester, 1980.
54. Gupta, R. R. *Physical Methods Heterocyclic Chemistry; General Heterocyclic Chemistry Series*; Wiley: New York, 1984.
55. Ding, L.; Wang, S.; Gregory, R. V. *Synth Met* 1999, 104, 73.
56. Moon, Y. B.; Can, Y.; Smith, P.; Heeger, A. *J Polym Commun* 1989, 30, 196.
57. Zhou, O.; Fleming, R. M.; Murphy, D. W. *Science* 1994, 263, 744.
58. Van der Pavw, L. *J Philips Rev Report* 1958, 13, 1.