# Copolymers of Aniline and o-Methoxyaniline: Synthesis and Characterization

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**Abstract:** High-conversion (HC) copolymers of aniline and o-methoxyaniline (o-anizidine) were synthesized for the first time by chemical oxidative copolymerization by using various polymerization techniques (simultaneous or consecutive introduction of comonomers into the polymerizing system). Low-conversion (LC) copolymers have also been synthesized for comparison. The polymers obtained were characterized by using ^{1}H-NMR, infrared, and electronic absorption spectroscopy; differential scanning calorimetry; and electrical conductivity measurements. Solubility characteristics and composition of different fractions of the copolymers were also determined. It was shown that, in contrast to the LC copolymers, HC copolymers reveal relatively poor solubility. Electrical conductivity of copolymers and also of o-methoxyaniline homopolymer is lower as compared to polyaniline, which correlates with notable hypsochromic (blue) shift of the bands in electronic absorption spectra. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1822–1828, 2005

**Key words:** characterization; conducting polymers; copolymerization; polyaniline

## INTRODUCTION

Polyaniline (PAni) has attracted considerable attention because of its unique electrical, optical, and electrooptical properties and numerous real and potential applications.[1–5]

One of the key problems related to the application of PAni is its poor processability due to the rigid-rod macromolecular chains and strong interchain interactions. Several approaches have been attempted to solve this problem: (i) doping induced processability of PAni, suggesting the use of the so-called functionalized protonic acids (such as dodecylbenzenesulfonic and camphorsulfonic acid) in the protonation of PAni, resulting in enhanced solubility;[6–9] (ii) preparation of PAni composites with thermoplastic polymers either *in situ* by polymerizing aniline in the presence of the second polymer constituent or by dispersing preliminarily prepared PAni in solution or in the melt of the second polymer constituent, followed by processing of the blend by using conventional methods;[3,5] (iii) homopolymerization of aniline derivatives (e.g., ring-substituted anilines) or their copolymerization with aniline,[10–17] resulting in improved solubility of the polymers obtained.

In our previous studies,[18–30] we applied the first two approaches to improve pocessability of PAni.

Concerning the homo- and copolymerization of aniline derivatives, there have been several reports on the synthesis and properties of alkyl[10–14] and alkoxyl[14–17] ring- substituted anilines. It has been found that anilines with such electron-donating substituents are more reactive than the unsubstituted aniline in the oxidative polymerization reaction due to the lower oxidation potential. Syntheses in the presence of two different monomers has shown preferential polymerization of the monomer with lower oxidation potential.[12,14,16,17] ^{1}H-NMR determination of the composition of aniline-o(m)-toluidine[12] and aniline-o-ethoxy aniline[16] copolymers versus comonomer feed composition has revealed that the actual molar fraction of substituted aniline monomer units in the copolymer is much higher than its content in the comonomer feed, up to 60–70% of the substituted comonomer. Thus, in low conversion copolymers aniline-toluidine[12] and aniline-o-ethoxyaniline[16] at 50% aniline derivative in the comonomer feed, the molar fraction of substituted aniline units in the copolymer was higher than 90%. In both cases, the low yields that are required for determination of the reactivities of monomers were achieved by employing a low molar ratio (ca. 0.25 : 1) of the oxidant to the comonomers.

Under similar conditions of low conversion chemical copolymerization (oxidant/comonomers ratio ca. 0.3 : 1), using an equimolar comonomer feed composition, copolymers of aniline and o-methoxyaniline have been obtained.[15] The yield, however, has not been specified. Based on FTIR and electronic absorp-

tion spectroscopy, differential scanning calorimetry (DSC), and electrical conductivity measurements, it was concluded that random copolymer of excellent solubility in its undoped form in several organic solvents (such as *acetone* chloroform, dimethylsulfoxide, N-methylpyrrolidone, etc.) has been prepared. However, neither quantitative solubility data in various solvents, nor the real composition of the poly(aniline-co-o-methoxyaniline) copolymers, have been presented.

From the technological point of view, it is important to synthesize and characterize high conversion (HC) polyaniline copolymers. The purpose of the present study was to prepare for the first time copolymers of aniline (Ani) and o-methoxyaniline (Mani) with high yield using various polymerization techniques: simultaneous (S) or consecutive (C) introduction of comonomers into the polymerizing system, in the latter case either aniline (C-Ani) or metoxyaniline (C-Mani) being added first. For comparison, low-conversion (LC) polymers have also been synthesized. The polymers obtained were characterized by using $^1$H-NMR, infrared, and electronic absorption spectroscopy; DSC; and electrical conductivity measurements. Solubility characteristics and composition of different fractions of the copolymers were also determined.

## EXPERIMENTAL

### Materials

Aniline (Ani) and o-methoxyaniline (Mani), both purchased from Merck, were doubly distilled under vacuum prior to use. Sulfuric acid and ammonium peroxydisulfate (APS) reagent grade were also obtained from Merck and used as received. The solvents N-methylpyrrolidone (NMP) and chloroform (both from Fluka) were used without further purification.

### Synthesis

*One-stage polymerization.* To prepare *high-conversion* copolymer HC-S, a mixture consisting of 0.9 mL Ani (0.01M) and 1.1 ml Mani (0.01M) was dissolved in 190 mL 0.5M $H_2SO_4$. This solution was maintained at 0–5°C in an ice bath and constantly stirred for about 30 min. To this solution was added dropwise with continuous stirring another solution prepared by dissolving 4.56 g (0.02M) APS in 10 ml distilled water. The reaction mixture was stirred at 0–5°C for 6 h and then kept at 10°C for 20 h. The green precipitate (doped copolymer in the form of emeraldine salt) obtained was filtered and washed repeatedly with 0.5M $H_2SO_4$ until the filtrate became colorless. To prepare the emeraldine base (undoped) form of the copolymer, 1 g of the copolymer salt was suspended in 250 mL 0.1M $NH_4OH$ solution and stirred for 6 h at

room temperature. It was afterwards filtered and washed with aqueous ammonia having pH > 12 until the disappearance of the color of the filtrate. It was dried under vacuum to constant weight.

A similar procedure was also followed to get both doped and undoped homopolymers polyaniline and poly(o-methoxyaniline).

*Two-stage polymerization.* To prepare *high-conversion* copolymer HC-C-Ani, 0.9 mL Ani (0.01M) were dissolved in 190 mL 0.5M $H_2SO_4$. This solution was maintained at 0–5°C in an ice bath and constantly stirred for about 30 min. Another solution prepared by dissolving 2.28 g (0.01M) APS in 5 ml distilled water was added dropwise to this solution with continuous stirring. When the color of the reaction mixture turned green (1 h after addition of the oxidant), 1.1 mL Mani (0.01M) and solution of 2.28 g (0.01M) APS in 5mL distilled water were added consecutively and stirred at 0–5°C for 5 h, then kept at 10°C for 20 h. Changing the order of comonomer addition, high-conversion copolymer HC-C-Mani was also obtained. Further procedure for the isolation of the doped copolymers and preparation of their undoped form was the same as described above for one-stage polymerization.

Following similar procedures the *low-conversion* copolymers LC-S, LC-C-Ani, and LC-C-Mani, as well as homopolymers PAni and PMani, were prepared by using lower oxidant to comonomers molar ratio of 0.25 : 1, instead of 1 : 1 as employed in the preparation of high- conversion polymers.

### Characterization

Solubility determination and spectroscopic and calorimetric characterization were performed by using the undoped "emeraldine base," EB, form of the polymers. The doped "emeraldine salt," ES, form was used for conductivity measurements.

Solubility was determined by dissolving 100 mg of the undoped form in 10 mL of chloroform of acetone when stirring at room temperature for 8 h followed by filtering, washing, and drying under vacuum.

The NMR spectra were obtained on a Bruker Avance DRX-250 spectrometer, operating at 250.13 MHz for $^1$H using a dual 5 mm probe head. The measurements were carried out in DMSO-d$_6$ solution at ambient temperature. The chemical shifts were referenced to the resonance signal of the solvent (DMSO-d$_6$) at 2.49 ppm. Standard 1D experiments with pulse width 30°, 1 s relaxation delay, 16K time domain points, zero-filled to 64K for protons were performed. Hard pulses with 90° pulse width of 11.6 $\mu$s for the protons at a power level of 3 dB below the maximum output were used.

Electronic absorption spectra were measured on a Carl Zeiss UV–vis spectrometer by using DMSO solutions and thin films cast therefrom.

| Designation | Yield % | $\sigma^*$ | Composition | | Acetone soluble fraction % | Chloroform insoluble fraction | | | | Chloroform soluble fraction | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $f_{Ani}$ | $f_{Mani}$ | | % | $f_{Ani}$ | $f_{Mani}$ | $\sigma^*$ | % | $f_{Ani}$ | $f_{Mani}$ | $\sigma^*$ |
| HC-S | 71 | $5.10^{-2}$ | 0.47 | 0.53 | 8 | 60 | 0.78 | 0.22 | $3.10^{-1}$ | 40 | 0.38 | 0.62 | $2.10^{-2}$ |
| HC-C-Mani | 73 | $1.10^{-1}$ | 0.47 | 0.53 | 8 | 62 | 0.76 | 0.24 | $1.10^{-1}$ | 38 | 0.38 | 0.62 | $4.10^{-2}$ |
| HC-C-Ani | 86 | $1.10^{-1}$ | 0.67 | 0.33 | 9 | 59 | 0.92 | 0.08 | $4.10^{-1}$ | 41 | 0.30 | 0.70 | $1.10^{-2}$ |
| PAni | 91 | 2.0 | 1.0 | 0.0 | 4 | 95 | 1.0 | 0.0 | - | 5 | - | - | - |
| PMani | 64 | $6.10^{-2}$ | 0.07 | 0.93 | 11 | 0 | - | - | - | 100 | 0.05 | 0.95 | - |

*Electrical conductivity was measured using doped films.
$f_{Ani}$ and $f_{Mani}$: molar fraction of Ani and Mani, respectively.

Infrared spectra of films cast from the NMP solution were registered on a Bruker Vector 22.

DSC studies were performed on a Perkin–Elmer DSC 7 differential scanning calorimeter in argon atmosphere in the temperature range of 0–350°C and heating rate of 10°C min$^{-1}$. Samples of about 10 mg were sealed in aluminum pans with holes. The instrument was calibrated with an indium standard for temperature and heat change.

Electrical conductivity, $\sigma$, of thin films of ES form obtained by HCl doping of the EB films cast from the NMP solution was measured by the conventional four-probe technique.

## RESULTS AND DISCUSSION

### High-conversion polymers

Table I presents data for polymerization yield, solubility, composition, and electrical conductivity of the homo- and copolymers of aniline (Ani) and o-methoxyaniline (Mani) prepared under different conditions. Solubility and composition were determined by using the undoped "emeraldine base," EB, form of the polymers. The doped "emeraldine salt," ES, form was used for conductivity measurements.

#### Yield

The polymers were obtained with yields approximately equal to or higher than 70%. Monomer conversion in the one-stage process (HC-S) is lower than in the two-stage process, particularly when Ani was added first (HC-C-Ani). When Mani was introduced into the reaction system before Ani (HC-C-Mani), the yield was approximately the same as in the one-stage process (HC-S), but lower than in the case of HC-C-Ani.

#### Solubility and composition

First of all, it is hardly to say that the high conversion poly(aniline-co-o-methoxyaniline)s, at least the high-conversion copolymers listed in Table I, reveal exellent solubility in acetone and chloroform as stated by Pandey and coworkers.[15] As mentioned in the Introduction, they do not specify the yield, although low-conversion polymerization conditions (oxidant/comonomers ratio ca. 0.3 : 1) have been used. Neither quantitative solubility data in different solvents, nor the real composition of the Ani-Mani copolymers, have been presented.

As is seen from Table I, poly(o-methoxyaniline) (PMani) is completely soluble in chloroform, and poorly soluble (11 wt % as 1 wt % solution) in acetone, while the soluble fractions of PAni are 5% and 4% by weight, respectively. Irrespective of the polymerization procedure, all the copolymers reveal poor solubility in acetone (ca. 8–9 wt % of the copolymer). The solubility of the copolymers in chloroform is much higher, approximately 40 wt % being the soluble and 60 wt % the insoluble fraction.

The molar fractions of the Ani and Mani units in copolymers, $f_{Ani}$ and $f_{Mani}$, respectively, and in their chloroform soluble and insoluble fractions were deduced by $^1$H-NMR spectroscopy. Figure 1 shows the proton NMR spectral characteristic of PAni, PMani, and copolymer HC-S (as illustrative examples). The copolymers exhibit a signal centered at about 3.8 ppm assigned to the protons of the -OCH$_3$ group as does PMani. As expected, this signal is not observed in the spectrum of PAni. The fractions of methoxyaniline and aniline units in the copolymers were estimated from the integral intensity of the resonance peaks of the aliphatic and aromatic protons (in the 7.0 ppm range). The results are presented in Table I.

When the comonomers were added simultaneously (HC-S) or when Mani was first introduced in a two-stage process (HC-C-Mani), copolymers of nearly equimolar composition, that is, approximately the same as the composition of the comonomer feed, have been obtained. When Ani was first added in a two-stage process (HC-C-Ani), a polymer enriched of Ani units ($f_{Ani} = 0.67$) was obtained.
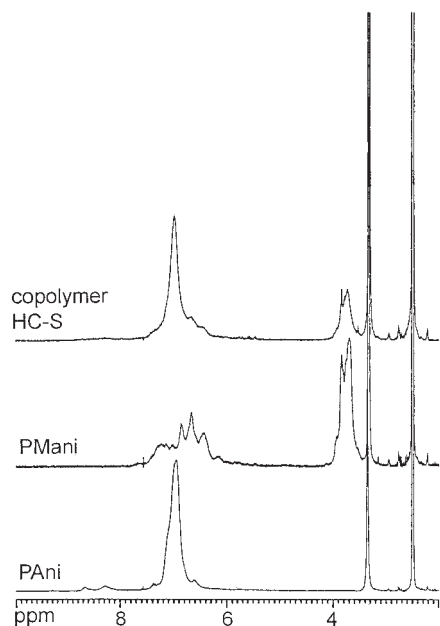
**Figure 1** $^1$H-NMR spectra of polyaniline (PAni), poly(o-methoxyaniline) (PMani), and high-conversion copolymer HC-S.

*Insoluble in chloroform factions* of the polymers obtained either by the one-stage process (HC-S) or by the two-stage process adding Mani (HC-C-Mani), first are predominantly real copolymers enriched of aniline units, the molar fraction of Mani units being about 0.23. Since the Mani homopolymer is completely soluble in chloroform, its presence in these fractions has to be excluded and Mani units are obviously involved in copolymer chains. The presence of PAni homopolymer, however, cannot be excluded, since it is insoluble in chloroform. But if PAni presents in a considerable amount, the real copolymer has to be enriched with Mani units and it has to be soluble in chloroform, which is not the case. In contrast, the composition of the chloroform insoluble fraction of the copolymer obtained by a two-stage process adding first Ani (HC-C-Ani) is very close to the aniline homopolymer, the Mani molar fraction being only 0.08.

*Soluble in chloroform fractions* of all the copolymers studied are obviously real copolymers enriched with Mani units. The presence of aniline homopolymer in these fractions has to be excluded, and Ani units ($f_{Ani} \cong 0.3$–0.4) are bound in copolymer chains. The presence of PMani homopolymer, however, cannot be excluded since it is soluble in chloroform. However, if PMani presents in a considerable amount, the real copolymer has to be enriched with Ani units and it has to be insoluble in chloroform, which is not the case. Besides, the fact that the content and composition of the soluble fraction is approximately the same irrespective of the polymerization procedure indicates that this is a real copolymer.

Obviously, homopolymer of Mani does not present in the final product even in the case when Mani was introduced first into the polymerizing system in a two-stage process (HC-C- Mani). After introduction of the second monomer (Ani), it copolymerizes with the initially formed Mani homopolymer chains rather than forming Ani homopolymer, since the oxidation potential of the polymer chains is lower than the oxidation potential of the aniline monomer[1] and a copolymer (random or block) enriched in Mani (chloroform soluble fraction) has been formed. In further polymerization, copolymer fractions enriched with Ani units (chloroform insoluble fraction) have been formed due to the exhaustion of Mani from the comonomer feed. By analogy, when Ani was introduced first into the polymerizing system (HC-C-Ani), after introduction of Mani it copolymerizes with the initially formed polyaniline homopolymer chains rather than forming Mani homopolymer due to the same reason—lower oxidation potential of polymers as compared to monomers. And finally, in the one-stage process, Mani polymerizes preferentially due to the higher reactivity as compared to unsubstituted Ani, and random copolymer enriched with Mani (chloroform soluble fraction) has been formed. In further polymerization, random copolymer enriched with Ani units (chloroform insoluble fraction) has been obtained due to the exhaustion of Mani from the comonomer feed.

Unfortunately, the available resolution of $^{13}$C-NMR spectra appears to be insufficient to allow the positive identification of the type of copolymers (random or block) by determination of the microstructure of the copolymer chains, that is, the sequence distribution of comonomer units.

Infrared and electronic absorption spectra

As seen from Figure 2, FTIR spectra of the EB form of PAni, PMani, and the copolymer HC-C- Mani (shown as an illustrative example), as well as the copolymers HC-S and HC-C-Ani (not shown in Fig. 2), revealed vibrational bands at the following wave numbers (cm$^{-1}$), assignment being performed according to Harada and coworkers[31]:

3281–3312 and 2931–2938 (NH stretching);
1617–1675 (C =O stretching, indicating the presence of quinoid moieties);
1593–1603 and 1504–1514 (ring stretching in quinoid and benzenoid rings, respectively);
1300–1328 (CN stretching + CH bending);
822–835 (CH out-of-plane bending).

Only PMani and the copolymers showed bands at 1260 and 1030 cm$^{-1}$, assigned to C- O-C stretching of the alkyl aryl ether linkage.[17]
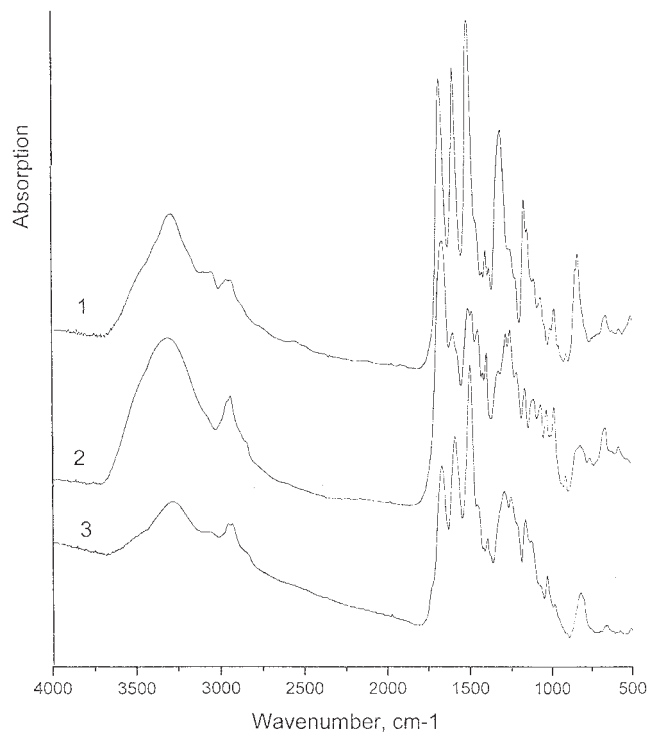
**Figure 2** Infrared spectra of polyaniline (PAni), 2 - poly(o-methoxyaniline) (PMani), and high-conversion copolymer HC-C-Mani.

Electronic absorption spectra of PAni, PMani, and the copolymers in EB form were measured both in thin films and in solution in DMSO. In all the spectra, two bands are present: the first one at about 320 nm is usually ascribed to the $\pi - \pi^*$ transition in benzene rings of the tetrameric repeat unit, whereas the second band at about 630 nm is attributed to an exitonic- type transition between the HOMO orbital of the benzenoid ring and the LUMO orbital of the quinoid ring.[4] The exact position of the absorption maxima, $\lambda_{max}$, of these bands for the polymers studied is shown in Table II.

Notable hypsochromic (blue) shift of the bands was observed for PMani and copolymers as compared to PAni, the shift being larger for PMani than for the copolymers, and for HC-S copolymer than for HC-C-Mani and HC-C-Ani copolymers. This is indicative of lower conjugation length (i) in Mani homo- and co-polymers as compared to PAni; and (ii) in HC-S co-polymer than for HC-C-Mani and HC-C-Ani copolymers. The effective conjugation length is a result of equilibrium between the conjugation that favors planar chain structures and steric factors that tend to give twisted chains. Evidently, steric hindrance connected with methoxy substituent results in twisting, thus lowering the conjugation length. Besides, the solid state spectra differ slightly from the solution one, thus showing a solvatochromic effect.

### Electrical conductivity

As is seen from Table I, electrical conductivity of the ES form of copolymer HC-S is of the same order of magnitude ($10^{-2}$ S/cm) as for PMani, while the copolymers with consecutively added comonomers (HC-C-Ani and HC-C-Mani) reveal an order of magnitude higher conductivity ($10^{-1}$ S/cm). Conductivity of PAni is 2 S/cm. These results correlate fairly well with the above discussed differences in blue shift in the electronic spectra and in conjugation length, respectively. Conductivity of soluble and insoluble in chloroform fractions of the copolymers is about $10^{-2}$ and $10^{-1}$ S/cm, respectively, which also correlates with aniline content.

### Differential scanning calorimetry

Calorimetric characterization was performed by using the undoped EB form of the polymers. Only a single glass transition, $T_g$, was visible on DSC traces both of homopolymers PAni (56°C) and PMani (105°C), and of copolymers HC-S (82°C), HC-C-Mani (78°C), and HC-C-Ani (63°C). The single $T_g$ for the copolymers located between the corresponding relaxation transitions of the homopolymers is evidence that real copolymers, perhaps random copolymers, have been formed. Obviously, the blocks of Mani and Ani units, if any, are not long enough to give rise to two different glass transitions, characteristic of both type of blocks. The composition of the copolymers HC-S and HC-C-Mani is nearly equimolar ($f_{Ani} = 0.47$), while the copolymer HC-C-Ani is enriched in Ani units ($f_{Ani} = 0.67$), resulting in its lower $T_g$ as compared to the other copolymers.

### Low-converision polymers

Table III presents data for the polymerization yield, solubility, composition, and electrical conductivity of homo- and copolymers obtained under conditions of low-conversion oxidative polymerization.

As is seen, low-conversion copolymers (yield in the range of 18–23%) are either entirely (LC-S and LC-C-Mani) or partially (LC-C) soluble in chloroform. The molar fraction of Ani units in entirely soluble copoly-

**TABLE II**
**Wave Length of the Absorption Maxima in the Electronic Absorption Spectra, $\lambda_{max}$, nm**

| Designation | Film | | Solution | |
|---|---|---|---|---|
| PMani | 310 | 605 | 315 | 615 |
| PAni | 320 | 635 | 315 | 640 |
| HC-S | 312 | 625 | 325 | 619 |
| HC-C-Mani | 314 | 626 | 318 | 625 |
| HC-C-Ani | 315 | 630 | 320 | 631 |

**TABLE III**
**Yield, Solubility, Composition, and Electrical Conductivity ($\sigma$, S/cm) of Low-Conversion)**
**Homo- and Copolymers of Aniline and o-Methoxyaniline**

| Designation % | Yield | $\sigma^*$ | Composition | | Chloroform insoluble fraction | | | Chloroform soluble fraction | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $f_{Ani}$ | $f_{Mani}$ | % | $f_{Ani}$ | $f_{Mani}$ | % | $f_{Ani}$ | $f_{Mani}$ |
| HC-S | 23.5 | $3.10^{-2}$ | 0.12 | 0.88 | 0 | - | - | 100 | - | - |
| HC-C-Mani | 17.6 | $2.10^{-2}$ | 0.14 | 0.86 | 0 | - | - | 100 | - | - |
| HC-C-Ani | 21.1 | $6.10^{-2}$ | 0.60 | 0.40 | 44 | 0.81 | 0.19 | 56 | 0.05 | 0.95 |
| PAni | 20.2 | 2.0 | 1.0 | 0.0 | 99 | - | - | 1 | - | - |
| PMani | 14.7 | $2.10^{-2}$ | 0.05 | 0.95 | 0 | - | - | 100 | - | - |

*Electrical conductivity was measured using doped films.
$f_{Ani}$ and $f_{Mani}$: molar fraction of Ani and Mani, respectively.

mers is only 0.12–0.14. Obviously, the soluble copolymer obtained by Pandey and coworkers,[15] as mentioned above, is similar to LC-S copolymer with a very low content of Ani units.

Thus, when Mani was introduced into the reaction system either simultaneously with (LC-S) or prior to Ani (LC-C-Mani), it polymerized preferentially due to its higher reactivity as a result of lower oxidation potential as compared to Ani. In both cases, soluble in chloroform real copolymers of very low content of Ani units have been obtained, neither homopolyaniline nor copolymers of higher content of Ani units being formed (there is no chloroform insoluble fraction). Of course, the presence of Mani homopolymer cannot be excluded, particularly in LC-C-Mani. In the two-stage process, when Ani was introduced first into the reaction system (LC-C-Ani), naturally its homopolymerization takes place initially. Next to the Mani addition, two polymer fractions are formed: (i) a chloroform soluble fraction consisting of highly enriched in Mani copolymer ($f_{Mani}$ = 0.95); and (ii) a chloroform insoluble fraction consisting of real copolymer ($f_{Mani}$ = 0.19), all the Mani units being involved in copolymer chains. The presence of Ani-homopolymer in the second fraction cannot be excluded. However, having in mind the above-discussed results for high-conversion copolymers, showing that copolymers of $f_{Mani}$ up to 0.20–0.25 are chloroform insoluble (Table I), it can be concluded that the second fraction consists predominantly of Ani-Mani copolymer.

Electrical conductivity of copolymer films of LC-S and LC-C-Mani (ca. $10^{-2}$ S/cm) is approximately the same as for Mani homopolymer, LC-C-Ani being an order of magnitude more conductive (ca. $10^{-1}$ S/cm) due to the considerably higher content of Ani-units. The highest conductivity of 2 S/cm revealed low-conversion PAni, which is the same value as for high-conversion PAni. As has already been discussed for high-conversion polymers, low- conversion Mani homo- and copolymers also revealed lower conjugation length as compared to PAni, as evidenced by hypsochromic (blue) shift of the band at 625 nm in the electronic absorption spectrum of PAni into the range of 586 nm for PMani and 594–604 nm for the copolymers.

In conclusion it can be stated that high-conversion poly(aniline-co-methoxyaniline) copolymers were prepared by chemical oxidative copolymerization by using various polymerization techniques (simultaneous or consecutive introduction of comonomers into the polymerizing system). In contrast to the low-conversion copolymers, they reveal relatively poor solubility. Electrical conductivity of copolymers and also of o-methoxyaniline homopolymer is lower as compared to polyaniline, which correlates with a notable hypsochromic (blue) shift of the bands in electronic absorption spectra.

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