

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 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 using ¹H-NMR, infrared, and electronic absorption spectroscopy, differential scanning calorimetry, and electrical conductivity measurements. Solubility characteristics and composition of different fractions of the copoly-

mers 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 compared to polyaniline, which correlates with notable hypsochromic (blue) shift of the bands in electronic absorption spectra.
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Key words: polyaniline; copolymerization; conducting polymers; characterization

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 preliminary prepared PAni in solution or in the melt of the second polymer constituent, followed by processing of the blend 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 articles^{18–30} we applied the first two approaches to improve the processability 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 alkoxy^{14–17} ring-substituted anilines. Anilines with such electron-donating substituents are more reactive than the unsubstituted aniline in the oxidative polymerization reaction due to the lower oxidation potential. Synthesis in the presence of two different monomers has shown preferential polymerization of the monomer with lower oxidation potential.^{12,14,16,17} ¹H-NMR determination of the composition of aniline-*o*(*m*)-toluidine¹² and aniline-*o*-ethoxy aniline¹⁶ 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-toluidine¹² and aniline-*o*-ethoxyaniline¹⁶ 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 (~0.25 : 1) of the oxidant to the comonomers.

Under similar conditions of low-conversion chemical copolymerization (oxidant/comonomers ratio ~0.3 : 1), using an equimolar comonomer feed composition, copolymers of aniline and *o*-methoxyaniline

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have been obtained.¹⁵ The yield, however, has not been specified. Based on FTIR and electronic absorption 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) 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 methoxyaniline (C-Mani) being added first. For comparison, low-conversion (LC) polymers have also been synthesized. The polymers obtained were characterized using ¹H-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 H₂SO₄. 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 H₂SO₄ 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 NH₄OH solution and stirred for 6 h at room temperature. It was afterward 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) was dissolved in 190 mL 0.5M H₂SO₄. 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 oxidant), 1.1 mL Mani (0.01M) and solution of 2.28 g (0.01M) APS in 5 mL distilled water were added consecutively and stirred at 0–5 °C for 5 h and 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 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 a lower oxidant to comonomer 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 using the undoped "emeraldine base," EB, form of polymers. Doped "emeraldine salt," ES, form was used for conductivity measurements.

Solubility was determined by dissolving 100 mg of undoped form in 10 mL of chloroform or 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 ¹H 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, 16 K time domain points, zero-filled to 64 K for protons were performed. Hard pulses with 90° pulse width of 11.6 μs for the

TABLE I
Yield, Solubility, Composition, and Electrical Conductivity (σ , S/cm) of High-Conversion Homo- and Copolymers of Aniline and *o*-Methoxyaniline

Designation	Yield (%)	σ^a	Composition		Acetone soluble fraction (%)	Chloroform insoluble fraction				Chloroform soluble fraction			
			f_{Ani}	f_{Mani}		%	f_{Ani}	f_{Mani}	σ^a	%	f_{Ani}	f_{Mani}	σ^a
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	—

^a Electrical conductivity was measured using doped films.

Note. f_{Ani} and f_{Mani} molar fraction of Ani and Mani, respectively.

protons at a power level of 3 dB below the maximum output were used.

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

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

DSC studies were performed on a PerkinElmer 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, σ , of thin films of ES form obtained by HCl doping of EB films cast from NMP solution was measured using a 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 using the undoped EB form of polymers. Doped ES form was used for conductivity measurements.

Yield

The polymers were obtained with yields approximately equal to or higher than 70%. Monomer conversion in a one-stage process (HC-S) is lower than in a 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, it is hard to say that poly(aniline-*co*-*o*-methoxyaniline)s, at least high-conversion copolymers listed in Table I, reveals excellent solubility in acetone and chloroform as stated by Pandey et al.¹⁵ As mentioned in the Introduction, they do not specify the yield although low-conversion polymerization conditions (oxidant/comonomers ratio ~0.3:1) have been used. Neither quantitative solubility data in different solvents nor the real composition of the Ani-Mani copolymers has been presented.

As 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 (~8–9 wt % of copolymer). The solubility of the copolymers in chloroform is much higher, approximately 40 wt % for the soluble and 60 wt % for the insoluble fraction.

The molar fractions of Ani and Mani units in copolymers, f_{Ani} and f_{Mani} , respectively, and in their chloroform soluble and insoluble fractions were deduced by ¹H-NMR spectroscopy. Figure 1 shows the proton NMR spectral characteristic of PAni, PMani, and copolymer HC-S (as an illustrative example). The copolymers exhibit a signal centered at ~3.8 ppm assigned to the protons of the -OCH₃ 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, i.e., approximately the same as the composition of the comonomer feed, were ob-

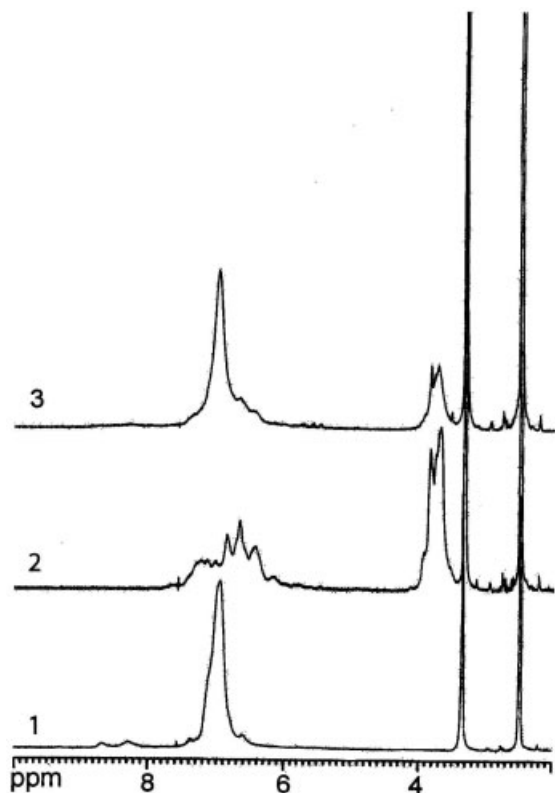


Figure 1 $^1\text{H-NMR}$ spectra of: (1) polyaniline (PANi); (2) poly(*o*-methoxyaniline) (PMani); (3) high-conversion copolymer HC-S.

tained. When Ani was first added in a two-stage process (HC-C-Ani), polymer enriched with Ani units ($f_{\text{Ani}} = 0.67$) was obtained.

Insoluble in chloroform fractions of the polymers obtained either by one-stage process (HC-S) or by two-stage process adding first Mani (HC-C-Mani), are predominantly real copolymers enriched of aniline units, with the molar fraction of Mani units being ~ 0.23 . Since Mani homopolymer is completely soluble in chloroform, its presence in these fractions must 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 is present in a considerable amount, the real copolymer must be enriched with Mani units and it must be soluble in chloroform, which is not the case. In contrast, the composition of chloroform insoluble fraction of the copolymer obtained by a two-stage process adding first Ani (HC-C-Ani) is very close to aniline homopolymer, with 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 this fraction must be excluded and Ani units ($f_{\text{Ani}} \cong 0.3\text{--}0.4$) are bounded in copolymer chains. The presence of PMani homopolymer, however, cannot be

excluded since it is soluble in chloroform. However, if PMani is present in a considerable amount, the real copolymer must be enriched with Ani units and it must be insoluble in chloroform, which is not the case. Besides, the fact that the content and composition of soluble fraction are approximately the same irrespective of the polymerization procedure indicates that this is a real copolymer.

Obviously, the 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 to form Ani homopolymer, since the oxidation potential of the polymer chains is lower than the oxidation potential of aniline monomer¹ 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 compared to the monomers. And finally, in the one-stage process Mani polymerizes preferentially due to the higher reactivity 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 $^{13}\text{C-NMR}$ spectra appears to be insufficient to allow the positive identification of the type of copolymers (random or block) by determination of the microstructure of copolymer chains, i.e., 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}), with the assignment being performed according to Harada et al.³¹

3281–3312 and 2931–2938 (NH stretching);

1617–1675 (C = O stretching indicating the presence of quinoid moieties);

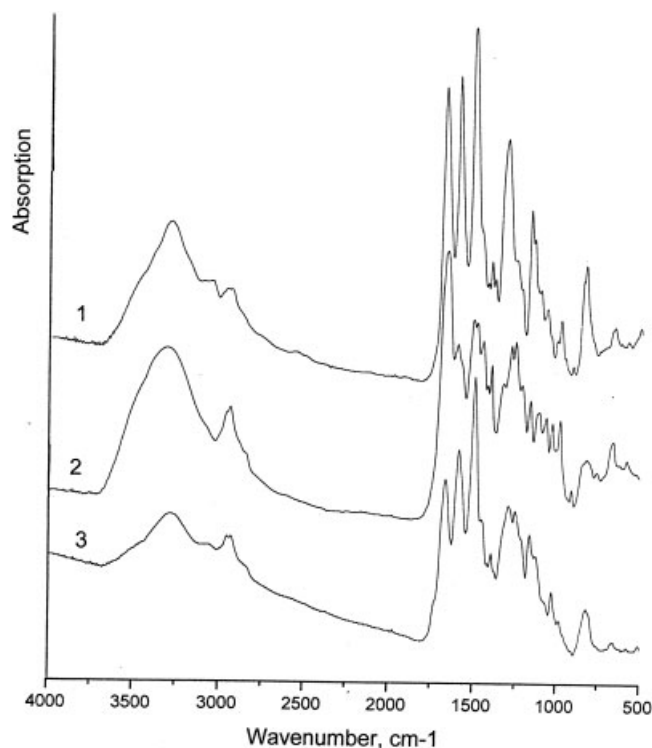


Figure 2 Infrared spectra of: (1) polyaniline (PAni); (2) poly(*o*-methoxyaniline) (PMani); (3) high-conversion copolymer HC-C-Mani.

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 alkyl aryl ether linkage.¹⁷

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 spectra two bands are present: the first one at ~ 320 nm is usually ascribed to $\pi-\pi^*$ transition in benzene rings of the tetrameric repeat unit, whereas the second band at ~ 630 nm is attributed to an excitonic-type transition between HOMO orbital of the benzenoid ring and LUMO orbital of the quinoid ring.⁴ The exact position of the absorption maxima, λ_{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 compared to PAni, with the shift being larger for PMani than for the copolymers and for the HC-S copolymer compared to HC-C-Mani and HC-C-Ani copolymers. This is indicative of lower conjugation length: (i) in Mani homo- and copolymers compared to PAni and (ii) in HC-S copolymer compared to HC-C-Mani and HC-C-Ani copolymers. The effective conjugation length is a result of equilibrium between the conjugation, which

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 seen from Table I, electrical conductivity 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 $\sim 10^{-2}$ and 10^{-1} S/cm, respectively, which also correlates with aniline content.

Differential scanning calorimetry

Calorimetric characterization was performed using the undoped EB form of polymers. Only 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 types of blocks. The composition of the copolymers HC-S and HC-C-Mani is nearly equimolar ($f_{\text{Ani}} = 0.47$), while the copolymer HC-C-Ani is enriched in Ani units ($f_{\text{Ani}} = 0.67$), resulting in its lower T_g compared to the other copolymers.

Low-conversion polymers

Table III presents data for the polymerization yield, solubility, composition, and electrical conductivity of

TABLE II
 Wavelength of the Absorption Maxima in the Electronic Absorption Spectra, λ_{max} (nm)

Designation	Film		Solution	
	1	2	1	2
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 (σ , S/cm) of Low-Conversion Homo- and Copolymers of Aniline and *o*-Methoxyaniline

Designation	Yield (%)	σ^a	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	—	—

^a Electrical conductivity was measured using doped films.

Note. f_{Ani} and f_{Mani} molar fraction of Ani and Mani, respectively.

homo- and copolymers obtained under conditions of low-conversion oxidative polymerization.

As shown, 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 copolymers is only 0.12–0.14. Obviously, the soluble copolymer obtained by Pandey et al.¹⁵ as mentioned above is similar to the LC-S copolymer with very low content of Ani units.

Thus, when Mani is introduced into the reaction system either simultaneously with (LC-S) or prior to Ani (LC-C-Mani), it polymerizes preferentially due to its higher reactivity as a result of lower oxidation potential compared to Ani. In both cases chloroform-soluble real copolymers of very low content of Ani units have been obtained, with 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) chloroform-soluble fraction highly enriched in Mani copolymer ($f_{Mani} = 0.95$); and (ii) chloroform-insoluble fraction consisting of real copolymer ($f_{Mani} = 0.19$), with all the Mani units being involved in copolymer chains. The presence of Ani-homopolymer in the second fraction cannot be excluded. However, keeping 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 ($\sim 10^{-2}$ S/cm) is approximately the same as for Mani homopolymer, with LC-C-Ani being an order of magnitude more conductive ($\sim 10^{-1}$ 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 been already discussed for high-conversion polymers, low-conversion Mani homo- and copolymers also revealed lower conjugation length compared to PAni, as evidenced by hypsochromic (blue) shift of the band at 625 nm in 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-*o*-methoxyaniline) copolymers were prepared by chemical oxidative copolymerization 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 compared to polyaniline, which correlates with notable hypsochromic (blue) shift of the bands in electronic absorption spectra.

References

- Gospodinova, N.; Terlemezyan, L. *Progr Polym Sci* 1998, 23, 1443.
- Kang, E. T.; Neoh, K. G.; Tan, K. L. *Progr Polym Sci* 1998, 23, 277.
- Anand, J.; Palaniappan, S.; Sathyanarayana, D. N. *Progr Polym Sci* 1998, 23, 993.
- Pron, A.; Rannou, P. *Progr Polym Sci* 2002, 27, 135.
- Pud, A.; Ogurtsov, N.; Korzenko, A.; Shapoval, G. *Progr Polym Sci* 2003, 28, 1701.
- Cao, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1992, 48, 91.
- Cao, Y.; Treacy, G. M.; Smith, P.; Heeger, A. J. *Appl Phys Lett* 1992, 60, 2711.
- Cao, Y.; Colaneri, N.; Heeger, A. J.; Smith, P. *Appl Phys Lett* 2001, 1994, 65.
- Kulkarni, V. G.; Campbell, J. C.; Mathew, W. R. *Synth Met* 1993, 55–57, 3785.
- Dhawan, S. K.; Trivedi, D. C. *Synth Met* 1993, 60, 63.
- Huang, M.-R.; Li, X.-G.; Yang, Y.-L.; Wang, X.-S.; Yan, D. *J Appl Polym Sci* 2001, 81, 1838.
- Wei, Y.; Hariharan, R.; Patel, S. A. *Macromolecules* 1990, 23, 758.
- Savitha, P.; Sathyanarayana, D. N. *Polym Int* 2004, 53, 106.
- Matosso, L. H. C.; Manohar, S. K.; MacDiarmid, A. G.; Epstein, A. J. *J Polym Sci A Polym Chem* 1995, 33, 1227.

15. Pandey, S. S.; Annapoorni, S.; Malhotra, B. D. *Macromolecules* 1993, 26, 3190.
16. Liao, Y.-S.; Angelopoulos, M.; Levon, K. *J Polym Sci A Polym Chem* 1995, 33, 2725.
17. Rehan, H. H.; Al-Mazroa, S. H.; Al-Fawzan, F. F. *Polym Int* 2003, 52, 918.
18. Gospodinova, N.; Mokreva, P.; Terlemezyan, L. *J Chem Soc Chem Commun* 1992, 923.
19. Stejskal, J.; Kratochvil, P.; Gospodinova, N.; Terlemezyan, L.; Mokreva, P. *Polymer* 1992, 33, 4857.
20. Gospodinova, N.; Terlemezyan, L.; Mokreva, P.; Stejskal, J.; Kratochvil, P. *Eur Polym Mater* 1993, 29, 1305.
21. Stejskal, J.; Kratochvil, P.; Gospodinova, N.; Terlemezyan, L.; Mokreva, P. *Polym Int* 1993, 32, 401.
22. Gospodinova, N.; Mokreva, P.; Tsanov, T.; Terlemezyan, L. *Polymer* 1997, 38, 743.
23. Tsanov, T.; Mokreva, P.; Terlemezyan, L. *Polym Polym Composites* 1997, 5, 299.
24. Tsanov, T.; Terlemezyan, L. *Polym Polym Composites* 1997, 5, 483.
25. Tsanov, T.; Terlemezyan, L. *Polym Polym Composites* 1998, 6, 39.
26. Terlemezyan, L.; Mokreva, P. *Int J Polym Mater* 2002, 51, 23.
27. Tsocheva, D.; Tsanov, T.; Terlemezyan, L. *J Therm Anal Cal* 2001, 66, 415.
28. Tsocheva, D.; Tsanov, T.; Terlemezyan, L. *J Therm Anal Cal* 2002, 68, 159.
29. Terlemezyan, L.; Radenkov, M.; Mokreva, P.; Radenkov, Ph.; Atanasov, A. *J Polym Mater* 2003, 20, 213.
30. Tsocheva, D.; Terlemezyan, L. *J Therm Anal Cal* 2004, 75, 739.
31. Harada, I.; Furukawa, Y.; Ukeda, F. *Synth Met* 1989, 29, E303.