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Synthesis and NMR characterization of a novel polyaniline derivative

The copolymer of 2-methoxyaniline and 3-aminobenzenesulfonic acid

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Summary

The synthesis and solution-state NMR investigation of the structure of a novel type of water-soluble polyaniline (PANI) derivative in leucoemeraldine and emeraldine oxidation states is presented. Copolymers of 3-aminobenzenesulfonic acid and 2-methoxyaniline (PMAOMA) with various monomer molar ratios were synthesized by chemical polymerization in a hydrochloric acid medium. Due to a large difference in the reactivities of 2-methoxyaniline (OMA) and 3-aminobenzenesulfonic acid (MA), the content of OMA in the copolymers was much higher (over 0.65 of the mole fraction) than in the reaction mixture. Structural characterization of the reaction products was performed using one- (^{1}H, ^{13}C) and two-dimensional (GHSQC and GCOSY) NMR spectroscopy. The NMR data indicated an almost block structure of OMA sequences of variable length separated by shorter sequences of MA units. It was also shown that the incorporation of MA units in the copolymer chains favors the formation of a less oxidized material.

Introduction

Polyaniline (PANI) has been extensively studied as a promising material for a number of commercial applications such as sensors, rechargeable batteries, electrochromic displays, selective membranes, charge dissipative coatings, corrosion resistant coatings, etc. However, PANI is insoluble in organic solvents (especially in doped-conductive form) due to a stiff molecular chain and strong intermolecular interactions, which is reflected in its rather poor processability. The polymers of ring or N-substituted aniline derivatives, such as alkyl [1,2], alkoxy [3] and aryl [4] aniline, show increased stability, wider colour ranges, lower electrical conductivity and good solubility in solvents like 1-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF) or tetrahydrofuran (THF). The water-soluble PANIs are a special class of PANIs which have been doped externally by a free strong acid and internally (self-doping) by sulfonate [5-9], carboxy [10] or phosphate [11] groups bound to the polymer backbone.

PANI derivatives are usually prepared by modifying the polymer chain by: (i) the post-treatment of the parent PANI base, i.e., by a substitution reaction; (ii) the chemical or electrochemical homopolymerization of aniline derivatives; (iii) the copolymerization of aniline with ring or N-substituted derivatives. For example, sulfonic groups can be introduced onto polymer chains by direct sulfonation of PANI [9] or by chemical or electrochemical copolymerization of aniline and sulfonated aniline derivatives such as alkyl- [12, 13] and alkoxy-sulfonated [14] aniline, 2,5-diaminobenzenesulfonic acid [15] or aminobenzenesulfonic acid [5-8]. The chemical and electrochemical homopolymerizations of 3-/2-aminobenzenesulfonic acid do not take place under mild conditions due to the strong electron-withdrawing effect and steric hindrances of the sulfonic group [5-9]. The introduction of an electron donating group (e.g. methoxy) into the aromatic ring improves its reactivity and, thus, 2-methoxy-5-sulfonic acid can homopolymerize under basic conditions [16]. However, homopolymerization of alkoxy-sulfonated aniline does not take place, probably due to the bulkiness of the substituent [14]. Namely, steric hindrance can prevent the initial bimolecular coupling of substituted ANI molecules, which is the rate-determining step in this type of polymerization [14, 17].

For the synthesis of sulfonated aniline copolymers, a reactive aniline derivative (i.e. alkyl or alkoxy aniline) can be used instead of aniline. Electrochemical copolymerization of *N*(3-sulfopropyl)-aniline with *N*-methylaniline [18], and 2-aminobenzenesulfonic acid with 3-methylaniline and 3-ethylaniline [19] have already been reported. Our intention was to synthesize a fully substituted PANI derivative by the chemical copolymerization of 3-aminobenzenesulfonic acid (MA) and 2-methoxyaniline (OMA). The structures of the emeraldine and leucoemeraldine base forms of the copolymers (PMAOMA), as well as that of the homopolymer POMA, were characterized by one- and two-dimensional solution-state NMR spectroscopy.

Experimental

Synthesis

The copolymers of OMA and MA were prepared using a similar procedure as for the copolymerization of ANI with MA [7,8], i.e. the oxidation of the substituted anilines by ammonium persulfate in acidic aqueous medium (1M HCl, Merck). The synthesis was performed at room temperature for 20 h. The molar feed fraction of OMA (f_1) was varied from 0.2 to 1.0; in the latter case the homopolymer POMA was obtained (Table 1). The oxidant ammonium peroxodisulfate ($(NH_4)_2S_2O_8$, Fluka) was added (mole ratio oxidant/monomers=1) to a constantly stirred 0.014 M solution of monomers OMA (Fluka) and MA (Aldrich) in the selected molar ratio. After 10 to 15 min the solution started to take on a red-to-purple color and a precipitate was formed. After 20 h it was filtered off and extensively washed: first with 1 M HCl (750 ml) in order to remove all oligomers and monomers, and then with acetone (250 ml). "As-synthesized" POMA and PMAOMA hydrochloride salts were dried under vacuum for 48 h at room temperature. POMA and PMAOMA salts were reduced to leucoemeraldine bases (LB) with hydrazine hydrate (Fluka) for 20 hours under argon. The reduced products were evaporated in a vacuum rotary evaporator at 50 °C. The residues were then washed with acetone and dried.

Characterization

The sulfur content was determined by atomic emission spectroscopy based on inductively coupled plasma (ICP-AES) on a sequence ICP atomic emission spetrophotometer Atomcsan 25 (Thermo Jarrell Ash). Elemental analysis was carried out on a CE440 LeemanLabs (CHN) analyzer. The fraction of OMA units in the copolymer (F_1, Table 1) was calculated from the mole fraction of MA (sulfur to nitrogen (S/N) ratio) and also, using ^{1}H NMR, from the integral ratio of methoxy protons at around 3.7 ppm and aromatic protons at around 7 ppm. ^{1}H and ^{13}C NMR spectra of the samples were recorded on a Varian VXR 300 MHz spectrometer; the gradient heteronuclear single quantum coherence (GHSQC) and gradient shift correlated (GCOSY) spectra were recorded on a Varian Inova 600 MHz spectrometer. ^{13}C NMR spectra were measured using a 90 degree pulse, a relaxation delay of 2 sec, an acq. time of 1.637 sec and up to 45,000 repetitions (45 hours). ^{1}H NMR spectra were recorded using a 4.5 degree pulse, a relaxation delay of 3 sec, an acq. time of 4 sec and 500 repetitions (1 hour). The GHSQC spectrum was measured for about 29 hours using a relaxation delay of 1 sec, an acq. time of 0.345 sec, 192 repetitions and 2 x 200 increments. GCOSY was measured for about 19 hours using a relaxation delay of 2 sec, an acq. time of 0.345, 56 repetitions and 2 x 256 increments. 10 % solutions of samples were prepared in a mixture of 1-methyl-2-pyrrolidinone (NMP, Aldrich), triethylamine (TEA, Aldrich) and DMSO-d_6 (70:10:20). TEA was added to increase the solubility of the copolymer hydrochloride salts by converting them into the emeraldine base forms. The chemical shift values were quoted relative to tetramethylsilane (TMS), an internal standard taking into account the DMSO-d_6 peak at 39.5 ppm.

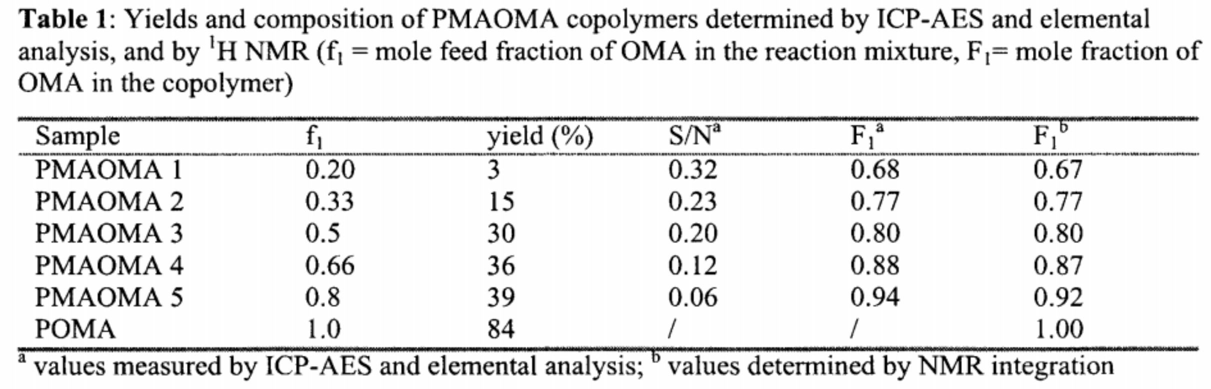


Table 1: Yields and composition of PMAOMA copolymers determined by ICP-AES and elemental analysis, and by ^{1}H NMR (f_1 = mole feed fraction of OMA in the reaction mixture, F_1= mole fraction of OMA in the copolymer)

Sample	f_1	yield (%)	S/N[a]	F_1[a]	F_1[b]
PMAOMA 1	0.20	3	0.32	0.68	0.67
PMAOMA 2	0.33	15	0.23	0.77	0.77
PMAOMA 3	0.5	30	0.20	0.80	0.80
PMAOMA 4	0.66	36	0.12	0.88	0.87
PMAOMA 5	0.8	39	0.06	0.94	0.92
POMA	1.0	84	/	/	1.00

[a] values measured by ICP-AES and elemental analysis; [b] values determined by NMR integration

Results and discussion

Chemical synthesis

The reactivities of MA and OMA monomers depend on the steric and electronic effects of the substituents. A bulky sulfonic group with an electron-withdrawing effect reduces the polymerizability of MA [9]. For OMA, the electron-donating effect of the methoxy substituent accelerates the rate of the oxidative polymerization reaction by stabilization of the intermediate free radical cations [1], which predominates over the steric effect. Thus, the reactivity of OMA is much higher than that of MA and, consequently, the mole fraction of OMA in the copolymers (F_1) is much higher than in the reaction mixtures (f_1) (Table 1). This is also reflected in an increase in copolymer yield for copolymers with high f_1 values; at low f_1 mainly soluble oligomers were formed. Table 1 shows that there is quite a good agreement between the ICP-AES/elemental analysis and ^{1}H NMR for the estimation of F_1.

NMR characterization

The NMR investigation of the structure of PANI and its derivatives is complicated due to the complexity of the emeraldine oxidation state ("as-synthesized" form) and the poor spectral resolution [20]. Highly soluble leucoemeraldine bases (LB) are formed by the reduction of PANI or its derivatives. LBs have uniform structures and show well resolved NMR spectra which makes resonance assignment easier. For this reason, we began our studies of the leucoemeraldine base forms of homopolymer POMA (LB-POMA) and copolymer PMAOMA 3 with F_1=0.8 (LB-PMAOMA) (Figures 1-4).

The ^{13}C NMR spectrum of LB-POMA shows seven signals corresponding to the carbons denoted 1b-7b (Table 2) and some minor signals ascribed to various side products (Figure la). The ^{1}H NMR spectrum of LB-POMA shows an intense singlet for proton 3b and two doublets for protons 5b and 6b (Figure 2a). The ^{13}C and ^{1}H NMR spectra of the copolymer LB-PMAOMA (Figures 1b and 2b) have all the signals found in the LB-POMA spectra, as well as additional low intensity signals ascribed to the carbons and protons of MA units (positions 1a-6a). The slight broadening of OMA signals 1b-7b and some small additional signals in the ^{13}C and ^{1}H NMR spectra can be ascribed to the vicinal OMA and MA units forming heterogeneous sequences (1bs'-7bs') and 1bs'-7bs'). The low intensity of the signals belonging to the MA units and to the heterogeneous sequences in LB-PMAOMA indicates that a low fraction of MA units were incorporated into the copolymer. This is due to the lower reactivity of MA compared to that of OMA. Hence, the copolymer chains consist of long homogenous OMA sequences separated by MA units or short sequences.

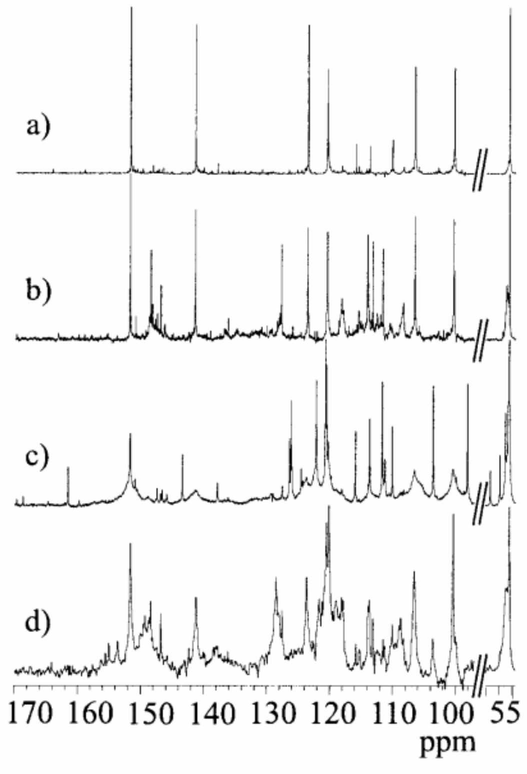


Figure 1. The ^{13}C NMR spectra of (a) LB-POMA, (b) LB-PMAOMA, and of (c) POMA and (d) PMAOMA in the "as-synthesized" forms

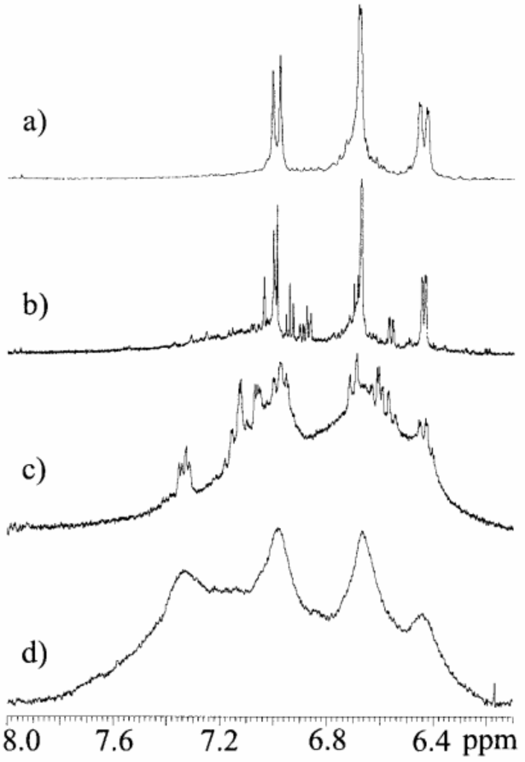


Figure 2. The ^{1}H NMR spectra of (a) LB-POMA, (b) LB-PMAOMA, and of (c) POMA and (d) PMAOMA in the "as-synthesized" forms

In the two-dimensional GHSQC spectrum of LB-PMAOMA (Figure 3), the signals above 123 ppm on the ^{13}C axis show no correlations to the proton signals and were assigned to quaternary carbons bearing sulfonate and methoxy substituents and to carbons bonded to an amine nitrogen. Their assignment in Table 2 was made considering the spectrum of LB-POMA (Figure 1a) and the calculated chemical shifts based on the assignment of LB-PANI

[8,20], LB-SPAN [8] and additivity parameters for methoxy and sulfonic substituents [21]. The signals at 123.5, 151.6 and 141.4 ppm were ascribed to carbons 1b, 2b and 4b of the OMA units, while the signals at 148.2, 146.8 and 127.6 ppm were assigned to carbons 4a, 2a and 1a of the MA units [8].

According to the ^{13}C-^{1}H couplings in the GHSQC spectrum of LB-PMAOMA (Figure 3), the carbon signals at 100.3, 106.5 and 120.4 ppm show intense correlation signals to proton signals at 6.67, 6.44 and 7.00 ppm and were attributed to the 3b, 5b and 6b carbons and protons of the OMA units (Table 2). The carbons with signals at 111.5, 114.0 and 113.2 ppm are coupled with protons having signals at 7.04, 6.56 and 6.94 ppm and were ascribed to the 3a, 5a and 6a positions of the MA units. The methoxy substituent (7b) shows a correlation to the carbon signal at 55.0 ppm and the proton signal at 3.7 ppm. ^{1}H-^{1}H couplings in the two-dimensional GCOSY spectrum (Figure 4) confirmed the assignment based on GHSQC spectrum. For OMA units, an intense out-of-diagonal correlation signal for the adjacent proton coupling 5b-6b and weak correlation signals for long-range 5b-3b and 6b-3b proton couplings were observed. The coupling of MA 5a-6a protons and the very weak coupling of MA 3a-5a protons was also observed. The weak correlation signal for proton resonances at 6.74 and 6.90 ppm could be due to the long-range coupling of the protons in the chlorinated OMA units.

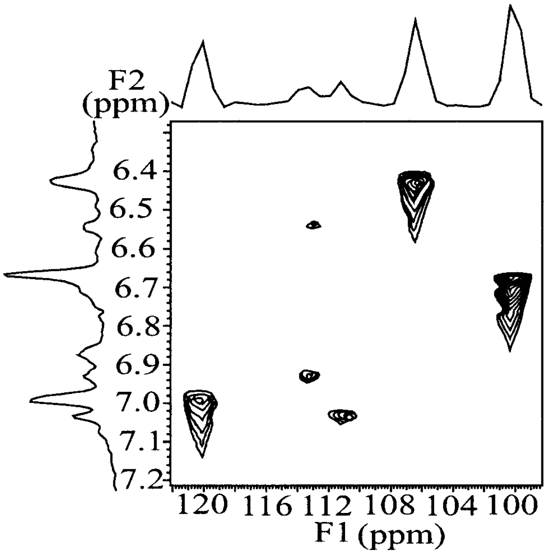


Figure 3. The two-dimensional GHSQC spectrum of LB-PMAOMA

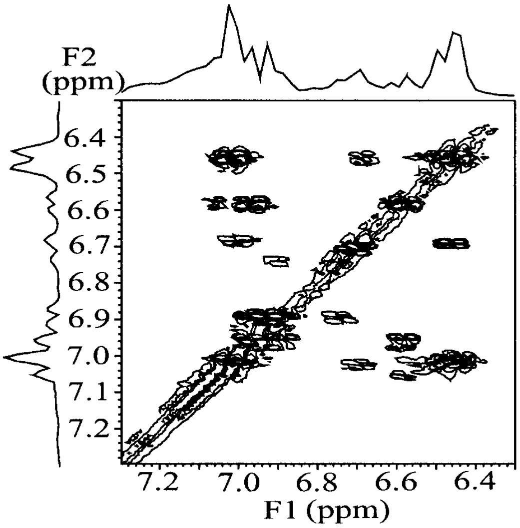
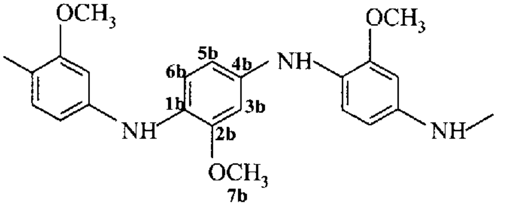
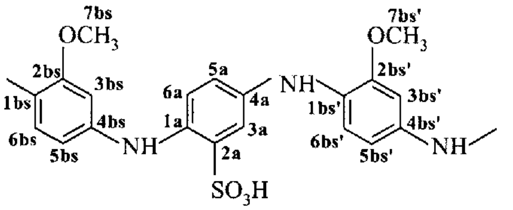
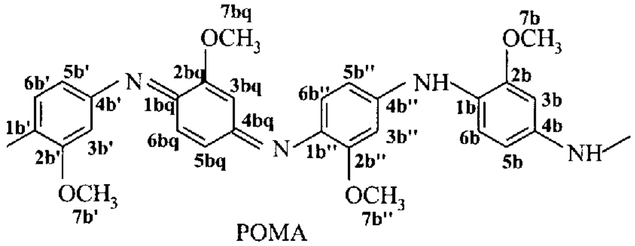
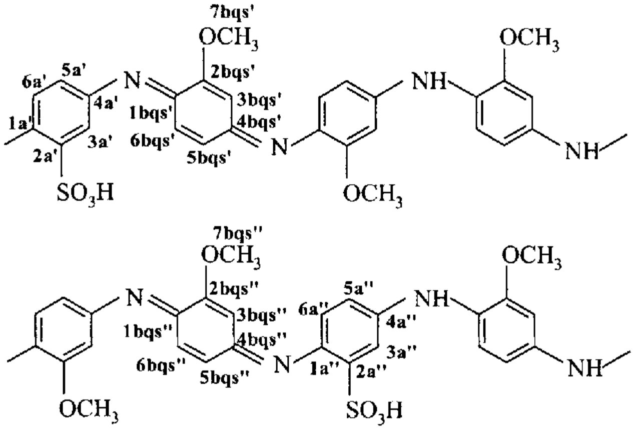


Figure 4. The two-dimensional GCOSY spectrum of LB-PMAOMA

Other weak signals in the ^{1}H and ^{13}C NMR spectra of LB-PMAOMA are due to the various sequences of both comonomers, the possibility of head-to-head and tail-to-tail arrangements, and defect sites caused by end groups, the residue of quinoid rings, chlorination, degradation by hydrolysis and other side reaction [8,20]. The ^{13}C signals at around 110, 114 and 116 ppm which are present in the LB-PMAOMA and LB-POMA spectra could be ascribed to the chlorination of the methoxy substituted benzene ring, while signals at 118 and 108 ppm, which are especially intense in the LB-PMAOMA spectrum, could be ascribed to the end sulfonated group.

Table 2: Assignment of the observed carbon chemical shifts in ^{13}C NMR spectra of LB-POMA, LB-PMAOMA, POMA and PMAOMA polymers

Structure	Position of carbon	Chemical shift (ppm)
 LB-POMA	1b	123.5
	2b	151.6
	3b	100.3
	4b	141.4
	5b	106.5
	6b	120.4
	7b	55.0
	1a	127.6
 LB-PMAOMA	2a	146.8
	3a	111.5
	4a	148.2
	5a	114.0
	6a	113.2
	1bq, 6bq (cis)	145.7-148.7
	2bq (cis)	169.5
	2bq (trans)	159.5
	3bq (trans)	108.2
	3bq (cis)	124.5
 POMA	4bq	168
	5bq (cis)	137.8
	5bq (trans)	114
	6bq (trans)	127.5
	7bq	58.1
	1b'	126.1
	1b''	126.4
	2b'	161
	2b''	151.6[a]
	3b'	98.1
 PMAOMA	3b''	103.6
	4b'	150.9
	4b''	143.3
	5b'	111.3
	5b''	111.6
	6b'	122.1
	6b''	120.7
	7b'	56.5
	7b''	55.0
	1a'	153.6
	1a''	149.2
	2a'	136.1
	2a''	128.4
	4a'	155.5
	4a''	155.0
	5a', 6a'', 3a', 5a'', 6a' 3a''	122 - 108

[a] 2b'' overlapping with 2b

The ^{13}C NMR and ^{1}H spectra of POMA in the "as-synthesized" (emeraldine) form (Figure 1c and 2c) show a number of new signals that are absent in the spectra of reduced LB-POMA. Assuming head-to-tail arrangements of OMA units, two benzenoid units (1b'-7b' and 1b"-7b") in the neighborhood of the quinoid unit (1bq-7bq) are present in POMA. The new signals in the ^{13}C NMR spectra were assigned as summarized in Table 2 considering the calculations made on the basis of the emeraldine PANI and SPAN chemical shifts [8,20] and the additive parameters of the methoxy substituent [21]. The signals characteristic of LB-POMA (1b-7b) at 151.6, 141.3, 123.6, 120.2, 106.5, 100.3 and 55.0 ppm become broader and of lower intensities. In addition to the signals at 115.9, 113.7 and 110.1 ppm ascribed to the chlorinated benzenoid OMA rings, some smaller signals appear which are ascribed to head-to-head and tail-to-tail arrangements, other possible chain conformations about the quinoid ring, and defect sites.

The ^{13}C NMR spectrum of PMAOMA in the "as-synthesized" form (Figure 1d) contains all the signals characteristic of LB-PMAOMA (1a-6a and 1b-7b), as well as those characteristic of the POMA emeraldine base (1b'-7b', 1bq-7bq and 1b"-7b"). However, the comparison of the "as-synthesized" POMA and PMAOMA spectra shows that the relative intensity of the carbon signals marked 1b'-7b', 1bq-7bq and 1b"-7b" is much lower and of the carbon signals characteristic of LB-POMA marked 1b-7b (benzenoid units surrounded by benzenoid units) is significantly higher in the PMAOMA spectrum than their intensities in the "as-synthesized" POMA spectrum. This indicates a lower content of quinoid units and a higher content of benzenoid units in the "as-synthesized" PMAOMA compared to POMA. Similar conclusions were reported for SPAN copolymers where a linear correlation was observed between the content of MA units and the proportion of reduced oxidation states [8].

The assignment of new signals in the "as-synthesized" PMAOMA ^{13}C NMR spectrum was made under the following assumptions: the majority of MA units remain in the benzenoid form; quinoid units are mostly derived from OMA units; and, most of the monomer units are in a head-to-tail arrangements. Due to the asymmetry of the MA units, at least three different quinoid units should be present in the copolymer: (i) those in longer POMA sequences (C1bq-C7bq); (ii) those in the vicinity of an MA unit head (C1bqs"-C7bqs"); and (iii) those in the vicinity of an MA unit tail (C1bqs'-C7bqs'). These new signals (C1bqs'-C7bqs' and C1bqs"-C7bqs") shift downfield and upfield depending on the signals of homogenous emeraldine OMA sequences (C1bq-C7bq). Owing to the low spectral resolution and intensity of these signals a detailed assignation was not made. The signals assigned to sulfonated units (C1a'-C6a' and C1a"-C6a") in the vicinity of quinoid rings (bqs' and bqs") were partly overlapped by other signals; their assignment is given in Table 2.

The ^{1}H NMR spectra of "as-synthesized" PMAOMA (Figure 2d) show a broad, poorly resolved multiplet of aromatic protons in the region from 6.0 to 8.0 ppm with the aliphatic, methoxy protons at around 3.7 ppm.

Conclusions

The chemical synthesis of copolymer poly(2-methoxyaniline-co-3-aminobenzensulfonic acid) (PMAOMA) is reported for the first time. Due to the high reactivity of 2-methoxyaniline (OMA) and the very low reactivity of 3-aminobenzensulfonic acid (MA), the actual fraction of OMA in the copolymers (F_1), estimated by ^{1}H NMR and elemental analysis is higher than its feed fraction (f_1). The NMR investigation of the PMAOMA structure indicated an almost block structure of OMA sequences of variable length separated by MA units of shorter sequences. A comparison of the NMR spectra of the "as-synthesized" POMA homopolymer and the PMAOMA copolymer show that the incorporation of MA units reduces the content of quinoid units and increases the content of benzenoid units. This means that more a reduced oxidation state is favored in the formation of the PMAOMA copolymer.

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