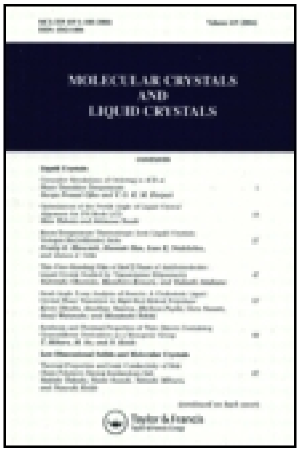

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EPR and Optical Study of the Aminonaphthalene Sulfonic Acids and Aniline New Conducting Copolymers

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EPR and Optical Study of the Aminonaphthalene Sulfonic Acids and Aniline New Conducting Copolymers

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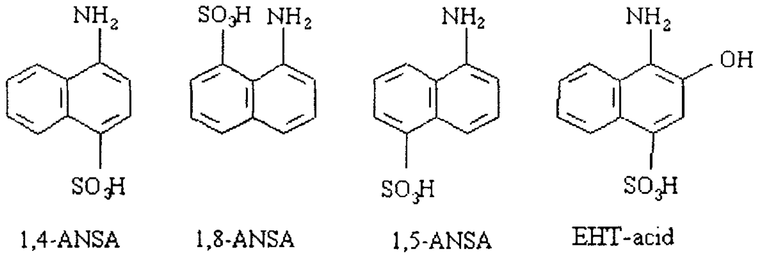
The effects of the molecular structure of isomeric aminonaphthalene sulfonic acids (ANSA) on the EPR and optical spectra of its copolymers with aniline (An) have been investigated. As it has been indicated by EPR and IR-spectroscopy, the higher spin concentration is observed for (1,4-ANSA+An) copolymer when the ortho-para position coupling between ANSA and An takes place. According to UV-spectroscopy of the copolymer films on SnO_2 surface the absorption bands near 400-440 nm (cation-radical species) and 800-900 nm (delocalized conducting electrons) are observed in all the cases. The shape of maxima is depend on ANSA molecular structure.

Keywords: copolymers, structure, EPR, optical spectra, magnetism

INTRODUCTION

Synthesis and investigation of a new conducting copolymers with aminonaphthalene and sulfonic groups are of substantial interest because their using as potential electrode materials[1] and molecular-based magnets[2]. The ferromagnetic behavior below T = 4 K of HCl-doped (5,2-ANSA) and aniline copolymer is reported[2]. But the characteristics of this copolymer are not given.

In order to study the effect of structure on the electronic properties of copolymers the EPR, IR, UV- spectra of ANSA and aniline (An) copolymers have been investigated in the present work. The isomeric ANSA with different mutual position of substitutes were used: 1-amino-4-naphthalene sulfonic acid (1,4-ANSA); 1-amino-8-naphthalene sulfonic acid (1,8-ANSA); 1,5-ANSA; 1-amino-2-hydroxy-4-naphthalene sulsonic acid (EHT-acid). Structures of ANSA are presented in Fig.1.



1,4-ANSA 1,8-ANSA 1,5-ANSA EHT-acid

FIGURE 1. Chemical structure of aminonaphthalene sulfonic acids

EXPERIMENTAL

Copolymers were synthesized both by oxidative polymerization of ANSA+An mixtures in sulfuric acid solution and electropolymerization on SnO_2 electrodes at current density 0,1 mA/cm^2. The structure of copolymers have been investigated by IR-spectroscopy (KBr pellets, Specord M-80) at frequency range 400-4000 cm^{-1}.EPR measurements have been performed with X-band RE-1306 spectrometer operating in the high frequency (100 kHz) modulation mode of magnetic fields in temperature range 4,2-300 K. Electronic absorption spectra in 350-1000 nm region were obtained with spectrophotometer SP-700 A. Magnetic measurements have carried out as described in [3].

RESULTS AND DISSCUSSION

In acid solution ANSA undergoes to anodic oxidation through amino group, while the sulfonic group and naphthalene cycle does not intervene[1,4]. Oxidation of aniline proceeds at the potential range near to ANSA oxidation which leads to possibility of copolymer products formation, suggested by IR-spectroscopy (broad bands at 3280 - 3300 cm^{-1}). The bands at 790-820 cm^{-1} (deformation oscillation of C-H bond in naphthalene ring substituted in 1 and 4 position) suggested the para-coupling products formation. In the IR spectra of (1,4-;1,5-ANSA+An) copolymers maximum at 1150, 780, 758 cm^{-1} are corresponded to ortho-substituted naphthalene cycle, the bands at 1630-1650, 1450-1456 cm^{-1} indicate the coupling throuth C-C- bonds (FIGURE 2).

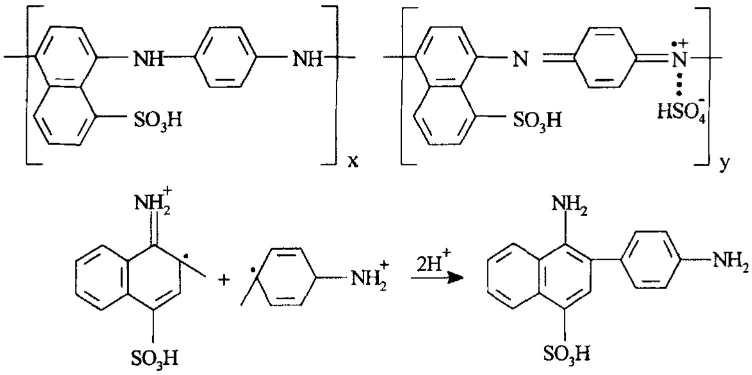


FIGURE 2 Scheme of (ANSA+An) copolymers formation

As it was found from EPR spectroscopy in the 4,2-300 K temperature interval all copolymers demonstrate the signal shape in general similar that to poly-An powders [5,6].The line parameters weakly depend on temperature between 77 and 300 K, but at $T < 50$ K the signal shape becomes more intensive. It's found that shape of signal is depended on the ANSA. An molar ratio (FIGURE 3). The g-values are in the range 2.0025-2.0034, which is typical for free radicals of the π-system 2 of aromatics. It's also indicates that radical defects trapped in the poly(ANSA-An) network are present[6]. Parameters of EPR-spectra are presented in the TABLE 1.

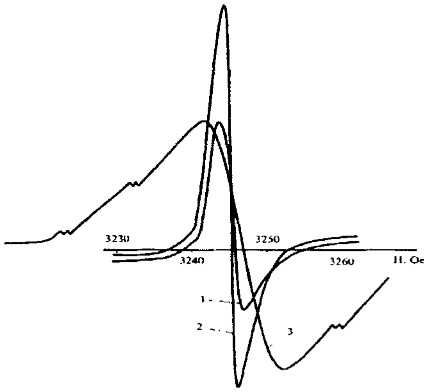


FIGURE 3. EPR- spectra of (ANSA-An) copolymers at the T = 298 K: 1,3-(1,8-ANSA+An);2-(1,4-ANSA+:An);, molar ratio 1:1 (2,3); 1:3(1).

TABLE 1. Parameters of EPR-spectra of $(ANSA+An)_n$ at T = 298 K

Copolymer	Molar ratio	$g \pm 0.0002$	ΔH_{pp}, Oe	N_s, 1/ g
Poly-An	0 :1	2.0034	3.1	$5{,}5 \bullet 10^{19}$
$(1{,}4\text{-}ANSA+An)_n$	1: 1	2.0028	3.1	$1{,}2 \bullet 10^{20}$
	1: 3	2.0028	3.1	$1.7 \bullet 10^{19}$
$(1{,}8\text{-}ANSA +An)_n$	1 : 1	2.0026	7.5	$3.7 \bullet 10^{19}$
	1 : 3	2.0025	4.0	$7.2 \bullet 10^{19}$
$(EHT+An)_n$	1 : 3	2.0031	3.2	$4.9 \bullet 10^{18}$

As it is seen from the Table 1, increasing of the paramagnetic centers concentration (N_s) is observed in the case of (1,4-ANSA+An) copolymer (1:1), when the ortho-position coupling between ANSA and An takes place. The N_s is higher by about one order of magnitude in comparison with poly-

An doped by sulfuric acid[4] synthesized at the same conditions. In the case of $(1,8\text{-ANSA+An})_n$ the para-coupling is prevalent. This one leads to any loss of spin density due to spin-spin interaction (bipolaron formation). The (EHT-An) copolymer is characterized by lowest spin density may be caused by presence of radical-acceptor hydroxyl group in naphthalene rings[1]. In UV-spectra of (co)polymer films in all cases two or three absorbtion maximums were observed. (Fig. 4): 400-440 nm (cation-radicals or polarons), 750-900 nm (delocalized electrons of conductivity or bipolaronic states). Peak near the 550-650 nm could be associated with the π -π^* transition of the polymer units with quinoid structure. The λ_{max} of this peak are found to be red-shifted in copolymers as it was compared with corresponding $(\text{ANSA})_n$ probably due to extention of the π-conjugation.

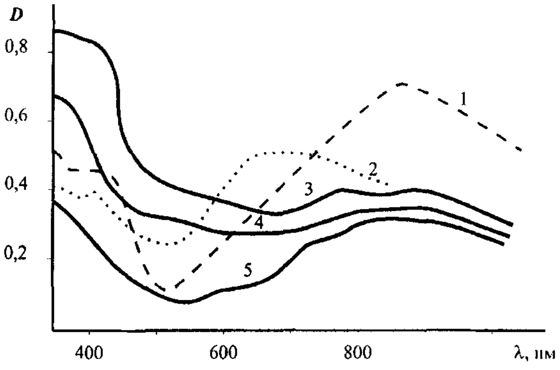


FIGURE 4. Optical spectra of (co)polymer films on the SnO_2: 1-poly-An; 2-$(1,8\text{-ANSA})_n$; 3-$(1,8\text{-ANSA+An})_n$; 4-$(1,5\text{-ANSA+An})_n$;5-$(1,4\text{-ANSA+An})_n$.

Keeping in mind the higher spin density of $(1,4\text{-ANSA+An})_n$ the magnetic properties of this copolymer was examined. Temperature dependence of the magnetic susceptibility at low-temperature region is shown at the FIGURE 5. The linear extrapolation of $1/\chi$ curve at the range below 4.2 K intersects the temperature axis at $T_c = 2.8$ K, indicating the weak ferromagnetic interaction[2]. Parameters of EPR together with UV-vis. spectra clarified that spins of (ANSA+An)copolymers had a polaronic nature delocalizing over the amino- naphthalene rings and polyaniline fragments. Differences in unpaired spin con-centration is caused by space structure of copolymers. A higher N_s value of$(1,4\text{-ANSA+An})_n$ may be explained both by the presence of π-conjugation in copolymer chain and steric effect of radical trapped ortho-substitute in naph-thalene rings. In this case a weak ferromagnetic interaction has been observed.

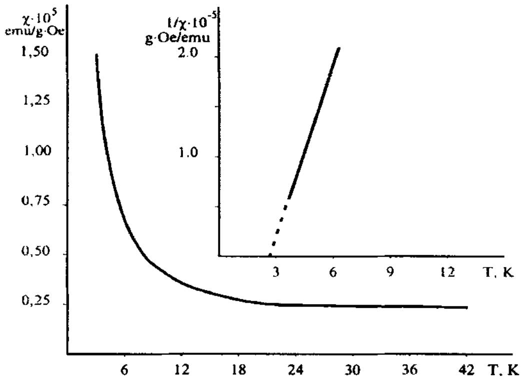


FIGURE 5. Temperature dependence of magnetic susceptibility of $(1,4\text{-ANSA+An})_n$ (1:1) at H = 1000 Oe.

References

[1.] M.C.Pham, M. Mostefai M., M.Simon et al., *Synth. Metals,* **63**, 7 (1994)

[2.] H. Mizobushi, T. Kawai, E. Trobland et al., Ibid, **69**, 239 (1995).

[3.] E.I. Aksimentyeva et al., *Physika Tverdogo Tela,* **30**, 1133 (1996).

[4.] Chernilevska G.S., Aksimentyeva E.I.,Novikov V.P. *Theoreticheskaya i Eksper. Khimia,* **33**, 22 (1997).

[5.] H.S. Javadi et al. *Synth.Metals,***29**, 439 (1989)

[6.] O.I. Aksimentyeva et al., *Ext.Absi.XVII Congr. AMPERE*(Kazan), **1**, 395. (1994)