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Matrix Polymerization of Aniline in the Presence of Polysulfonic Acids

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Abstract: **Aniline matrix polymerization in the presence of polysulfonic acids with different chemical structure and molecular mass in water and water-2-propanol mixtures is investigated. It is found that aniline matrix polymerization leads to formation of soluble polyelectrolyte complexes where polyaniline is in emeraldine form. The dimensions of polyaniline-polyelectrolyte complex particles do not depend on the molecular mass and chemical structure of polyelectolyte in water. Obtained complexes are stabilized not only with electrostatic but also with non-ionic, e.g. Van der Waals' interactions. The proton conductivity of polyelectrolyte complexes of PANI-MF-4SK is investigated and it is found the proton conductivity can be controlled with varying of ANI amount in the initial reaction mixture.**

Keywords: **polyaniline, matrix polymerization, Nafion, proton and electron conductivity**

I INTRODUCTION

Polyaniline (PANI) is an electron conducting polymer which has potential application in different areas of the industry. Due to its rather high electron conductivity, environmental stability and ease of preparation polyaniline may be used in electrochromic devices, antistatic and anticorrosion coatings, supercapacitors and organic wires. The main disadvantages of polyaniline are the poor solubility in common solvents and low thermal stability of electron conductivity (because HCl is volatile and polyaniline is dedoping on heating). There are a lot of solutions of this problem but the simplest is the matrix polymerization of aniline in the presence of polyacid. Polyacid organizes aniline molecules during its polymerization and stabilizes polyaniline macromolecules making them soluble in water. In this work the main features of aniline matrix polymerization in the presence polystyrenesulfonic and polyacrylamidomethylpropanesulfonic acid and the properties of PANI obtained in their presence were studied.

However poly-(2-acrylamido-1-methylpropanesulfonic) acid (PAMPS) and poly(4-styrenesulfonic) acid (PSS) do not form with PANI films with good mechanical properties. The possibility of aniline matrix polymerization in the presence of film forming polyelectrolyte Nafion® and its analogue MF-4SK in 2-propanole and the properties of films of obtained interpolyelectrolyte complexes (IPEC) were studied in present work.

II EXPERIMENTAL

A Raw materials

For aniline matrix polymerization aniline hydrochloride (ANI, Sigma Aldrich) was used as a monomer, ammonium persulfate (APS, ICN Biomedicals) was used as an oxidizer. PAMPS (M_w = 2 000 000, Sigma Aldrich), PSS (M_w = 70 000, Sigma Aldrich), Nafion® (Sigma Aldrich, DuPont) and MF-4SK (JSC "Plastpolymer", 8.2% solution in 2-propanol) were used as polyelectrolyte matrices (PEM).

B Aniline matrix polymerization in the presence of PAMPS and PSS

0.0389 g of ANI and 0.0883 g of APS were dissolved in 10 ml of distilled water. Freshly prepared ANI solution was mixed with polyacid solution ([ANI]/[PEM] = 1) and stirred during 30 min. Then APS solution was added to the mixture of ANI and PEM at the vigorous stirring ([APS]/[ANI] = 1.25 and 5), after that the mixture was briefly stirred and left to polymerize at room temperature during 24 hours.

C ANI matrix polymerization in the presence of Nafion® and MF-4SK

0.0066 g of ANI was dissolved in 10 ml of mixture of distilled water and 2-propanol and 0.0144 g of APS was dissolved in 10 ml of mixture of 2-propanol and distilled water. Then freshly prepared ANI solution was mixed with appropriate amount of MF-4SK solution or 8.2% solution of Nafion® in 2-propanol ([ANI]/[Nafion® (MF-4SK)] = 0.05 - 1). The volume fractions of 2-propanol were 3.4, 25, 50, 75 and 88.67 vol.%. The mixture was stirred during 30 min and APS solution was added on the constant stirring ([APS]/[ANI] = 1,25). Then reaction mixture was left to polymerize at room temperature during 24 hours.

Solutions of PANI prepared in the presence of Nafion analogue (MF-4SK) with 2-propanol content 88.67 vol.% were casted in a Petri dishes and dried in air. The obtained films were conditioned in boiling 1M HCl for 3 h and in boiling water for 3 h.

Proton and electron conductivity of conditioned films was measured using two-probe technique with impedance meter Agilent 4285A (Sweden) at frequency range 20Hz – 2MHz at 25-100°C with temperature interval of 5°C.

The morphology of PANI-PEM composite was investigated using transmittance electron microscope Leo 912 AB Omega (Zeiss, Germany).

The electron spectra of the reaction mixtures containing ANI, APS and PEM at different time intervals were collected using spectrophotometer Helios α, USA.

The experiments of dynamic light scattering were carried out using "PhotoCor Complex" instrument ("Fotocor", Russia) with real-time correlator "PhotoCor-FC" (288 channels) and one-mode helium-neon laser (λ_0 = 632.8 nm). Obtained autocorrelation functions were processed using inverse Laplase transform on DynaLS software. This processing gives relaxation times distribution function $\tau = 1/Dq^2$ of the investigated solutions. All studied solutions have distribution functions with one peak which is inherent for diffusion character of the observed processes. The diffusion coefficient of water soluble PANI was found as a slope of dependence of $1/\tau$ from $q = \frac{4\pi n}{\lambda_0}\sin(\theta/2)$, where n is refraction index of solvent, θ is scattering angle (30-130°). The hydrodynamic radii (R_h) of complexes were calculated using Einstein-Stocks equation $R_h = \frac{kT}{6\pi\eta_0 D}$, where η_0 = 0.893 cP for water.

Water soluble PANI obtained in the presence of PEM was dedoped using 1M NaOH solution, the pH of the resulting solution was adjusted to 11.

III DISCUSSION

During ANI oxidation with APS in the presence of the PEM the mixture solution color becomes dark green via blue, however the appearance of PANI precipitate is not observed which indicates that obtained PANI is involved in IPEC with a polyelectrolyte matrix. In the electron spectra (data are not shown) of the reaction mixtures the absorbance at 350 nm and 630 nm is linearly increasing during 15 min of the polymerization. Then the absorbance at 350 nm shifts to 370 and the shoulder-like band at 420 nm appears. The peak at 630 nm shifts dramatically to 730 nm. The band at 350 nm is π-π*-electron transitions in benzene rings, 630 nm is attributed to an absorbance of exitone transitions in quinoid rings, while the 370 nm peak corresponds to a protonated emeraldine salt, 420 nm band corresponds to appearance of cation-radicals [1] and 730 nm band – to polarons [2]. Such spectral behavior can be connected with the reduction of partially oxidized polyaniline and its transformation to emeraldine salt.

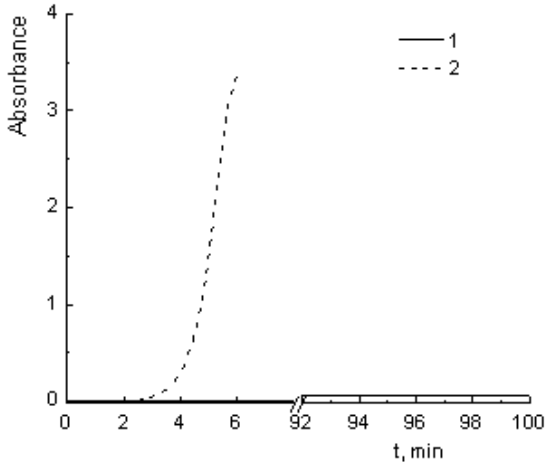

Fig. 1. The dependence of absorbance of the reaction mixtures containing ANI and APS at 630-640 nm from time for reaction mixtures 1) without matrix and 2) in the presence of PSS (M_w = 70 000), ([APS]/[ANI] = 1.25, [ANI] = 2×10^{-3} mol/l)

To confirm this conclusion ANI polymerization with 5-fold excess of APS was carried out. The polymerization with 5-fold excess of oxidizer has no red shift of absorption band from 630 nm to 730 nm but after the absorption peak at 630 nm reaches its maximum value it starts to decrease and shifts to blue region due to the oxidative destruction of polymerization product. Thus the red shift of band at 630 nm in electron spectra of the reaction mixture is attributed to reduction of partially oxidized form of PANI to emeraldine form.

It was found that polyelectrolyte matrix reduces the period of ANI polymerization, i.e. the polymerization of ANI in the presence of low molecular weight dopant (HCl) at [ANI] = 10^{-3} mol/l does not take place even after 100 min. While the one in the presence of PAMPS or PSS was found to finish after 5-7 min (Fig. 1).

The dynamic light scattering data showed that the hydrodynamic radii R_h of forming IPECs rise at the initial stages of ANI polymerization and become constant after red-shift of peak at 630 nm. The R_h was found to be 20 nm for IPEC PANI-PSS and 30 nm for PANI-PAMPS, while the R_h of PSS is 5 nm and 18 nm of PAMPS. These data allow to propose that observed particles if IPECs consist of aggregates including PANI chains and from 5 to 80 chains of PEM (for PAMPS and PSS correspondingly).

It is known that PANI does not dissolve in water and its particles should be stabilized with PEM loops in water solution due to electrostatic interaction between PANI and PEM. Deprotonation of emeraldine salts by alkali causes the formation of non-charged emeraldine base [3]. Thus, the addition of NaOH should destroy the IPEC PANI-PEM. pH increase of the PANI-PEM solution leads to decrease of the absorbance at 730 nm. Decrease and appearance of a new absorption band at 540 nm is corresponded to emeraldine base [3]. The precipitation of PANI was not observed. This shows, that the polyelectrolyte matrix stabilizes polyaniline not only with ionic but also with other, e.g. Van der Waals' interactions.

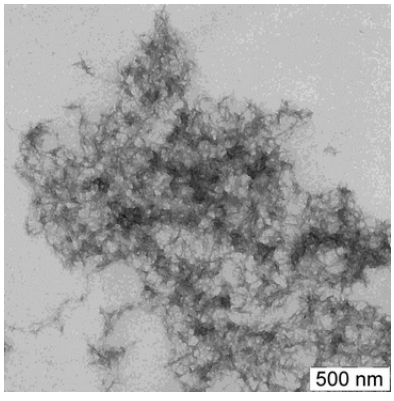

Fig. 2. Microphotograph of polyaniline particles obtained in the presence of PAMPS

The morphology of the products of the ANI matrix polymerization was investigated with the transmission electron microscopy. Figure 2 shows the microphotograph of the polyaniline stabilized with the PAMPS.

As it is seen from the fig. 2 polyaniline obtained in the presence of PAMPS consists of the numerous fiber aggregates. Polyaniline obtained by chemical polymerization without polyelectrolyte matrix forms the spherical particles of 100-500 nm. Hence the presence of PE in ANI polymerization mixture leads to the change of resulted PANI morphology.

The electron conductivity of the IPECs is about 2 powers less than polyaniline obtained without the polyelectrolyte matrix ($3 \cdot 10^{-2}$ S/cm for PANI:PAMPS and $7 \cdot 10^{-2}$ S/cm for PANI:PSS).

As it is mentioned above the obtained IPECs PANI-PAMPS and PANI-PSS do not form stable films thus matrix polymerization of ANI in the presence of Nafion® and MF-4SK was studied. Due to Nafion and MF-4SK do not dissolve in water. 2-propanol was chosen as a most appropriate solvent for PEM, ANI and APS.

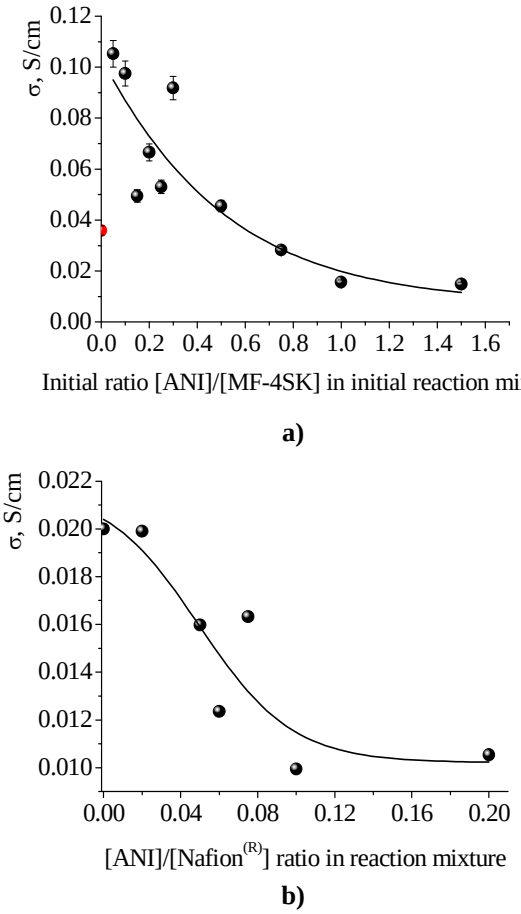

Fig. 3 Dependence of proton conductivity of PANI-MF-4SK (a) and PANI-Nafion® (b) films on the [ANI]/[MF-4SK(Nafion®)] ratio in the initial reaction mixture

Aniline polymerization in the presence of Nafion® and MF-4SK was carried out. It was found that rate and induction period of polymerization depends on the 2-propanol/water ratio. The rate of polymerization reaches the maximum at 25 vol.% 2-propanol content and decreases on 2-propanol content decreasing. The induction period of polymerization increases with 2-propanol content decrease. It is known that during aniline polymerization cation-radicals are formed in the reaction mixture, thus polymerization rate should depend on the solvent polarity as in case of the ionic polymerization. Hence the reduction of the induction period and the rate of ANI polymerization can be explained by decrease of solvent dielectric constant. The decrease of the reaction rate at high water content in the reaction mixture may be concerned with solvatation and hydrogen bonds rearrangements effect of water.

Aniline polymerization in the presence of Nafion® with molar ratio [aniline]/[Nafion®] 0.01-0.25 in 2-propanol/water mixture leads to the formation of soluble polyelectrolyte complex containing polyaniline and Nafion®.

The films of IPEC PANI-Nafion® and PANI-MF-4SK were prepared from 88.67 vol.% 2-propanol solution. Fig. 3 shows the dependence of proton conductivity of PANI-MF-4SK (a) and PANI-Nafion® (b) films on the [ANI]/[MF-4SK(Nafion®)] ratio in the initial reaction mixture.

It was found that films' proton conductivity increases with PANI content decreasing, reaches maximum at [ANI]/[MF-4SK] = 0.05 and is 3 times higher comparing to the one for the pristine MF-4SK (Fig. 3(a)). For PANI-Nafion® films the proton conductivity tends to increase on ANI amount decreasing and reaches maximum at [ANI]/[Nafion®] = 0.02 which is equal to proton conductivity of pristine Nafion® film (Fig. 3(b)).

It can be proposed that proton conductivity of PANI-MF-4SK films increase at small amount PANI contents is caused by the rearrangement of MF-4SK clusters and channels system by PANI and creation the additional network of hydrogen bonds which increase the films' hydratation degree and increase the ionic transport through film. The proton conductivity of PANI-MF-4SK films decreases with increase of [ANI]/[MF-4SK] that can be explained by ionic bonds formation between MF-4SK and PANI which leads to proton immobilization and formation of the hydrophobic sites of IPEC PANI-MF-4SK via charge compensation and decreases the films water uptake. For PANI-Nafion® membranes the only decrease of proton conductivity is observed which also can be attributed to formation the hydrophobic sites of IPEC and decrease the films water uptake.

In order to confirm this suggestion the obtained films were studied by IR-spectroscopy (Fig. 4).

As it is seen from the Fig. 4, the intensity of the absorption band at 3400 cm^{-1} in the spectra of PANI-MF-4SK films attributed to stretching vibrations of O-H bond of water clusters $H_{2n+1}O^{n+}$ bonded with MF-4SK sulfonic groups [5] decreases on ANI content, increasing in the initial reaction mixture. This decrease is concerned with decrease of water clusters $H_{2n+1}O^{n+}$ amount bonded with MF-4SK sulfonic groups which provide the proton conductivity of PANI-MF-4SK films.

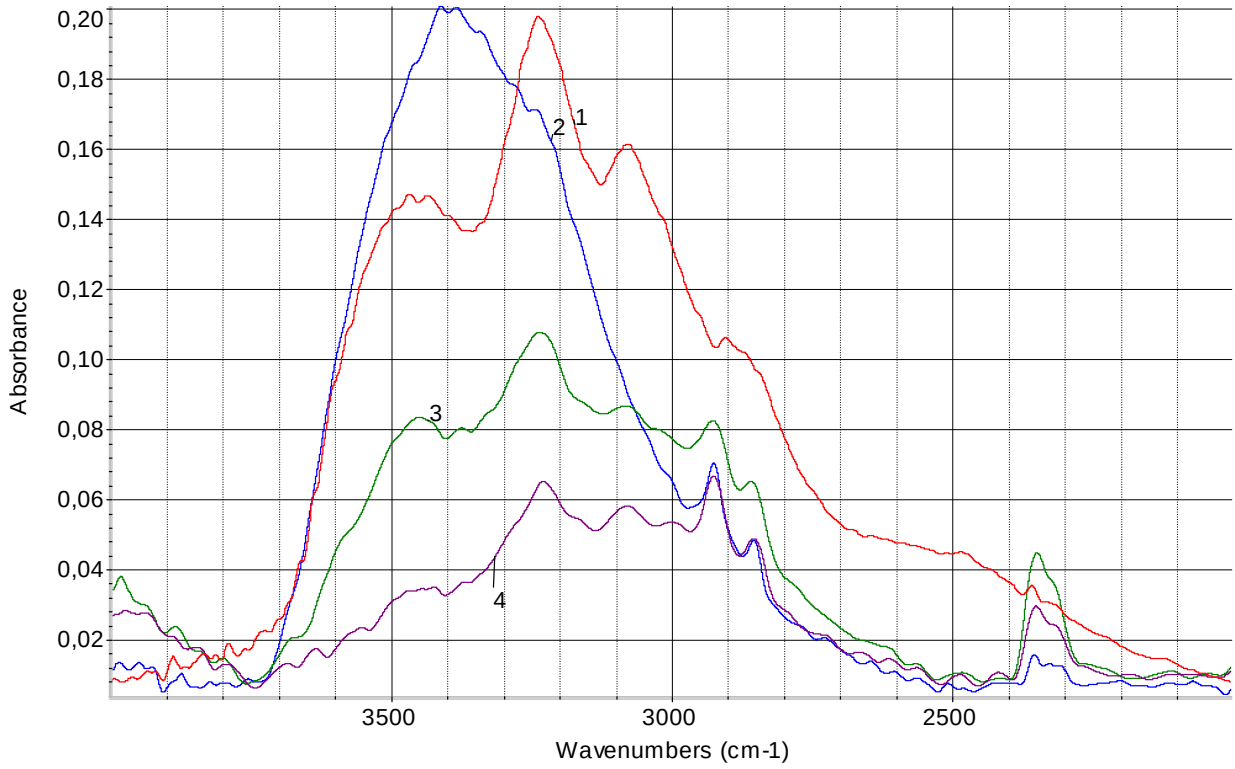

Fig. 4 The IR-spectra of MF-4SK pristine film (1) and films of PANI-MF-4SK with ratios [ANI]/[MF-4SK] 0.1 (2), 0.5 (3) and 0.75 (4) in the initial reaction mixture.

IV CONCLUSION

Thus aniline matrix polymerization in the presence of polysulfonic acids was investigated in water and 2-propanol solutions. It was found that PE reduces ANI polymerization time and leads to formation of soluble products containing PANI and PE which are involved in IPEC. These IPECs are stabilized not only by ionic but also by non electrostatic interactions and have electron and proton conductivity. The proton conductivity of these complexes can be varied by changing ANI amount in the initial reaction mixture.

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Žanna Boeva, Olga Piškina, Vladimirs Sergeyevs. Polianilīna matricas polimerizācija polisulfonskābju klātbūtnē.
Salīdzinoši augstās elektronu vadāmības, vides izturības un vienkāršās pārstradājamības dēļ polianilīnu izmanto elektrohromatiskajās ierīcēs, antistatiskajos un antikorozijas pārklājumos superkondensatoros un organiskajos vados. Tajā pašā laikā polianilīna galvenie trūkumi ir zemā šķīdība tradicionālajos šķīdinātājos un elektronu vadāmības zemā termiskā stabilitāte (jo hlorūdeņradis ir gaistošs un polianilīns karsējot pārdopējās). Minētajai problēmai ir vairāki risinājumi, no kuriem vienkāršākā ir anilīna matricas polimerizācija poliskābes klātbūtnē. Šajā darbā apskatīta anilīna polimerizācija poli-(2-akrilamīd-1-metilpropānsulfoskābes) un poli(4-stirolsulfonskābes) klātbūtnē. Ievērojot, ka veicot anilīna polimerizāciju poli-(2-akrilamīd-1-metilpropānsulfoskābes) un poli(4-stirolsulfonskābes) klātbūtnē ir grūti iegūt plēvītes ar labām mehāniskajām īpašībām, vienlaicīgi apskatīta iespēja veikt anilīna matricas polimerizāciju plēvi veidojoša polielektrolīta Nafion® vai tā analoga MF-4SK 2-propanolā klātbūtnē. Vienlaicīgi darbā pētītas iegūto interpolielektrolītu kompleksu plēvju īpašības. Parādīts, ka anilīna matricas polimerizācija noved pie šķīstošu polielektrolītu kompleksu veidošanās, kuros polianilīns ir emeraldīna formā. Polianilīna-polielektrolīta

kompleksa ūdenī daļiņu izmēri nav atkarīgi no polielektrolīta ķīmiskās struktūras un molekulmasas. Noteikts, ka iegūtie kompleksi stabilizēti ne tikai ar elektrostatiskiem, bet arī ne-jonu, t.i., van der Valsa mijiedarbības spēkiem. Pētīta polianilīna-MF-4SK polielektrolītu kompleksu protonu vadāmība un noskaidrots, ka protonu vadāmība ir regulējama, mainot anilīna daudzumu sākotnējā reakcijas maisījumā.

Жанна Боева, Олга Пышкина, Владимир Сергеев. Матричная полимеризация анилина в присутствии полисульфоновых кислот.

Полианилин (ПАНИ) - электронно проводящий полимер, обладающий достаточно высокой электронной проводимостью, стабильностью в окружающей среде и легкостью приготовления, имеющий потенциал применения в электрохромных устройствах, антистатических и антикоррозионных покрытиях, суперконденсаторах и органических проводах. Основными недостатками ПАНИ являются низкая растворимость в обычных растворителях и термическая стабильность электроннопроводимости (поскольку хлороводород является неустойчивым и полианилин дедопируется при нагревании). Существует множество вариантов для решения данной проблемы, но наиболее легкий матричная полимеризация анилина в присутствии поликислоты. В данной работе показаны основные особенности матричной полимеризации анилина в присутствии поли-(4-стиролсульфоновой) и поли-(2-акриламид-1-метилпропанолсульфоновой) кислот. Однако данные кислоты не образуют с полианилином пленки с хорошими механическими свойствами, по этому была рассмотрена возможность матричной полимеризации анилина в присутствии пленкообразователя полиэлектролита Nafion® и его аналога MF-4SK в 2-пропанол. В работе также были изучены свойства интерполиэлектролитных комплексов. Обнаружено, что при полимеризации анилина в присутствии полиэлектролитной матрицы образуются растворимые полиэлектролитные комплексы, в которых ПАНИ находится в форме соли эмеральдина. Установлено, что размеры комплексов полианилина в воде не зависят от молекулярной массы полиэлектролитной матрицы и ее химической структуры. Установлено, что эти комплексы стабилизированы за счет электростатических сил и Ван-дер-ваальсовых сил. Изучена протонная проводимость пленок полиэлектролитных комплексов на основе ПАНИ и МФ-4СК, показано, что протонной проводимостью можно управлять, изменяя содержание анилина в исходной реакционной смеси.