Polymeric Sulfonic Acids as Molecular Templates for Preparing Conducting Polymers with Tunable Morphology, Electrochemical and Spectral Properties

A.A. Nekrasov

A.N. Frumkin Institute of Electrochemistry, Moscow, Russia,

e-mail: secp@elchem.ac.ru

Possible application areas of polyaniline

- Conductive coatings (printable electronics, electromagnetic shielding, antistatic coatings)
- Anticorrosion coatings
- Hole-injection layers (organic light-emitting diodes - OLED)
- Electrochromic coatings (adjustable optical filters, “smart windows”, displays)
- Electromagnetic field modulation
- Sensors and biosensors (pH, oxidizing-reducing agents, some biomolecules)

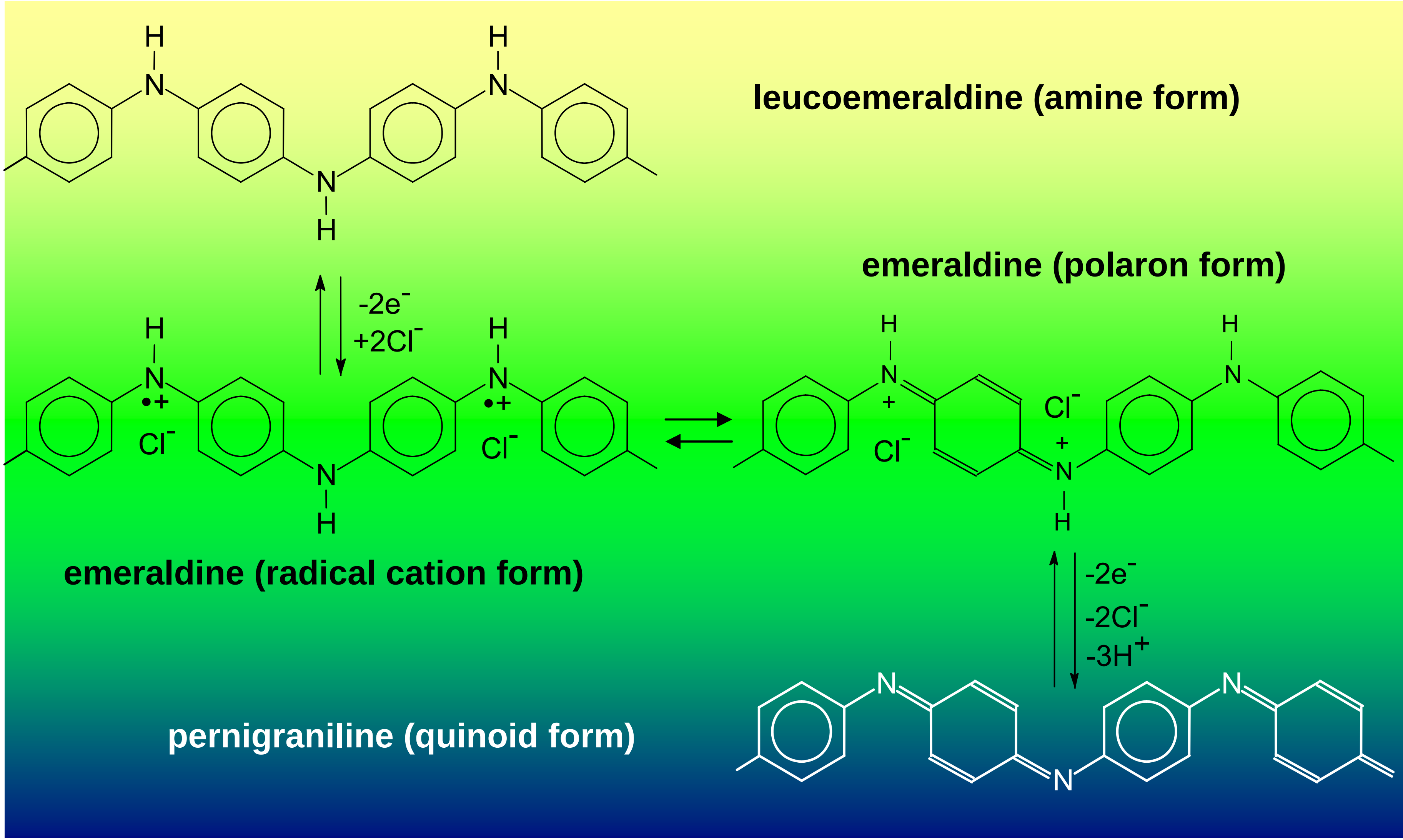
Main technological drawbacks

- Bad mechanical and film-forming properties
- Adhesion problems (some substrates)
- pH- and moisture-dependent characteristics (undesirable for some applications)
- Insoluble in common organic solvents (solution processing is hardly possible)

Outlines

- **Background studies (ordinary polyaniline):**
- **Electrochemical matrix polymerization of aniline in the presence of polymeric acids**
- **Chemical matrix polymerization of aniline in the presence of polymeric acids**
- **Characterization of the films**
- **Advantageous features in some possible applications**
- **Electrochromic device**
- Conclusions
- Acknowledgements

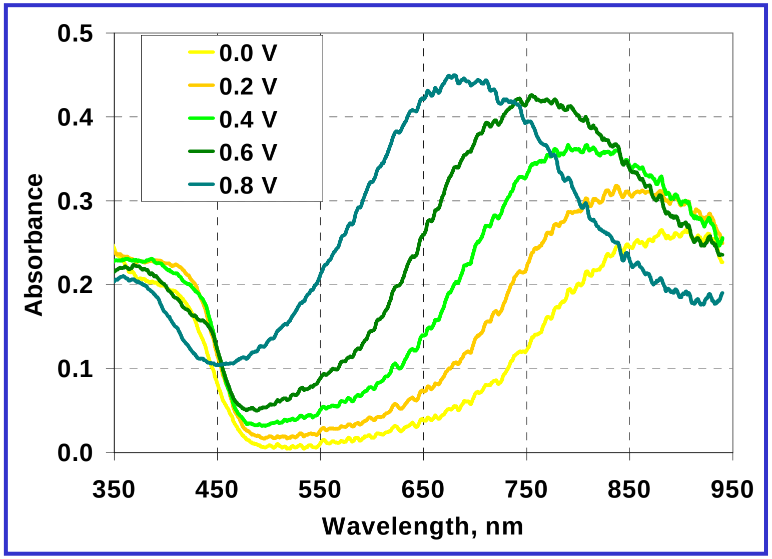
Scheme Of Different Forms Of Polyaniline And Redox Transitions Between Them

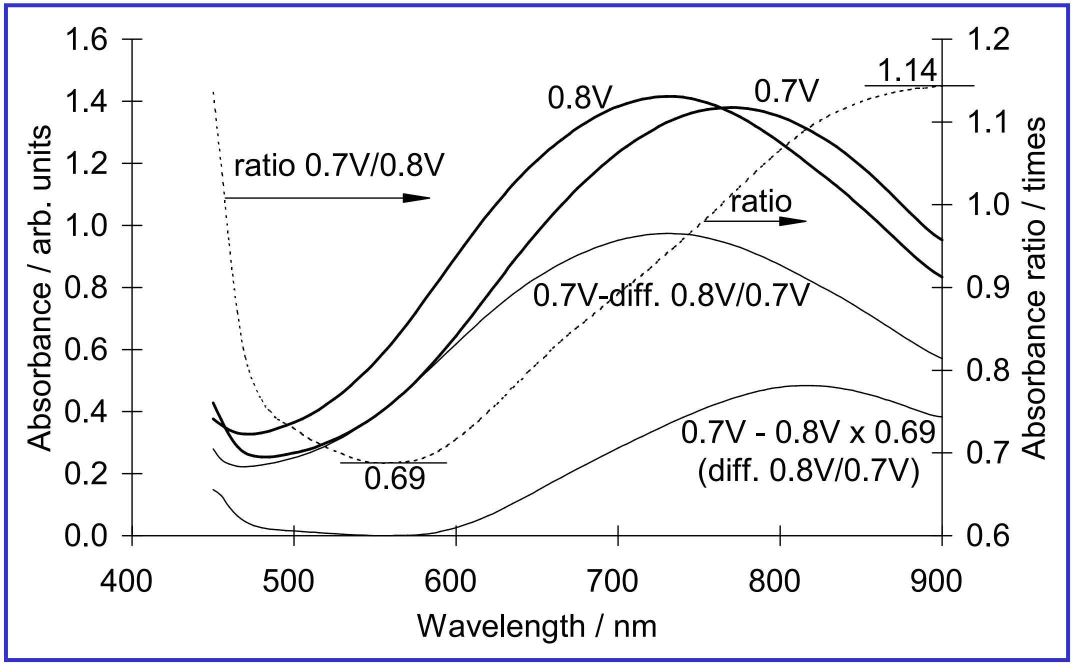


Basic principle of separation of individual absorption bands using Alentsev-Fok method

A.A. Nekrasov, V.F. Ivanov, A.V. Vannikov, J. Electroanal. Chem. 482 (2000) 11.

PANI-HCl





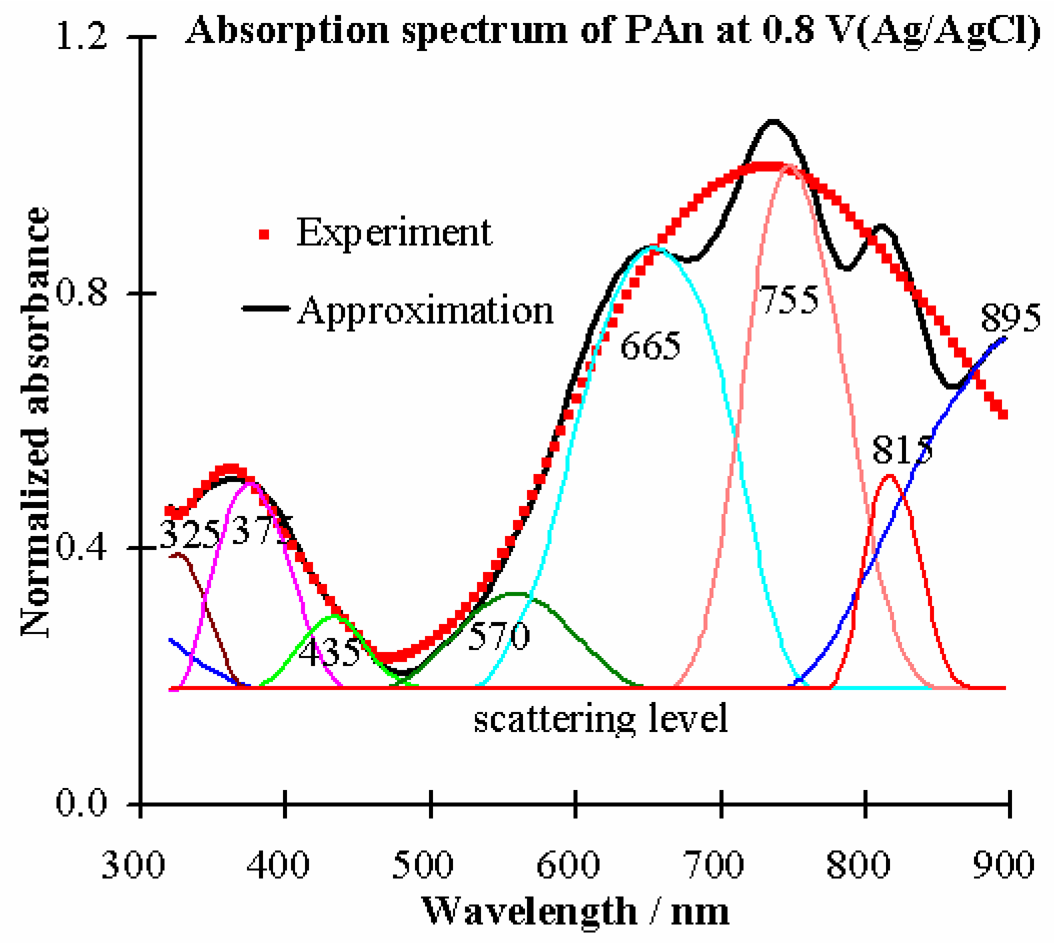
No preliminary notion about possible shape of individual absorption bands (Gaussian, Loretzian or hybrid type) is necessary.

No suppositions about possible number of the bands are required

Individual absorption bands in polyaniline

A.A. Nekrasov, V.F. Ivanov, A.V. Vannikov, J. Electroanal. Chem. 482 (2000) 11.

- On the basis of **spectroelectrochemical data** obtained at different potentials
- using **Alentsev-Fock** method
- **nine individual absorption bands** were separated within UV-Vis spectrum of PAn in the range **300-900 nm**



Derivative Cyclic Voltabsorptometry (DCVA)

Electrochemical process: ***Red* - *ne* ↔ *Ox***

From a combination of Beer's and Faraday's laws it follows:

$$A_{\lambda}^{Ox} = \varepsilon_{\lambda}^{Ox} Ql / nFV$$

A - optical absorption of ***Ox*** at λ *(maximum of absorption band of* ***Ox****)*

ε - extinction coefficient of ***Ox*** at λ *(presumably constant)*

Q - charge consumed in the reaction

l - film thickness

V - film volume

Ratio ***l / V*** *is constant*

n - number of electrons participating in the reaction *(presumably constant)*

F - Faraday number *(constant)*

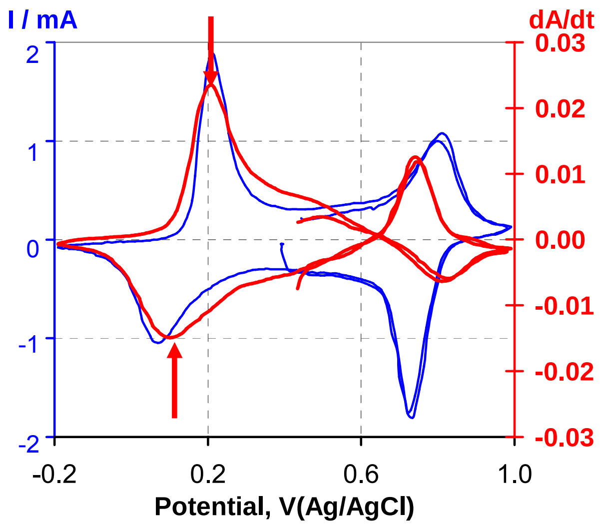
So, **optical absorption linearly** depends on **charge**

Cyclic Voltammetry (CVA)	Derivative Cyclic Voltabsorptometry (DCVA)
i = dQ/dt = f (E,w)	*dA/dt = f (E,w)*

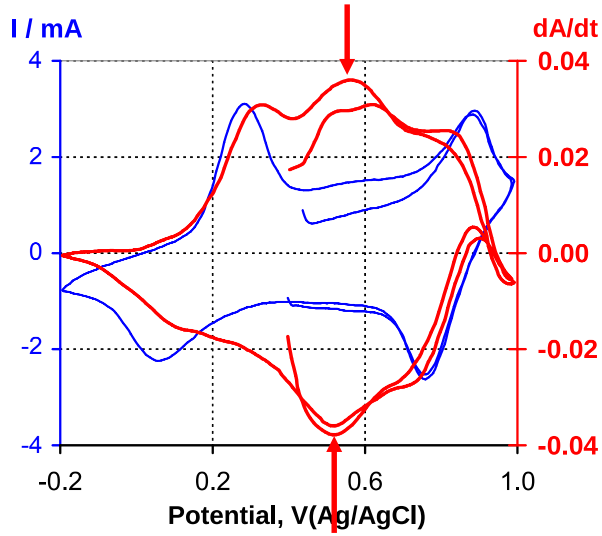
Attribution of individual absorption bands: DCVA results

A.A.Nekrasov, V.F.Ivanov, O.L.Gribkova, A.V.Vannikov Electrochim. Acta. 50 (2005) 1605.

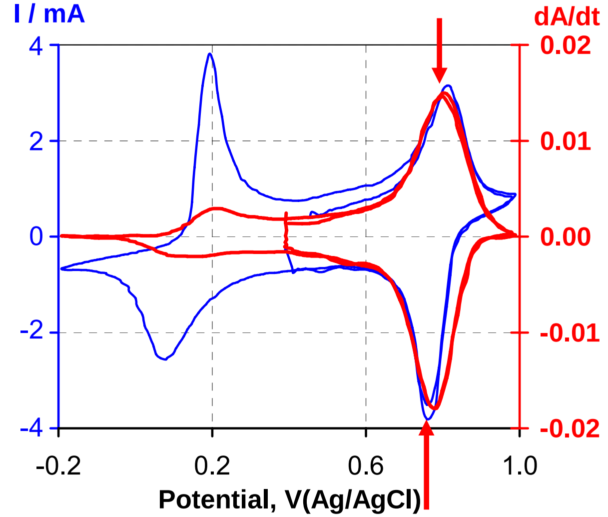
755 nm
PANI synthesized in HCl
Cycled in $HClO_4$ at 10 mV/s



665 nm
PANI synthesized in HCl
Cycled in HCl at 50 mV/s



570 nm
PANI synthesized in HCl
Cycled in $HClO_4$ at 20 mV/s

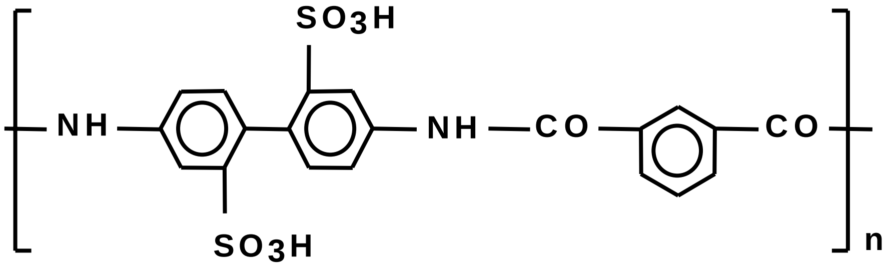


"Localized" polarons generated by **FIRST** **electrochemical** process

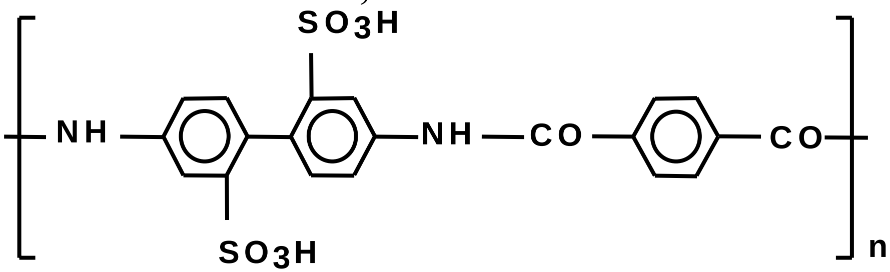
Cation-radical dimers (presumably) generated by **chemical** process

Quinoid structures generated by **SECOND** **electrochemical** process

Interpolymer complexes of PANI with polymeric sulfonic acids

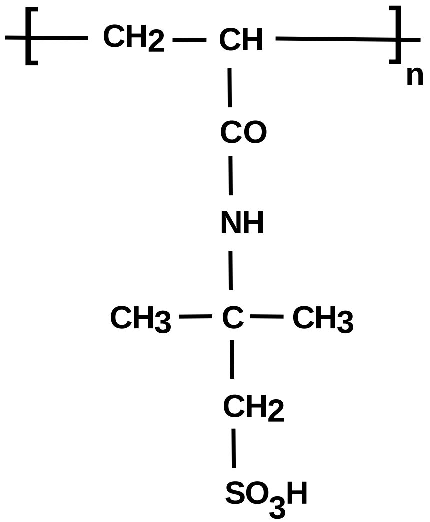


poly-p,p’-(2,2’-disulfoacid)-diphenylen-iso-phthalamid
(iso-PASA, SEMI-RIGID BACKBONE)
DOUBLE base; MW~40000 ~ 80 units

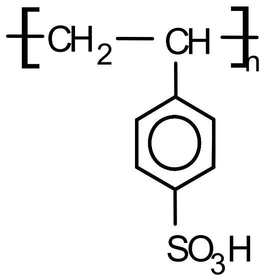


poly-p,p’-(2,2’-disulfoacid)-diphelylen-tere-phthalamid
(tere-PASA, RIGID BACKBONE)
DOUBLE base; MW~40000 ~ 80 units

Copolymer of i-PASA and t-PASA = co-PASA



poly(2-acrylamido-2-methyl-1-propanesulfonic acid)
(PAMPSA, FLEXIBLE BACKBONE)
SINGLE base
MW~2000000 ~10000 units



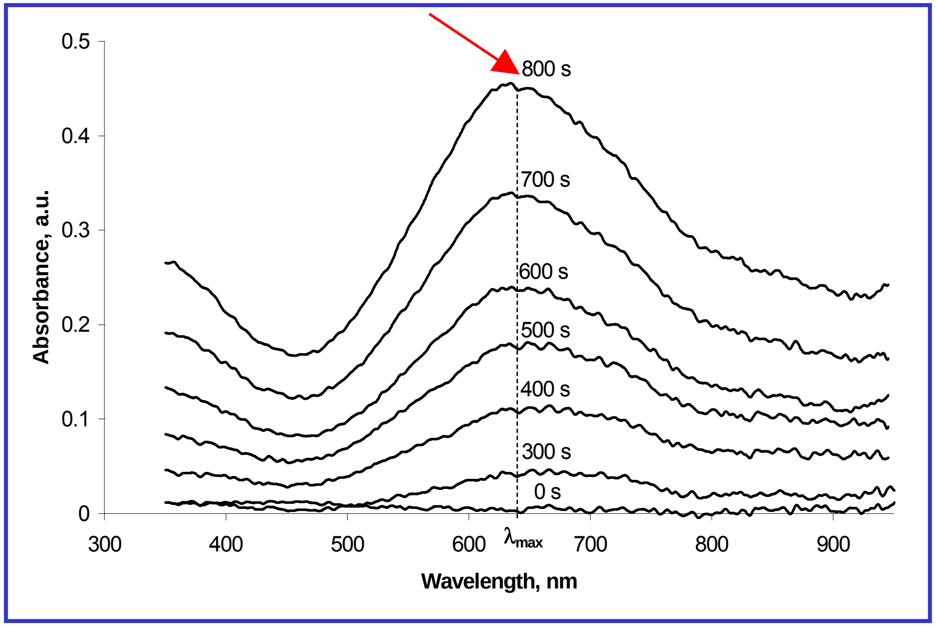
poly(styrene-sulfonic acid)
(PSSA, FLEXIBLE BACKBONE)
SINGLE base
MW~70000
~380 units

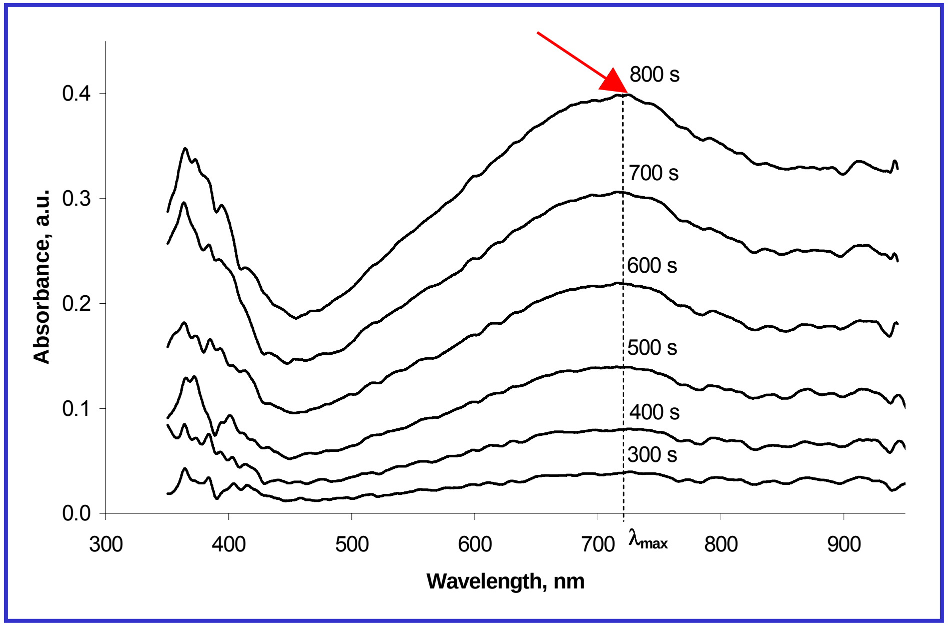
- soluble in water
- good film-forming properties
- high ionic conductivity
- high optical transparence

Evolution of absorption spectra during the electrochemical matrix polymerization

Nekrasov A.A., Gribkova O.L., Eremina T.V., Isakova A.A., Ivanov V.F., Tverskoj V.A., Vannikov A.V. Electrochim Acta 53 (2008) 3789

Potentiostatic synthesis at 0.75V vs. Ag/AgCl (No background electrolyte)





PAMPSA, PSSA, HCl

i-PASA, t-PASA, co-PASA

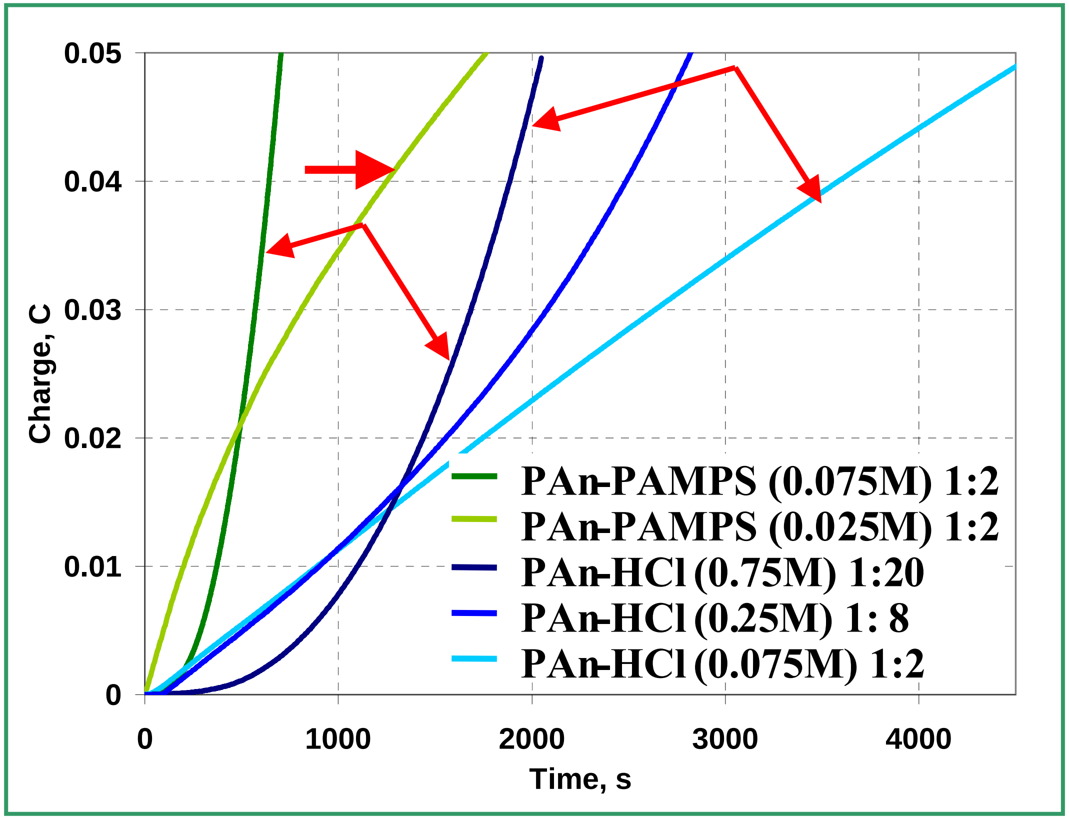
Polyacid with flexible backbone behaves more like ordinary inorganic acid

Rigid-chain polyacid →

Shape of spectra is distorted

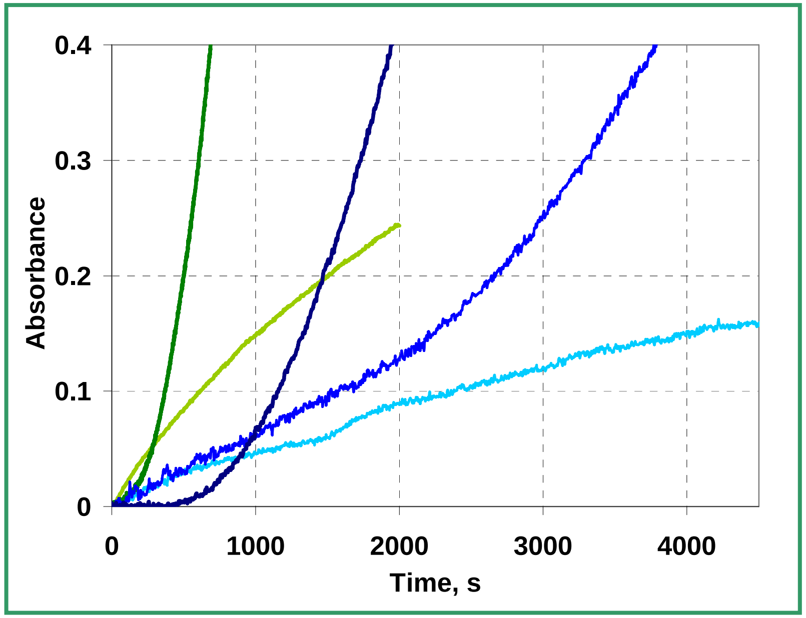
Electrochemical matrix synthesis of polyaniline (1)

Flexible-backbone polyacid (PAMPSA) and HCl



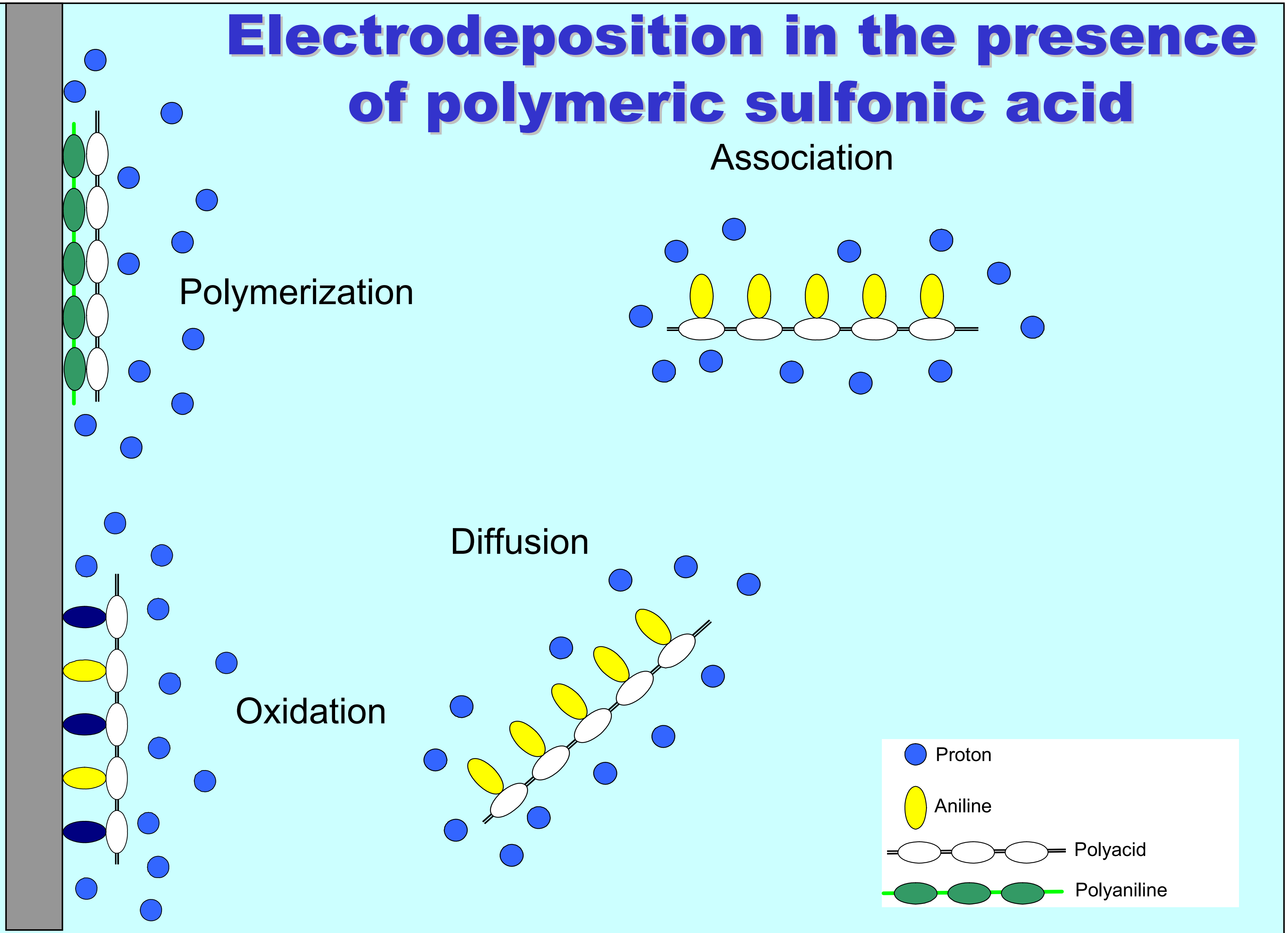
Initial solutions: aniline/PAMPSA (1:2) and aniline/HCl

0.75 V (vs. Ag/AgCl). S=2.25 cm^2.



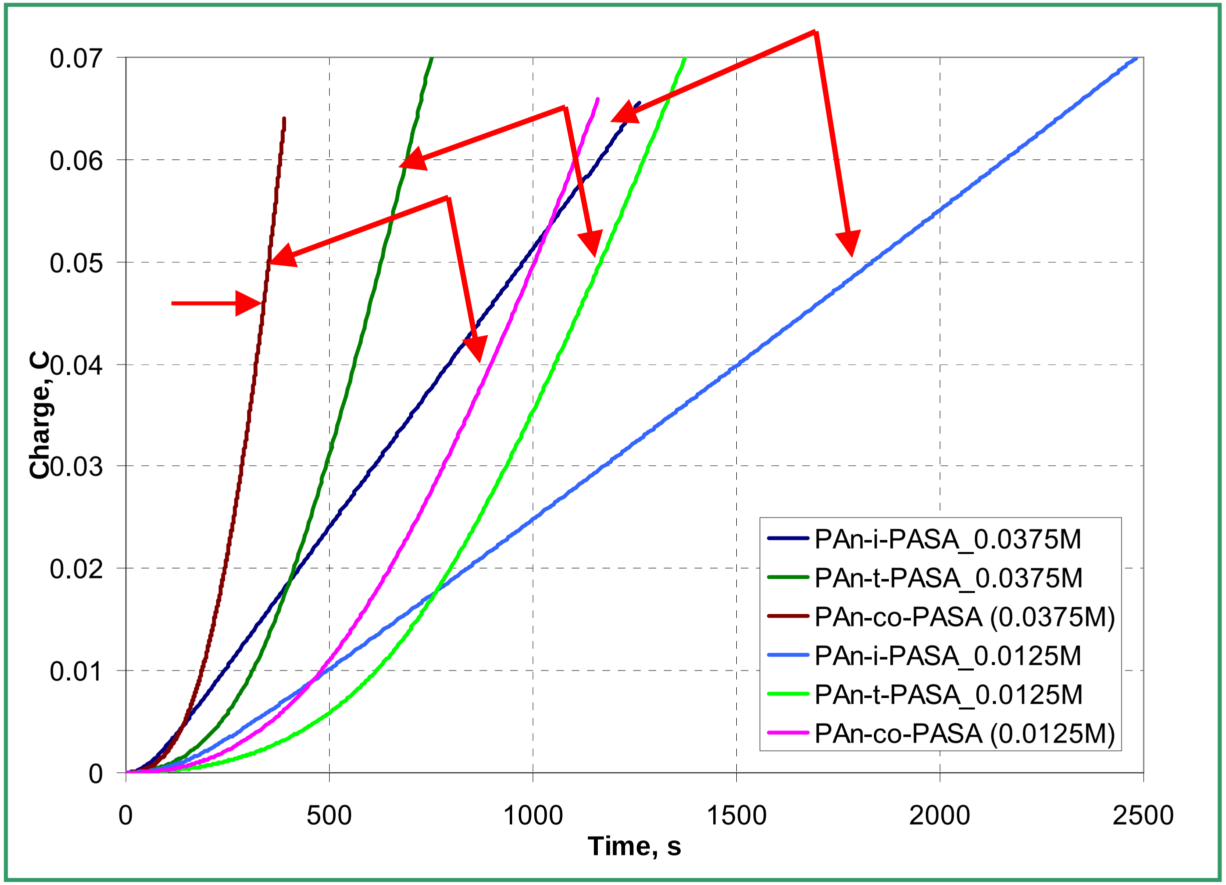
- non-sigmoid shape of the dependence in HCl in the same concentration as PAMPSA
- standard sigmoid shape is observed at 10 times higher concentration of HCl
- higher local concentration of protons near the polyacid backbone
- non-sigmoid shape of the dependence in very low concentration of PAMPSA
- higher polymerization rate on polymeric acid due to association of aniline with the sulfonic groups

Electrodeposition in the presence of polymeric sulfonic acid



Electrochemical matrix synthesis of polyaniline (2)

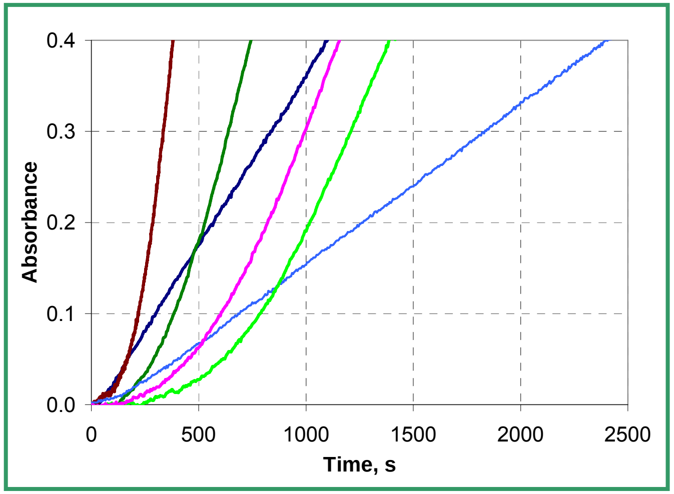
Rigid-chain polyacids t-PASA, i-PASA and co-PASA



Initial solutions: An/t-PASA, An/i-PASA and An/co-PASA

Reagents ratio: 1:1

0.75 V (vs. Ag/AgCl). S=2.25 cm^2.

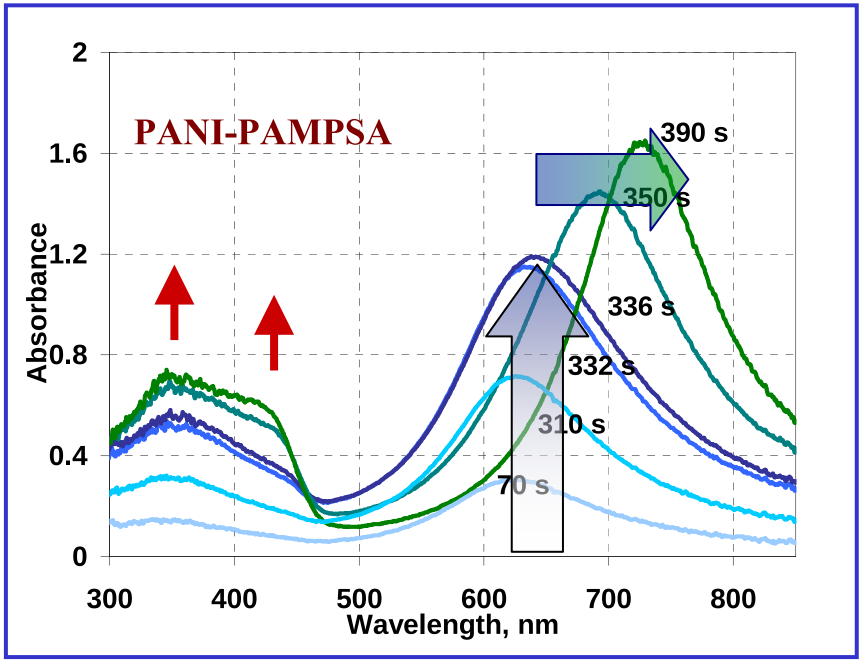


i-PASA: **no nucleation stage of electropolymerization for all concentrations**

t-PASA and co-PASA: **standard autocatalytic synthesis for all acid concentrations**

co-PASA: **highest polymerization rate among all polyacids studied**

Chemical matrix synthesis of polyaniline

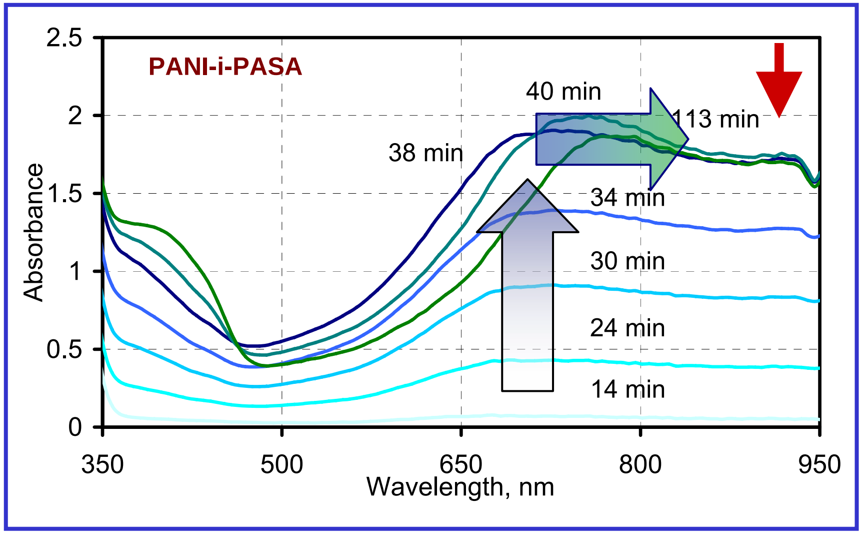


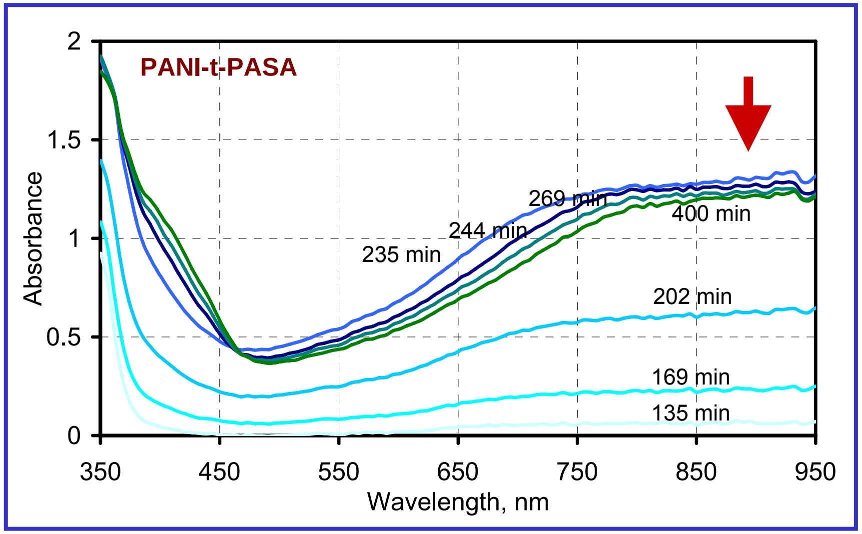
O.L. Gribkova, A.A. Nekrasov, M. Trchova, V.F. Ivanov, V.I. Sazikov, A.B. Razova, V.A. Tverskoy, A.V. Vannikov Polymer 52 (2011) 2474

Initial solution: Aniline/polyacid
molar ratio aniline/sulfonic group : 1:2
Aniline concentration: 6 mM
Oxidant: ammonium persulfate (1:1)

1 stage: growth of absorption near 320 nm and 650 nm – accumulation of amine and quinoid form
2 stage: rapid shift of the absorption maximum to the area near 750 nm – formation of localized polarons

intense absorption in the near-IR region for rigid and semi-rigid polyacids

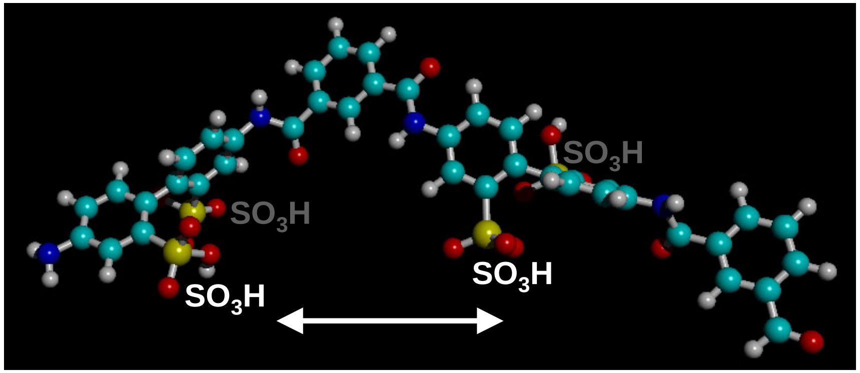




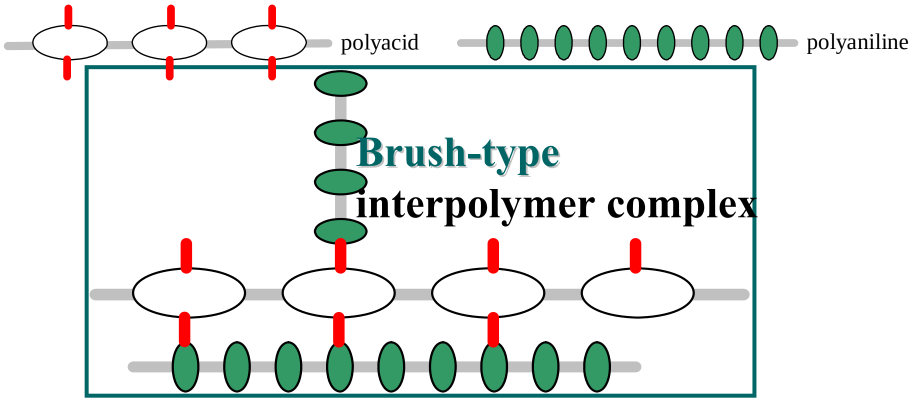
Interpolymer compelxes: Structural aspects

affecting the matrix polymerization of aniline in the presence of rigid-chain polyacids

i-PASA (semi-flexible)

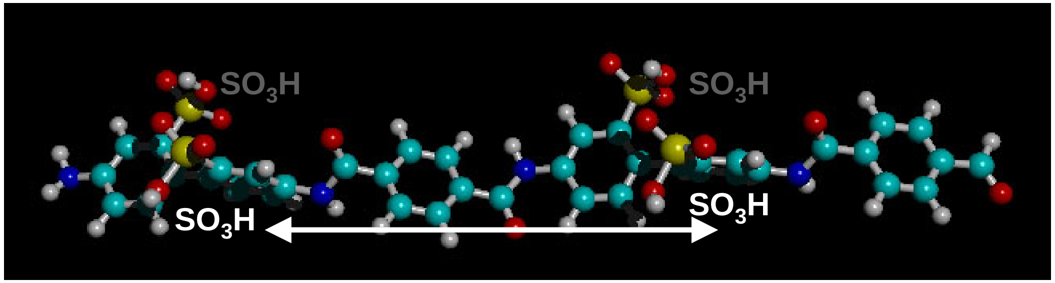


non-autocatalityc character of the synthesis

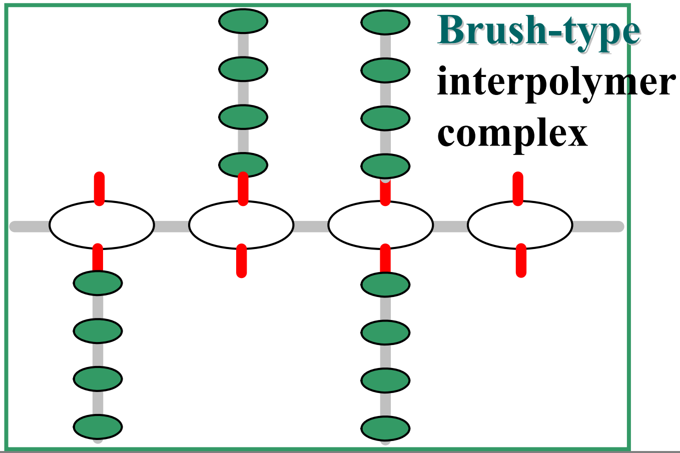


Double-strand interpolymer complex

t-PASA (rigid)



standard autocatalityc character of the synthesis

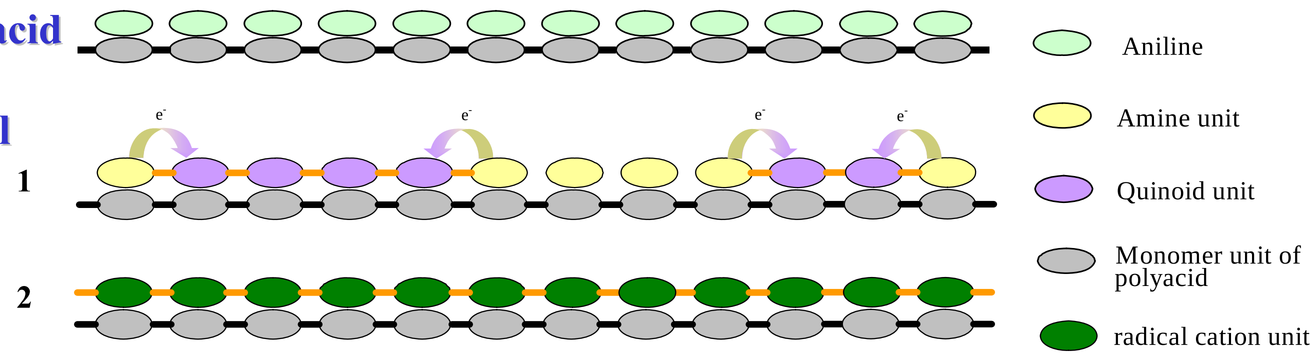


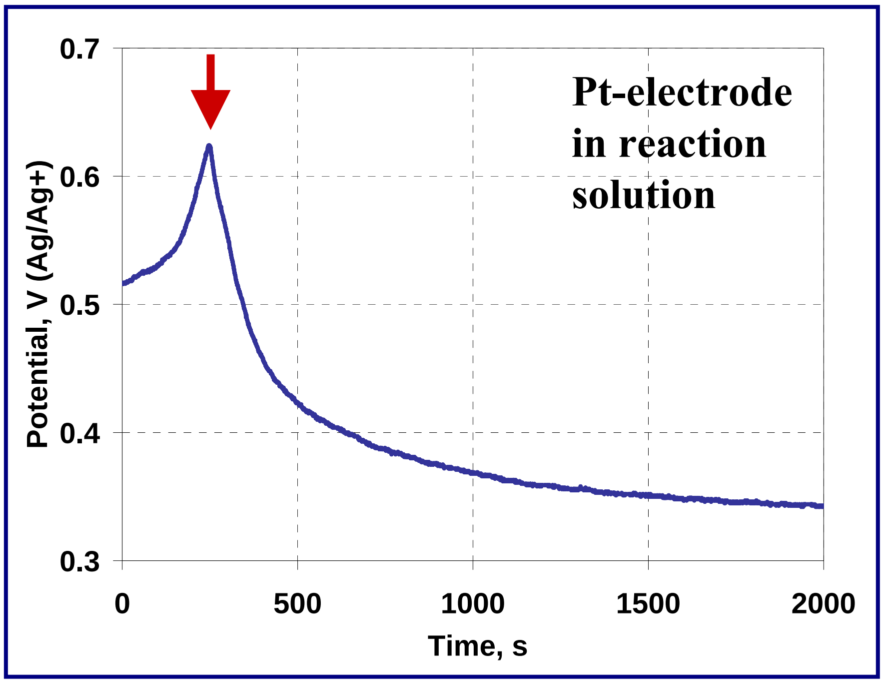
Scheme of aniline chemical polymerization in the presence of polyacids

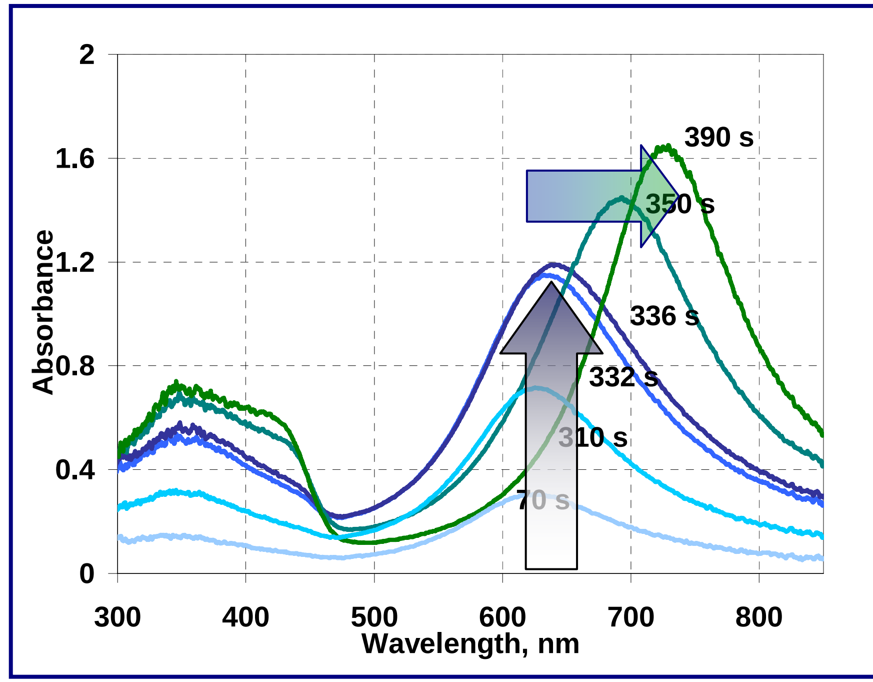
aniline associates with the polyacid

quinoid forms oxidize the initial aniline and amine forms

quiunone-amine interaction gives semi-oxidized emeraldine

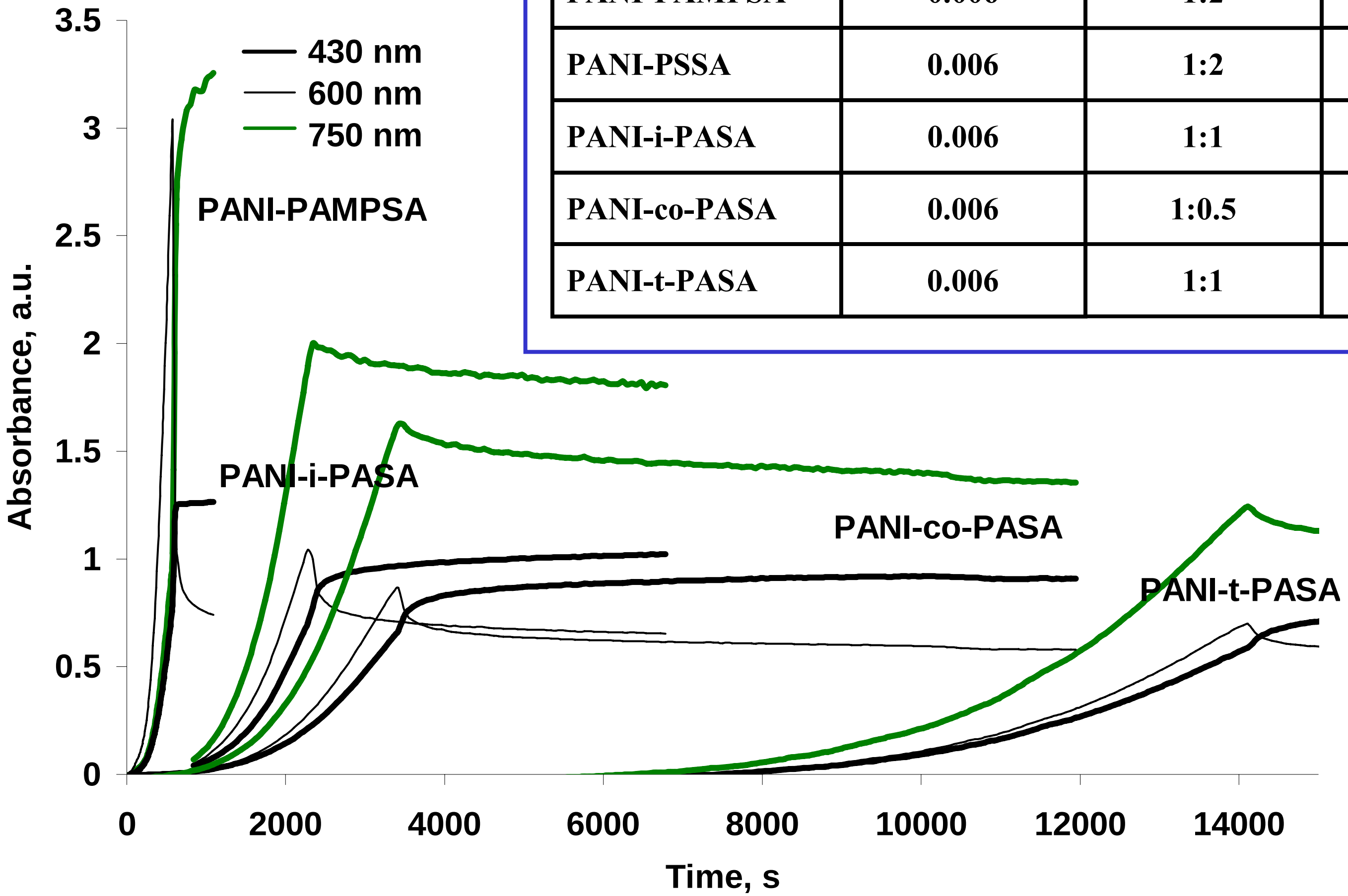






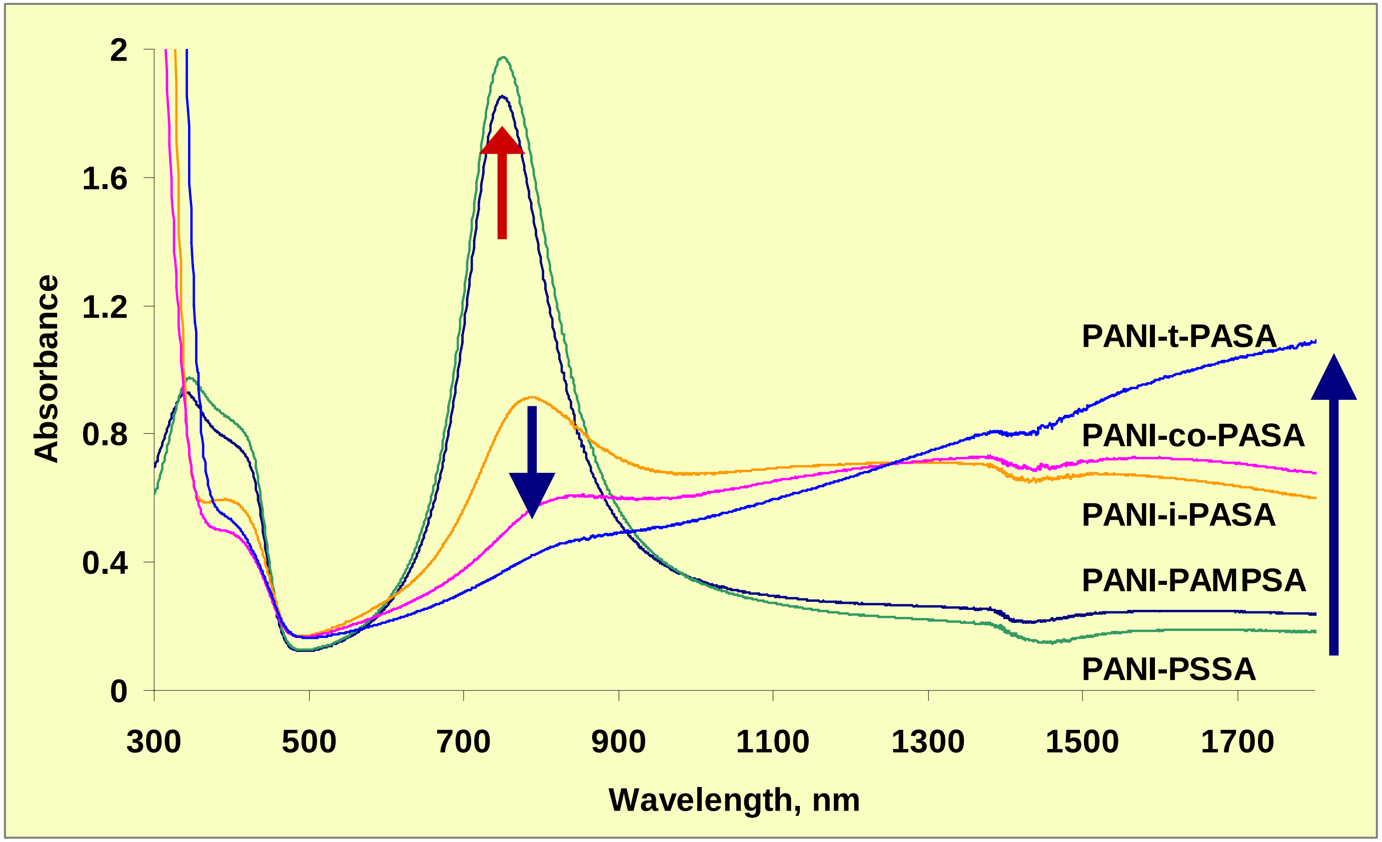
Optical absorbance changes at characteristic wavelengths during synthesis

	Aniline concentration, mol/l	Aniline to monomer unit	pH after adding aniline	First stage duration, s
PANI-PAMPSA	0.006	1:2	2.58	680
PANI-PSSA	0.006	1:2	2.52	790
PANI-i-PASA	0.006	1:1	2.48	2340
PANI-co-PASA	0.006	1:0.5	2.62	3420
PANI-t-PASA	0.006	1:1	2.52	14110



UV-Vis-NIR absorption spectra of solutions of PANI-polyacid complexes

O.L. Gribkova, A.A. Nekrasov, M. Trchova, V.F. Ivanov, V.I. Sazikov, A.B. Razova, V.A. Tverskoy, A.V. Vannikov Polymer 52 (2011) 2474



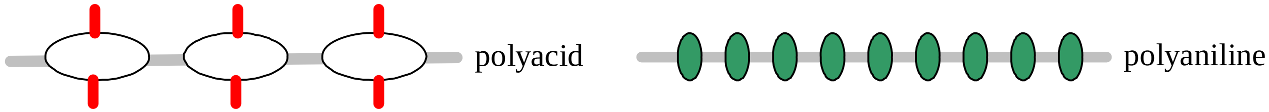
PANI-flexible polyacids: weak interaction between adjacent PANI chains gives higher absorption of localized polarons.

PANI-rigid polyacids: high absorption of delocalized polarone may be due to π-π stacking of adjacent polyaniline molecules

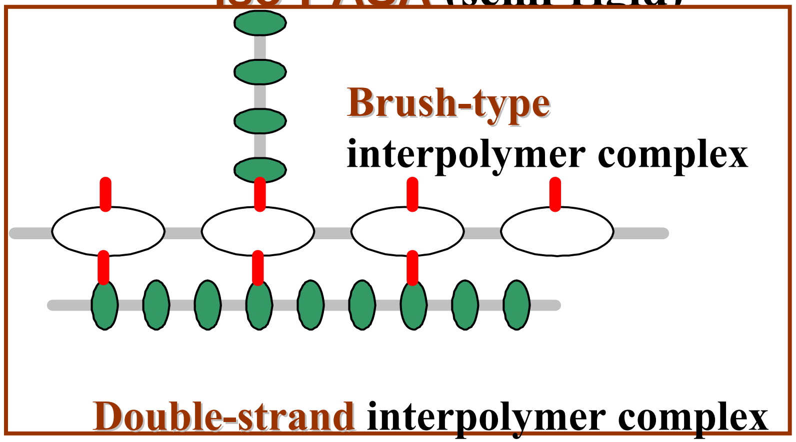
Similar spectra are observed for solution-cast films

Films are soluble in water. So, prior the experiments the films should be cross-linked by bivalent cations, Ca^{2+} or Ba^{2+}

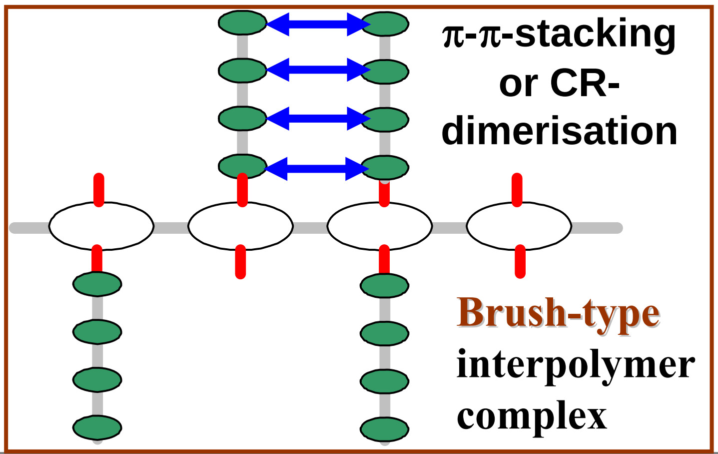
Interpolymer compelxes: Structural aspects



iso-PASA (semi-rigid)

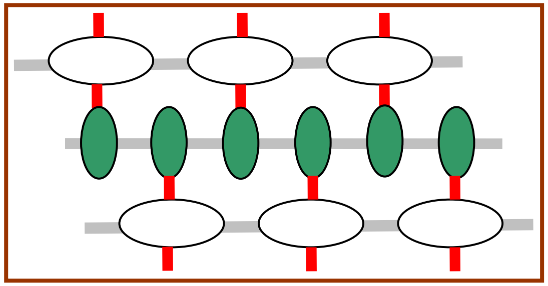


tere-PASA (rigid)



PANI-PAMPSA (1:2)

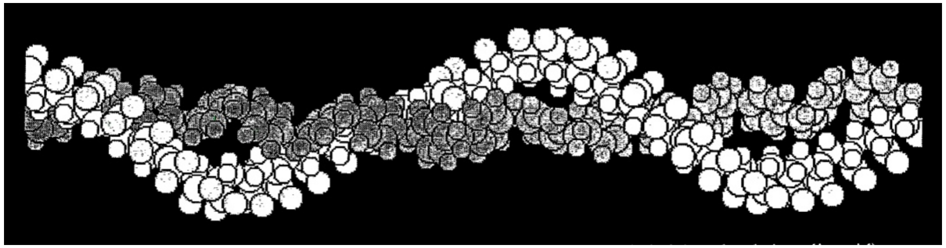
Double-strand interpolymer complex



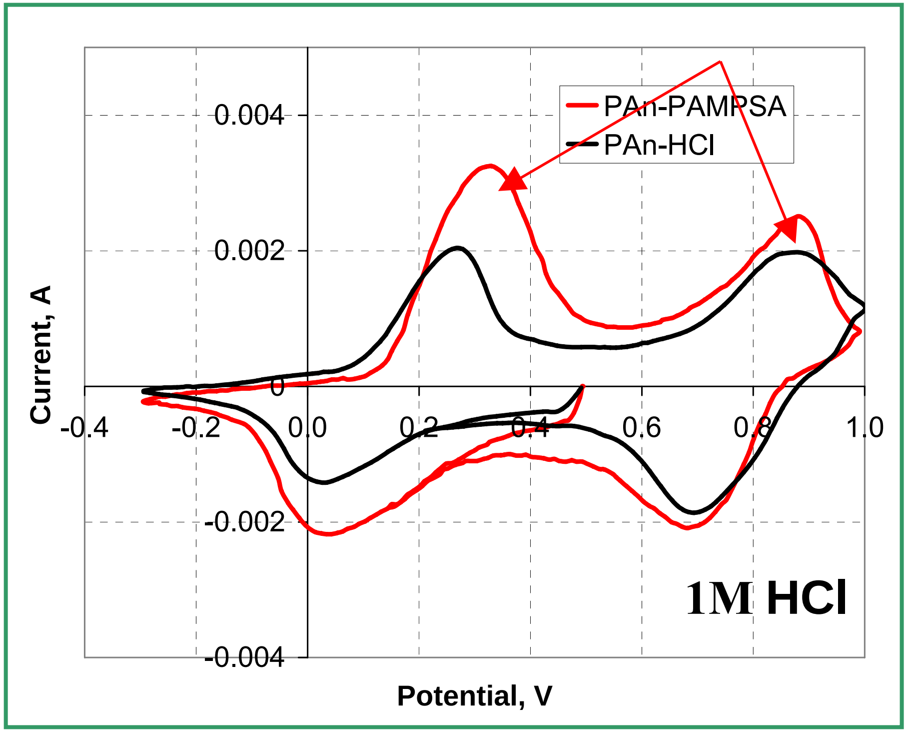
PANI-chains isolated from each other

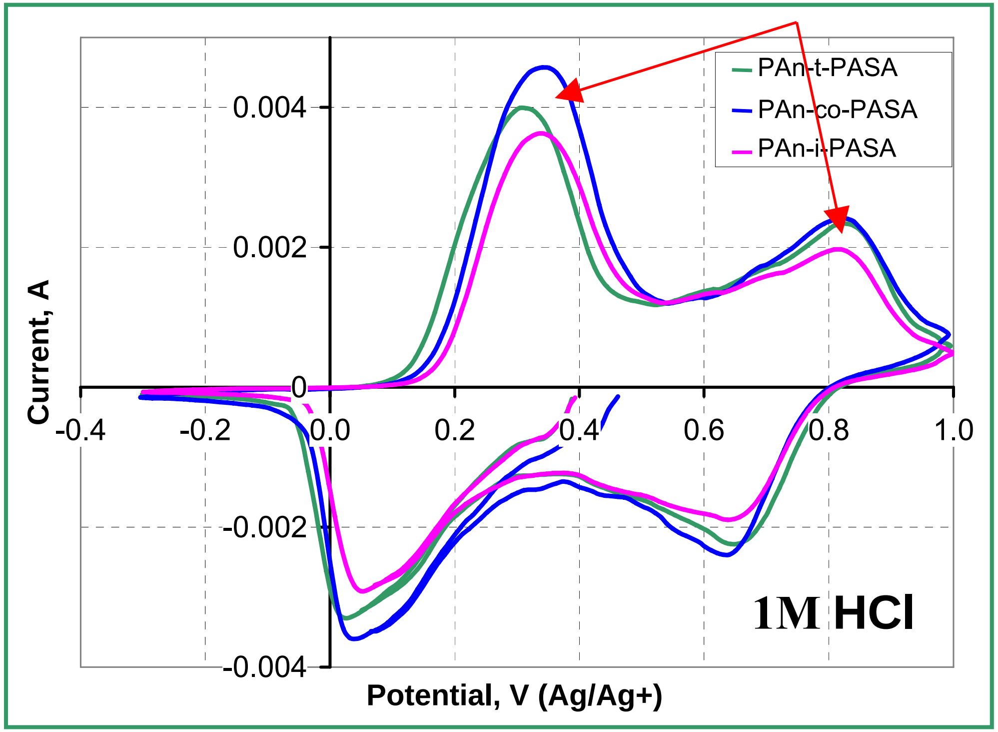
Analog: PANI-poly(acrylic acid)

L. Sun, L.-M. Liu, R. Clark, S.C. Yang, Synth. Met. 84 (1997) 67



CV of electrodeposited matrix polyaniline





CV is similar to standard polyaniline

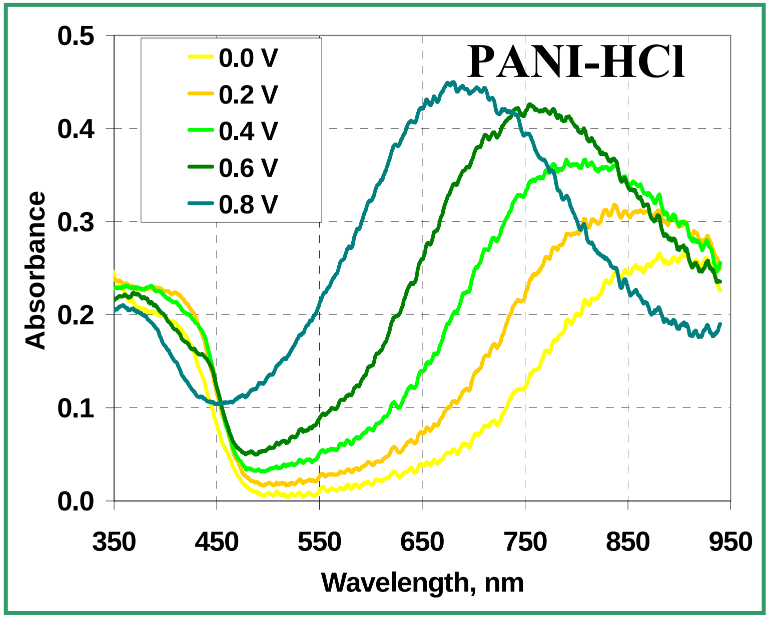
Polyacid with flexible chain can adapt its structure to polyaniline

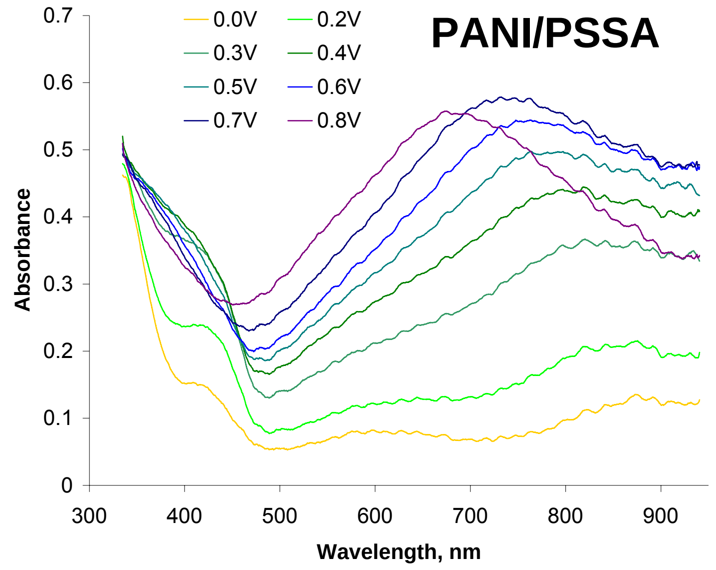
	Potential, V					
	E^1_a	E^1_c	$E^1_{1/2}$	ΔE^1	E^2_a	E^2_c
HCl	0.268	0.026	0.147	0.242	0.882	0.694
PAMPSA	0.330	0.034	0.182	0.296	0.881	0.682
t-PASA	0.314	0.024	0.169	0.290	0.831	0.653
i-PASA	0.338	0.049	0.194	0.289	0.818	0.647
co-PASA	0.341	0.042	0.192	0.299	0.821	0.631

Formation of quinoid fragments is hindered

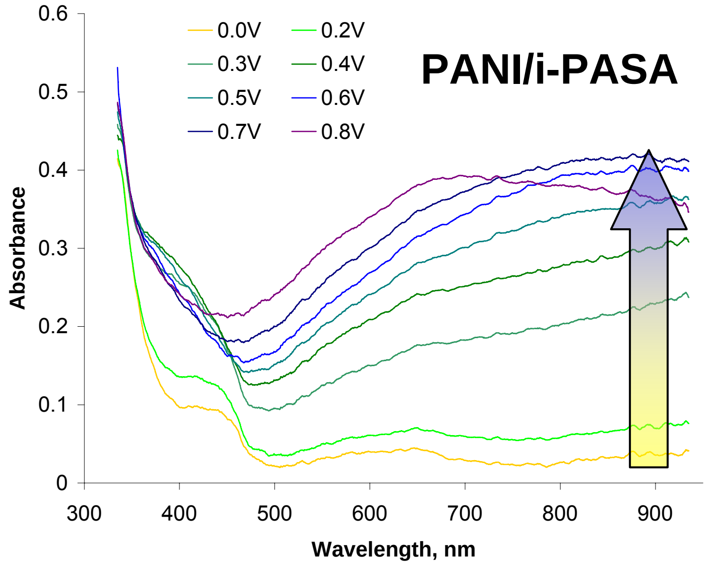
In the case of polyacid with rigid polymer backbone polyaniline has to adapt its structure to the structure of polyacid

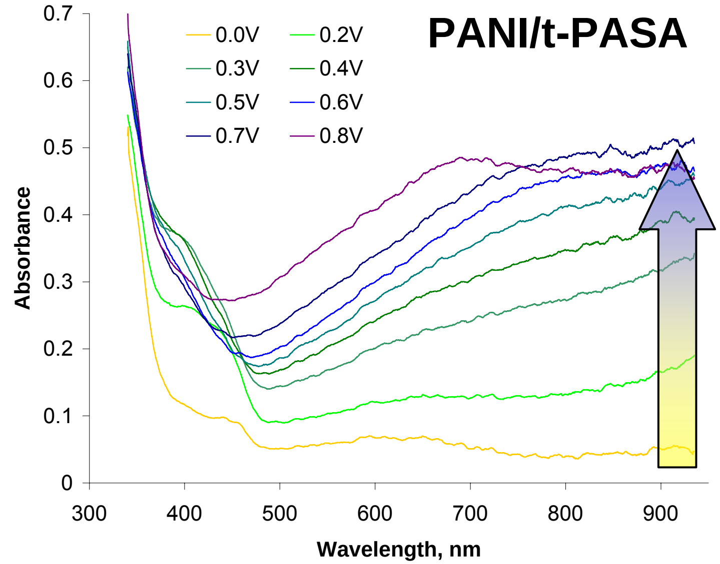
UV-Vis spectroelectrochemistry



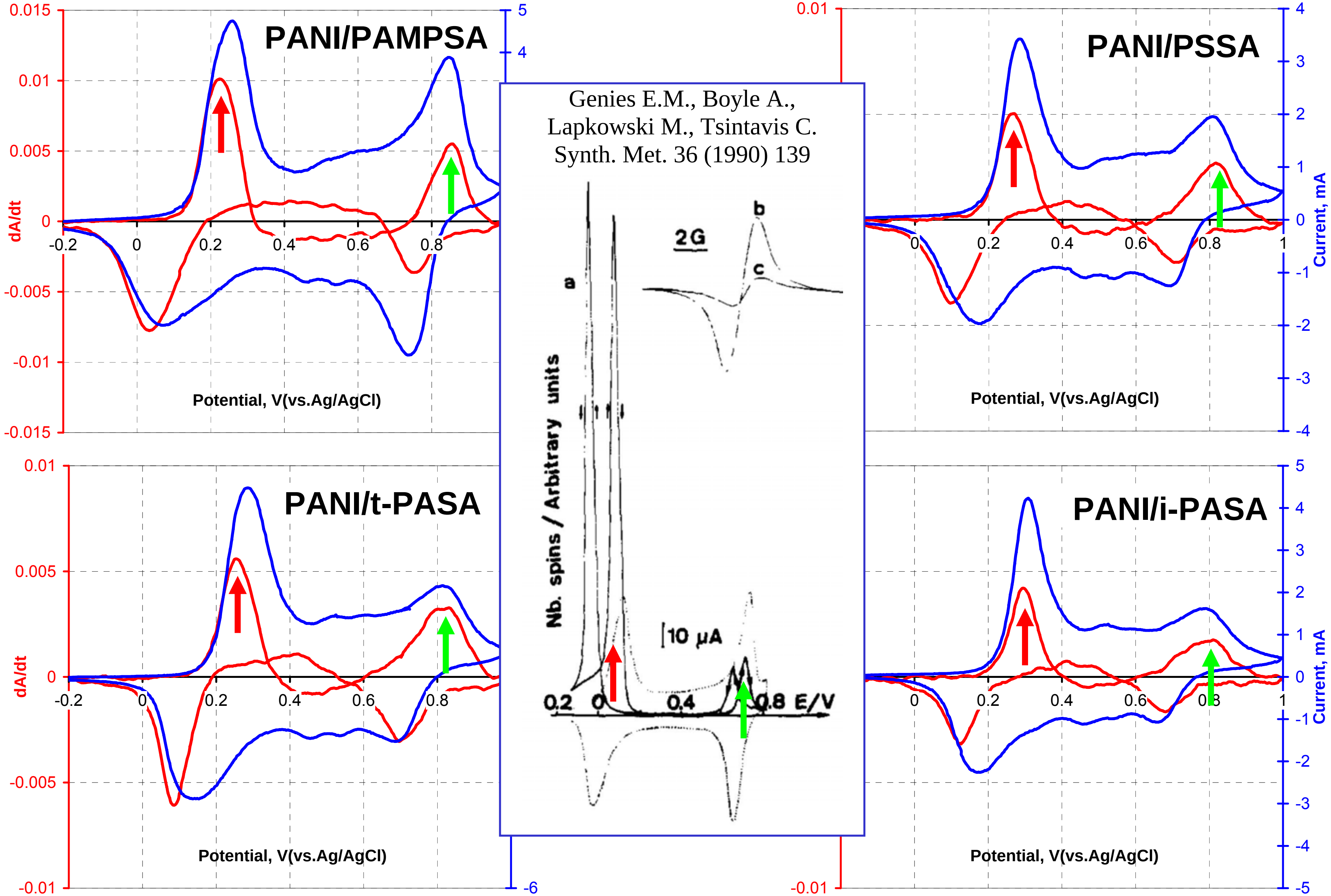


1M aqueous HCl

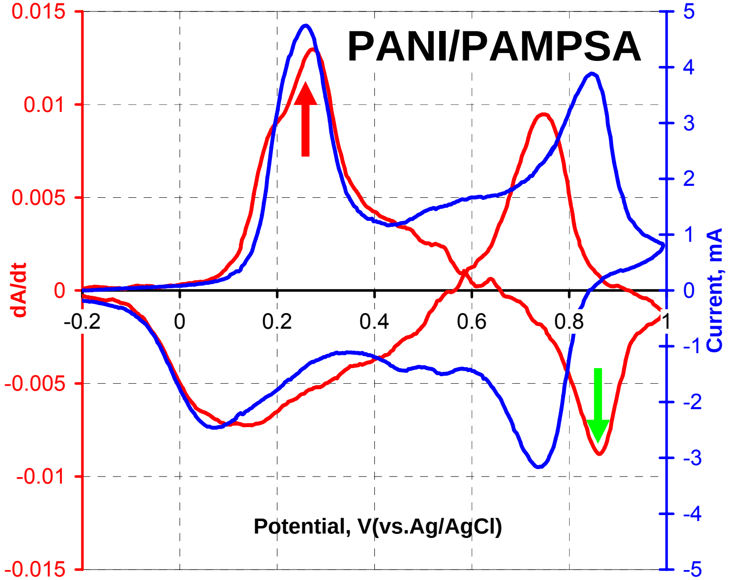


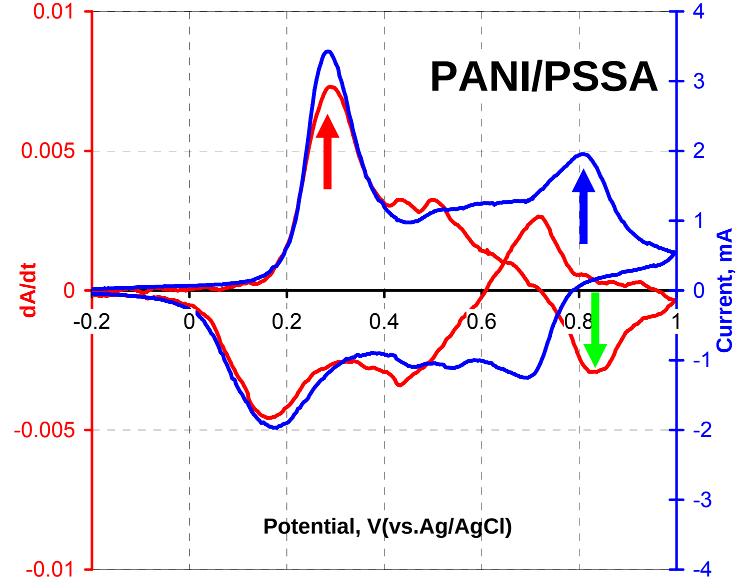


DCVA-435 nm, radical cations



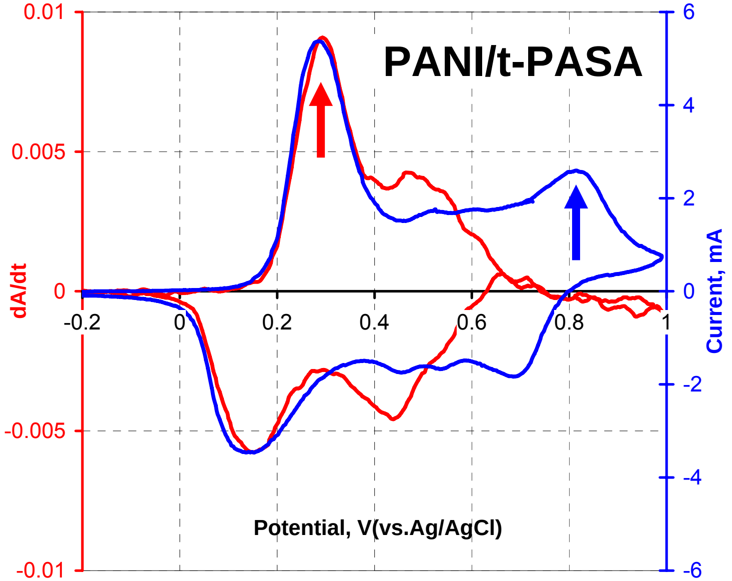
DCVA-755 nm, localized polarons

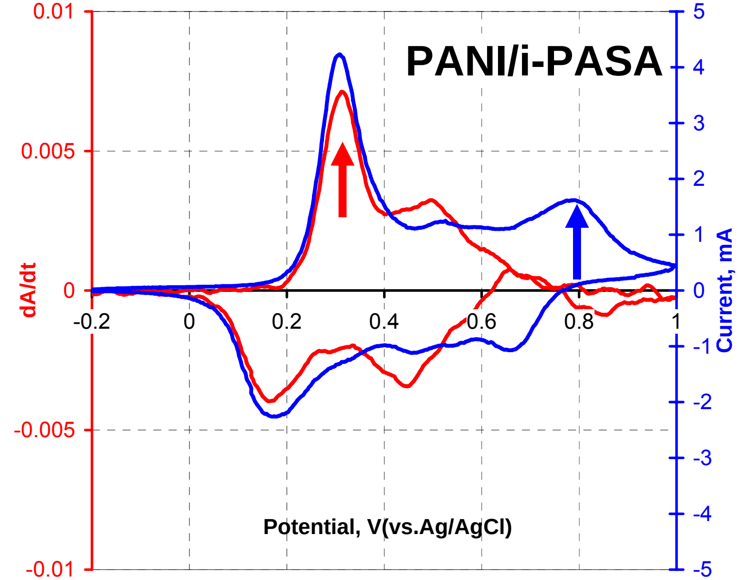




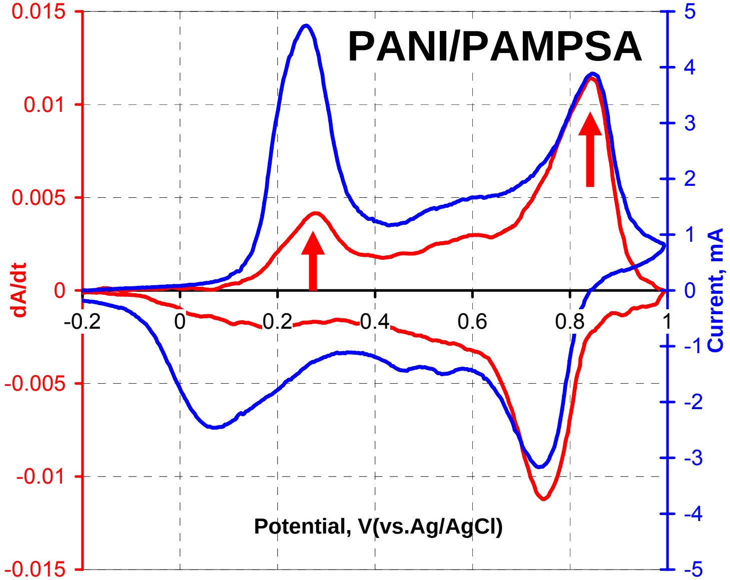
20mV/s

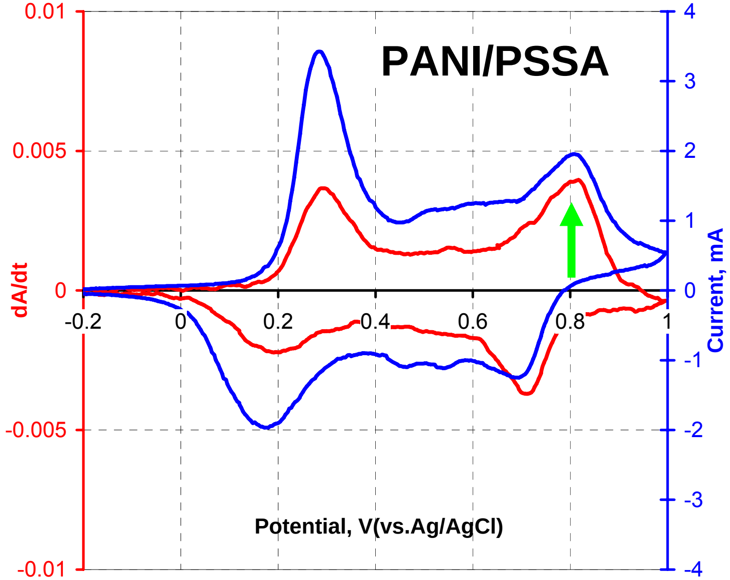
1M aqueous HCl





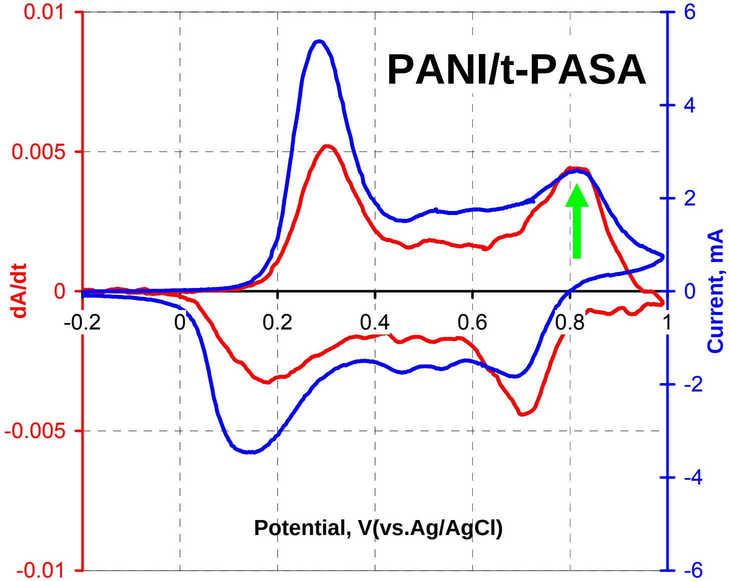
DCVA-570 nm; quinoid structures



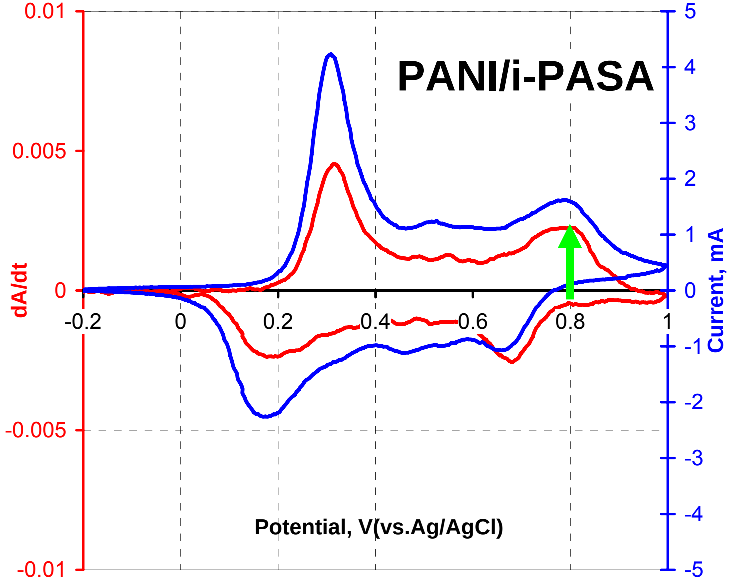


20mV/s

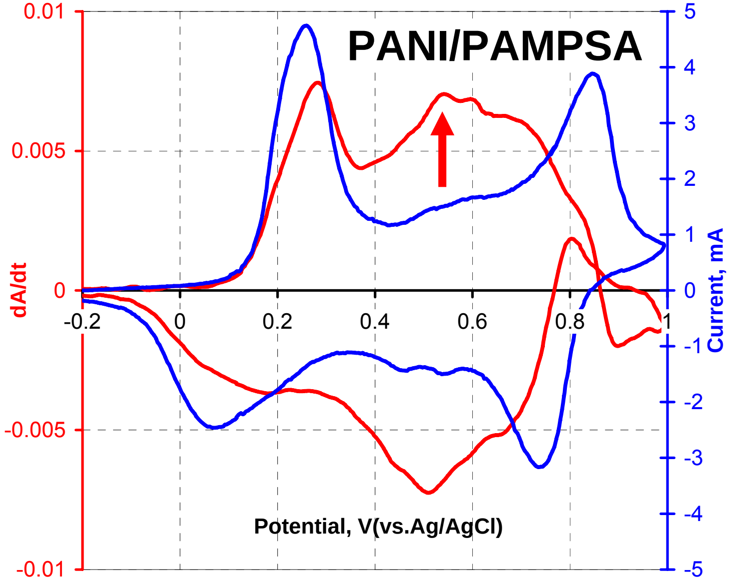
1M aqueous HCl

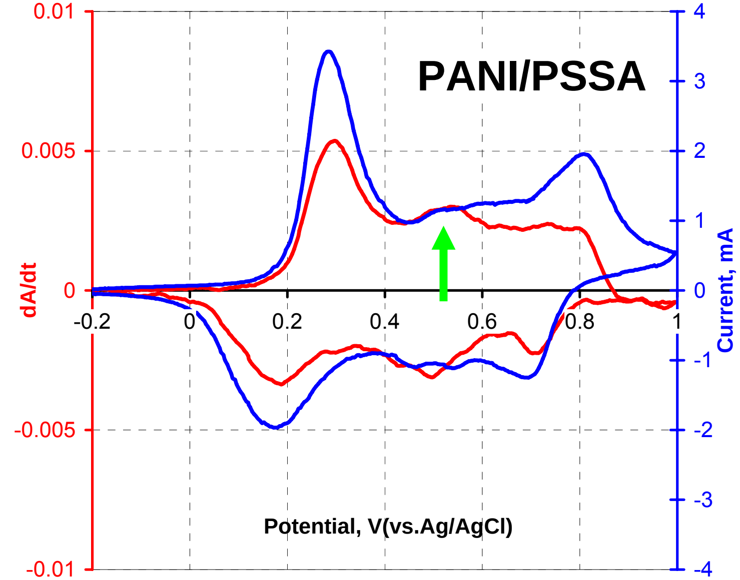


Formation of quinoid structures is hindered



DCVA-665 nm, radical cation dimers?

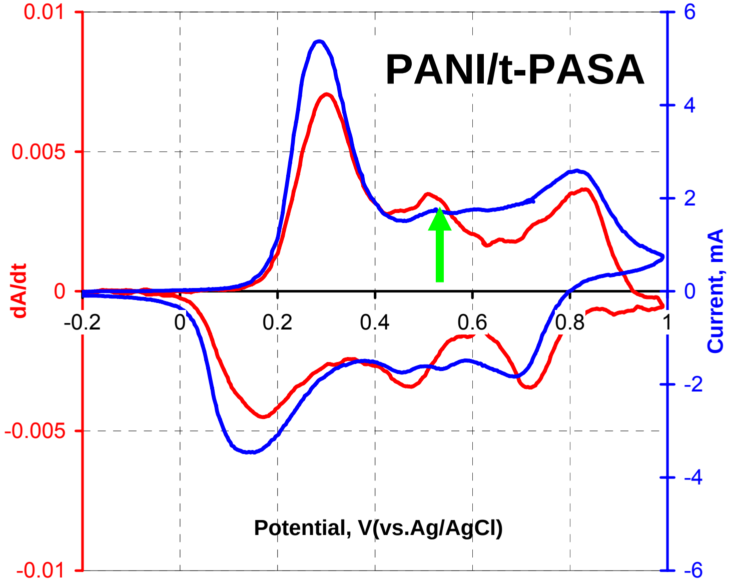


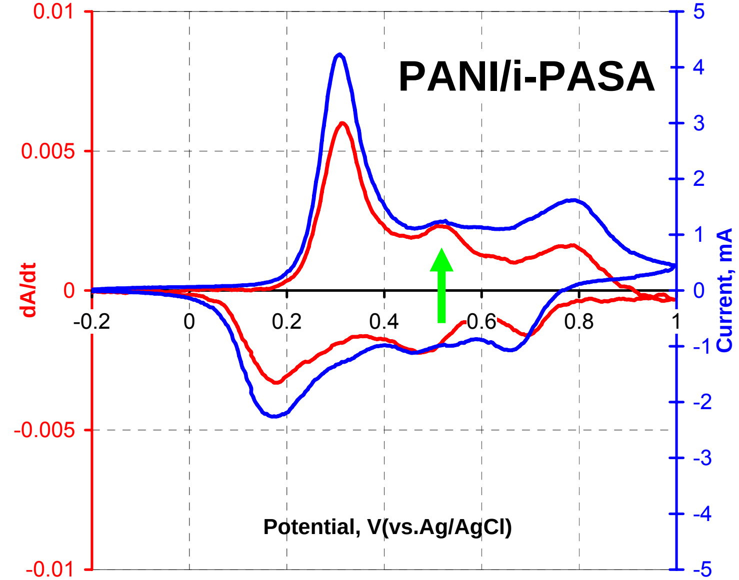


20mV/s

1M aqueous HCl

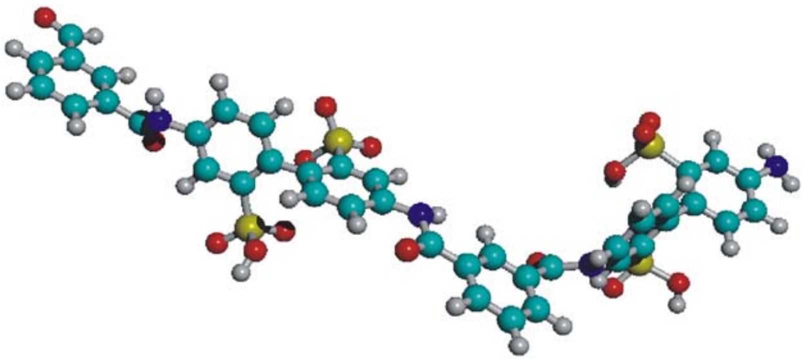
DCVA similar to DCVA 570



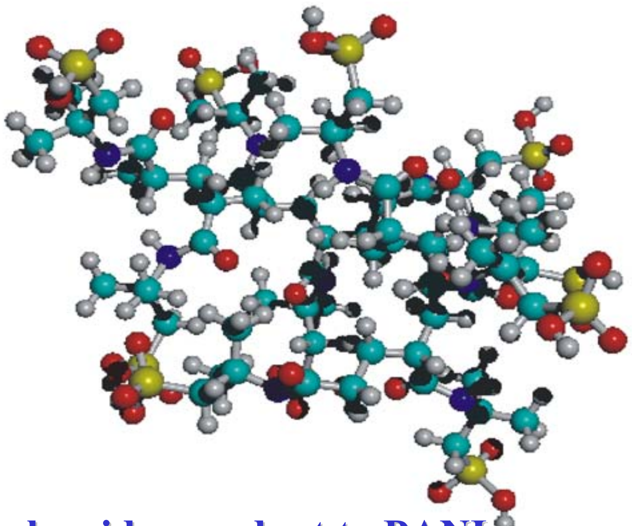


Polymeric acids: molecular modeling

iso-PASA dimer (semi-rigid)

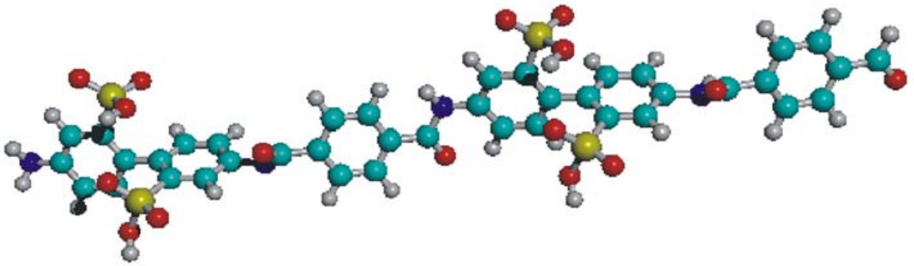


PAMPSA decamer (flexible)



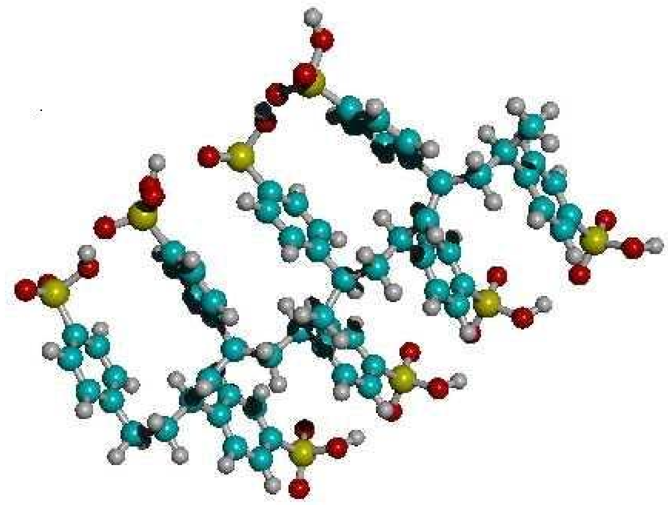
polyacid can adapt to PANI

tere-PASA dimer (rigid)



much more rigid polymer backbone which is slightly bent in the case of the iso-polymer → lower conformational adaptability → PANI adapt to polyacid

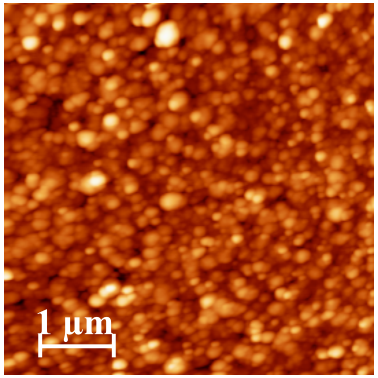
PSSA octamer (flexible???)



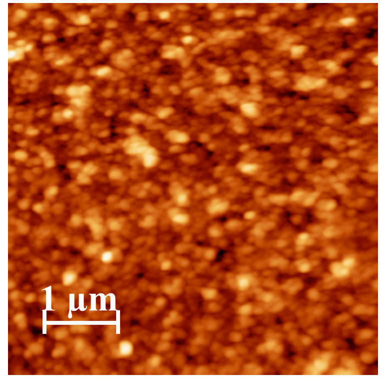
Flexible polymer backbone **BUT…**
short benzene-containing side chains hinder chain bending → lower conformational adaptability

Morphology of PANI-polyacids films: AFM studies

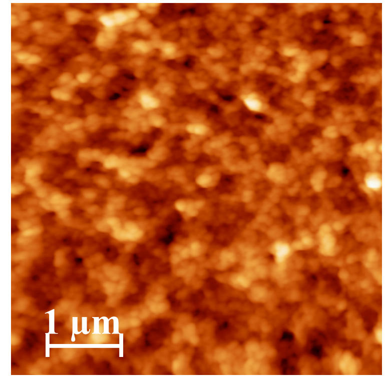
PANI-i-PASA



PANI-t-PASA

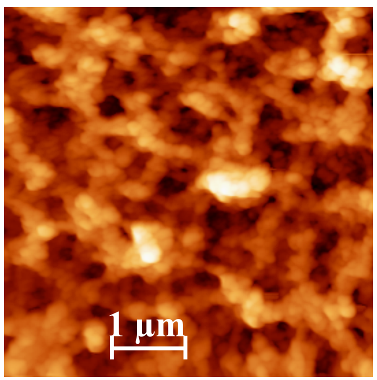


PANI-co-PASA



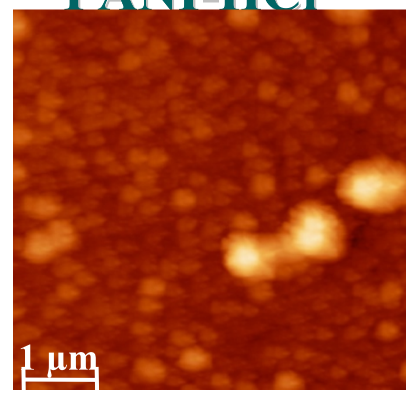
Association of aniline along the polyacid molecule → Preforming of polyaniline clusters →More uniform nucleation → More uniform structure

PANI-PAMPSA



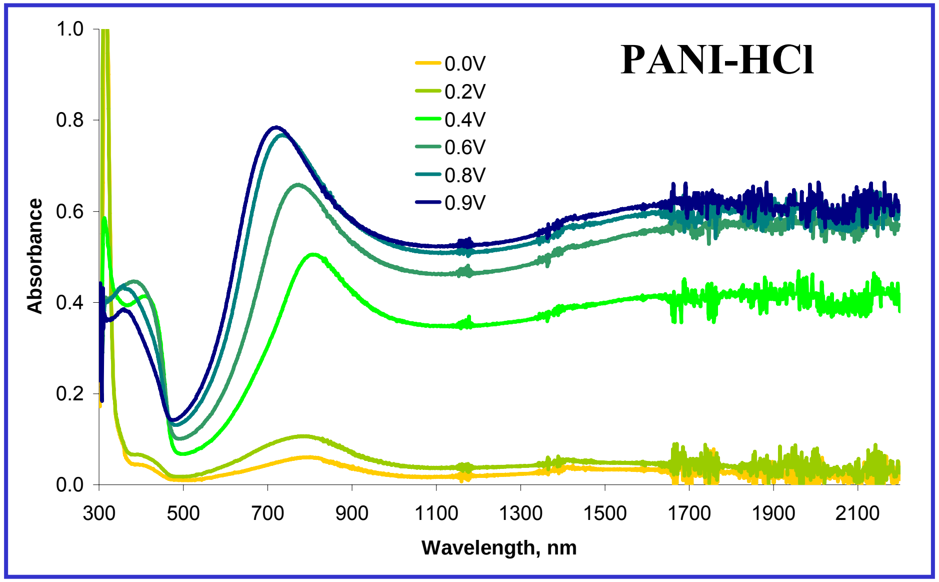
- objects size is bigger in the case of PAMPSA with greater molecular weight
- for thick films - “velvet-like” surface

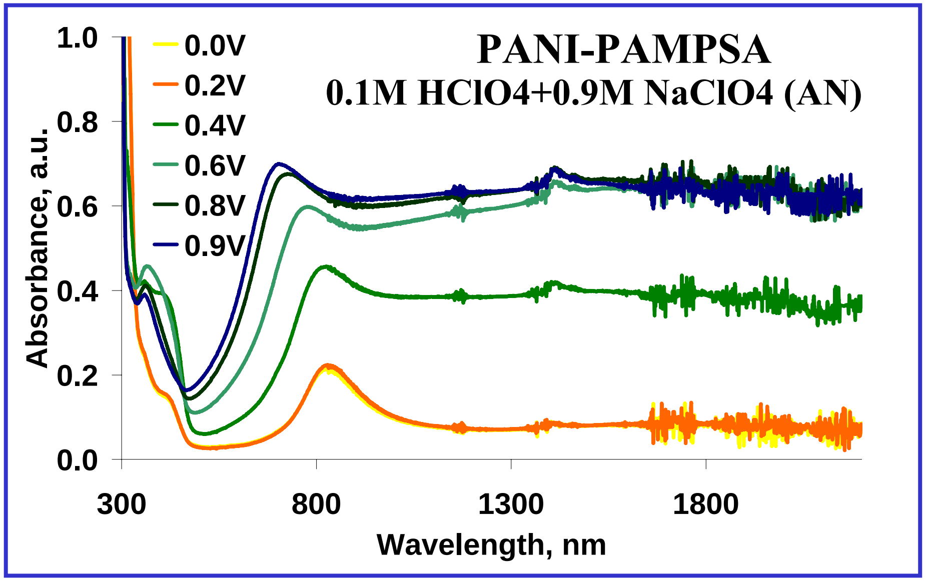
PANI-HCl

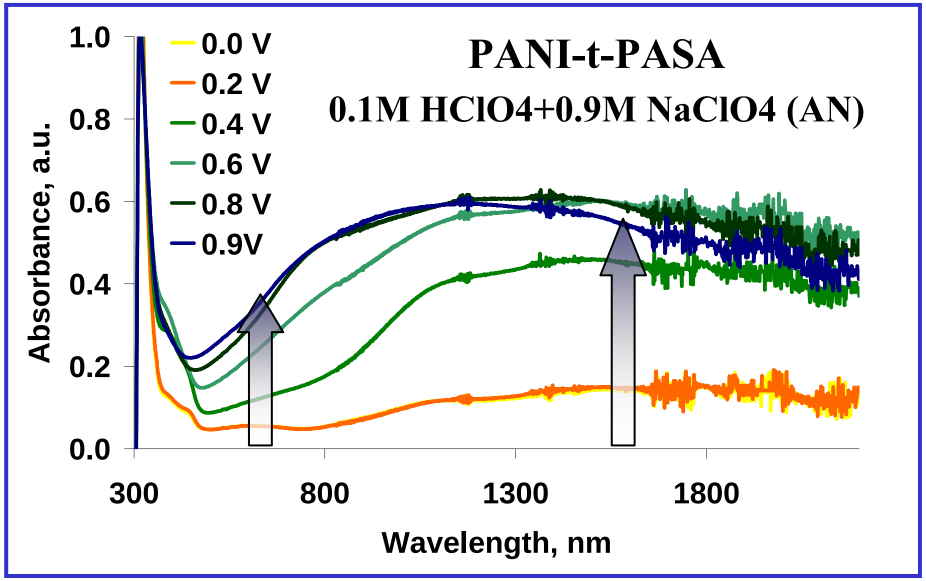


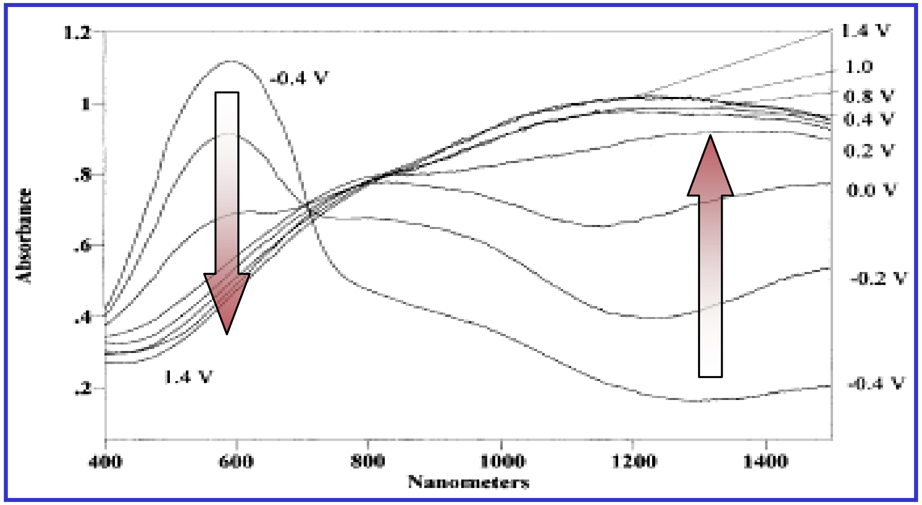
Irregular surface morphology:
Objects size ranges from 0.1 to 2 microns.
Result of irregular nucleation process and development of the defects due to autocatalytic character of the synthesis.

Spectroelectrochemistry of electrodeposited PANI-polyacid films (UV-Vis-NIR)









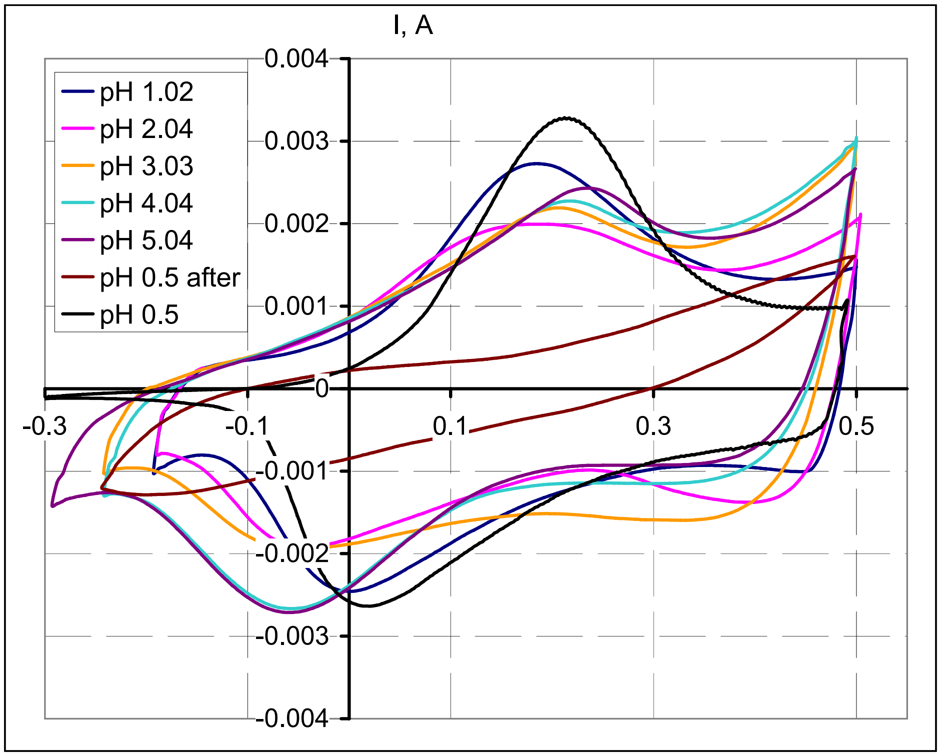
PEDOT M. Łapkowski, A. Pron,
Synthetic Metals 110 (2000) 79–83

Electroactivity at high pH

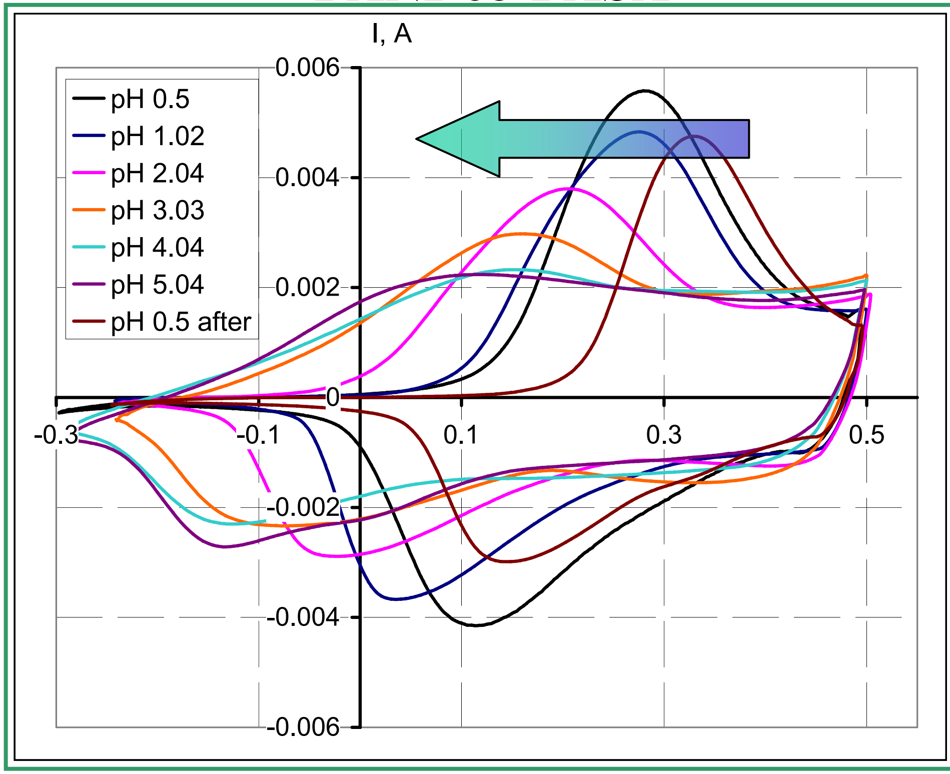
A.A. Nekrasov, O.L. Gribkova V.F. Ivanov, A.V. Vannikov J Solid State Electrochem 14 (2010) 1975

Medium: aqueous $HClO_4$ +NH_4ClO_4; Electrode: SnO_2

PANI-HCl



PANI-co-PASA



- ➔ "normal" cathodic shift of peak position within the pH-range 0.5-2
- ➔ After cycling at pH 5 the film lost electroactivity even in 1M $HClO_4$

- ➔ "normal" cathodic shift of peak position within the pH-range 0.5-5
- ➔ Probably, bulky unmovable acidic dopant adjusts pH inside the film

Electroactivity at high pH (2)

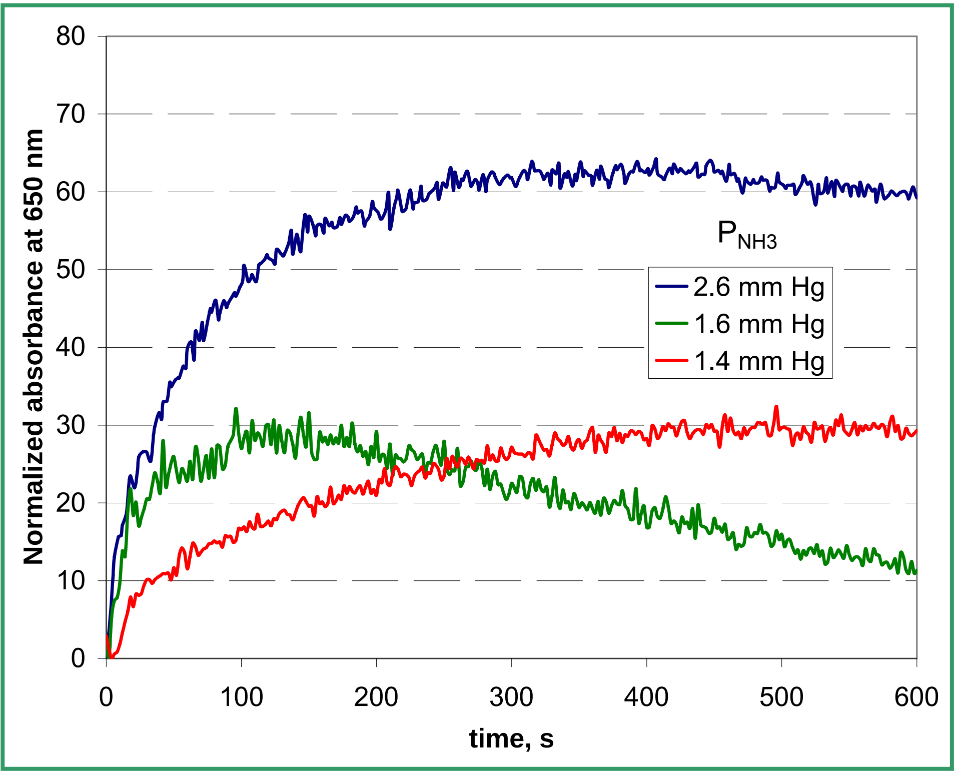
A.A. Nekrasov, O.L. Gribkova V.F. Ivanov, A.V. Vannikov J Solid State Electrochem 14 (2010) 1975

PANI-acid	Anode peak position, V pH						
	0.5	1.02	2.04	3.03	4.04	5.04	0.5(after)
PANI-HCl	0.214	0.187	0.181	0.208	0.222	0.236	-
Δ*E*		-0.027	-0.006	0.027	0.014	0.014	
PANI-i-PASA	0.296	0.272	0.206	0.173	0.128	0.084	0.323
Δ*E*		-0.024	-0.066	-0.033	-0.045	-0.044	0.212
PANI-t-PASA	0.261	0.267	0.201	0.153	0.157	0.166	0.347
Δ*E*		0.006	-0.066	-0.048	0.004	0.009	0.095
PANI-co-PASA	0.281	0.277	0.206	0.163	0.147	0.098	0.332
Δ*E*		-0.004	-0.071	-0.043	-0.016	-0.059	0.183
PANI-PAMPSA	0.261	0.277	0.196	0.158	0.167	0.128	0.367
Δ*E*		0.016	-0.081	-0.038	0.009	-0.039	0.133

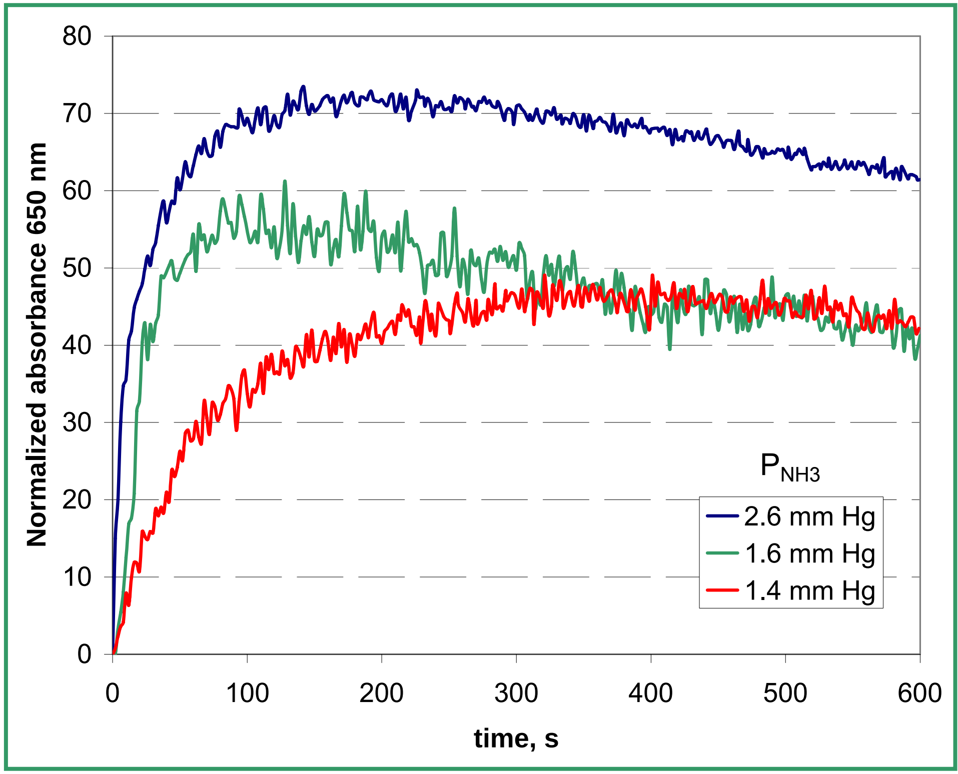
- → PANI-i-PASA interpolymer complexes have widest pH-range of electroactivity
- → followed by PANI-co-PASA (also has i-PASA fragment in the structure)
- → mixed structure of the interpolymer complex and abnormal course of the synthesis

NH_3-sensing properties

PANI-HCl



PANI-i-PASA



- ➔ **main drawback of common PANI-HCl - formation after exposition to ammonia vapors of solid ammonium chloride**
- ➔ **interplymer complexes can be completely washed off the hydrochloric acid without any significant deprotonation.**

Response time and amplitude at 1.4 mm Hg

PANI-acid	Δt (s)	ΔA, %
PANI-HCl	24	8.3
PANI-i-PASA	70	30.5
PANI-t-PASA	91	14.4
PANI-co-PASA	106	20.3
PANI-PAMPSA	42	22.2

Main advantages of using polyacids for aniline matrix polymerization (conclusion)

- **Low concentration of reagents (compared to synthesis in inorganic acids)**
- **Fast polymerization** and **low content of byproducts** in the final polymer
- **Improved film-forming** and **mechanical properties** of the resulting polymer, **good adherence** to different substrates
- **Possibility to modify the structure** of the polymer with the purpose **to change its optical** and **electrical properties**
- **Improved morphology and structural uniformity** of the films
- **Wide pH-range of electroactivity**
- **Improved resource characteristics** of the films in various applications
- **The rigidity** of polymer chain of polyacid **molecular template** produce cardinal **influence** on the **spectroelectrochemical processes** in the **interpolymer complexes** of polyaniline**: flexible-chain** polyacid can **adapt** its structure **to** the structure of **polyaniline,** while in the complex with **rigid-chain** polyacid **polyaniline** is forced to **change its conformation,** which results in disturbing of the spectroelectrochemical properties
- **The adaptability** of the polyacid molecular **template** is dependent not only on the **flexibility of the polymeric backbone,** but also on the **length and the structure of side chains**

ELECTROCHROMIC ALL-SOLID THIN-FILM LIGHT MODULATORS

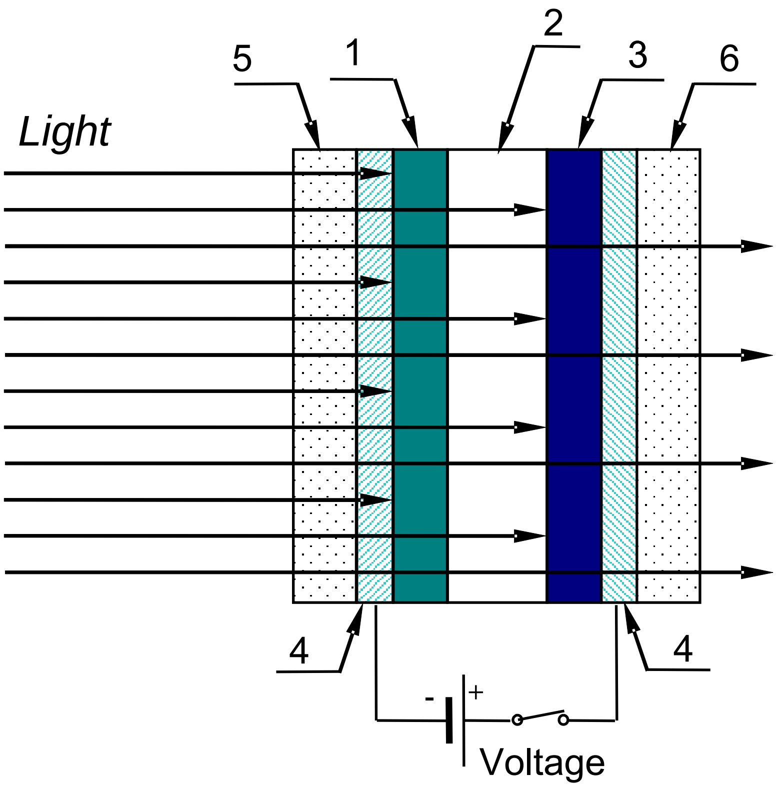
Main advantages of electrochromic optical modulators:

1) isotropic optical medium (high contrast, which is practically independent of the viewing angle);
2) energy-independent state of maximal transmittance;
3) “memory” effect for each of the intermediate states of transmission;
4) gradual change of transmittance;
5) simplicity of design and manufacture.

Main advantages of all-solid thin-film electrochromic cells:

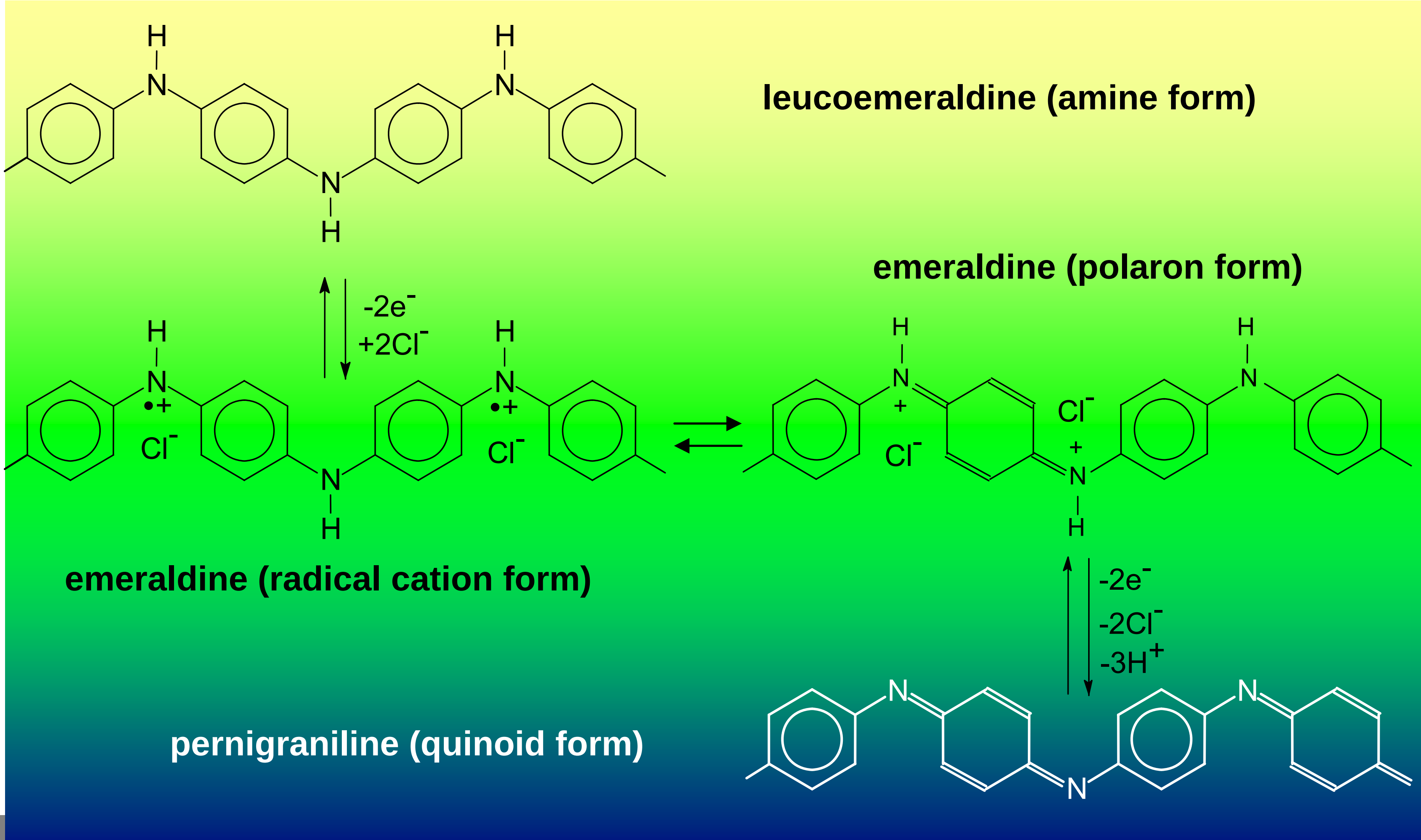
1) low optical response time (electrochromic substance immobilized on electrode);
2) response time is less temperature dependent (relay-race ion transfer in semi-solid electrolyte instead of diffusion);
3) wide temperature range of operation;
4) leak-proof.

SCHEME OF DUAL-LAYER ELECTROCROMIC DEVICE



1. Cathodic electrochromic layer (WO_3)
2. Optically transparent electrolyte (on the base of PAMPSA)
3. Anodic electrochromic layer (PANI)
4. Optically transparent electrodes (ITO, FTO)
5. Optically transparent support (glass, polymer film, e.j. PET)
6. Support (optically transparent – optical filter with adjustable transmission or modulator; optically reflecting – display or auto-dimming rearview mirror

SCHEME OF COLOR TRANSITONS IN POLYANILINE



CATHODIC ELECTROCHROMIC MATERIAL

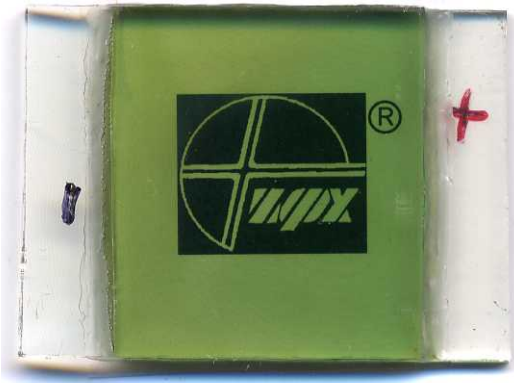
Tungsten trioxide

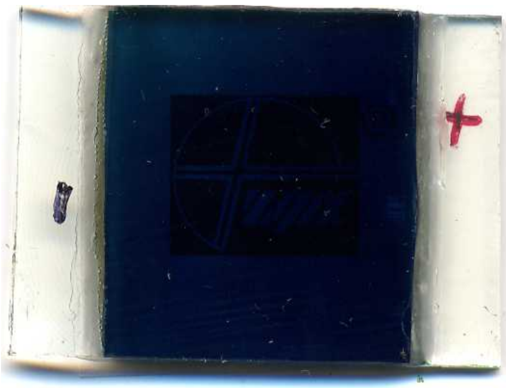
$$WO_3 + \chi e + \chi H^+ \leftrightarrow H_\chi WO_3$$

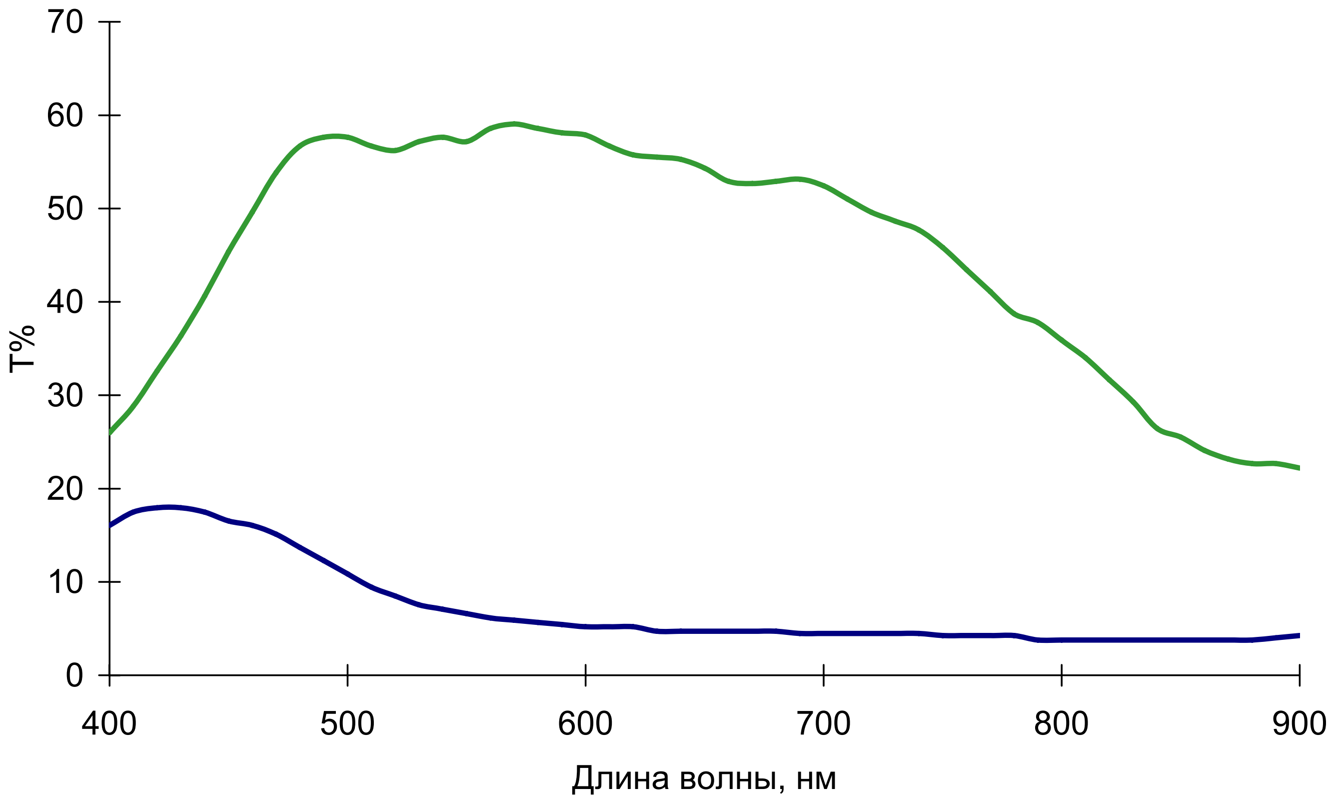
colorless **blue**

$$WO_3 + \chi e + \chi Li^+ \leftrightarrow Li_\chi WO_3$$

Transmittance spectra of PAn/WO_3 cell

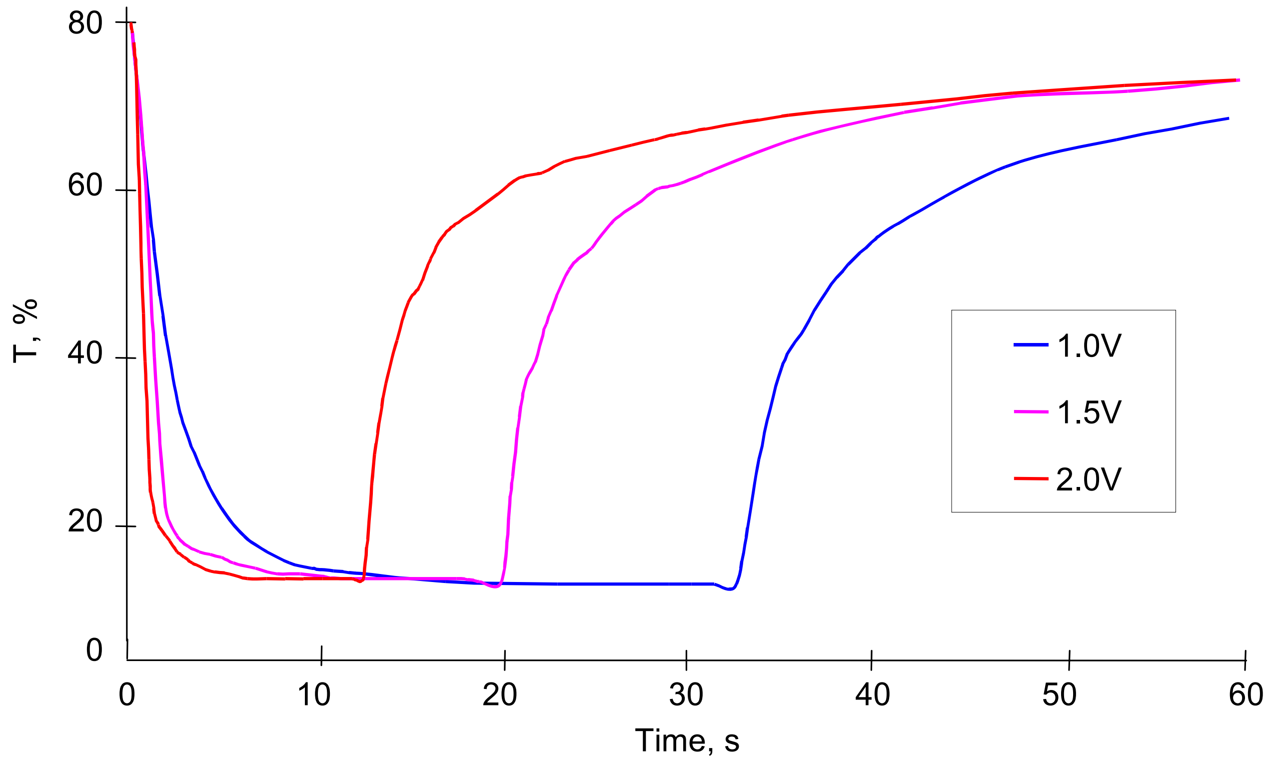






Semisolid polymer electrolyte (PAMPSA+H_3PO_4)

Kinetics of transmittance change at 550 nm



Semisolid polymer electrolyte (PAMPSA+H_3PO_4)

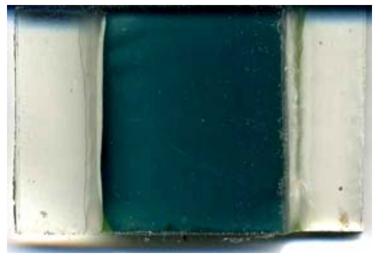
CHARATERISTICS OF SOLID-STATE ELECTROCHROMIC OPTICAL FILTER

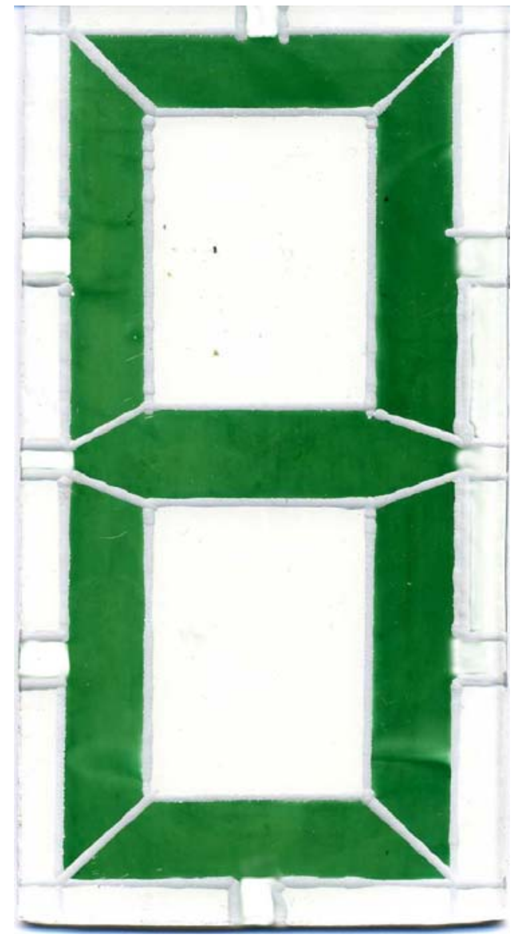
	Our prototype	**Typical parameters of all-solid electrochromic devices described in the literature**
Operation voltage, V	0-3	0-10
Optical response time, s	< 2	5-15
Number of operation cycles	1 000 000	100 000
Spectral range of transmittance modulation, nm	450-800	400-800

Possible Applications

1. switchable filters for light and heat (for various types of optical devices);
2. architectural glazing (for energy efficient windows, controlling the flow of light and heat);
3. electrochromic panels for automotive and aerospace application (auto-dimming sunroofs, windshields, visors, illuminators and rearview mirrors)
4. switchable sunglasses and so on

ELECTROCHROMIC DECADE INDICATOR





Non-transparent electrolyte possessing high diffuse reflectance

Acknowledgements

Head of Laboratory: **Prof. Anatoly Vannikov**

Colleagues: **Prof. Victor Ivanov,**

Prof. Vladimir Tverskoj (Moscow University of Fine Chemical Technology)

Dr. Oxana Gribkova

Dr. Alexandra Isakova

Ph.D. Students: **Ol'ga Omel'chenko**

Graduate students: **Tat'yana Eremina, Anna Razova, Vadim Sazikov**

The Russian Fund for Basic Research for financial support of the researches (projects No. No.12-03-01087-a, 12-03-90435-Ukr_a)

Thank you for your kind attention