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## SYNTHESIS OF CATIONIC POLYELECTROLYTES FOR TREATMENT OF NATURAL AND WASTE WATERS

Cationic polyelectrolytes, based on 2-methyl-5-vinylpyridine and halogen alkyls of various molecular masses, have been synthesized by spontaneous and radical VPS polymerization and radical VPS polymerization without their intermediate isolation. Viscosity, electrochemical properties and the efficiency of their application as flocculating agents in natural and waste water treatment have been studied.

The existing methods of cationic polyelectrolyte syntheses may be classified among two main groups:

polymer-similar transformation of polymerization and polycondensation linear polymers,

polymerization of ionogenous monomers.

In the first case cationic polyelectrolytes are received from chemical transformations of polymer non-containing ionogenous groups (polystyrene, polyvinyl toluene) or containing low basic ionogenous groups (polyvinylpyridine, polyvinylhynoline).

Non-ionogenous polymers are chloromethylated and aminated by various tertiary amines, i.e. triethylamine, triethanolamine, etc. In order to receive highly basic polyelectrolytes at the basis of polymers containing low-basic functional groups, they are treated with different alkylating agents (halogen alkyls, dialkylsulphates, etc).

The above methods for synthesis of cationic polyelectrolytes are multistage ones; that is why their production is complicated, accessory reactions lead to structure formation of polymers and creation of unregular in content polymers. Moreover, the obtained cationic polyelectrolytes are characterized by comparatively low values of molecular masses.

Having this in mind, one-stage process of polymerization of ionogenous unsaturated monomers is more perspective since it allows us to obtain highly molecular anionites with maximum content of ionogenous groups.

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The initial material used for the synthesis of highly basic water-soluble polyelectrolytes were quaternary vinylpyridine salts (QVPS) on the base of vinylpyridine and various alkylating agents, which ensured an extremely high reactivity of these salts and the availability of raw materials.

Monomeric vinylpyridine salts enter easily into polymerization because of high polarization of double bond due to positive charge on nitrogen atom. Since the polarization of double bonds is higher in the ortho- and para-positions, in most cases it is not possible to obtain unlimited quaternary salts on the base of 2- and 4-vinylpyridines, because the polymeric products are immediately released.

At the same time the reaction of 2-methyl and 5-vinylpyridines (2M5V) and various alkylating agents results in stable formation of quaternary vinylpyridine salts (QVPS) due to a lower activity of the double bonds.

Polymerization of vinylpyridine salts was performed by three methods:

1. Spontaneous QVPS polymerization in concentrated water solutions by specific ion mechanism.

2. Radical QVPS polymerization in water ethanol solutions.

3. Radical QVPS polymerization without their intermediate isolation.

Until now general attention of researches has been directed at studying a spontaneous polymerization of quaternary vinylpyridine salts.

KABANOV and his colleagues (1966, 1971) after detailed kinetic investigations of quaternary salts on the base of vinylpyridine with dimethylpyridine with dimethylsulphate spontaneous polymerization reaction have stated that the reaction proceeds by specific

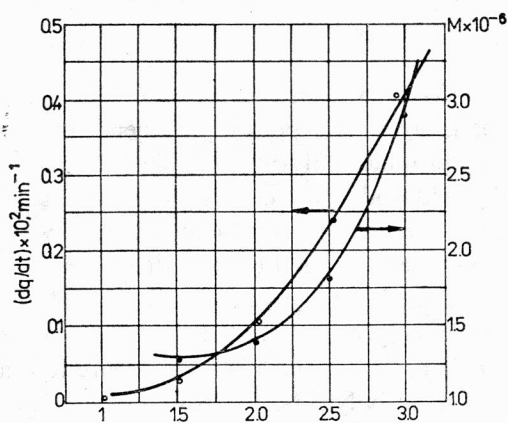


Fig. 1. Initial rate of MVP-C<sub>2</sub>H<sub>5</sub>-Br salt polymerization and molecular masses of resulting polymers versus initial monomer concentration  
Rys. 1. Początkowa szybkość polimeryzacji soli MVP-C<sub>2</sub>H<sub>5</sub>-Br i masy cząsteczkowe powstałych polimerów w zależności od początkowego stężenia monomeru

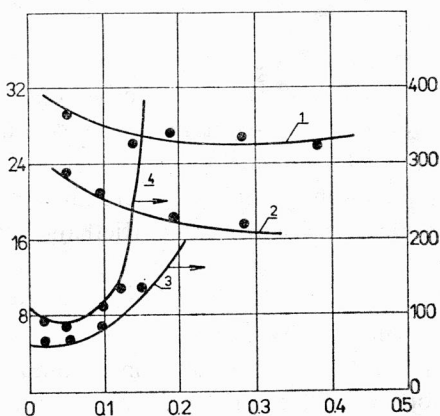


Fig. 2. Reduced viscosity of water solutions of VPS-11 polyelectrolyte versus their concentrations for various values of molecular masses

1 - 4.0, 2 - 3.2, 3 - 6.0, 4 - 8.3

Rys. 2. Zredukowana lepkość roztworów wodnych polielektrolitu VPS-11 w zależności od ich stężenia dla różnych wartości mas cząsteczkowych

1 - 4,0, 2 - 3,2, 3 - 6,0, 4 - 8,3

anion mechanism. This reaction result in formation of quaternary polymer salts of highly molecular weight, their use as flocculants for natural and waste waters treatment is thus of a great importance.

It should be emphasized that the reaction occurs at low temperatures (25–30°C) without initiators.

The investigations have shown that polymerization rate decreases rapidly when monomeric salt concentration in solution is reduced.

It is of interest to note that at QVPS concentration of 1 mole/dm<sup>3</sup> and lower the reaction does not proceed.

Analogical relationship has been found for molecular weights of obtained polymers (fig. 1).

The nature of anti-ions has great influence on spontaneous rate of QVPS polymerization.

At 2M5V–METSА salt the yield of a 4 hour polymerization is 17% of the theoretical one, while at 2M5V–CH<sub>3</sub>B<sub>2</sub> salt it amounts to 52% and it is highly probable due to different nucleophilicity and mobility of anions initiating spontaneous polymerization reaction.

Total duration of spontaneous polymerization in concentrated water solution ranges from 24 to 48 h, depending on the character of polymerized monomer salt (tab. 2).

The second method of the synthesis of cationic polyelectrolytes, i.e. radical polymerization of QVPS, is distinguished by its high productivity (tab. 2).

From the given data it may be seen that in this case reaction duration is 6–10 hours.

However, molecular masses (characteristic viscosities) of synthesized polysalts are significantly lower than those of polyelectrolytes obtained by spontaneous polymerization. The peculiarity of quaternary vinylpyridine salts radical polymerization is the influence of media in which the reaction takes place (GEORGIYEVA, ZUBOV, KABANOV, 1970). First of all it depends on the presence of ionogenous groups, while the strength of inter-ionic and inter-molecular interactions of reacting particles and the activity of reaction centers depend on the dissociation degree of these groups.

The rate of 1-ethyl-2-methyl-5-vinylpyridine bromide polymerization in water-spirit solutions increases approximately 4 times when transferring it into a less ionizing solvent (absolute ethanol) with respect to the same value in highly polar solvent (water).

Table 1

Yield (% wt.) of QVPS depending of the nature of halide alkyl and radical length  
Wydajność (% wagowe) QVPS w zależności od rodzaju i długości halogenu alkilowego

Halides	Alkyl radicals				
	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>	C <sub>4</sub> H <sub>9</sub>	C <sub>3</sub> H <sub>5</sub>
J	80	65	40	15.0	60
Br	78	60	5.0	—	42
Cl	15	—	—	—	—

Table 2

Reaction duration and yield of PVP salts versus the methods of their synthesis  
Czas reakcji i wydajność soli PVP w zależności od metod ich syntezy

Kind of salt	Method of synthesis	Duration hour	Polymer yield %	Z* hundr./cm <sup>3</sup> /g
MVP-C <sub>2</sub> H <sub>5</sub> Br	Spontaneous polymerization	24	95	8.7
	Radical polymerization	10	93	0.7
	Without monomer salt isolation	12	98	0.3
MVP-C <sub>2</sub> H <sub>5</sub> J	Spontaneous polymerization	48	91	3.9
	Radical polymerization	8	98	0.6
	Without monomer salt isolation	12	97	0.24

\* — intrinsic viscosity in 0.5 m KBr solution

The rate of QVPS radical polymerization depends on the nature of monomer salt.

Thus, the increase of radical length from CH<sub>3</sub> to C<sub>3</sub>H<sub>7</sub> at QVPS nitrogen atom reduces approximately three times the reaction rate.

Comparison of polymerization rates constants of iodine and bromine salts shows that the latter are polymerized slower than the former (tab. 3). In all probability the difference in kinetic characteristics of these salts is connected with different ionization degree of monomers molecules and growing macroradicals (GEORGIYEVA, ZUBOV, KABANOV, 1970).

Table 3

Values of initial rates and total constants of QVPS polymerization in 50% water ethanol solution  
Wartości początkowych szybkości i stałych polimeryzacji w 50% wodnym roztworze etanolu

Monomer	Initiator — azodiisobutyronitrile		K × 10 <sup>2</sup>
	Temperature	V <sub>0</sub> × 10 <sup>4</sup> mole/sec	
2M5V-CH <sub>3</sub> J	70	—	9.84
2M5V-C <sub>2</sub> H <sub>5</sub> J	70	2.14	5.56
	75	2.96	7.70
2M5V-CH <sub>3</sub> Br	75	1.50	3.90
2M5V-C <sub>2</sub> H <sub>5</sub> Br	75	0.99	2.57
2M5V-C <sub>3</sub> H <sub>7</sub> Br	75	0.57	1.49

Water-soluble highly basic polyelectrolytes can be obtained not only by methods of spontaneous and radical polymerization of non-limiting QVPS, but also by radical polymerization of the latter without their intermediate isolation.

Such a one-stage method of synthesis of cationic polyelectrolytes is of interest for two reasons:

1. Firstly, the isolation of monomer vinylpyridine salts being not required, the process is simplified significantly.

2. Secondly, this method is unchangeable in cases when the yields of monomer salts are low or the salts cannot be isolated from the a reaction zone. For example, monomer salts at the base of 4-vinylpyridine and different haloid alkyls cannot be isolated, therefore of all the above mentioned ways the last method is the only possible one.

Therefore it should be concluded that all three methods may be used.

The choice of method depends on the definite area and conditions of synthesized polymers application.

#### PROPERTIES AND APPLICATION OF CATIONIC POLYELECTROLYTES AT THE BASE OF 2-METHYL-3-VINYLPYRIDINE

For preliminary estimation of the applicability of cationic polyelectrolytes as flocculants, it is of importance to investigate their behaviour in water solutions. In particular, the investigation of viscous and electrochemical properties of polyelectrolyte solutions reveal the structure forms of polymer macromolecules in solution, its ionogenous abilities, associations of antiions and polyions.

These investigations allowed us to state that for water solutions of polymer quaternary salts at vinylpyridines base there occurs a non-linear increase of the viscosity with dilution, usual for polyelectrolytes. However, for polyelectrolytes of highly molecular weight obtained by spontaneous polymerization of quaternary vinylpyridine salts, the viscosity isotherms pass through minimum at a definite concentration  $C_0$  of polyelectrolytes in solution (fig. 2). At  $C > C_0$  concentration, the viscosity increases due to the aggregation of macromolecules at the expense of intermolecular interactions.

Studies on electroconductivity of polymer and monomer vinylpyridine salts have shown their significant difference.

Firstly, equivalent electroconductivity of polymer salts is lower than that of monomers (tab. 4). Secondly, isotherms of electroconductivity for polymers have curvilinear concave shape.

These features of electrochemical properties of solutions depend on a series of specific characteristics distinctive only for polyelectrolytes (counterion connection, association of ions). The values of probable constant ionization, calculated from Kachalcky-Spitnik equation, are extremely high, ranging within 3.9–4.85 and indicating the presence of counterion association in polyelectrolyte water solutions.

Table 4

Equivalent electrical conductivity of water solutions of QVPS and polyelectrolytes at 0.015 mole/dm<sup>3</sup> concentration  
 Równoważnikowa przewodność właściwa wodnych roztworów QVPS i polielektrolitów przy ich stężeniu 0,015 mola/dm<sup>3</sup>

Polyelectrolyte	Description Monomeric salt	Equivalent electrical conductivity		Hund. cm <sup>3</sup> /g
		Monomer	Polymer	
VPS-1	2M5V-METSA	49	16	2.0
VPS-6	2M5V-CH <sub>3</sub> J	88.5	17.9	1.0
VPS-7	2M5V-C <sub>2</sub> H <sub>5</sub> J	83.5	15.2	1.2
VPS-8	2M5V-C <sub>3</sub> H <sub>7</sub> J	80.5	12.85	0.9
VPS-10	2M5V-CH <sub>3</sub> Br	92.0	30.6	3.2
VPS-11	2M5V-C <sub>2</sub> H <sub>5</sub> Br	85.0	36.5	4.0

The investigations of the treatment of natural and waste water using synthesized polyelectrolytes have shown their high efficiency.

Thus, the investigation of flocculating capability of polymeric halogen containing vinylpyridine salts in removal of humus substances from natural water was carried out together with the Voronezh State University of Lenin's Komsomol.

The investigations were carried out on water solutions of humic acid and fulvic acid of 2-10 mg/dm<sup>3</sup> concentration. The concentration of ionogenous groups of fulvic acids was 5.57 mg equiv/g. The content of carboxylic groups and the total concentration of carboxylic and fenolic groups of humic acids are turned out to be 1.41 mg equiv/g and 3.52 mg equiv/g, respectively. VPS-6, VPS-7 and VPS-11 in salt and OH-form were used as the flocculants. The conversion into the OH-form is accompanied by yield of weakly basic groups in polyelectrolytes.

By isomerization of hydroxide alkyl vinylpyridine formed when changing the hallogen-ions to OH-groups; as a result the methylene bases containing tertiary amino groups are formed.

Table 5

The flocculants capacity determined from the data of potentiometric titration  
 Pojemność flokulantów oznaczona na podstawie danych z miareczkowania potencjometrycznego

Flocculant type	Capacity, mequiv./g	
	Acc. to highly basic groups E <sub>1</sub>	Acc. to summary of highly and weakly basic groups E <sub>2</sub>
VPS-6	2.41	4.27
VPS-7	3.45	4.32
VPS-11	3.45	5.50

Exchange volume of polyelectrolyte, found according to highly basic groups and the total highly and weakly basic groups, is given in tab. 5.

The presence of acid groups in humus substances and general functional groups in flocculants allow us to suppose that the yield of humic and fulvic acids occurs at the expense of chemical interaction of these groups. In this case, the polymer consumption should be calculated according to the formulas:

$$G = \frac{E_{HA}}{E_F} C,$$

$$G = \frac{E_{FA}}{E_F} C$$

where:

$G$  — polyelectrolyte dose, mg/dm<sup>3</sup>,

$C$  — concentration of humic and fulvic acids in water, mg,

$E_F$ ,  $E_{FA}$  and  $E_{HA}$  — exchange volumes of the flocculant, fulvic acid and humic acid, respectively, mg equiv/g.

However, the calculated doses of polyelectrolytes in OH-form exceed extremely those of flocculants found experimentally (tab. 6).

Table 6

Designed and defined experimentally doses of flocculants  
Planowane i wyznaczone doświadczalnie dawki flokulantów

Flocculant type	Designed doses of flocculants mg/mg						Experimental doses of acids mg/mg	
	E <sub>1F</sub>			E <sub>2F</sub>			Humic acid	Fulvic acid
	E <sub>1HA</sub>	E <sub>2HA</sub>	E <sub>FA</sub>	E <sub>1HA</sub>	E <sub>2HA</sub>	E <sub>FA</sub>		
VPS-6	0.59	1.46	2.30	0.31	0.82	1.30	0.8-0.9	0.6-0.7
VPS-7	0.41	1.02	1.62	0.32	0.81	1.25	0.9-1.0	0.6-0.7
VPS-11	0.42	1.06	1.70	0.25	0.64	1.1	0.6-1.2	0.6-0.7

This points to the fact that the flocculation process is determined not only by the volume of humus and polybasic substances but also by the molecular sizes of these compounds.

As it has been established, the cationic polyelectrolytes on the basis of vinylpyridines may be used successfully for treatment of industry wastewater. Highly-molecular polyvinylpyridine salts, obtained by spontaneous polymerization of QVPS are the most efficient flocculants.

Thus, the utilization of VPS-11 flocculant of 700,000 molecular weight permits the treatment of wastewater containing acid dyes, petroleum products, dissolved and emul-

sificated organic substances with 95–100% efficiency. The results of application of synthesized polyelectrolytes in treatment of industrial wastes are given in the report *Investigation of the wastewater treatment with flocculant utilization* by I. N. MYASNIKOV, L. V. GANDURINA and L. N. BUTZEVA.

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#### SYNTEZA KATIONOWYCH POLIELEKTROLITÓW DO OCZYSZCZANIA WÓD NATURALNYCH I ŚCIEKÓW

Polielektrolity kationowe, oparte na 2-metylo-5-winylopirydynie i chlorowcopochodnych alkilach o różnych masach cząsteczkowych, syntezowane były w samorzutnej oraz rodnikowej polimeryzacji soli winylopirydyny, a także w rodnikowej polimeryzacji tych soli bez wydzielania produktów pośrednich. Zbadano ich lepkość, własności elektrochemiczne oraz efektywność flokulacji w wodach naturalnych i ściekach.

#### SYNTHESE VON KATIONENAKTIVEN POLYELEKTROLYTEN ZUR WASSERAUFBEREITUNG UND ABWASSERREINIGUNG

Synthetisiert wurden kationenartige Flockungsmittel, die auf 2-Methylo-5-Vinylopyridin und auf Halogenderivaten von Alkylen unterschiedlicher Molekulargewichte basieren; dies war eine selbstvorgehende Synthese und eine Radikalpolymerisation von Vinylopyridinasalzen, ohne einer Ausscheidung von Zwischenprodukten. Untersucht wurde die Viskosität der Flockungsmittel, deren elektrochemische Eigenschaften und die Flockulationswirkung in natürlichen Wässern und Abwässern.

#### СИНТЕЗ КАТИОННЫХ ПОЛИЭЛЕКТРОЛИТОВ ДЛЯ ОЧИСТКИ ПРИРОДНЫХ И СТОЧНЫХ ВОД

Катионные полиэлектролиты, основанные на 2-метил-5-винилпиридине и галогеннопроизводных алкилах с различными молекулярными массами, были синтезированы в самопроизвольной, а также радикальной полимеризации этих солей без выделения промежуточных продуктов. Исследована их вязкость, электрохимические свойства, а также эффективность флокуляции в природных и сточных водах.