

SYNTHESIS AND STUDY OF NEW WATER-SOLUBLE (CO)POLYMERS OF POLYELECTROLYTE NATURE BASED ON AMINES, ACRYLIC ACID AND EPOXYCOMPOUNDS

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ABSTRACT: *New water-soluble polymers of polyelectrolyte nature have been obtained on the basis of acrylic acid, propylene oxide, epichlorohydrin and various amines as well as their derivatives with the aid of reactions of polymerization, copolymerization, oxypropylation, chloroxypropylation, neutralization and quaternization. With respect to the charge of polymer chain, synthesized polymers may have different nature, i.e. they may be aniono-active, cationo-active or aniono-cationo active. Composition and structure of the obtained polyelectrolytes have been identified by various complex physico-chemical methods.*

KEY WORDS: *Polimerization, water-soluble polymers, polyelectrolyte, aniono-cationo active polymers.*

AMİNLER, AKRİLİK ASİD VE EPOKSİKOMPONENTLERİNDEN ÇIKARAK YENİ, SUDA ÇÖZÜNEBİLEN POLİELEKTROLİT (KO)POLİMERLERİNİN SENTEZLENMESİ VE ARAŞTIRILMASI

ÖZET: *Akrilik asit, propilen, epiklorohidrin ve çeşitli aminlerde olduğu gibi onların türevlerinden yola çıkarak, polimerizasyon, kopolimerizasyon, oksipropilasyon, kloroksispropilasyon, nötralizasyon ve katerizasyon reaksiyonları ile suda çözünebilen yeni polielektrolit yapıda polimerler elde edilmiştir. Polimer zincirinin yüküne göre farklı yapılaraya sahip, örneğin anyon-aktif, katyon aktif ya da anyon-katyon aktif polimerler sentezlenmiştir. Elde edilen polielektrolitlerin yapı ve bileşenleri değişik fiziko-kimyasal yöntemlerle belirlenmiştir.*

ANAHTAR KELİMELER: *Polimerizasyon, suda çözünen polimerler, polielektrolit, , anyon- katyon aktif polimerler.*

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I. INTRODUCTION

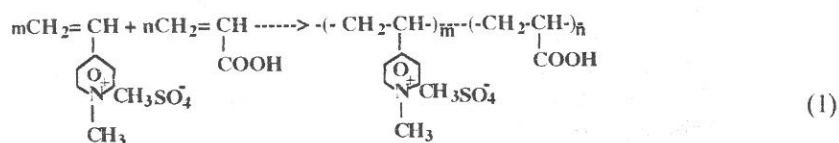
Water-soluble polymers containing functional groups with different charges obtained from acrylic monomers are not numerous. So, synthesis of new water-soluble acrylic copolymers containing non-ionogene and positively charged fragments attract interest because these groups should give macromolecules an additional stability in strongly mineralized waters. For insertion of cationo-active units into the main polymer chain it is very important to choose comonomers having corresponding structure, properties and capability to be involved in polymerization process of acrylic acid (AA) and its derivatives. Quaternary salts of 4-vinyl pyridine (4-VP) with dimethylsulphate (DMS) and methyl iodide (MI) and in some cases 4-VP itself meet these requirements.

Synthesis and specifications of polymerization of the quaternary salts of 4-VP with DMS and MI are described in detail in literature [1-4]. It is shown that the quaternary salts of 4-VP with DMS 1-methyl-4-vinyl pyridinium methyl sulphate (1-M-4-VPMS) and with MI 1-methyl-4-vinyl pyridinium iodide (1-M-4-VPI) are stable in dimethylsulphoxide (i.e. absence of polymerization) in the air.

Synthesis of water-soluble acrylic copolymers having non-ionogene oxypropyl fragments and units of 4-VP seems practically expedient by way of radical copolymerization. This is stipulated by propensity of the indicated quaternary salts of 4-VP (especially 1-M-4-VPMS) to radical polymerization.

II. RESULTS AND DISCUSSION

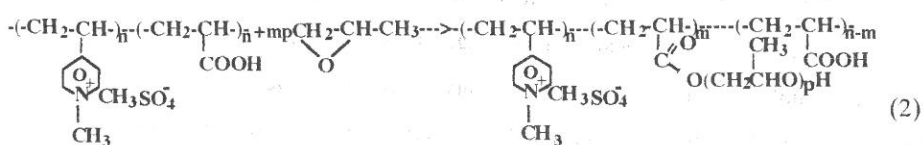
The copolymer of 1-M-4-VPMS with AA was synthesized both in ethanol and water:



In ethanol azo-diisobutyronitrile (ADIBN) was used as initiator. The amount of ADIBN was 1% of the total mass of comonomers by weight. Concentrations of comonomers were 0.4 mol/l. The temperature was kept at 70 °C for 8 hours. As the reaction proceeded, the larger part of the product precipitated in the form of white sediment (acid number was 70.4 mgKOH/g) and the remaining part was removed from the solution by evaporation of liquid phase. Despite to the presence of different acidic units in the chain, both fractions of copolymer were dissolved well in fresh water.

In aqueous medium ammonium persulphate (APS) was used as initiator. The amount of APS was 1% of the sum of the comonomers by weight. Concentrations of comonomers were 0.49 mol/l, the time of reaction was 11 hours at 50 °C. In contrast to the ethanol medium, the solution was homogeneous. The acid number of the final copolymer was 235.1 mg KOH/g.

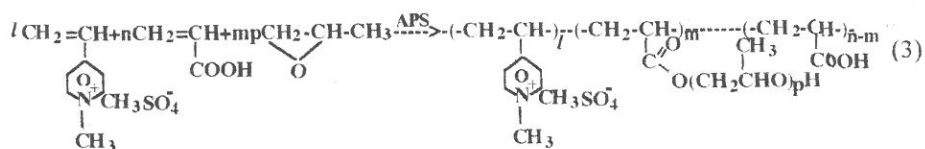
The synthesized copolymer of 1-M-4-VPMS and AA was undergone oxypropylation in water at 20°C. Molar ratio of AA and propylene oxide (PO) was 1:2.06. The concentration of AA units at oxypropylation step was equal to 0.06 mol/l and that of PO 0.12 mol/l. After 20 hours of the reaction conversion of PO was registered at the level 59.8 %, acid number of the final product of modification was 174.9 mg KOH/g. The scheme of modification represented as follows:



Such a chemical modification becomes successful only in the case of use of copolymer in aqueous solution. In the case of ethanolic solution the copolymer of 1-M-4-VPMS with AA does not undergo oxypropylation, though the triple molar excess of PO was taken with regard to AA units. Non-addition of PO to copolymer in ethanol solution is a consequence of hydrogen bonding, between alcohol and PO molecules and secondly, between alcohol molecules and carboxylic groups of the copolymer, respectively [5-7].

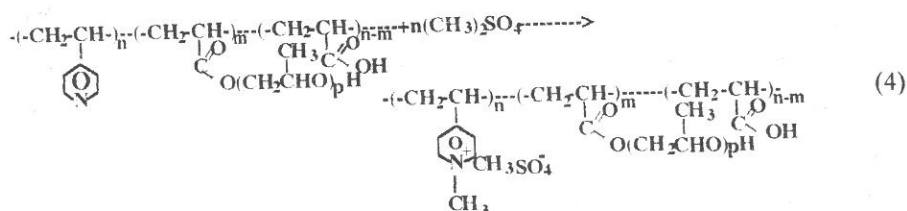
From practical point of view it seems more expedient to obtain the oxypropylated copolymer of 1-M-4-VPMS with AA "in statu nascendi", i.e. to conduct radical copolymerization of the indicated comonomers in aqueous media in the presence of PO. At the initial concentrations of 1-M-4-VPMS, AA and PO of 0.49 mol/l, APS of 1% of the total mass of comonomers within 12.5 hours at 50 °C, a complete conversion of PO was reached. Acid number of the copolymer was measured as 175.7 mg KOH/g.

The reaction scheme may be represented in the following form:



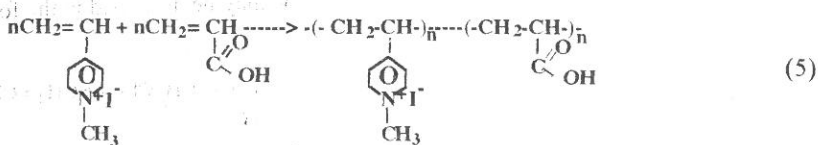
Composition and structure of the obtained copolymer were identified by H-NMR spectroscopy (spectrometer "Tesla BS-487 C", Chekhoslovakia). The analysis of spectra recorded in D₂O showed that oxypropylation reaction of carboxylic group in polymatrix leads to an appearance of resonance signals due to -CH₃ (doublet at 1.38-1.5 ppm) and -CH₂- protons (doublet at 1.55-1.65 ppm), -CH- proton (multiplet at 3.48-3.83 ppm) and OH-proton (singlet at 4.0 ppm). Entry of 1-M-4-VPMS to the polymer chain is a reason of resonance signals of the counterion CH₃SO₄⁻ (singlet at 3.0-3.1 ppm), the positively charged group -N⁺-CH₃ (singlet at 4.42-4.63 ppm). Resonance signals of pyridiniring in the copolymer was appeared in the range of 7.95-8.93 ppm.

The synthesized copolymer has a particular solubility. It dissolves well in hard strata waters but forms an opaque solution in fresh and sea waters. The copolymer synthesized on the basis of AA, PO and 1-M-4-VPMS may also be obtained by another way with reverse consequence of the steps. First, the copolymer containing units of free organic base (4-VP), AA and PO (time of the reaction is 10 hours) were obtained by copolymerization of 4-VP with AA in the presence of PO (the concentration of all three reagents is 0.9 mol/l) under an influence of APS (1% of the total mass of 4-VP and AA) at 50°C in aqueous media. Conversion of PO is 24.1%, acid number of the product was 94.7 mg KOH/g. Then free units of 4-VP of copolymer were alkylated according to Menshutkin reaction scheme in water at 20 °C with agitation :



Viscosity of the system increased as the reaction proceeded. An increase in polymatrix mass caused all the free units of 4-VP to be converted to units of quaternary salts. Studies for obtaining the copolymers based on AA, 1-M-4-VPI and PO, by the method of radical copolymerization had also been carried out. The presence of iodide-ion capable

of oxidizing complicates application of APS in aqueous copolymerization. So, under an attempt to copolymerize the indicated salt with AA (concentrations of comonomers are correspondingly 0.37 and 0.39 mol/l) in water under the action of APS (1% of the total mass of comonomers) a red-brown colour appeared and the dark residue-iodine (it gives a dark-blue colour with starch) precipitated both in absence and presence of PO. Therefore, iodide-anion of 1-M-4-VPI was oxidized in the presence of APS with iodine formation. Due to the indicated circumstance it is expedient to use ADIBN as initiator. This way, it is possible to involve 1-M-4-VPI into copolymerization with AA both in ethanol (concentration of comonomers is 0.11 mol/l) and aqueous media (concentration of comonomers is 0.47 mol/l) at 70 °C:



In both cases ADIBN at the amount of 1% of the total mass of the comonomers was introduced to the system in a small volume of acetone. In aqueous media the yield of the copolymers was quantitative. Acid number of the copolymer, measured, was 169.8 mgKOH/g.

Oxypropylation reaction of the copolymer may be carried out in aqueous solution. Use of ethanol solution of the copolymer for oxypropylation does not lead to the goal. The same situation is also observed in the case of the copolymer of 1-M-4-VPMS with AA as a result of inhibiting effect of alcohol. Oxypropylation of the copolymer in aqueous solution was conducted "in statue nascendi". This way permits, as in the case of the analogous copolymer of 1-M-4-VPMS to bring about addition of PO to acrylic units, though extent of conversion of PO is slightly lower. Apparently, even small amounts of acetone influences the efficiency of oxypropylation.

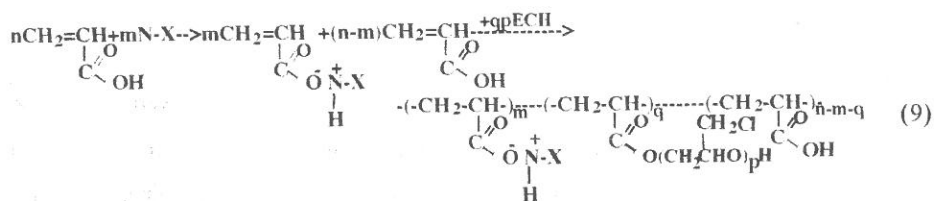
Oxypropylated copolymer of 1-M-4-VPI with AA may also be obtained through synthesis being successful in the case of 1-M-4-VPMS and including copolymerization of 4-VP with AA in the presence of PO and subsequent alkylation of the obtained copolymer according to Menshutkin reaction scheme:

The obtained salts (in the form of aqueous solutions) were polymerized at 55 °C in the presence of APS (1% of salt mass). The time of polymerization was 46-50 hours. In the case of salts, based on triethylamine and tributylamine, a partial sedimentation of polymer from the solution was observed. In other cases solutions were homogeneous. Yields of polymers as well as of monomer salts are given in Table 1.

Table 1. Yields of monomer salts based on COPEAA and amines as well as of their polymers

Monomer salt	Yield of monomer salt, %	Yield of polymer, %
COPEAA+ piperidine	75.9	64.8
COPEAA + triethylamine		23.9 23.9
COPEAA + triethanolamine	100	80.3
COPEAA + ethylenediamine	100	91.9
COPEAA + diethanolamine	94.3	100
COPEAA + monoethanolamine	76.1	65.8
COPEAA + ammonia water	100	99.5
COPEAA + methylamine		50.4 61.8
COPEAA + tributylamine		6.5 45.3
COPEAA + diethylamine		30.1 34.2

Some new water-soluble copolymers containing relatively strongly ionizing salt groups in addition to non-ionic chloroxypropyl groups and weakly ionizing carboxylic groups, were synthesized on the basis of AA, ECH and various amines. To carry out copolymerization and chloroxypropylation, initially the salts of AA with different amines were obtained (concentration of AA 0.19 mol/l). AA was neutralized by amines to the extent of 25, 50 and 75 % (8-10 hours, room temperature). Piperidine, pyridine and triethanolamine were used as amines. Then, copolymerization of AA with acrylate salt was conducted in aqueous media at 60 °C with following chloroxypropylation of free carboxylic groups. The initiating agent of copolymerization was APS (2.5 % of the total mass of comonomers). Time of the reaction was 10-12 hours. The reaction scheme may be represented by the following form:



where X is amine fragment.

Final degrees of conversions of ECH are given in Table 2.

Table 2. Final conversions of ECH

Amine	Final conversions ECH %		
	25 % neutralization	50 % neutralization	75 % neutralization
Piperidine	46.4	88.8	0.0
Pyridine	0.0	0.0	0.0
Triethanolamine	8.90	0.0	100

As may be seen from the table, addition of ECH to the carboxyl group of polymatrix has an extreme character depending on the degree of neutralization of monomeric acid by piperidine. The largest conversion of ECH (88.8 %) was observed at 50 % neutralization. At 25 % neutralization the conversion of ECH was equal to 46.4 %. At 75 % neutralization by piperidine ECH does not add to carboxyl group. The maximum conversion of ECH took place at 75 % neutralization of the acid by triethanolamine. When pyridine was used as a neutralizing agent, addition of ECH to carboxyl group did not occur. It was apparently related to the formation of very unstable complexes of pyridine with AA units. A copolymer containing ethylenediamine fragment was also obtained. Neutralization of AA by ethylenediamine was carried out at 25 % degree at room temperature for 8 hours. The copolymer of AA with acrylate salt was synthesized in water at 60 °C. Concentration of AA was 0.11 mol/l and of acrylate salt 0.05 mol/l. APS (25 % of the total mass of comonomers) served as initiator. Subsequent chloroxypropylation of the copolymer (molar ratio AA:ECH = 1:0.5) was unsuccessful. It may be related to formation of complexes of polymatrix free carboxyl groups with amino groups of ethylenediamine which hinders diffusion of ECH molecules to carboxyl groups.

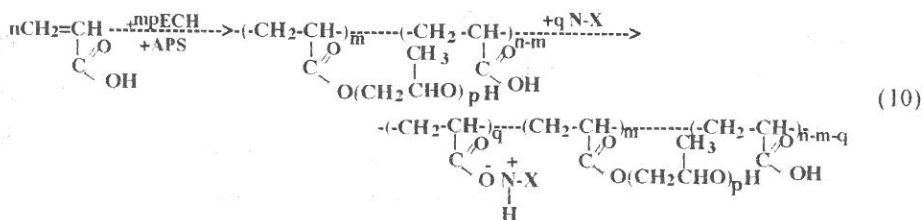
H-NMR-spectra of chloroxypropylated polyacrylic acid (COPPAA) neutralized by piperidine at the degrees of conversions of 25 and 50 % and by triethanolamine of 75 %

have been recorded. Resonance signals of protons from CH₂- and CH- groups of ECH residue and protons of N-CH₂, NH and OH-groups from the fragment of the corresponding salt are observed in the spectra. Chemical shift of protons are shown in Table 3. COPPAA partially neutralized by amines may also be obtained by another way. Consequence of steps was changed for this purpose. Firstly, using equimolar ratio of AA and ECH (0.29 mol/l) in aqueous media at 60 °C, the corresponding copolymer, COPPAA was obtained. The process was initiated by APS (2 % of the mass of AA). The conversion of ECH was 30-40 %. Then, the "ready" copolymer was neutralized by triethanolamine or piperidine at room temperature. Neutralization by amines has been carried out at 25, 50 and 75 % mol of COPPAA.

Table 3. Chemical shifts of protons in neutralized COPPAA

Chemical shifts of protons, ppm			
Protons	COPPAA neutralized by piperidine by 50 %	COPPAA neutralized by piperidine by 25 %	COPPAA neutralized by triethanolamine by 75 %
CH ₂	1.75-3.0	1.75-3.0	1.75-3.0
CH	3.5-3.8	3.65-3.9	4.0-4.2
N-CH ₂	4.0-4.2	4.0-4.2	4.5-4.75
NH	4.45-4.7	4.45-4.7	5.9-6.0
OH	-	-	5.3-5.5

The scheme of the synthesis is given below:



where X is amine fragment.

Final degrees of conversions of amines are given in Table 4.

Table 4. Final conversions of amines

Amine	Final conversion of amines		
	25 % neutralization	50 % neutralization	75 % neutralization
Piperidine	25.9	25.2	100
Triethanolamine	47.1	100	92

It is seen that with an increase of the amount of amine, its conversion, in general, rises. Such dependency may be explained by coordination of amines both with carboxyl and chloroxypropyl fragments. Neutralization of COPPAA by ethylenediamine and monoethanolamine at 50 % degree was carried out. Very high levels of conversions of amines (respectively, 100 and 93.6 %) were reached.

REFERENCES

- [1] K.V. Aliyev, Asadov V.A. "On the mechanism of zwitterionic polymerization of 4-vinylpyridine quaternary salts in organic media", III. UPAC Macro Mainz 26-th Int. Symp. Macromol. Mainz, Prepr. Short Commun. Vol. I. Mainz, s.a., pp. 242-245, 1978.
- [2] Z.H. Asadov, "Polymerization of quaternary salts of 4-vinylpyridine in organic media. II New aspects of petrochemical synthesis", Moscow, *Institute of Petrochemical Synthesis*, pp. 64-71 (in Russian), 1978.
- [3] Z.H. Asadov, "Polymerization of quaternary salts of 4-vinylpyridine in organic media.", II Materials of scientific Conference of Chemical Faculty of Moscow State University. Moscow, pp. 242-246 (in Russian), 1977.
- [4] Z.H. Asadov, "Mechanism of zwitterionic polymerization of N-alkyl-4-vinylpyridinium in solution and under conditions modelling spontaneous polymerization in media of low polarity", II. Mechanism of polymerization processes and new fields of use of polymers. Moscow, Institute of Petrochemical Synthesis, pp. 51-63 (in Russian), 1980.
- [5] Z.H. Asadov, A.D. Aga-zade, A.A. Kasimov, V.S. Aliyev, "Regularities and mechanism of oxypropylation reaction of polyacrylic acid partially neutralized by sodium hydroxide", II. *Vysokomolekulyarniy soyedineniya (High-molecular compounds)*, Vol. 32, B. N:10, pp. 792-797 (in Russian), 1990.
- [6] Z.H. Asadov, "Dissertation for the grade" Doctor of Chemical Science, Baku, Institute of Chemical Additives of Azerbaijan Academy of Sciences, 1992.

[7] Z.H. Asadov, A.D.Aga-zade, Akhmedova G.A., Nasibova Sh. M., Kasimov A.A., Aliyev V.S., "Synthesis, Kinetic regularities and mechanism of process for obtaining of water-soluble polymeric surface-active substances based on acrylic acid and propylene oxide". II Abstracts of the materials of the 1-ST Azerbaijan-Turkey Polymer Symposium. Baku. P. 365-366, July 8-11, 1991.