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## **SYNTHESIS AND STUDY OF POLYELECTROLYTES ON THE BASIS OF GLYCIDYL ESTER OF METHACRYLIC ACID**

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The synthesis of reticulated polyelectrolytes possessing ion-exchange properties, remains a topical task in chemistry. The constant widening of the application fields of such polymers in experimental studies and industry stipulates a more and more increasing interest to the problem of their preparation.

It is known [1-4], that ion-exchangers on the basis of epoxy-containing homo- and copolymers possess sufficiently high physico-chemical and sorption characteristics.

In this connection, glycidyl ester of methacrylic acid (GEMA), containing an easily polymerized double bond and reactive oxirane group in the structure is one of the promising epoxidized monomers.

The present work aims at synthesis and study of physico-chemical properties of polyfunctional anion-exchangers on the basis of GEMA copolymers and chloranhydride of methacrylic acid (1), GEMA and methylmethacrylate (2) with polyamines of different nature.

In the process of polycondensation of copolymers with polyamines of aliphatic (polyethyleneimine [3], polyethylenepolyamine [4]) and aromatic (poly-2-methyl-5-vinylpyridine [5]) rows optimum conditions and regularities of anionites formation have been established.

Concentrations of reacting substances, temperature and reaction duration have been varied upon the choice of the factors, effecting the properties of the final products.

The data on the influence of the ratio copolymer/aminizing agent (mass parts) show that static exchange capacities (SEC) and the content of nitrogen in the composition of crosslinked polyelectrolytes increase proportionally with an increase in the content of polyamine in the initial mixture (Table 1).

**Table 1.** The influence of aminizing agent upon exchange capacity and the content of nitrogen in ionites  
(t = 15 hours).

Polyelectrolytes based on	copolymer : amine, mass parts	SEC by 0,1N HCl solution, mg-equ/g	N, %	T, K
1/3	1,0 : 0,75	8,10	11,34	373
	1,0 : 5,00	9,80	13,72	
	1,0 : 7,50	10,25	14,35	
	1,0 : 10,0	10,80	15,12	
1/4	1,0 : 0,3	7,34	10,27	373
	1,0 : 0,6	9,00	12,60	
	1,0 : 0,9	9,45	13,23	
	1,0 : 1,2	9,93	13,90	
1/5	1,0 : 1,0	6,05	8,47	373
	1,0 : 3,0	6,89	9,63	
	1,0 : 7,5	8,10	11,34	
	1,0 : 10,0	8,55	11,97	
2/3	1,0 : 0,5	7,39	11,03	353
	1,0 : 3,0	8,48	12,23	
	1,0 : 5,5	10,09	15,34	
	1,0 : 8,0	11,24	17,46	
2/4	1,0 : 0,6	4,79	7,11	353
	1,0 : 1,5	5,69	8,64	
	1,0 : 3,0	7,14	11,35	
	1,0 : 7,5	8,14	13,27	
2/5	1,0 : 1,0	1,82	2,82	353

	1,0 : 3,0	3,89	6,18	
	1,0 : 5,0	4,37	7,38	
	1,0 : 7,5	4,45	7,86	

An increase in the amount of aminizing agent higher than the indicated limits leads to the formation of soluble and weakly crosslinked anionites of large swelling and low mechanical strength.

An increase of the polycondensation temperature from 333 K up to 393 K, upon the equal duration of the process ( $t = 15$  hours) results in some change of ionite exchange capacity (Table 2).

Table 2. Dependence of SEC of anionites on the reaction temperature ( $t = 15$  hours).

T, K	SEC of anionites by 0,1N HCl solution, mg-equ/g					
	1/3	1/4	1/5	2/3	2/4	2/5
333	9,45	9,38	8,33	5,94	6,74	4,00
353	10,15	9,80	8,46	10,09	7,14	4,37
373	10,80	9,93	8,55	9,50	7,32	4,60
393	10,67	10,05	8,10	9,30	6,14	4,73

As it is seen from the table, with an increase in the temperature there is observed first an increase, and then a decrease in SEC anionites. An increase in the temperature seems to entail a partial desamination of reticulated polyelectrolytes, stipulated by different nature of aminogroups, included in the content of anionites.

Furthermore, the dependence of the change of final products properties on the duration of polycondensation has been studied (Table 3).

Table 3. The effect of the reaction duration upon SEC and nitrogen content in polyelectrolytes.

Polyelectrolytes based on	t, hour	SEC by 0,1N HCl solution, mg-equ/g	N, %	T, K
2/3	4	7,29	11,32	373
	8	7,84	12,14	
	15	8,71	14,12	
	22	6,17	9,86	

2/4	5	6,25	9,95	393
	10	6,14	9,10	
	15	8,00	13,23	
	24	6,90	11,50	
2/5	5	3,90	6,40	353
	10	4,13	5,90	
	15	4,00	6,80	
	24	6,39	11,00	

Incidentally it has been established, that the process of aminizing finishes in 15 hours for polyelectrolyte on the basis of 2/3, 2/4 and a further increase in the time of hardening does not lead to significant change of the properties of polyelectrolytes. In case of anionite 2/5 maximum capacity is observed in case of 24 hours of hardening. It is connected with the fact that upon the further increase in the reaction duration there occurs an increase in the density of cross links in polymers and due to this accessibility of active centers for ion-exchange decreases.

Polyelectrolytes 1/3 and 1/5 possess high SEC value (10,80 and 8,55 mg-equ/g) with the reaction duration of 15 hours, and 10 hours for 1/4 (9,98 mg-equ/g). The further increase in the polycondensation time results in destructive processes, which lead to an increase in SEC and nitrogen content in ionites.

An important characteristic of quality of ion-exchangers is their chemical stability in relation to solutions of acids (5N H<sub>2</sub>SO<sub>4</sub>), bases (5N NaOH) and oxidizers (10 % H<sub>2</sub>O<sub>2</sub>, 1N HNO<sub>3</sub>). The measure of chemical stability is a degree of capacity loss upon their treatment by the given solutions. The studies have shown, that the synthesized ion-exchangers possess high chemical stability (70-98 %), and for ionite 2/3 after treatment by 5N solution of caustic soda some increase in exchange capacity. This can be explained by washing of low molecular and soluble intermediates of polycondensation out of polymer net and an increase in accessibility of active groups in the phase of ionite.

With the purpose of comparative investigation of thermal properties of ionites thermogravimetric studies have been carried out in the air. The curves of mass losses of all the studied samples possess a stepwise character. It seems to be explained by different thermal stability of ionogenic groups and ionite matrixes.

The structures of initial substances and final products have been investigated by IR-, NMR <sup>13</sup>C, <sup>1</sup>H-spectroscopy methods. The analysis data of IR-spectra testify to the fact that deformation oscillations, characteristic for epoxy group (910, 1250 cm<sup>-1</sup>) are present in GEMA monomer and in copolymers (1 and 2), synthesized on its basis, but are absent in the products of their interaction with polyamines, which proceeds due to epoxy group of non-ionic polymer and aminogroups of aliphatic and aromatic polyamines with the formation of polyfunctional polyelectrolytes of spatial structure. Thus, absorption bands of deformation oscillations of aminogroups appear in IR-spectra in the fields of 1580-1600, 1620

cm<sup>-1</sup>, C-N (1020-1220 cm<sup>-1</sup>) and C-OH (1720 cm<sup>-1</sup>), the appearance of which testifies to the opening of an epoxy ring.

In IR-spectra of anionites with poly-2-methyl-5-vinylpyridine there appear peaks of deformation oscillations of pyridine bases in the fields of 1030, 1490 cm<sup>-1</sup>, and in 1/5 a chlorine-substituted residue is partially preserved in the fields of 750, 1360 cm<sup>-1</sup>.

The curves of potentiometric titration testify to an average-basic character of polyfunctional anionites on the basis of copolymers 1 and 2.

Thus, polyelectrolytes of spatial structure, possessing anion-exchange properties have been obtained by chemical modification of epoxy groups of GEMA copolymers - methacrylic acid chloranhydride and GEMA - methylmethacrylate with polyethylenepolyamine, polyethyleneimine and poly-2-methyl-5-vinylpyridine.

## References

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