Synthesis of Copolymers Based on Vinyl morpholine, Acrylic Acid, and Colloidal Silica and Their Properties

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ABSTRACT

This article presents the synthesis and properties of copolymers based on vinylmorpholine, acrylic acid and colloidal silica as well as the dependence of the number of monomers on the molecular weight in the copolymerization reaction of vinylmorpholine and acrylic acid

Keywords: vinylmorpholine, copolymer, component, monomer, heteroatom, vinylmorpholine, colloidal siliconisol

Nowadays silica-based materials obtained as a result of sol-gel process with the presence of colloidal silica and organic compounds constitute a wide group of organic-inorganic composites. Using such an approach makes it possible to include a virtually unlimited number of functional compounds, including thermodynamically incompatible ones, into the composition of the synthesized composites. This applies, above all, to three-dimensional structures, which are polymer networks consisting of components that are not chemically bound, but not separated by mechanical migration of the chains. The importance of organosilicon compositions in such systems is that they regulate the formation of the structure in the composition, allow us to control the size of nanoparticles and physical and chemical properties of the material. In this case, the component of the composition - silicon dioxide - contains no functional groups. Functional organic low molecular weight or high molecular weight compounds act as carriers of chemically active fragments.

A number of world scientists on the synthesis of nitrogen-containing vinyl derivatives based on acetylene: B.A.Trofimov, O.N.Temkin, R.M.Flid, L.B.Fisher, I.L.Kotlyarevskiy, A.A.Petrov, B.Gusev, A.V.Shelkunov, Paru Ram Pao, L.Panivnika, Yoko Yamamoto, Biao Jiang the studies of others have a special place[1-5].

In Uzbekistan in this direction A.G.Maxsumov, K.M.Axmerov, T.S.Sirliboev, D.Yusupov, A.Ikromov, B.F.Muxiddinov, S.E.Nurmonov, R.Nazirova, F.A.Magrupov, A.Raxmonberdiev, A.T.Jalilov and others have synthesized various acetylene compounds and ionic compounds, and research in vinylation of active hydrogen organic compounds has been and continues to be conducted[6-8].

Synthesis of vinyl derivatives of heterocyclic compounds, development of process technology at atmospheric pressure,

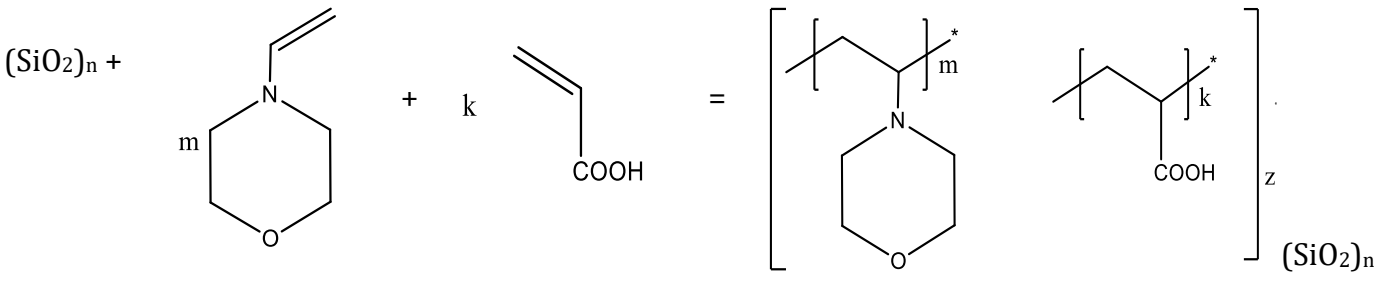
search for alternative reaction conditions, implementation of mathematical modeling of vinylation process, synthesis and technology of copolymers is one of the actual directions. issues of modern organic chemistry and chemical technology of organic compounds. This dissertation work is aimed at solving such problems as the synthesis of ionic products based on the vinylidation process with extensive use of local raw materials, as well as the study of these processes[9-11].

High molecular weight products based on derivatives of nitrogen-containing heterocyclic compounds can be shown to be promising components for the preparation of hybrid organic-inorganic compositions in your country. Having effective physical and chemical properties (possibility of chemical modification, harmlessness, solubility in water) such compounds can serve as an organic matrix for sorbents, proton-transfer membranes, emulsifiers, drugs, etc. When analyzing scientific works of researchers there was practically no information concerning obtaining, properties and application of hybrid polymer systems based on sol-gel synthesis products with participation of vinyl derivatives of nitrogen-containing heterocyclic compounds. On this basis, the research in this direction is of both theoretical and practical importance.

When synthesizing copolymers based on vinyl morpholine, acrylic acid and colloidal silica vinylization of morpholine was first carried out in high-base systems. In a four-neck flask equipped with a reflux condenser, stirrer and nozzle for the introduction of acetylene, 1.68 g KOH (10% weight of morpholine) and 50 ml DMSO were added and the mixture was heated to 97-100°C with constant stirring, then 16.98 ml (0.2 mol) of morpholine was added to the cooled to 35^0C and acetylene was passed through the mixture at 90^0C. After 3 hours the process was stopped and the reaction mixture was cooled, extracted with ether, dried with sodium sulfate, after which the solvent was removed and the residue was evacuated under vacuum in the presence of hydroquinone inhibitor. The fraction with boiling point corresponding to vinylmorpholine 92-94 ºC was collected. When moving in vacuum (10-13 mm Hg) T boiling= 40,5-41 ºC. The product yield is 27% (of the theory) $d_4^{20} = 1{,}0011\,г/см^3$, $n_D^{20} = 1{,}4559$

Hybrid composites based on colloidal silica sol and vinylmorpholine were prepared from synthesized vinylmorpholine at room temperature using the following procedure: 0.3 g of vinylmorpholine was dissolved in 5 ml of absolute ethyl alcohol, and 1 ml of colloidal silica sol and 0.4 ml of 0.5 M NaOH solution was added to the resulting solution. The duration of the reaction was from 1 to 24 hours. As a result, turbidity of the mixture and formation of a precipitate are observed. The resulting precipitate is washed several times with water and dried in a vacuum desiccator until constant weight is reached.

The copolymerization of the colloidal silica system of vinylmorpholine in the presence of acrylic acid was carried out in the presence of azobisic acid dinitrile (DAK) in dimethylformamide (DMF) solution at 60 °C for 6 hours. White powdery products soluble in alcohol, DFA, DMSO, tetrahydrofuran (THF) were obtained. The radical copolymerization proceeds along the vinyl group. The reaction of vinylmorpholine in the presence of acrylic acid in a colloidal silica matrix proceeds according to the following scheme.



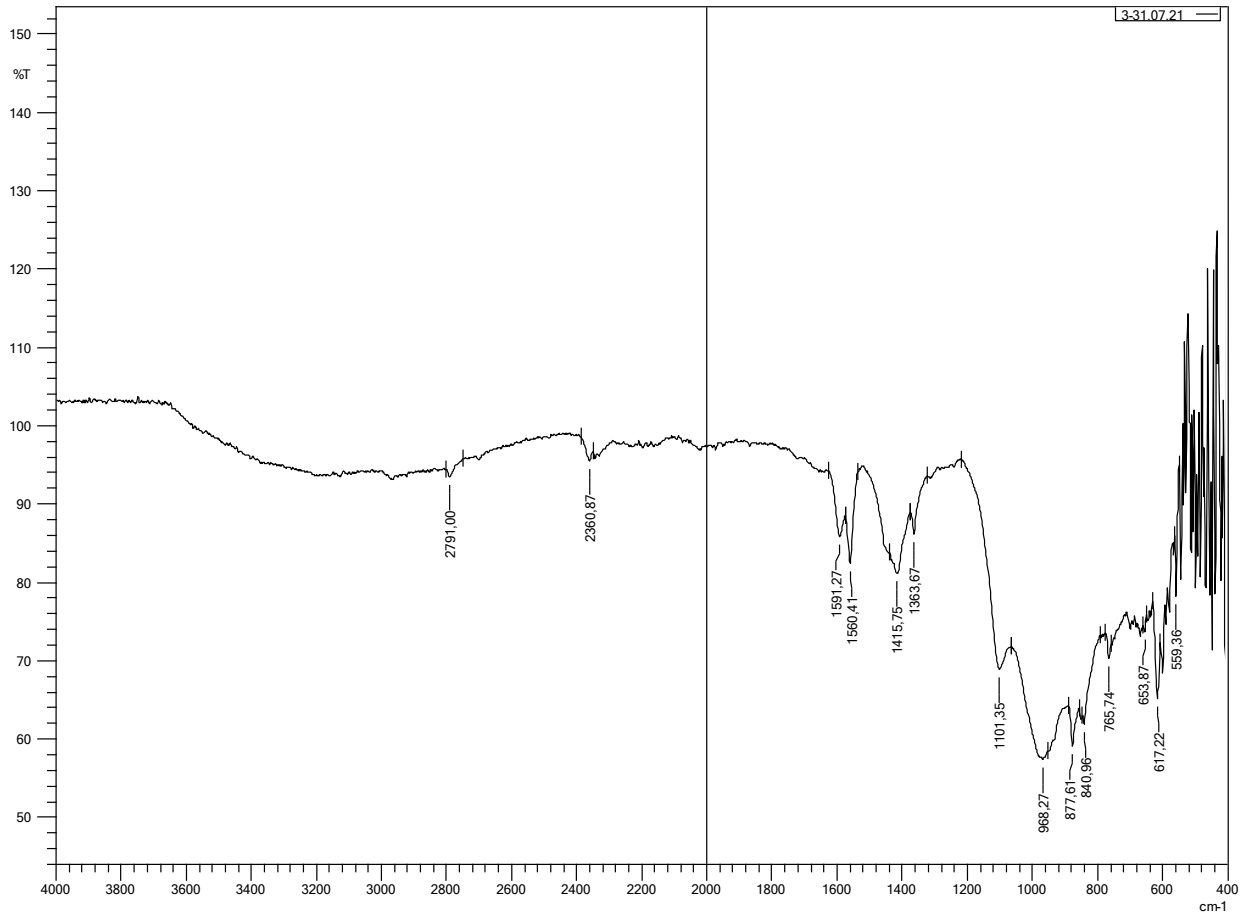


Figure 1: IR spectrum of the synthesized VM-AK-KK composite.

In IR spectra of copolymers after polymerization there are no absorption lines related to vinyl group (960, 1680 sm^{-1}) and vibrational lines of rings of morpholine molecule (1600, 1580, 1490, 1020 sm^{-1}) remain. The C=O vibration lines (1720-1750 sm^{-1}) are also observed, indicating the presence of VM and BA fragments in the copolymer.

The effect of the amount of initial reacting components on the yield, viscosity and molecular weight of the resulting product was investigated. The number of reacting components varied in the range from 1:9 to 9:1. As indicated above, DAK was used as the initiator, the reaction was carried out at 60 ^{0}C.

Molecular weights of copolymers were determined by cryoscopic method, their sizes varied from 110 000 to 300 000 (Table 1).

Table 1
Nitrogen-containing heterocyclic compounds (M_1)
Copolymerization with vinyl monomers retaining carbonyl (M_2).
(DMFA, DAC - 1.5% by weight, 60°C, 6 hours)

Molar ratio of the reagents		Yield %	Molecular mass of the copolymer (M)
M_1	M_2		
Vinylmorpholine-acrylic acid			
0.10	0.90	44	110 000
0.20	0.80	47	130 000
0.30	0.70	52	145 000
0.40	0.60	53	155 000

0.50	0.50	58	165 000
0.60	0.40	59	177 000
0.70	0.30	61	200 000
0.80	0.20	65	266 000
0.90	0.10	70	300 000

An increase in the proportion of vinyl monomer holding the carbonyl in the initial mixture causes an increase in the molecular weight of the copolymers. This, in turn, is due to the high tendency of the vinyl group to polymerize.

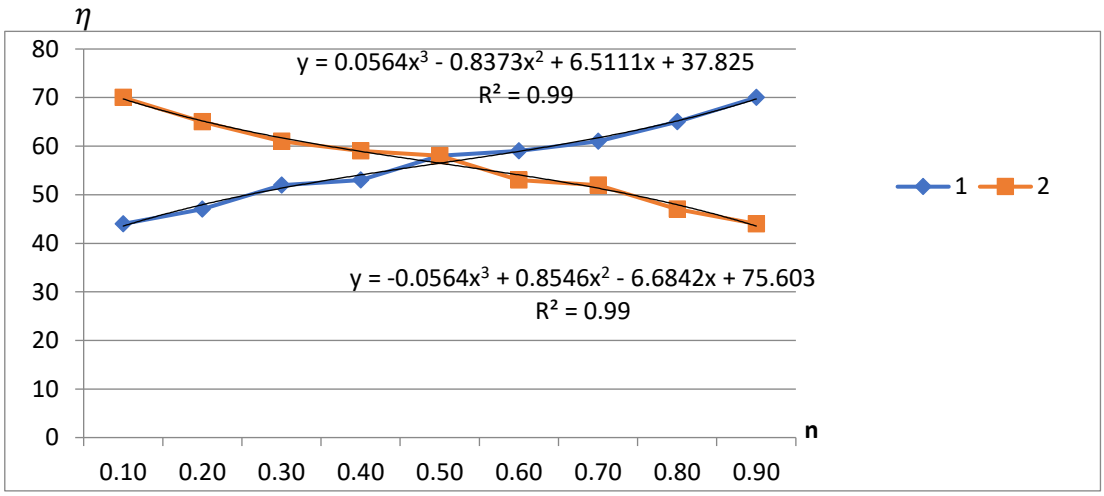
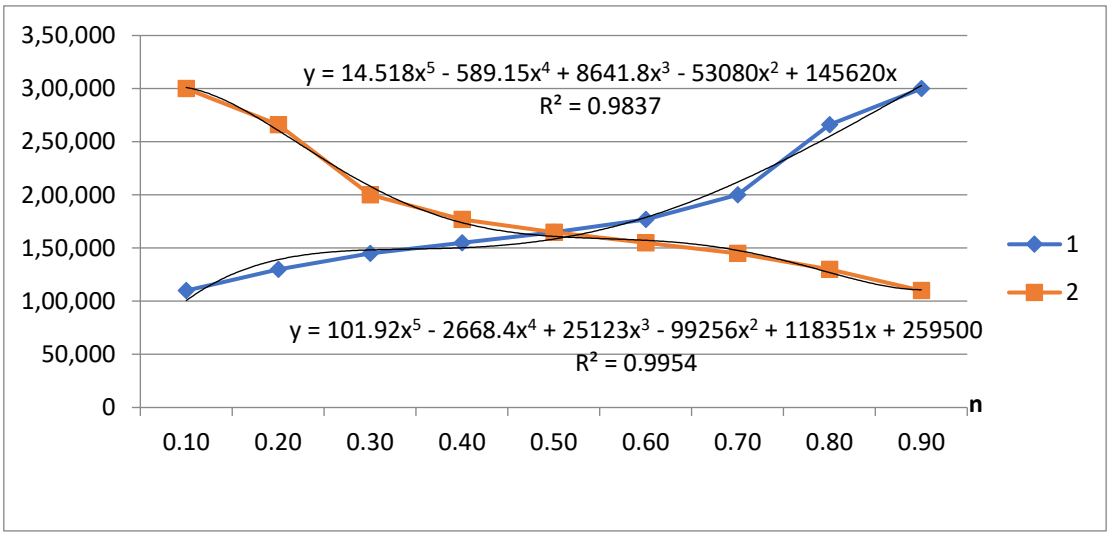


Figure 1: Dependence of the amount of monomers in the reaction of copolymerization of acrylic acid with morpholine
1- Dependence of the amount of vinyl morpholine on the product.
2- dependence of the amount of acrylic acid on the product
reaction product: number of n-moles

As can be seen from Figure 1, when analyzing the dependence of the number of reacting monomers on the performance based on the mathematical program, the value of R in the regression equation obtained from the mathematical processing of the obtained results is close to one. Not only shows that the obtained results coincide with the mathematical processing, but also the completeness of the results confirms its deafness. Also, the inverse proportionality of the regression equation and the lines obtained for each of the monomers confirms the correctness of the results. It is shown that the change in the amount of both monomers is carried out by the same equation. The theoretical calculations complement the practical experiments.
In Figure 2, the results of the dependence of monomer quantity on molecular weight coincide with the results of mathematical treatment and the same regression equation confirms the correctness of the results. Also each mathematical treatment for one monomer confirms the results with inverse proportionality. For the regression equation, $R^2 = 0.9954$ and $R^2 = 0.9835$ indicate agreement between the mathematical report and the experimental results.

Mr

Figure 2. Dependence of monomer quantity on molecular weight in the copolymerization reaction of vinylmorpholine and acrylic acid
1 Dependence of the amount of vinylmorpholine on the molecular weight. 2- Dependence of the amount of acrylic acid on the molecular weight.
Mr-molecular weight: number of n-moles



The presence of nitrogen heteroatoms in copolymers indicates their ability to complex. The block of long chains of nitrogen-containing monomers allows efficient ion transport, and the carbonyl-containing fragments are necessary for obtaining highly elastic membranes on their basis. All this provides a basis for the synthesis of hybrid composites based on the obtained copolymers. The absorption property of some intermediate elements was studied on the basis of the complexation property. Based on the results obtained, it was found that the intermediate metals can be effectively used for separation, purification and collection.

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