

# SYNTHESIS OF STYRENE COPOLYMERS WITH 3,5-DIMETHYL-4-VINYLPYRAZOLE AND STUDY OF THEIR FUNCTIONAL PROPERTIES

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Received: 06 november 2024

Accepted: 11 december 2024

Published: 24 december 2024

The article presents the results of studies on the synthesis of styrene copolymers with 3,5-dimethyl-4-vinylpyrazole in the presence of the initiator di-tert-butyl peroxide (DTBP) (0.2-0.5%). The copolymerization process was carried out in the block, at temperatures of 120-140°C and a time of 10 to 20 hours. The monomer ratio is 2:1 (mol). It was found that the maximum yield of copolymers (90%) is achieved at a temperature of 140°C for 10 hours. Properties of copolymers: softening temperature (in a capillary) 136-144 °C;  $\eta_{sp}/c$  0.5% benzene solutions 0.47-0.49.

**Keywords:** styrene, vinylpyrazole, nitrogen-containing heterocyclic compounds, copolymerization.

## INTRODUCTION

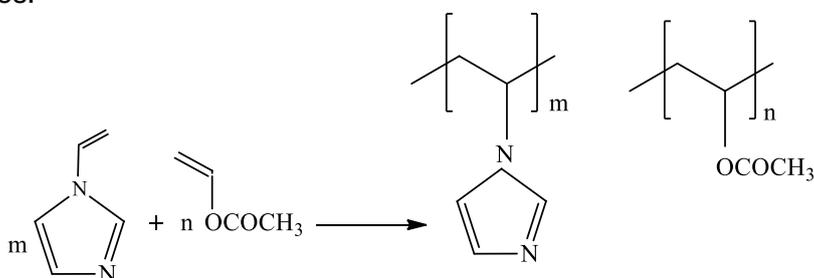
Nitrogen-containing heterocyclic compounds occupy one of the important places in modern technologies related to the production of metal corrosion inhibitors, pharmaceuticals, additives for oils and fuels, heat-resistant polymeric materials and other valuable products [1-4].

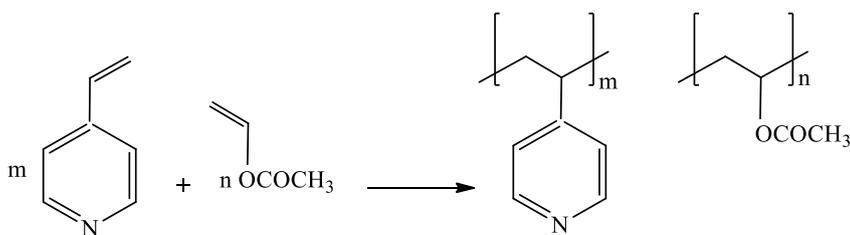
A promising direction in the chemistry of high-molecular compounds is the production of copolymers with nitrogen-containing heterocyclic fragments that have biological activity and can be used as biosensors, anticoagulants and antiseptics [5].

In recent years, new polymeric materials with specified properties have been developed by combining the products of tetraethoxysilane hydrolysis with poly-N-vinylazoles and polyvinylpyridine [5], as well as based on various copolymers of N-vinylpyrazole [7,8].

Using 1-vinylimidazole and 4-vinylpyridine as comonomers in the process of radical copolymerization with vinyl acetate, high-molecular compounds with molecular weights from 108 thousand to 300 thousand were obtained [9].

It was determined that copolymerization occurs on the vinyl group according to the schemes:





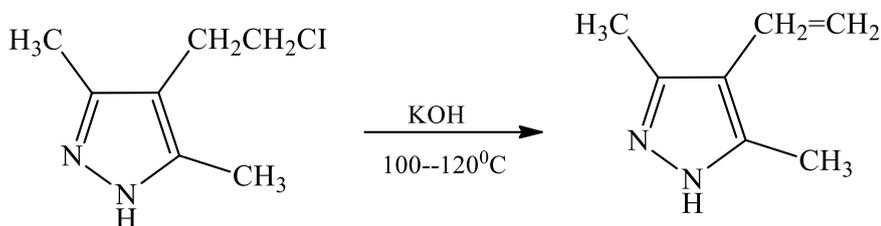
The synthesized copolymers were used in the compositions of composite sorption materials intended for the extraction of Pt (IV) from chloride solutions [10]. It was found that by using various nitrogen-containing copolymers in a composition with organosilicon compounds, it is possible to create hybrid chelate sorbents that are highly effective in the processes of concentrating noble metals from complex systems [11, 12].

As can be seen from the above material, conducting targeted studies on the study of copolymerization reactions of vinyl-substituted pyridines, pyrazoles and other nitrogen-containing compounds with other monomers allows us to create materials with useful properties [13, 14].

This article presents the results of studies on the process of double free-radical copolymerization of styrene with 3,5-dimethyl-4-vinylpyrazole in the presence of the initiator di-tert-butyl peroxide (DTBP). The influence of various factors was studied: temperature, amount of initiator (DTBP), monomer ratio and reaction time on the yields of double copolymers and their physicochemical properties.

## EXPERIMENTAL

Styrene (industrial monomer) and 3,5-dimethyl-4-vinylpyrazole were used as feedstock for the synthesis of double copolymers. The latter was obtained with a yield of 65% by dehydrochlorination of 3,5-dimethyl-4-(2-chloroethyl)pyrazole in the presence of KOH in a diethylene glycol (DEG) medium according to the scheme:



### Obtaining 3,5-dimethyl-4-vinylpyrazole.

6.72 g (0.12 mol) of KOH and 40 ml of diethylene glycol were loaded into a three-necked reaction flask equipped with a stirrer, thermometer and reflux condenser. The mixture was heated until the alkali was completely dissolved (at 100-1200). Then the temperature was gradually reduced to 50-600C and 7.92 g (0.05 mol) of 3,5-dimethyl-4-(2-chloroethyl) pyrazole were added to the mass in parts. The temperature was raised to 80-900C and the reaction was completed within 30-40 min. at this temperature. The mass was treated with water, the organic portion was extracted with sulfuric ether, washed with water, dried and subjected to vacuum distillation. The fraction 72-730C/1 mm Hg was collected,  $n_{D20}$ -1.5147;  $d_{420}$ -0.9542 g/cm<sup>3</sup>. Yield 3.67 g (~60%).

Copolymerization of styrene with 3,5-dimethyl-4-vinylpyrazole was carried out in a block with steel ampoules in the presence of the initiator di-tert-butyl peroxide (DTBP).

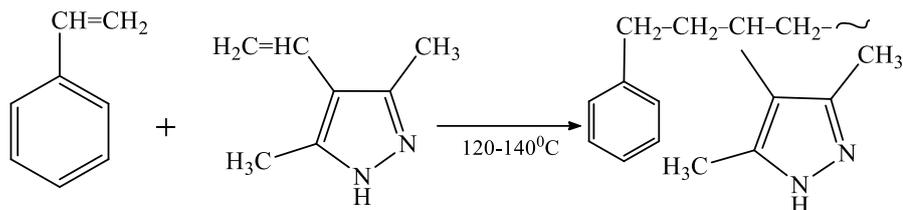
Calculated amounts of monomers and DTBP were loaded into prepared ampoules. The ampoules were cooled, pumped out and sealed in a nitrogen flow. Then, they were transferred to an oil bath with a given temperature, where they were kept for a certain time. Upon completion of the copolymerization process, the target copolymers were obtained by

precipitation of their benzene solutions in cooled heptane. The yields of copolymers, softening temperatures (in a capillary) and  $\eta_{sp}/c$  of 0.5% solutions in benzene at 25°C were determined. The structure of the copolymers was confirmed by IR spectroscopy data.

## DISCUSSION OF RESULTS

Block copolymerization of styrene with 3,5-dimethyl-4-vinylpyrazole was carried out at their ratio of 2:1 mol, temperature of 120 and 140°C, amount of DTBP initiator of 0.2-0.5% (calculated for the mixture of monomers) and duration from 5 to 20 hours.

The process proceeds according to the scheme:



The table 1 shows the results of studies on the effect of temperature and duration of the copolymerization process on the yields of target double copolymers and their properties.

**Table 1.** The effect of temperature and duration of the process on the yields of copolymers and their properties.

Temperature, °C	Time, hour	Copolymer yields, %	Properties of copolymers	
			Softening temperature, °C	in a 0.5% solution in benzene at 25°C
120	2	34,0	140-154	0,43
-----	3	47,2	140-158	0,46
-----	5	58,0	152-162	0,50
-----	7	67,4	153-164	0,52
-----	10	83,0	155-165	0,55
-----	20	88,4	160-167	0,57
140	2	65,0	130-132	0,35
-----	3	72,6	131-134	0,38
140	5	76,0	133-136	0,45
	7	80,5	135-140	0,47
	10	90,0	136-144	0,49
	20	92,8	146-153	0,52

Conditions: ratios of styrene:3,5-dimethyl-4-vinylpyrazole - 2:1 (mol), amount of initiator - DTBP-0.2% (on the mixture of monomers)

As can be seen from the table, temperature has a significant effect on the yield of the target double copolymers of styrene with 3,5-dimethyl-4-vinylpyrazole. The optimal process conditions, at which their high yield is achieved (90%), can be considered to be a temperature of 140°C, the amount of DTBP initiator is 2% and the process duration is 10 hours. A further increase in time to 20 hours is undesirable, since in this case the yield of copolymers increases by only 2.8%. As can be seen from the table, temperature has a significant effect on the yield of the target double copolymers of styrene with 3,5-dimethyl-4-vinylpyrazole. The optimal process conditions, at which their high yield is achieved (90%), can be considered to be a

temperature of 1400C, the amount of DTBP initiator is 2% and the process duration is 10 hours. A further increase in time to 20 hours is undesirable, since in this case the yield of copolymers increases by only 2.8%.

When copolymerization is carried out at 1200C, the yield is 83.0% for 10 hours, and 88.4% for 20 hours. Comparison of the properties of the obtained copolymers shows that at 1200C more high-molecular compounds are formed than at 1400C (ήприв 0.5% solutions of copolymers in benzene at 250C in the first case is on average 0.50-0.52, while in the second no more than 0.45-0.47).

It should be noted that the copolymers synthesized by us contain pyrazole units in their structures. They can find application in the compositions of polymer composite materials, sorbents for the extraction of heavy metals and radionuclides from water systems. In addition, they can be modified with nanoparticles of metals, their sulfides, oxides and other substances.

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