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## SCRUNITY OF POLYMERIZATION AND CO-POLYMERIZATION OF SOME BROMINE-CONTAINING MONOMERS VINYL SERIES

**Abstract:** The article extends the results of kinetic studies of some halogen-containing vinyl monomers. Analyzing the behavior of bromine-containing monomers in binary systems with amino compounds revealed the occurrence of spontaneous polymerization of some monomers with an active bromine atom when they interact with tertiary amines. This is clarified by the activity of the bromine atom, which manifests itself in the dependence of the structure of the bromine-containing component. The goal of the work was to study the influence of functional groups on the reactivity of a double bond in halogen-containing vinyl monomers. When researching the kinetics of the copolymerization of bromine-containing monomers with acrylonitrile, into the bargain, studying the mutual influence of the bromine atom and double bond in the monomers under study, it was shown that the presence of a reactive bromine atom greatly influences the copolymerization process and the properties of the resulting copolymers, which makes it possible to more purposefully, moreover to implement the synthesis of a number of macromolecular compounds, as well as their further chemical transformation.

**Key words:** polymerization, copolymerization, bromine-containing monomer, spontaneous polymerization, reaction kinetics, polymerization rate.

**Language:** English

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### Introduction

Halogen-containing polymers and copolymers are widely used as flame-retardant polymers, flame retardants, reactive polymers in various sectors of the economy.

The presence of a halogen atom in the structure of polymers and copolymers makes it possible to accomplish various polymer-analogous transformations with the aim of introducing functional groups into the macromolecule and imparting specific properties to the synthesized products [3,7].

### Discussion

It was launched that reactive halogen-containing monomers interact with amino compounds and in this case the initiation process occurs, as a result of which polymers are formed by polyelectrolyte properties. For a systematic study of the polymerization process, a homologous series of the following monomers was compiled: vinyl bromide, allyl bromide, bromostyrene, vinyl bromoacetate and vinylbenzyl bromide. The main indicators of the selected monomers are presented in table 1. To reap the kinetic indicators of the polymerization and copolymerization reactions, dilatometric and spectroscopic methods were used.

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For the time of study, it was found that not all bromine-containing monomers interact with amino compounds and spontaneous polymerization does not occur.

Based on preliminary studies, it was originated that vinyl bromide and bromostyrene do not

react with amino compounds. Along with allyl bromide reacts with tertiary amines and a quaternary monomeric salt is formed, which does not enter the polymerization reaction due to degradation chain transfer.

**Table 1 - Structural formula and main indicators of monomers**

No	Monomers	mol.mas	T bale, ° C	Refractive index	The results of the interaction with tertiary amines
1	Vinyl bromide $\begin{array}{c} \text{CH}_2=\text{CH} \\   \\ \text{Br} \end{array}$	107	14-15	1,5286	The reaction does not proceed
2	Allyl bromide $\begin{array}{c} \text{CH}_2=\text{CH} \\   \\ \text{CH}_2\text{Br} \end{array}$	121	71-72	1,3980	Quaternary salt forms
3	Bromostyrene $\begin{array}{c} \text{CH}_2=\text{CH} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{Br} \end{array}$	183	68-69 at 1.33 kPa	1,5415	The reaction does not proceed
4	Vinyl bromoacetate $\begin{array}{c} \text{CH}_2=\text{CH} \\   \\ \text{O} \\   \\ \text{O}=\text{C}-\text{CH}_2\text{Br} \end{array}$	165	32-33 at 1,33k Pa	1,4526	Spontaneous polymerization occurs
5	Vinyl benzyl bromide $\begin{array}{c} \text{CH}_2=\text{CH} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{CH}_2\text{Br} \end{array}$	197	82-84 at 1,33 k Pa	1,5932	Spontaneous polymerization occurs

The results of experimental studies showed that the interaction of vinylbenzyl bromide (WBB) and vinyl bromoacetate (WBA) with tertiary and polyamines in organic solvents such as ethyl alcohol, dioxane, benzene undergoes spontaneous polymerization at relatively low temperatures. Studying the interaction of allyl bromide with amino

compounds showed that the process is limited by the Menshutkin reaction — the formation of a quaternary ammonium monomer salt due to the low polymerization ability of allyl monomers despite the appearance of charged atoms in the monomer molecule. At the same time, under the same conditions, vinyl bromide and bromostyrene do not

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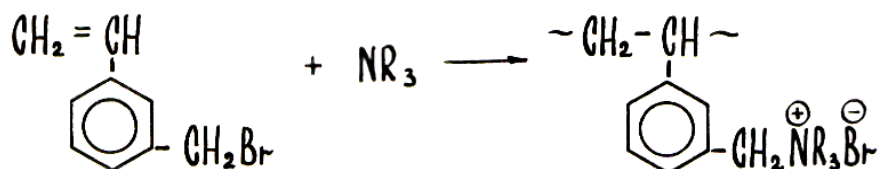
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enter into the Menshutkin reaction due to the low mobility of the bromine atom.

### Results

The increased activity of the bromide atom of the WBB group is explained by resonance stabilization, where an aromatic ring is involved in the resonance and the charge is distributed between the side chain



where NR<sub>3</sub> are tertiary amines.

In this instance, high molecular weight products are formed containing quaternary ammonium groups in each aromatic nucleus, i.e. only quaternized vinylbenzyl bromide molecules enter into the

atoms and ring atoms [4]. As a result, vinylbenzyl bromide easily reacts with Menshutkin in the reaction with tertiary amines (TAs). As a result, the nitrogen atom is positively charged, which enhances the polarization of the double bond. This, in turn, contributes to the course of spontaneous polymerization according to the following scheme:

reaction, which is proved by potentiometric titration of aqueous polymer solutions into bromine ions (Table 2), which are close to the theoretically calculated content (25.16% for PVBB: DMA; 31.25% for PVBB: TMA) and to the results of elemental analysis for bromine.

**Table 2 - Polymerization conditions and some physicochemical properties of polymers obtained based on the interaction of vinylbenzyl bromide with tertiary amines (conversion = 25%)**

T, °C	liquid	The molar ratio of WBB: TA	Bromine content, %		η <sub>pr</sub> (1% aqueous solution) dl / g	Exchange capacity, mEq / g
			Потенциометрическое титрование Potentiometric titration	Analysis element		
Vinylbenzylbromide + dimethylaniline						
30	Ethanol	1:1	24,6	24,5	0,19	2,8
40	-	1:1	24,9	24,9	0,16	3,0
50	-	1:1	24,8	24,7	0,11	2,8
40	Dioxane	1:1	25,1	24,8	0,20	3,0
40	Benzene	1:1	24,9	24,9	0,25	2,9
40	Inmass	1:1	24,8	24,9	0,30	2,9
50	Dioxane	1:1	25,1	25,0	0,18	3,0
50	Dioxane	2:1	23,5	25,0	0,17	2,4
Vinylbenzylbromide + trimethylamine						
0	Ethanol	1:1	30,8	30,6	1,48	3,7
0	Dioxane	1:1	31,1	31,0	1,42	3,8
25	Dioxane	1:1	30,9	31,0	1,30	3,8
25	Dioxane	1:2	30,5	30,6	1,32	3,8
25	Dioxane	2:1	27,8	31,2	1,25	3,6

The individuality of the obtained polymers is also confirmed by the removal of UV spectra, where in the region of 250-260 nm there is an absorption band characteristic of quaternary ammonium groups.

In the EPR spectra of the vinylbenzyl bromide + dimethylaniline system, taken under various conditions directly and indirectly, radical formation is not observed.

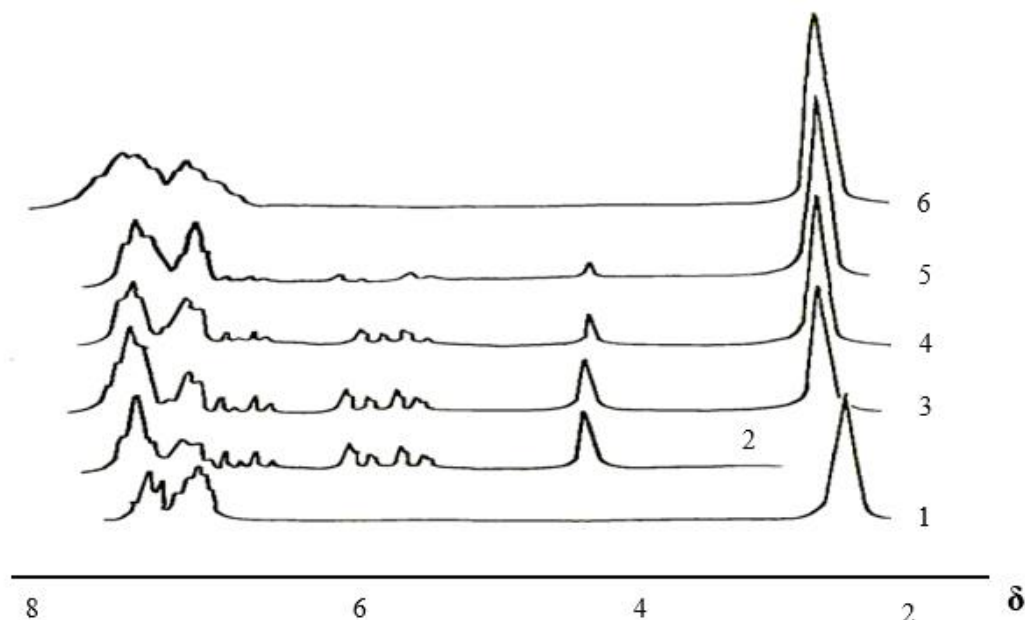
For collation, the IR spectra of polyvinylbenzyl bromide (PVBB) and polyvinylbenzyl dimethyl phenyl ammonium bromide (PVBDMFAB) were studied. The absorption band in the 1225 cm<sup>-1</sup>

region, related to the deformation vibrations of the CH<sub>2</sub>Br group, is completely absent in the spectrum of PVBDMFAB obtained at an equimolar content of the starting materials. This indicates the complete quaternization of dimethylaniline with vinyl benzyl bromide, accompanied by spontaneous polymerization.

To clarify the reaction between vinylbenzyl bromide and amino compounds, the NMR spectra of the starting components and their mixtures in time were recorded (Figure 1).

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**Figure 1 - PMR spectra of the system vinylbenzyl bromide + dimethylaniline: 1- dimethylaniline; 2 – vinylbenzyl bromide; 3 - immediately after the draining of the initial components; 4 - after 1 hour; 5 - after 2 hours; 6 - in 24 hours.**

In the NMR spectrum, taken 5 minutes after mixing the components (vinylbenzyl - bromide + dimethylaniline), all the signals of both components are preserved, but the signal circuit changes significantly:

- the signal from the proton of the methyl group at the nitrogen atom, detected in the spectrum of dimethylaniline in the form of a three-proton singlet (2.5 ppm), began to shift to a weak field (2.65 ppm) obviously due to the quaternization of the nitrogen atom of dimethylamine groups
- there is a decrease in signal intensity during a chemical shift of 4.1 ppm, related to the protons of methylene - CH<sub>2</sub>Br-group of vinylbenzyl bromide;
- the proton signals of the vinyl groups of vinylbenzyl bromide (5.25 and 6.65 ppm) are slightly shifted to a weak field (5.35 and 6.75 ppm).

These data confirm the formation of monomeric salt in the early stages of the process occurring during

the interaction of vinylbenzyl bromide with dimethylaniline. The time dependence of the change in the intensity of the signals of -CH<sub>2</sub>Br and CH<sub>3</sub>-N-CH<sub>3</sub> groups can be expressed as the quantitative timing of the Menshutkin reaction.

For this day forward, a decrease in the signal intensity of the zrotons of not only the CH<sub>2</sub>-Br group, but also the protons of the vinyl group of vinylbenzyl bromide is observed. This indicates that the salt formation of vinylbenzyl bromide is accompanied by spontaneous polymerization.

In the NMR spectrum, taken after 24 hours, there are no signals of protons of the vinyl and bromomethyl groups, which indicates the cessation of polymerization and the complete consumption of the initial components of the protons of the vinyl and bromomethyl groups, which indicates the cessation of polymerization and the complete consumption of the initial components.

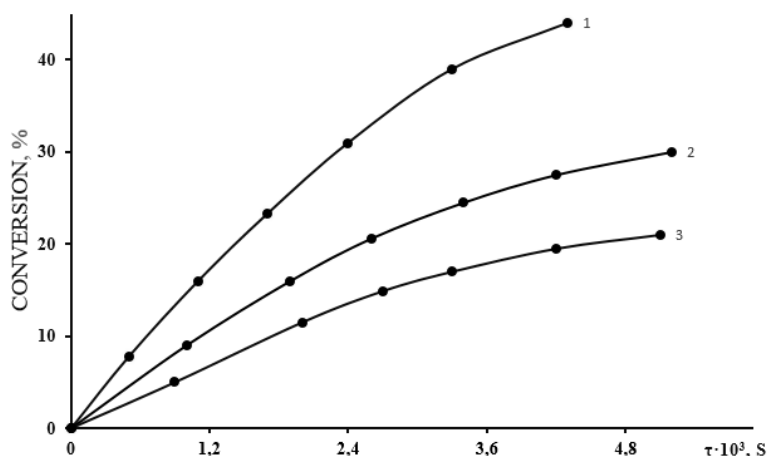


Figure 2 - Effect of the nature of the medium on the spontaneous polymerization rate of vinylbenzyl bromide with dimethylaniline  $T = 40^{\circ}\text{C}$ , 1 - ethanol, 2 - benzene, 3 - dioxane

A study of the impact of the nature of solvents on the process of spontaneous polymerization showed that the reaction rate in polar media is greater than in nonpolar media (Figure 2). The increase in the rate of spontaneous polymerization during the interaction of vinylbenzyl bromide with dimethylaniline with an increase in the polarity of the medium is apparently associated with an acceleration of the Menshutkin reaction, which is the initial stage of the process and with an increase in the degree of dissociation of the quaternary salt in polar media, which leads to the

appearance of a positive charge on the nitrogen atom. This, in turn, leads to an increase in polarization of the double bond and acceleration of spontaneous polymerization.

To clarify the effect of temperature on the rate and to calculate the total activation energy of spontaneous polymerization of vinylbenzyl bromide in the interaction with dimethylaniline, average reaction rates were determined at the initial stage of the stationary process at temperatures of 30, 40, 50  $^{\circ}\text{C}$ .

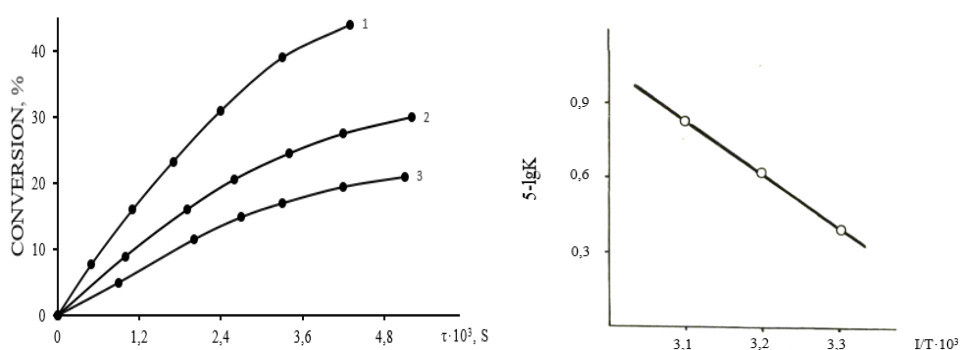


Figure 3 - Dependence of polymer yield on reaction time at temperatures: 1 - 30  $^{\circ}\text{C}$ , 2 - 40  $^{\circ}\text{C}$ , 3 - 50  $^{\circ}\text{C}$  (a) and calculation of activation energy (b)

Perceivable from Figure 3a, with an increase in temperature, the rate of spontaneous polymerization increases.

The activation energy of the reaction of spontaneous polymerization of vinylbenzyl bromide with dimethylaniline, which is 38.25 kJ / mol, was determined from the dependence of the reaction rate constants on temperature in arrhenius coordinates

(Fig. 3b). The value of K turned out to be close to the value of the activation energy, a characteristic Menshutkin reaction, which is the initial stage of the process. This suggests that the Menshutkin reaction is at the same time a limiting stage of the process. This is also confirmed when determining the order of reactions for the starting components.

Installed results of the study, it can be assumed

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that, with the equimolar ratio of vinylbenzyl bromide to tertiary amine or with an excess of tertiary amine, polymerization is highly selective and whose mechanism, by analogy with the mechanism proposed in [89], includes three stages:

Based on the studies, it was shown that with an excess of tertiary amine, polymerization is highly selective and a mechanism is proposed that includes three stages:

- chemical activation as a result of salt formation;
- initiation by the formation of an intermediate zwitterions
- chain growth by the addition of a monomeric salt to a zwitterion and a growing chain.

To determine the reactivity of the selected

monomers, we studied the processes of their copolymerization with acrylonitrile in the presence of various initiators and under different conditions.

As can be seen from the results obtained, the copolymerization rate in the presence of dicyclohexylperoxydicarbonate is greater than in the presence of benzoyl peroxide and dinitrileisobutyricacid. This, apparently, is explained by a higher decomposition rate of dicyclohexylperoxydicarbonate under the reaction conditions than benzoyl peroxide and dinitrileisobutyricacid.

Regardless of how, the high decay rate of the initiator leads to its rapid consumption and part of the free radicals at the same time reacts with growing macroradicals, which leads to a decrease in the molecular weight of the copolymers (table 2).

**Table 2 - Effect of the nature of the initiator on the yield and intrinsic viscosity of the copolymers, T = 600°C; [I] = 0.035 mol / L; [M] = 7.35 mol / L.**

Copolymer	The initial ratio of monomers, mol, %	Initiator	Liquid	Time, $1 \times 10^{-3}c$	Output, %	$[\eta]$ dl / g
VB + AN	50:50	PB	DMFA	7,2	11,5	0,82
		DAK	DMFA	7,2	9,2	0,70
		DSPDK	DMFA	3,6	13,0	0,55
BC + AN	50:50	PB	DMFA	7,2	18,0	0,84
		DAK	DMFA	7,2	9,8	0,72
		DSPDK	DMFA	3,6	12,0	0,57
VBB + AN	50:50	PB	DMFA	7,2	10,3	0,22
		DAK	DMFA	7,2	14,5	0,20
		DSPDK	DMFA	3,6	16,8	0,15
VBA+AN	50:50	PB	DMFA	7,2	10,0	0,53
		DAK	DMFA	7,2	9,3	0,20
		DSPDK	In mass	3,6	11,5	0,18
AB + AN	5:95	PB	DMFA	7,2	16,8	0,15
		DAK	DMFA	7,2	9,0	0,26
		DAK	In mass	3,6	10,2	0,45

To study the influence of the nature of the medium on the copolymerization of bromine-containing monomers with acrylonitrile, the reaction was carried out in various solvents of different polarity. Studies have shown that the copolymerization reaction proceeds at a higher rate in the medium of dimethylformamide than ethanol and benzene. This, apparently, is explained by the fact that in a polar solvent medium (EDMFA>Vetanol>Ebenzene), the polarization of double bonds of polar monomers is enhanced, which increases their tendency to polymerization.

The influence of the structure of monomers on the activity of vinyl groups was also studied. The vinyl group of these monomers is not a rigidly fixed, strictly localized system, the cloud of  $\pi$  electrons of the

double bond is mobile, dynamically covers all systems connected by conjugation. In vinyl bromide, the bromine atom is located directly at the double-bonded carbon, and the mutual influence of the double bond and the bromine atom is explained by the conjugation between the free bromine electrons and the double bond. As a result of this pairing, the carbon-bromine bond receives a doubly bound character. Thus, carbon and bromine are bound together by more than one pair of electrons and the carbon-bromine bond is stronger than if it were a purely simple bond.

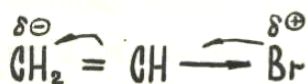
The dipole moment of the coupling decreases, since the induction component of the dipole moment and the much smaller moment arising due to the conjugation are directed in different directions [4]

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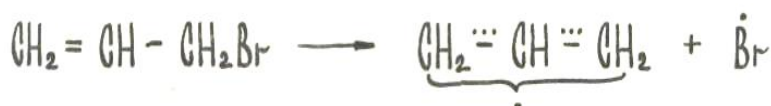
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In this structure, the bromine atom naturally carries a positive charge, and the carbon atom is negative. The induction effect of the bromine atom greatly reduces the electron density of the double bond, making it difficult to break the double bond.

In the bromstyrene molecule, the bromine atom is located directly at the carbon of the ashless ring and the mutual influence of the double bond, the benzene



The overlapping of the p-orbital with the  $\pi$ -cloud of the double bond leads to stabilization of the radical.

In vinylbenzyl bromide, the  $\pi$ -electrons of the vinyl group enter into conjugation with the  $\pi$ -electrons of the benzene ring ( $\pi$ ,  $\pi$ -conjugation), which, apparently, reduces the double bond cleavage energy, and the presence of a methylene group increases the activity of the bromine atom. This is indicated by the calculated values of activation energy (EBVB = 86 kJ / mol) and a relatively large value of specific activity (QBBB = 0.326) compared with vinyl bromide (EBB = 101.5; QBB = 0.038).

In addition, the density of the C-Br bond electron cloud shifts to the more electron-negative bromine atom. As a result, bromine becomes mobile and participates in chain transfer reactions via the monomer and chain transfer constants increase in the order of SBB < SBB < SAB.

The above premises are confirmed by considering the quantum structure of these monomers [4]. As is known, the bromine atom is located directly at the double-bonded carbon and the carbon bearing the bromine atom has  $sp^2$  hybridization (rather than  $sp^3$ ), therefore the carbon-bromine bond is shorter and stronger (C - Br bond length 1.86 Å) and the

ring and the bromine atom is also explained by the conjugation between the free electrons of the bromine, benzene ring and the double bond. Therefore, the bond of bromine with carbon of the benzene ring becomes strong.

In allyl bromide, the bromine atom is very mobile, easily replaced. This is due to the high stability of the allyl radical due to the resonance effect. Each carbon - carbon bond in an allyl radical is neither double nor simple, but hybrid. A free electron is not localized on any of the carbons: it is delocalized, and it is equally distributed between two terminal carbon atoms:

molecules are more stable (breaking energy of the C - Br bond is DVB = 292.6 kJ / mol), for allyl bromide and vinylbenzyl bromide the carbon-bromine bond is formed due to  $sp^3$  hybridization, the bond length is 1.91 Å and therefore the C - Br bond is less stable (DBA = 196.6 kJ / mol, DBBB = 209.0 kJ / mol) [5].

Consequently, when studying the behavior of halogen-containing monomers in binary systems with amino compounds, the course of spontaneous polymerization of some bromine-containing monomers with an active halogen atom during interaction with tertiary amines was revealed.

### Conclusion

When researching the kinetics of the copolymerization of bromine-containing monomers with acrylonitrile, as well as studying the mutual influence of the bromine atom and double bond in the monomers under study, it was shown that the presence of a reactive bromine atom greatly influences the copolymerization process and the properties of the resulting copolymers, which makes it possible to more purposefully but to carry out the synthesis of a number of macromolecular compounds, as well as their further chemical transformation.

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