Synthesis and kinetic regularities of copolymers based on styrene and nitrogen-containing methacrylic monomers

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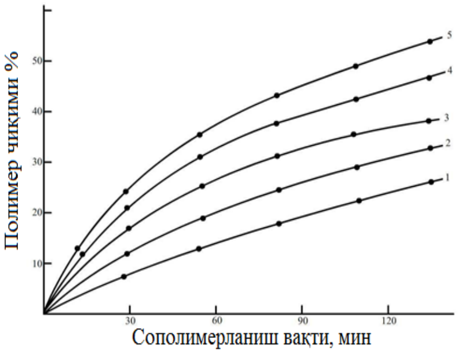
Abstract: In this study, the synthesis and kinetic regularities of the radical copolymerization of N-morpholin-3-chloropropylacrylate (MXIPMA) with styrene were investigated. The copolymerization was carried out in bulk at 70 °C in the presence of azobisisobutyronitrile (AIBN) as an initiator. The effects of monomer ratio, reaction time, and temperature on the conversion degree and copolymer composition were analyzed. The obtained results demonstrated that the introduction of a morpholine-containing nitrogen fragment into the methacrylate structure significantly affects the copolymerization rate and thermal stability of the resulting copolymers. Due to their high polarity and solubility, the synthesized copolymers show potential for use as lubricant modifiers.

Keywords: acrylates, polymer additives, copolymers, synthesis technology, performance properties, functional additives

Currently, in-depth study of radical copolymerization processes of nitrogen-containing methacrylic monomers is one of the important directions of functional polymer materials chemistry. The nitrogen atom and its functional groups contained in such monomers form additional active centers in the polymer chain, which allows to significantly improve the physicochemical properties of the polymer. In particular, products obtained by copolymerization with styrene are characterized by high mechanical strength, thermal stability and solubility.

The effects of various factors on the kinetics of radical copolymerization of nitrogen-containing methacrylic acid and styrene were studied: the ratio of initial monomer concentrations, temperature, reaction duration, and the nature of the solvent.

In order to study the effect of the initial mixture composition on the rate of the copolymerization reaction of nitrogen-containing methacrylic acid ester and styrene, the reaction was carried out in a dioxane solution with different molar ratios of the initial monomers at a temperature of 353 K in the presence of the initiator DAK (Figure 1).



1. Yield of MXIPMA and styrene copolymer as a function of reaction time at different ratios of starting monomers: 1 - 90 : 10; 2 - 25 : 75; 3 - 50 : 50; 4 -75 : 25; 5 - 90 : 10. [DAK]=3.79 10^{-3} mol/l. Solvent dioxane. T = 353 K.

As can be seen from Figure 1, the copolymer yield increases with increasing reaction time [1].

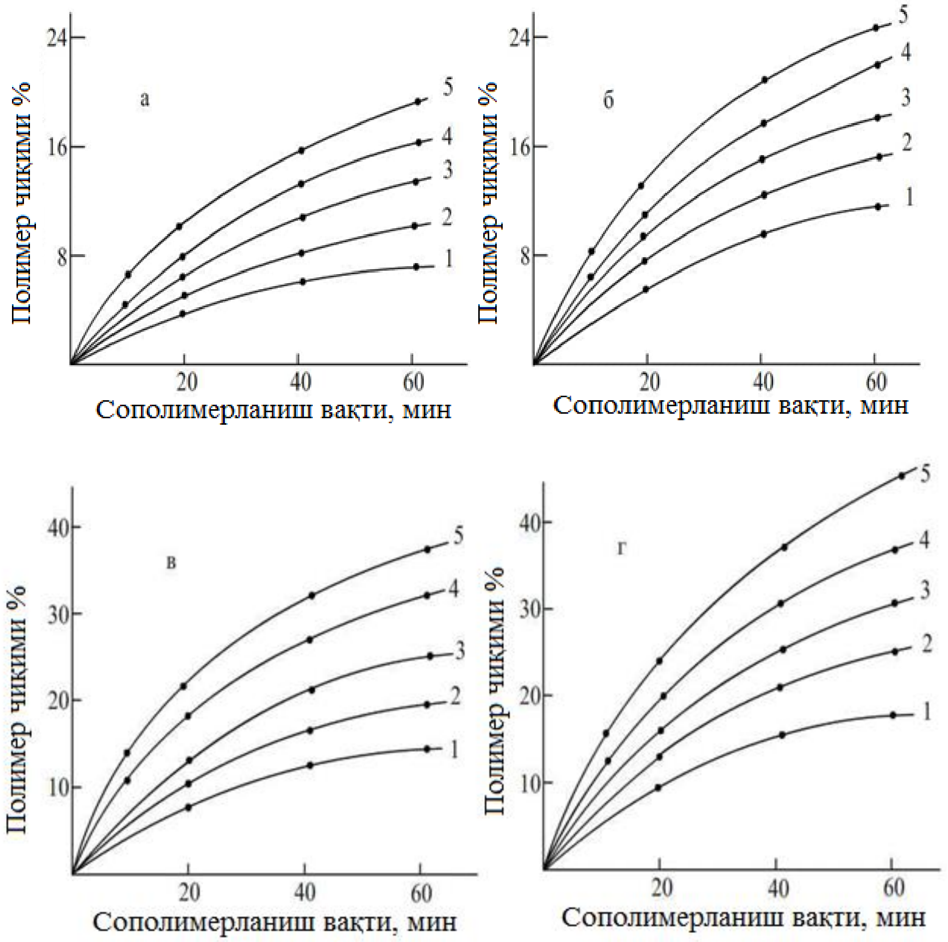


Figure 2. Dependence of the yield of MXIPA and styrene copolymers on the reaction time. Monomer ratio, mol.%: 1 - 10:90; 2 - 30:70; 3 - 50:50; 4 - 70:30; 5 - 90:10. Solvents: dioxane (a), benzene (b), dimethylformamide (c), dimethylsulfoxide (g).

Based on the experimental results, it was found that the copolymerization rate increases with increasing concentration of nitrogen-containing acrylic acid ester in the initial monomer mixture. The increase in the reaction rate can be explained as follows: the participation of the nitrogen-containing group in the initiation stage facilitates the formation of radicals in the chain extension reaction, as a result of which the number of active centers increases and the copolymerization rate increases. At the same time, the characteristic viscosity of the copolymer solutions decreases (Figure 2) [2].

The decrease in the characteristic viscosity of copolymer solutions with an increase in the amount of MXIPA in the initial monomer mixture can be explained by the participation of nitrogen-containing acrylic acid ester molecules in the chain termination and extension stages.

In order to study the effect of the nature of the solvent on the copolymerization kinetics, the reaction was carried out at a molar ratio of the starting monomers of 0.5:0.5 at temperatures ranging from 333 to 353 K (Figure 2). It can be seen that the process rate and the yield of copolymers increase with increasing temperature and polarization of the medium. The linear nature of this relationship indicates that the copolymerization reaction of MXIPA and styrene is a second-order kinetic equation with respect to the monomer [3].

Table 1

Kinetic parameters of the copolymerization reaction of MXIPA and styrene in different solvents [DAK] = 3.79 10 $^{-3}$ mol/l. Sm= 0.8 mol/l

Solvent	Temperature,K	Copolymer yield,%	Conversion x/a (a-x) 10 ^{2}	K 10 ^{5} sec $^{-1}$	E $_{f,}$ kJ
Dioxane	333	4.21	0.5068	2.82	56.31
	338	5.89	0.7158	3.98	
	343	7.36	0.9025	5.01	
	348	9.67	1.2166	6.76	
	353	12.62	1.6054	8.91	
Benzene	333	5.92	0.7157	3.98	53.59
	338	7.80	0.9669	5.37	
	343	10.08	1.2728	7.07	
	348	12.12	1.5670	8.71	
	353	15.92	2.1146	11.74	
DMFA	333	6.3	0.7617	4.23	46.80
	338	8.6	1.0661	5.92	
	343	10.2	1.2870	7.15	
	348	12.4	1.6040	8.91	
	353	16.7	1.9526	10.84	
DMSO	333	6.3	0.7617	4.23	43.90
	338	8.6	1.0661	5.92	
	343	10.2	1.2870	7.15	
	348	12.4	1.6040	8.91	
	353	16.7	1.9526	10.84	

The dependence of the characteristic viscosity of copolymer solutions on temperature was studied (Fig. 3). It is known that in homopolymerization, the characteristic viscosity decreases with increasing temperature. This phenomenon is characteristic for processes occurring in all solvents, both polar and non-polar solvents, and is associated with an increase in the initiation rate as a result of increasing temperature. There is a rather interesting phenomenon, namely, the characteristic viscosity increases as one passes from non-polar solvents to polar solvents. On the one hand, this is fully consistent with the possibility of an increase in the chain growth constant as a result of an increase in the molecular weight of the polymer, which is also consistent with the general situation of complex-radical copolymerization. On the other hand, with a change in the nature of the solvent, the relative activity of the monomers logically changes (Table 1) [4].

Therefore, during the chain extension stage, the initiator is ignored and used in very small amounts, 5·10-4 mol/l.

The molecular weight of the resulting copolymer was determined according to the Mark-Hoovink equation $[\eta] = 4.17*10^{4} M\ 0.60$ adopted for styrene in benzene solution.

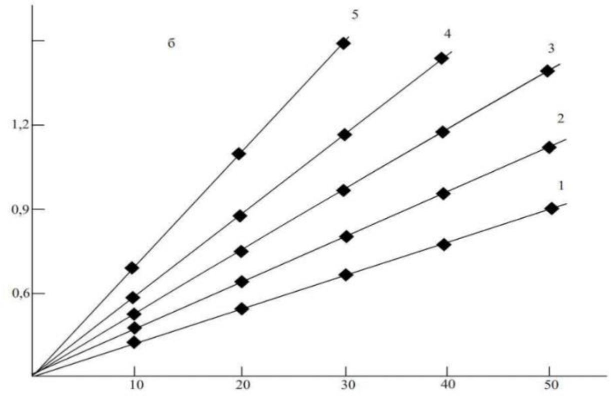


Figure 3. Conversion of MXIPA and styrene copolymerization LgK /a(a-x) dependence on reaction duration (in dioxane solution). 1 - 333; 2 - 343; 3 - 343; 4 - 348; 5 - 353 K

Figure 4 shows the dependence of LgK on 1/T, based on which the activation energy value for the initial stage of the copolymerization process in various solvent environments was determined, which is equal to 43.91 - 56.31 kDJ/mol for the reaction, which corresponds to the activation energy value of radical copolymerization of acrylic monomers. The yield of copolymers increases in the following solvent series: dioxane, benzene, dimethylformamide, dimethylsulfoxide [5].

It is evident that this association increases the probability of specific solvation due to the formation of hydrogen bonds. The activation energy of copolymerization of MXIPA and styrene in polar solvents is relatively low, and during this process, the monomers form an intermediate complex with the polar solvent molecule, which increases the chain growth rate.

To determine the participation of the MXIPA monomer molecule in the chain extension step, styrene copolymerization was carried out in the presence of MXIPMA at a low conversion rate of up to 1 wt.% (based on the mass of styrene) [6].

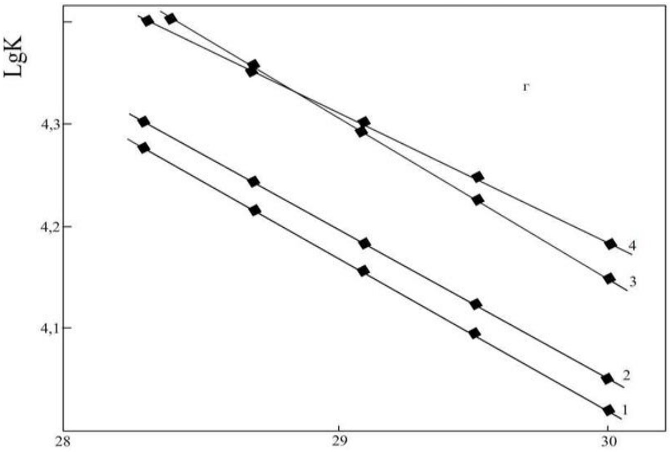


Figure 4. Dependence of LgK on 1/T.10 $^{-3}$ in the copolymerization of MXIPA and styrene in different solvents· 1-dioxane; 2-benzene; 2-dimethylformamide; 4 - dimethylsulfoxide.

It was found that the presence of a small amount of MXIPA does not affect the initial rate of polymerization of styrene, which allows the calculation of the chain transfer constant through the monomer using the Mayo equation. The chain transfer constant Sm for the MXIPA molecule was also calculated by the least squares method.

$$1/R = 1/R_o + S_m M_1 / M_2,$$

where, $P_o^{-1,}$ P^{-1} - the degree of polymerization without and with the participation of the extender, respectively. M_1 and M_2 - the concentration of the extender and monomer. $C_м$ - the chain transfer constant.

Table 2

Copolymerization performance of MXIPMA and styrene

Copolymerization conditions				Description of copolymers	
Temperature ^{0}C	MXIPMA	Styrene	Initiator amount, %	Yield, %	Yield, %
60	10	90	0.30	86.3	8000
65	20	80	0.40	89.5	8500
70	30	70	0.55	91.4	9000
70	40	60	0.60	93.5	9500
75	50	50	0.70	94.7	8700
75	60	40	0.75	92.5	8500
80	70	30	0.80	88.3	8000
85	80	20	0.90	87.1	7500
90	90	10	1.00	85.4	7000

The copolymer of MXIPA and styrene is a white powdery substance, soluble in dioxane, benzene, DMFA, DMSO, and chlorinated hydrocarbons, but insoluble in water, lower alcohols, and aliphatic hydrocarbons [7].

Thus, the results of the study indicate that the MXIPA molecule does not inhibit the copolymerization reaction, but rather actively participates in it, allowing the formation of copolymers with styrene and other monomers with complex properties [8].

The temperature of the copolymerization reaction solution with nitrogen-containing acrylic acid ester (MXIPA) and styrene at 60-90 ^{0}C, the initiator (DAK) dinitrile of diazomic acid at 0.3-1.0%, and the monomer ratios of 1:9 and 9:1 on the yield and molecular weight of the copolymer was studied, and the results are presented in Table 2.

As can be seen from the table, the ratio of MXIPA and styrene in the initial mixture of monomers in the copolymer composition in the ratio of 1:9 and 9:1 led to an increase in the yield and molecular weight of the copolymer at the ratio of MXIPA monomer to 1-4, and a decrease in the molecular weight of the copolymer at the ratio of 5-1 with styrene, which is explained by the high reaction activity of styrene. The study of the effect of temperature on the yield and molecular weight of copolymers showed that a change in temperature from 60 °C to 90 °C led to a decrease in the molecular weight without a significant effect on the yield of the copolymer. This is explained by the fact that an increase in temperature accelerates all chemical reactions, including the chain growth reaction during the formation of copolymers.

When the initiator concentration in the monomer mixture was studied in the range of 0.3-1.0%, the amount of diazomic acid dinitrile in the copolymerization reaction exceeding 0.7% led to a decrease in the molecular weight of the copolymer, while a decrease in its concentration led to a decrease in the copolymer yield. The results of the studies showed that the optimal conditions for ensuring a high value of the copolymer yield were the reaction temperature of 70°C, the proportion of styrene monomer of 50%, the amount of initiator of 0.7%, and the time of 3 hours, the yield of the copolymerization reaction was 94.7%.

Therefore, the yield and molecular weight of the copolymer depressant precursors can be controlled by varying the molar amounts of alkyl methacrylate and styrene monomers in the initial mixture of the copolymerization reaction, the temperature, and the amount of initiator used to synthesize them[9].

Conclusion

The study investigated the kinetics of radical copolymerization of nitrogen-containing methacrylic acid and styrene. The effect of various factors on the copolymerization process, including the ratio of initial monomer concentrations, temperature, reaction time, and solvent nature, was analyzed. The aim was to determine how these factors affect the polymerization rate, conversion level, and structural properties of the resulting copolymer. The results obtained will provide a scientific basis for improving the synthesis technology of high-performance copolymers that can be used as various functional additives and oil modifiers in the future.

References

1. Saidov J.E., Nazarov Sh.Yu., Sakhibov D.Z. Issledovanie processa sopolimerzatsiya methakrilovoy kisloty s N-morpholine-3-chloro isopropylacrylatom. Republican scientific and technical conference Novye komposisionnye materialy: Poluchenie i primenenie v razlich nyx otraslyax p romyshlennosti. -2022g. P.181-182.

2. 145. GOST 5066-2018. Determination of the onset of crystallization, freezing points of motor fuels.

3. GOST 22254-92 Diesel fuel. The method of determining the limit of filtration temperature in a cold filter.

4. Nazarov Shomurod, Idiyev Bahrom // BASIC ASPECTS OF ACRYLATE-BASED PREPARATION // (2025). Journal of Uzbekistan's Development and Research, 1(1), 163-168. DOI: https://doi.org/10.5281/zenodo.14711264

5. Sadirova Saodat Nasretdinovna, Idiev Bakhrom Bobir ugli // Sovershenstvovanie tekhnologii prisadkov na osnove akrilatov // sbornik materialov mejdunarodnoy nauchno - tekhnicheskoy konferentsii "PROBLEMY, INNOVATSIONNYE PREDLOJENIya I RESHENIya V OBLASTI KHIMII I TECHNOLOGII NEFTI I GAZA" BUKHARA-2023 82 P.

6. Kamoliddin, K., & Javlonbek, M. (2023). MODIFICATION OF CATALYTIC SYSTEMS IN THE PROCESS OF OBTAINING SYNTHETIC HIGH FATTY ACIDS THROUGH OXIDATION OF PARAFFIN HYDROCARBONS. Universum: technical science, (3-5 (108)), 37-40.

7. Kamoliddin Khujakulov et al 2021 IOP Conf. Ser.: Earth Environ. Sci. 839 042073 DOI 10.1088/1755-1315/839/4/042073

8. Khujakulov, KR, Narzullaeva, AM, Rayimov, ZX, Niyozova, RN, Jamilova, NQ, & Rakhmanov, BO (2020). Analysis of Physical and Mechanical Properties of Skin Oil Based on Secondary Petroleum Products. International Journal of Advanced Research in Science, Engineering and Technology, 7 (11), 15908-13.

9. Nazarov Sh.K., Olimov B.B., Akhmedov V.N. P redvaritelnyi quantovo-khimicheskii analysis synthezirovannyx monomerov s uchastiem vinylacetylene. International journal of Progressive Sciences and Technologies (IJPSAT) ISSN: 2509-0119. Special Issue September 2020, pp. 50-56