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SYNTHESIS AND STUDY OF THE POLYMERIZATION OF N-ALKYL-N-ALLYL-(β -CHLORO)ALLYLAMMONIUM DIHYDROPHOSPHATES

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The polymerization reactions of the synthesized N-alkyl(methyl, *n*-butyl, *n*-heptyl, *n*-dodecyl)-N-allyl-N-(β -chloro)allylamines (AABA) were carried out in solutions of mineral acids (HCl, HNO₃, H₃PO₄) in the presence of thermal initiators – ammonium persulfate (AP) and azo-*bis*-isobutyric acid dinitrile (ABD). Radical polymerization of AABA was performed using AP and ABD with initiator concentration $4 \cdot 10^{-4}$ mol/l and at a temperature 60°C, the reaction was 10–24 hours. In this way, it is not possible to obtain sufficiently high molecular mass of the polymerization products, although PA is more effective than ABD. However, during the photopolymerization of AABA in solutions of concentrated acids in the presence of photoinitiators – uranyldiaquadiacetate and uranyldipivalate with an initiator concentration of $4 \cdot 10^{-4}$ mol/l, water soluble polymers were obtained with sufficiently high characteristic viscosity for a given amine.

Keywords: *N-alkyl-N-allyl-N-(β -chloro)allylamines, mineral acids, thermal initiator, photo-initiator, polymerization, water, acetone.*

doi

Introduction

The polymers based on diallyl monomers occupy an important place among synthetic polyelectrolytes, which can be used as coagulants, flocculants, soil structuring agents, as well as for purification of drinking and waste water. Therefore, the synthesis of new diallyl monomers and polymers containing functional groups, as well as the corresponding polyelectrolytes with adjustable hydrophilic-hydrophobic balance is a very urgent task.

The study on the radical polymerization processes of diallyl monomers, in particular, on the basis of N-alkyl-N-allyl-N-(β -chloro)allylamines is of scientific and practical interest. It should also be noted that there are small data in the literature devoted to the study of the kinetic features of the polymerization of N-alkyl-N-allyl-N-(β -chloro)allylamines and their salts in protonated form, which would contain hydrophobic N-alkyl substituents.

In the literature, there are no data on the synthesis and polymerization of N-alkyl-N-allyl-N-(β -chloro)allylammonium dihydrophosphates. But there is information about the polymerization N-alkyl-N,N-diallylammonium dihydrophosphates [1, 2].

Experimental part

Methylamine – used a "pure" 25% water solution. N-Butylamine – b.p. 77.8°C, n_d^{20} – 1.4035, d_4^{20} – 0.7401. *n*-Heptylamine – b.p. 158.3°C, n_d^{20} – 1.4270, d_4^{20} – 0.7770. *n*-Dodecylamine – b.p. 248°C, m.p. 27–28°C rashly distilled allylchloride – b.p. 45°C, n_d^{20} – 1.4154, d_4^{20} – 0.9379. Freshly distilled (β -chloro)allylchloride – 94°C, n_d^{20} – 1.4600, d_4^{20} – 1.2080. Sodium hydroxide, sodium chloride, orthophosphoric acid (85% aqueous solution) brand products "ch. p.". Thermal initiators – ammonium persulfate (AP) (NH₄)₂S₂O₈ and dinitrile azobisisobutyric acid (ABD) N $\equiv$ C–C(CH₃)₂–N=N–C(CH₃)₂–C $\equiv$ N products of the brand "ch. f. a.". Recrystallized from water (AP) and ethyl alcohol (AID), dried in vacuum to constant mass. Photoinitiators – uranyl diaquadiacetate UO₂(OOCCH₃)₂·2H₂O (UA) and uranyl diaquadi-pivalate UO₂[OOC(CH₃)₃]₂·2H₂O (UP), brand products "ch. p." [3]. In all experiments, bidistilled water was used. Acetone, ethanol, isopropyl alcohol, diethyl ether were purified by the conventional method [4]: the solvents used corresponding to the table characteristics.

Synthesis of investigated compounds was made on case N-allyl-N-(β -chloro)allyl-N-methylamine (ABMA). A two-liter, four-necked flask equipped with a stirrer, reflux condenser, thermometer, dropping funnel, pour a portion of a 25% aqueous solution of methylamine 127 g (1 mol) and 76.5 g of allyl chloride drop by drop during 1 h and after 7 h 111 g (mol) (β -chloro)allyl chloride for 1 h and then a 50% aqueous solution of sodium hydroxide (80 g, 2 mol). The feed rate of the reagents is adjusted so that the temperature in the reaction mass does not exceed 30°C. To remove excess heat using a water bath with ice. After adding the sodium hydroxide solution, the reaction mass is slowly warmed to 70°C. After cooling the reaction mixture, the upper layer is separated and kept over granulated NaOH for 40 h. The amine aged above the alkali is fractionated on a column, keeping the reflux ratio 10:1. During distillation, fractions 68–70°C/2.67 kPa, n_d^{20} – 1.4630, d_4^{20} – 0.9445. Yield 60%. $MR_{D/found}$ 42.43. $MR_{D/calc.}$ 42.26. Found, %: C 57.78, H 8.62, N 9.73, Cl 24.25. $C_7H_{12}NCl$. Calculated, %: C 57.73, H 8.31, N 9.62, Cl 24.34.

Synthesis of N-allyl-N-(β -chloro)allyl-N-n-butylamine (ABBA). The reaction mixture of 7.3 g (0.1 mol) of butylamine, 7.6 g (0.1 mol) of allylchloride and 11.1 g (0.1 mol) (β -chloro)allylchloride, 0.8 g (0.2 mol) sodium hydroxide granules surrounded on air and 40 ml isopropyl alcohol is transferred to a special ampoule. After this, the reaction mixture is degassed on a vacuum unit and placed in an oil thermostat, where it is maintained at a temperature of 105–110°C for. 7-9 h. Then the reaction mixture is thoroughly washed by water, and the organic part is extracted by ether and after removing the ether, it is distilled by vacuum distillation: b. p. – 102–103°C/0.133 kPa. n_d^{20} – 1.4640, d_4^{20} – 0.9191. Yield – 55%. $MR_{D/found}$ – 55.55. $MR_{D/calc.}$ 56.21. Found, %: C 64.12, H 9.71, N 7.39, Cl 18.67. $C_{10}H_{18}NCl$. Calculated, %: C 63.99, H 9.67, N 7.46, Cl 18.89.

In a similar way obtained:

N-allyl-N-(β -chloro)allyl-N-n-heptylamine (ABHA) from heptylamine: b.p. 111–113°C/0.133 kPa. n_d^{20} – 1.4656, d_4^{20} – 0.9052. Yield – 52%.

$MR_{D/found}$ – 70.24. $MR_{D/calc.}$ 70.15. Found, %: C 68.14, H 10.60, N 6.06, Cl 15.35. $C_{13}H_{24}NCl$. Calculated, %: C 67.95, H 10.53, N 6.10, Cl 15.43.

N-allyl-N-(β -chloro)allyl-N-n-dodecylamine (ABDA) from dodecylamine: b.p. 134–135°C/0.133 kPa. n_d^{20} – 1.4660, d_4^{20} – 0.8870. Yield 50%. $MR_{D/found}$ – 93.66. $MR_{D/calc.}$ – 93.39. Found, %: C 72.15, H 11.52, N 4.72, Cl 11.74. $C_{18}H_{34}NCl$. Calculated, %: C 72.08, H 11.43, N 4.67, Cl 11.82.

Synthesis of N-allyl-N-(β -chloro)allyl-N-methylammonium dihydrophosphate (MHPH). Pre-dried and distilled N-allyl-N-(β -chloro)allyl-N-methylamine (ABMA) are placed in a beaker and mixed with an equivalent amount of orthophosphoric acid (85% aqueous solution). Mix thoroughly until a homogeneous mass, while the excess heat is removed in a water bath with ice. The mixture is thoroughly washed with cold ether and dried to a constant mass over P_2O_5 . Purified by recrystallization from a mixture of ether–absolute ethanol in the ratio 10:1. T_{melt} – 66°C. Yield – 75%. Found, %: C 34.67, H 6.28, N 5.69, Cl 14.43, P 12.77. $C_7H_{15}NCIPO_4$. Calculated, %: C 34.51, H 6.21, N 5.75, Cl 14.55, P 12.72.

In a similar way obtained other compounds.

N-allyl-N-(β -chloro)allyl-N-n-butylammonium dihydrophosphate (BHPH): m. p. – 73°C. Yield – 73%. Found, %: C 41.98, H 7.47, N 4.99, Cl 12.49, P 10.94. $C_{10}H_{21}NCIPO_4$. Calculated, %: C 42.04, H 7.41, N 4.90, Cl 12.41, P 10.85.

N-allyl-N-(β -chloro)allyl-N-n-heptylammonium dihydrophosphate (HHPH): m. p. – 92°C. Yield – 70%. Found, %: C 47.69, H 8.35, N 4.20, Cl 10.92, P 9.52. $C_{13}H_{27}NCIPO_4$. Calculated, %: C 47.63, H 8.30, N 4.27, Cl 10.81, P 9.46.

N-allyl-N-(β -chloro)allyl-N-n-dodecylammonium dihydrophosphate (DHPH): m. p. 99°C. Yield 65%. Found, %: C 54.40, H 9.43, N 3.43, Cl 8.81, P 7.86. $C_{18}H_{37}NCIPO_4$. Calculated, %: C 54.33, H 9.37, N 3.52, Cl 8.91, P 7.79.

Polymerization of N-alkyl-N-allyl-N-(β -chloro)allylamines in the environment of proton-donating acids. A weighed 0.2 mol/l of monomer was placed in concentrated solutions of acids (HCl, HNO_3 , H_3PO_4) and the initiator

($4 \cdot 10^{-4}$ mol/l) was added. The prepared solutions were divided into two parts and placed in a special ampoule. On part of the ampoules was placed in a thermostat at 60°C for 10–24 hours, the other part of the ampoules was photopolymerized at $0\text{--}20^{\circ}\text{C}$, при $\lambda=360$ nm. After the reaction was completed, the reaction mixture was gradually poured into dry acetone in portions. The resulting precipitates were filtered, thoroughly washed with dry acetone, and dried over P_2O_5 to constant mass. Yields are 15–45%.

Results and discussion

In connection with widespread use of cationic polyelectrolytes in various branches of industry, it seems natural for researchers to synthesize new polyelectrolytes which would have a complex of valuable properties with adjustable hydrophilic–hydrophobic balance basis on the diallyl monomers. To this end, we have a number of N-alkyl-N-allyl-N-(β -chloro)allylamines synthesized to the scheme [5, 6]:

The interaction of N-alkyl-N-allyl-N-(β -chloro)allylamines with of orthophosphoric acid

obtained N-alkyl-N-allyl-N-(β -chloro)allylammonium dihydrophosphates:

It is known that radical polymerization of tertiary amines in the form of free bases proceeds only with the formation of low molecular mass oligomers. This is due to the side effect of the monomer–radical cleavage of the hydrogen atom of the $-\text{CH}_2$ group of the allyl substituent, as is well known, which easily occurs in the case of diallylamines in the basic form. In this case, the chain transfer reaction to the monomer leads to the formation of a weakly reactive allylic transfer radical, the loss of the active radical center and the attenuation of the polymerization process. This reaction is characterized as a degradation chain transfer to the monomer [7]. This is mainly due to the presence of isolated degraded chain transfer to the monomer, which complicates the methods of their deep research. Therefore, the search for approaches to the synthesis of of N-alkyl-N-allyl-N-(β -chloro)allylamines which reduce the

contribution of the degradation chain to the monomer, can open the way to obtaining polymers with desired practical properties and high molecular mass (MM).

The reactions of radical polymerization of the amines synthesized by us earlier were carried out in solutions of various mineral acids (HCl , HNO_3 , H_3PO_4) in the presence of a thermal initiators ($T=60^{\circ}\text{C}$) and photochemical method ($T=20^{\circ}\text{C}$).

The radical polymerization of ABMA was performed using UA and AID with an initiator concentration of $4 \cdot 10^{-4}$ mol/l at 60°C , the reaction time was equal to 10–24 h. The results are shown in Table 1. As can be seen from table 1, in this way it is not possible to obtain sufficiently high values of the MM of the polymerization products, although PA is more effective than ABID. The polymer yield in all cases did not exceed 10%.

Table 1. The results of the polymerization reaction ABMA depending on the ratio of amine:acid

Acid	Ratio of ABMA:acid, mol/l	$[\eta]$ dl/g, 0.1 n NaCl	Initiator
HCl	1:1	0.028	AP
	1:2	0.028	AP
	1:1	0.028	AID
HNO ₃	1:1	0.037	AP
	1:2	0.037	AP
	1:1	0.029	AID
H ₃ PO ₄	1:1	0.048	AP
	1:2	0.048	AP
	1:1	0.039	AID

However, during the polymerization of ABMA (20°C, $\lambda=360$ nm) in solutions of concentrated acids in the presence of UA and UP with a concentration of $C_{in}=4 \cdot 10^{-4}$ mol/l, water-soluble polymers were obtained with sufficiently high characteristic viscosity for a given class of compounds. The results of photopolymerization are shown in Table 2, from which it is clear that highest MM polymer values were obtained in the case of ABMA in a solution of ortho-phosphoric acid (85% aqueous solution) in the presence of UA as an initiator, and the MM value does not depend on the amine/acid ratio. The MM values of the obtained polymerization products, as well as the yield of polymers, are higher in the case of polymerization of ABMA in mineral acids than in the case of polymerization in the presence of thermal initiators (60°C). It should be noted that in the absence of an initiating system, the reaction of polymerization of ABMA in acid is not observed.

Table 2. The results of the photopolymerization reaction ABMA depending on the ratio of amine: acid at a temperature of 20°C, $\lambda=360$ nm

Acid	Ratio of ABMA:acid, mol/l	Photoinitiator	Temperature, °C	$[\eta]$, dl/l, 0.1n NaCl
HCl	1:1	UA	20	0.180
	1:2	UA	20	0.14
	1:1	UP	20	0.08
HNO ₃	1:1	UA	20	0.29
	1:2	UA	20	0.25
	1:1	UP	20	0.19
H ₃ PO ₄	1:1	UA	20	0.76
	1:2	UA	20	0.77
	1:1	UP	20	0.33
	1:1	UA	20	0.92
	1:1	UP	20	0.41

As can be seen from table 2, UA is fairly effective initiating system. It is known that salts of uranyl when absorbed by a quantum of light are restored, chemically from U^{6+} to U^{4+} . When light is absorbed, the uranyl ion goes into an excited state to form the U^{5+} product.

In this case, the radicals either die due to intracellular reactions, or dissociate with the release of the radical $R^{\cdot}$, which initiates polymerization, into the bulk [8]. Chlorine anions have a strong inhibitory effect on the rate of photochemical reduction of the uranyl ion U^{6+} to U^{4+} , nitrate anions have a weak inhibitory effect, and ortho-phosphoric acid anions do not have a marked inhibitory effect [9]. Apparently, this fact contributes to the creation of an effective system in which ABMA is capable of polymerizing with the formation of a soluble polymer in water.

Analysis of ^{13}C NMR spectrum of the polymer suggests that the polymerization proceeds through the double bonds of the formation of a diallyl groups via a cyclo linear mechanism with the formation of a polymer with a pyrrolidine structure [10–12].

Conclusions

1. Radical polymerization of AABA was carried out in solutions of mineral acids (HCl, HNO₃, H₃PO₄) using thermal initiators – PA and ABD ($C_{in}= 4 \cdot 10^{-4}$ mol/l, at 60°C). It is shown that this method fails to obtain sufficiently high MM values of polymerization products. However, during the photopolymerization of AABA ($T=20^\circ C$, $\lambda=360$ nm) in solutions of concentrated acids in the presence of photoinitiators – uranyldiaquadiacetate and uranyldipivalate with an initiator concentration of $4 \cdot 10^{-4}$ mol/l, water-soluble polymers were obtained with sufficiently high characteristic viscosity for a given amine.

2. It was established that the polymerization of AABA proceeds through the double bonds of the diallyl groups via a cyclo linear mechanism with the formation of a polymer with a pyrrolidine structure.

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N-ALKİL-N-ALLİL-N-(β-XLOR)ALLİLAMMONIUM DİHİDROFOSFATLARIN SİNTEZİ VƏ POLİMERLƏŞMƏLƏRİNİN TƏDQİQİ

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Sintez edilmiş N-alkil-N-allil-N-(β-xlor)allilaminlərin (AABA) polimerləşmə reaksiyaları mineral turşular (HCl, HNO₃, H₃PO₄) məhlullarında termiki inisiatorlar – ammonium persulfat (AP) və azobisizoyağ turşusunun dinitrilinin (ABD) iştirakı ilə aparılmışdır. AABA-nın radikal polimerləşməsi PA və ABD-dən istifadə edilməklə inisiatorun 4·10⁻⁴ mol/l qatılığı, 60°C temperaturda və 10–24 saat müddətində aparılmışdır. Göstərilən üsulla kifayət qədər yüksək molekul kütləli polimerləşmə məhsulları almaq olmur, amma AP AİD-yə nisbətən daha çox effektivdir. Lakin AABA-nın fotopolimerləşməsini (T=20°C, λ=360 nm) qatı turşu məhlullarında fotoinisiatorlar – uranil diakvadiasetat və uranil diakvadipivalat iştirakı ilə inisiatorun 4·10⁻⁴ mol/l qatılığında aparın zaman hər bir amin üçün xarakteristik özlülüyün kifayət qədər yüksək qiymətli suda həll olan polimerləri alınmışdır.

Açar sözlər: N-alkil-N-allil-N-(β-xlor)allilaminlər, mineral turşular, termiki inisiator, fotoinisiator, polimerləşmə, su, aseton.

СИНТЕЗ И ИССЛЕДОВАНИЕ ПОЛИМЕРИЗАЦИИ N-АЛКИЛ-N-АЛЛИЛ-N-(β-ХЛОР)АЛЛИЛАММОНИЙ ДИГИДРОФОСФАТОВ

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Реакции полимеризации синтезированных нами ранее N-алкил(метил, n-бутил, n-гептил, n-додецил)-N-аллил-N-(β-хлор)аллиламинов (ААБА) проводили в растворах минеральных кислот (HCl, HNO₃, H₃PO₄) в присутствии термических инициаторов – персульфата аммония (ПА) и динитрила азо-бис-изомасляной кислоты (ДАК). Радикальную полимеризацию ААБА проводили с использованием ПА и ДАК с концентрацией инициатора – 4·10⁻⁴ моль/л, температура – 60°C, продолжительность реакции – 10–24 ч. Указанным способом не удается получить достаточно высокие значения молекулярных масс продуктов полимеризации, хотя ПА является более эффективным, чем ДАК. Однако при проведении фотополимеризации ААБА (T=20°C, λ=360 nm) в растворах концентрированных кислот в присутствии фотоинициаторов – диаквадиацетата уранила и диаквадипивалата уранила с концентрацией 4·10⁻⁴ моль/л были получены водорастворимые полимеры с достаточно высокими значениями характеристической вязкости для изученного амина.

Ключевые слова: N-алкил-N-аллил-N-(β-хлор)аллиламины, минеральные кислоты, термический инициатор, фотоинициатор, полимеризация, вода, ацетон.