CHEMICALLY INITIATED EMULSION POLYMERIZATION OF METHACRYLATE ESTER WITH DIETHYLETHYNYL CARBONATE IN THE MEDIUM OF NONIONIC EMULSIFIER OP-10

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Annotation. This paper examines the chemically initiated emulsion polymerization of methacrylic acid ester with diethyl ethynyl carbonate in the presence of the nonionic emulsifier OP-10. The study focuses on the influence of emulsion polymerization conditions, emulsifier concentration, and monomer ratio on the process kinetics, emulsion stability, and the physicochemical properties of the resulting polymer dispersions. It was found that the use of the nonionic emulsifier OP-10 promotes the formation of stable emulsions and ensures uniform polymerization. The resulting polymers are characterized by satisfactory molecular weight parameters, a high degree of conversion, and improved performance properties. The results of the study demonstrate the potential of this method for the synthesis of functional polymeric materials applicable in the fields of paints and varnishes, adhesives, and special polymer systems.

Keywords: monomer, initiation, methacrylic acid chloride, heat resistance, triethylamine, gel effect, diethylethynylcarbinol methacrylic ester, emulsifier, emulsion system.

Annotatsiya. Ushbu maqolada metakril kislota efirining dietil etinil karbonat bilan OP-10 noion emulsifikatori ishtirokida kimyoviy yo'l bilan boshlangan emulsiya polimerizatsiyasi o'rganiladi. Tadqiqot emulsiya polimerizatsiyasi sharoitlari, emulsifikator konsentratsiyasi va monomer nisbatining jarayon kinetikasiga, emulsiya barqarorligiga va hosil bo'lgan polimer dispersiyalarining fizik-kimyoviy

ISSN 3030-3907

xususiyatlariga ta'siriga qaratilgan. Noion emulsifikator OP-10 dan foydalanish barqaror emulsiyalarning hosil bo'lishiga yordam berishi va bir xil polimerizatsiyani ta'minlashi aniqlangan. Olingan polimerlar qoniqarli molekulyar og'irlik parametrlari, yuqori konversiya darajasi va yaxshilangan ishlash xususiyatlari bilan ajralib turadi. Tadqiqot natijalari ushbu usulning bo'yoq va laklar, yopishtiruvchi moddalar va maxsus polimer tizimlari sohalarida qo'llaniladigan funktsional polimer materiallarini sintez qilish uchun salohiyatini namoyish etadi.

Kalit so'zlar: monomer, initsializatsiya, metakril kislota xlorid, issiqlikka chidamlilik, trietilamin, jel effekti, dietil etinil karbinolning metakril efiri, emulsifikator, emulsion sistema.

Аннотация. В данной статье исследуется процесс химически инициированной эмульсионной полимеризации эфира метакриловой кислоты с диэтилэтинилкарбонатом в присутствии неионогенного эмульгатора OP-10. Основное внимание уделено изучению влияния условий эмульсионной полимеризации, концентрации эмульгатора и соотношения мономеров на кинетику процесса, стабильность эмульсии и физико-химические свойства полученных полимерных дисперсий. Установлено, что использование неионного эмульгатора OP-10 способствует образованию устойчивых эмульсий и обеспечивает равномерное протекание полимеризации. Полученные полимеры характеризуются удовлетворительными молекулярно-массовыми показателями, высокой степенью конверсии и улучшенными эксплуатационными свойствами. Результаты исследования демонстрируют перспективность данного метода для синтеза функциональных полимерных материалов, применимых в области лакокрасочных покрытий, клеевых композиций и специальных полимерных систем.

Ключевые слова: мономер, инициирование, хлорид метакриловой кислоты, термостойкость, триэтиламин, гелеобразующий эффект, метакриловый эфир диэтилэтинилкарбинола, эмульгатор, эмульсионная система.

INTRODUCTION.

In the context of modern polymer chemistry, particular attention is being paid to the development of efficient and environmentally friendly methods for synthesizing polymeric materials with desired properties. Emulsion polymerization occupies a leading position among polymer production methods due to its high process speed, the ability to control molecular weight characteristics, and the ability to produce stable aqueous dispersions that meet the requirements of "green" chemistry.

ISSN 3030-3907

The relevance of this study stems from the need for an in-depth study of chemically initiated emulsion polymerization of methacrylic acid esters with functional comonomers, particularly diethyl ethynyl carbonate, which allows for modification of the structure and properties of the resulting polymers. The use of nonionic emulsifiers, such as OP-10, is of practical interest due to their high emulsifying capacity, thermodynamic stability, and compatibility with various monomer systems.

Studying the effect of the nonionic emulsifier OP-10 on process kinetics, emulsion stability, and the properties of the resulting polymers is relevant for expanding theoretical understanding of emulsion polymerization and for creating new functional polymer materials. The results obtained can be used in the development of modern paints and varnishes, adhesives, and other highly effective polymer systems, highlighting the scientific and practical significance of this work.

As we know, today the polymerization of vinyl monomers in an emulsifier solution is one of the most widely used methods for the synthesis of acetylene, ethylene and propylene from local raw materials of some large-tonnage polymers.

Therefore, the demand for teaching the theoretical and experimental foundations for obtaining monomers and their transformation into polymers is required.

In recent years, of considerable interest has been the study of the polymerization of vinyl monomers containing in their composition, along with a double, a triple bond.

The purpose of this work to study the patterns of chemically initiated emulsion polymerization of methacrylic acid ester with diethylethynyl carbonate in an aqueous medium in the presence of non-ionic emulsifier OP-10, as well as to study the influence of process conditions and emulsifier concentration on the kinetic parameters of polymerization, emulsion stability and physicochemical properties of the resulting polymer particles.

Analysis of literary data. Emulsion polymerization is a method for polymerizing monomers dispersed in a liquid medium, resulting in the formation of aqueous dispersed systems with particle sizes of approximately 50–300 nm. Aqueous latexes are most widely used in practice.

The kinetic properties and mechanism of homo- and copolymerization depend on the nature of the monomers, as well as on the combination of chemical reactions and physical processes accompanying the formation of latex systems.

A number of theoretical approaches have been proposed, including theories of micellar nucleation of latex particles, homogeneous aggregation, and

ISSN 3030-3907

microemulsification, which allow for the existence of several mechanisms for this process [1].

However, a rigorous and universal theory for the emulsion polymerization of monomers that are partially or highly soluble in water has not yet been developed. Elucidating the role of the aqueous phase and the reactions occurring within it in the formation of polymer-monomer particles (PMPs) remains a significant scientific challenge.

In this regard, the study of the kinetics and mechanism of emulsion polymerization of 2-ethylhexyl acrylate (2-EHA), as well as its copolymerization with water-soluble monomers, is of particular interest.

Acrylonitrile-based copolymers have found wide application in various industries due to their combination of valuable performance characteristics, including high mechanical strength, heat resistance, and resistance to chemicals. The inclusion of isohexyl methacrylate units in the macromolecular chain allows for targeted modification of the properties of the resulting materials, specifically increasing their elasticity and improving frost resistance [1].

Acrylonitrile and isohexyl methacrylate copolymers are typically produced by radical polymerization in solution or emulsion media. The composition and structure of the copolymer are determined by the ratio of the starting monomers, as well as synthesis parameters such as process temperature, initiator concentration, and other process factors.

Scientific publications describe a wide range of methods for studying AN-IGMA copolymers, including NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, and other physicochemical analytical methods [2]. The use of these approaches allows us to evaluate the composition of copolymers, their molecular weight characteristics, degree of branching and a number of other parameters.

Such an increased attention to such monomers is due, on the one hand, to their insufficient research, and secondly, in most cases, the formation of polymers from them with increased heat resistance, semiconductor, magnets, and catalytic properties [3].

As is known, the emulsion polymerization of the corresponding vinyl monomers is one of the most widely used methods for obtaining a number of large-capacity polymers. Its main advantages compared to bulk polymerization and in the presence of organic solvents are as follows: Ease, removal of reaction heat and thus prevention of local overheating, formation of polymers with increased molecular weight, wide possibilities for controlling the process rate and the properties of the resulting products.

ISSN 3030-3907

Based on this, in this work, we also studied in detail the polymerization of acetylene monomers in the presence of nonionic emulsifiers OP-10 and OS-20, as well as anionic emulsifiers E-30 and APPK [4].

The discussion of the results. When choosing these substances, first of all, they proceeded from their belonging to different classes of emulsifiers and suspenders of organic compounds, the wide availability and cheapness of chemical sensitivity, the insolubility of the aqueous medium in them of the initial monomers, the ease of purification of possible impurities and a number of other factors.

The starting monomer (MAEDEA) of methacrylic ether of diethylethynylcarbinol was obtained by direct interaction of diethyleneylcarbinol with methacrylic acid chloride in the presence of triethylamine in a sulfuric ether medium. The monomer yield, depending on the synthesis conditions, was within 60–70% of the theoretical value. After double distillation, he had the following physico-chemical parameters; Tboil=350/10 C; d20=0.9643; n=1.5537; Rnid.=46,30; Rvych.=46,41.

The resulting monomer was obtained using the IR spectrumMAEDEK, in which the absorption frequency of alkynes with low intensity for three bonds (C□C) was shown in the region of 2100-2300cm-1, by vinyl connection, 1670-1780 cm^{-1} stretching vibrations.

Based on this and in accordance with the above tasks, in this section of the work, the emulsion polymerization of the synthesized acetylene monomers (MAEDEEK) was studied in detail using OP-10 as an emulsifier (condensation product of 10^{-12} moles of ethylene oxide with a mixture of mono- and dialkylphenols with alkyl residues , containing 8-10 carbon atoms).[3].

The conditions for the polymerization of the monomers were as follows: At the beginning, the polymerization of the monomers was carried out in the presence of various amounts of APPK (0,2-2,0 wt.%). In the aqueous phase and under the following other conditions, the concentration of DAC is $11{,}6 \cdot 10^{-3}$ mol/l, temperature 343 K, ratio of monomer and aqueous phase 1:3, reaction content and duration 1-4 hours. The obtained experimental data are presented in the figures [3].

ISSN 3030-3907

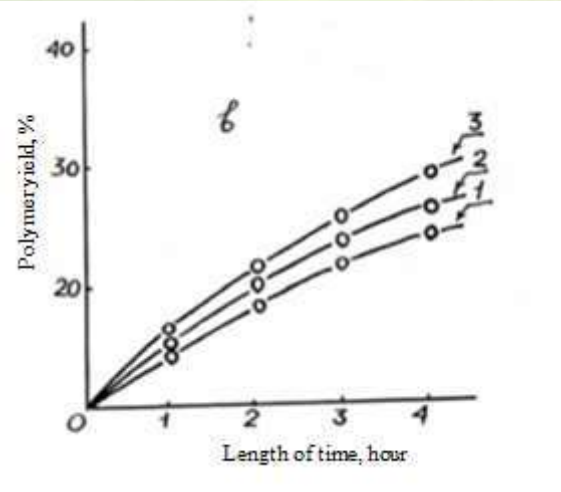


Fig.-1. Kinetics of chemical initiated emulsion polymerization of MAEDEEK at various ratios of monomer and aqueous phase: 1-1:1, 2-1:3, 3-1:5, [DAC] = 11,6 · 10^{-3} mol /l, [APPK] = 0,5 wt.%, T = 343K.

As follows from them, the polymer yield and, accordingly, the reaction rate depend little on the concentration of OP-10. This is obviously due to the sufficiency in all cases of the amount of dispersant to stabilize the monomer droplets in the aqueous phase. It should be noted that such an insignificant dependence of the rate on the concentration of water-soluble esters of mono- and dialkylphenols with alkyl residues containing 8-10 carbon atoms of emulsion polymerization of a number of other vinyl monomers [5, 6].

The observed some increase in the rate as the content of OP-10 increases, apparently, is associated with an increase in the number of monomer droplets in the aqueous phase.

At the same time, the rate of the studied processes under comparable conditions significantly exceeds that of bulk polymerization for all monomers. The reason for this, on the one hand, is due to the possibility of transferring the chain to OP-10 molecules and, as a result, obtaining from it additional initiating radicals with sufficient activity, and on the other hand, the efficiency of removing the reaction heat due to the process taking place in such a heat-consuming medium as water. , as a result, local overheating is to some extent prevented and the probability of formation of substances that inhibit polymerization is reduced.

In addition, during emulsion polymerization of the studied monomers, as in the case of other vinyl compounds, a protective layer of APPK is apparently formed first on the surface of monomer droplets and then on the surface of polymer-monomer particles, which prevents their coagulation. As a result, the rate of the chain termination reaction also decreases.

Thus, also by comparing the study of chemical initiated emulsion polymerization of acetylene monomers is described by the following equations:

ISSN 3030-3907

MAEDMEK w=[J]0.50 [APPK]0.30, MAEDEKli W=[J]0.52 [APPK]0.27, MAEMEEK w=[J]$^{0.54}$[APPK]0.26, MAEECG W=[J]0.55 [APPK] 0.23.

The emulsion polymerization of monomers, as in the case of the previous processes studied, is significantly affected by temperature. In this case, the reactions were carried out under the following conditions: temperature 333, 343 and 353 K, DAA concentration 11.6.10-3 mol/l, the ratio of monomers and the aqueous phase 1:3, the content of OP-10 0.5 wt. %. From the results obtained, it follows that with increasing temperature, in all cases, the formation of polymers increases, which is mainly due to an increase in the rate of chain initiation and growth. [8].

Based on the results obtained, E was calculated and its values for the polymerization of MAEDMEK, MAEMEEK, MAEDEEK, and MAEECG are 33.5, 32.3, 34.1, and 32.2 kJ/mol, respectively. It can be seen from the given data that the found values of E are significantly less than those of the chemically initiated polymerization of monomers in bulk, which is an advantageous advantage of carrying out the polymer formation reaction in an emulsion. In this case, one of the main reasons for the observed reduced values of E may be the difficulty of terminating growing chains due to the process occurring in microblocks stabilized by APPC.. As is known [3], as the concentration of the initiator increases, the yield of radicals from the components of the initial reaction mixture increases and, accordingly, the rate of the initiation reaction increases. In this case, obviously, on the process of initiation into succumbing under the action of the initiator, in the accumulating polymer.

It was found that the yield of the target product depends both on the temperature and on the concentration of the initiator. The rate of the process depends on the concentration of the initiator to the power of 0.56. The value of the activation energy is 32, kJ/mol.

These data indicate that the radical polymerization of MAEDEEK in an emulsion medium proceeds according to a free radical mechanism, predominantly with bimolecular termination of growing chains, the rate of chain termination reaction.

One of the important characteristics of polymers is their resistance to temperature effects (4). Based on this, the thermal stability of the synthesized polymer samples was studied in detail both in vacuum and in air at temperatures of 500 K and a heating duration of up to 10 hours. As can be seen from them, the samples synthesized in the emulsion turned out to be more thermally stable than those in the presence of organic solvents. This, obviously, is associated with a lower MW of polymers, in the second case, due to the significant chain termination both

ISSN 3030-3907

by periradicals from the solvent and as a result of chain transfer to its molecules. [5,6,7].

CONCLUSIONS

It was established that chemically initiated emulsion polymerization of methacrylic acid ester with diethyl ethynyl carbonate in the presence of the non-ionic emulsifier OP-10 proceeds effectively, forming stable polymer dispersions.

2. It was shown that the use of the non-ionic emulsifier OP-10 ensures high stability of the emulsion system, uniform distribution of monomer particles, and prevents their coagulation during polymerization.

3. The influence of emulsifier concentration and monomer ratio on the kinetic parameters of the process, degree of conversion, and molecular weight characteristics of the synthesized polymers was determined.

4. The resulting polymers are characterized by a sufficiently high degree of polymerization and satisfactory physicochemical and performance properties, confirming the effectiveness of the chosen synthesis method.

5. The results of the study confirm the potential of chemically initiated emulsion polymerization using OP-10 for obtaining functional polymeric materials suitable for practical application in the paint, varnish, adhesive and other branches of the polymer industry.

Spectral data also show that polymerization proceeds mainly due to the double bond of the monomer. The study of the solubility, density, thermal and heat resistance of the obtained polymers showed that these properties of poly-MAEDEA depend on the conditions of its synthesis.

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