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CHEMICALLY INITIATED EMULSION POLYMERIZATION OF METHACRYLIC ACID ESTER WITH DIETHYLETHYNYL CARBONATE USING NONIONIC SURFACTANT OP-10

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ABSTRACT	KEYWORDS
This article discusses the process of chemically initiated emulsion polymerization of methacrylic acid ester with diethylethynyl carbonate in an aqueous medium using the nonionic emulsifier OP-10. The features of the polymerization reaction, the effect of component concentration and synthesis conditions on the stability of the resulting emulsion, particle size and molecular characteristics of the polymer are studied. The data obtained indicate the high efficiency of OP-10 as an emulsifier, providing system homogeneity and latex stability. The results can be used in the development of new polymeric materials with specified physicochemical properties. The regularity of radical chemical initiation of emulsion polymerization of diethylethynylcarbinol methacrylic ether in the presence of APPK, OP-10, OS-10E-30 dispersant was studied.	Monomer, initiation, methacrylic acid chloride, heat resistance, triethylamine, gel effect, diethylethynylcarbinol methacrylic ester, emulsifier, emulsion system.

Introduction

It is well known that today the polymerization of vinyl monomers in the presence of emulsifiers is among the most commonly applied techniques for synthesizing high-tonnage polymers such as acetylene, ethylene, and propylene from locally sourced raw materials. [9].

Consequently, there is a growing need to teach both the theoretical and practical aspects of monomer synthesis and their subsequent polymerization. In recent years, significant attention has been directed toward the polymerization of vinyl monomers that contain not only double bonds but also triple bonds in their structure.

This heightened interest is primarily attributed to two factors: first, the limited extent of research on such monomers, and second, their ability—upon polymerization—to yield materials with enhanced thermal stability, semiconducting behavior, magnetic properties, and catalytic activity [1].

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.

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 [2].

Emulsion polymerization is a distinct chemical technique commonly employed to synthesize water-based resins that exhibit a range of colloidal and physicochemical characteristics. This type of heterogeneous free-radical polymerization involves dispersing hydrophobic monomers into water using oil-in-water emulsifiers. The polymerization is initiated by either water-insoluble initiators like sodium persulfate (NaPS) or oil-soluble ones such as 2,2′-azobisisobutyronitrile (AIBN) [3].

Frequently utilized monomers in this process include butadiene, styrene, acrylonitrile, acrylates, methacrylates, vinyl acetate, and vinyl chloride. As the polymerization advances, particle nuclei form and expand, resulting in a vast oil–water interfacial area. To stabilize these growing latex particles and prevent coagulation, effective stabilizing agents are necessary—such as ionic or non-ionic surfactants and protective colloids like hydroxyethyl cellulose and polyvinyl alcohol, which may adsorb onto or chemically bond with particle surfaces.

Colloidal stability is ensured through electrostatic stabilization, steric stabilization [4, 5], or a combination of both mechanisms. The resulting eco-friendly latex dispersions consist of numerous polymer particles (approximately 10–300 nm in diameter) suspended in water. These emulsion polymers are utilized in a broad spectrum of applications, including synthetic rubbers, thermoplastics, coatings, adhesives, binders, rheology modifiers, plastic pigments, calibration standards, immunodiagnostic assays, protein purification media, and drug delivery systems. A deep understanding of polymerization kinetics and mechanisms is essential for developing high-performance products tailored to specific requirements.

Emulsion polymerization is a highly intricate process due to the interplay between free radical polymerization mechanisms and various colloidal interactions that govern the nucleation, growth, and stabilization of polymer particles. One of the most notable aspects of this method is the confinement of free radicals within individual monomer-swollen polymer particles. This spatial separation significantly decreases the likelihood of bimolecular termination reactions, thereby enhancing the polymerization rate and yielding polymers with higher molecular weights—an advantage not attainable in bulk or solution polymerization.

Although the nucleation phase is brief, the formation of initial particle nuclei during the early stages of polymerization is critical, as it largely determines the ultimate size and size distribution of latex particles, and directly impacts the quality of the resulting latex. Controlling this nucleation step remains a complex and demanding challenge for researchers in the field.

The growth of polymer particles is influenced by the transport and distribution of monomers, free radicals, and surfactants among various domains: the aqueous phase, emulsified monomer droplets (acting as monomer reservoirs), monomer-swollen polymer particles (where the primary reaction occurs), and the oil–water interface. These transport processes are crucial in determining the dynamics of particle growth.

From both scientific and industrial perspectives, the colloidal characteristics of latexes are of paramount importance. Key properties include particle size and size distribution, surface charge density (zeta potential), surface coverage by stabilizing molecules, the structure of hydrophilic polymers adsorbed or chemically attached to particle surfaces, the type and concentration of surface functional groups, particle morphology, as well as the optical, rheological, and overall colloidal stability of the dispersion.

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, 1670-1780cm-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).[6].

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. 10-3 mol/l, temperature 343K, ratio of monomer and aqueous phase 1:3, reaction content and duration 1-4 hours. The obtained experimental data are presented in the figures [1].

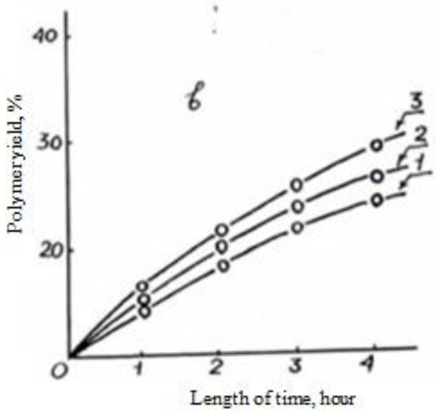

Fig.-1. Kinetics of chemical initiated emulsion polymerization of MAEDEEK at various ratios of monomer and aqueous phase: 1-1:1, 2-1:3, 3-1:5, [DAC] = 11.6 * 10-3 mol /l, [APPK] = 0.5 wt.%, T = 343K.

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 [6, 7].

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:

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. [8,9].

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

Conclusions

The conducted studies have shown that chemically initiated emulsion polymerization of methacrylic acid ester in the presence of diethylethynyl carbonate and nonionic emulsifier OP-10 is an effective method for obtaining stable polymer dispersions with specified colloidal and molecular characteristics. It was found that the use of OP-10 promotes the formation of a finely dispersed system and provides a high degree of stabilization of latex particles due to steric protection. The introduction of diethylethynyl carbonate as a co-initiating agent has a positive effect on the polymerization rate and the molecular weight of the resulting polymer. The obtained results confirm the prospects of this system for the development of environmentally friendly aqueous polymeric materials applicable in the production of coatings, adhesives and other functional products. 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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