



RADIATION SUSPENSION POLYMERIZATION OF ACETYLENE MONOMERS

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Abstract.

The regularity of the chemical initiation of ethacididimethylethyl ethynylate polymerization in the presence of solvents such as n-heptane and n-dioxane was studied. A uniform decrease in the relative velocity (W_s/W_m) of the studied processes with an increase in the solvent fraction is shown, which indicates the identity of the mechanism of their occurrence.

Keywords:

Monomer, initiation, itaconic acid acid chloride, thermal stability, triethylamine, gel effect.



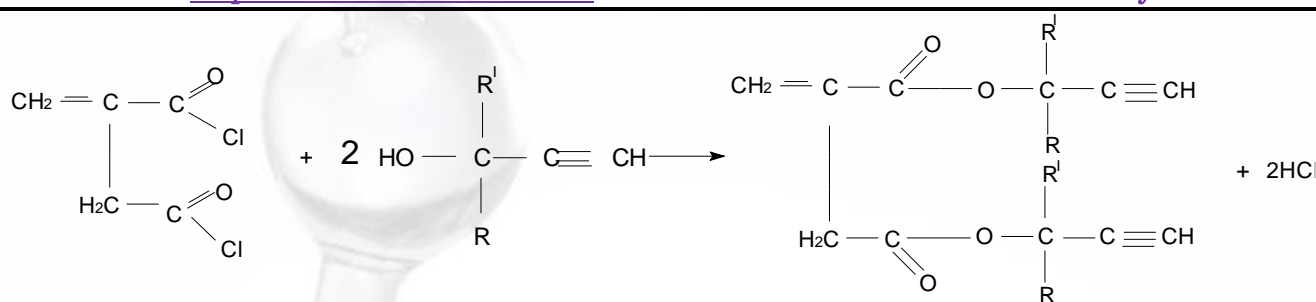
In recent years, various aspects of the polymerization and copolymerization of acetylene monomers containing both double and triple bonds in their molecules have been very intensively studied. Such increased attention to them is primarily due to the possibility of obtaining, on their basis, polyconjugated polymer products with dielectric and magnetic properties, increased thermal stability, and a number of other valuable physicochemical properties [1].

Acetylene monomers have also found some application as compressing agents in the process of improving the operational properties of some large-tonnage polymers, in the study of ion-exchange materials, complexing agents and catalysts [2].

The polymerization and copolymerization of acetylenic monomers can be carried out by various methods, but the most common is their chemical initiation. Moreover, these processes and they are carried out mainly on the double bonds of monomers, while their throne $-C\equiv C-$ bond, basically, does not participate in the reaction because of its known resistance to radical influences [2,3].

Methods for the synthesis of itaconic esters of acetylenic alcohols and diol. The synthesis of this kind of esters can be carried out in two ways: using the most unsaturated organic acid or its halogen anhydride, in particular chlorine anhydride. Carrying out the reaction of itaconic acid with AC and AD did not give the expected results and the ester yield did not exceed 5-8%. The use of itaconic acid chlorine anhydride turned out to be more effective when it interacts with AC in the presence of triethylamine (5,4).

The reaction proceeds according to the scheme:

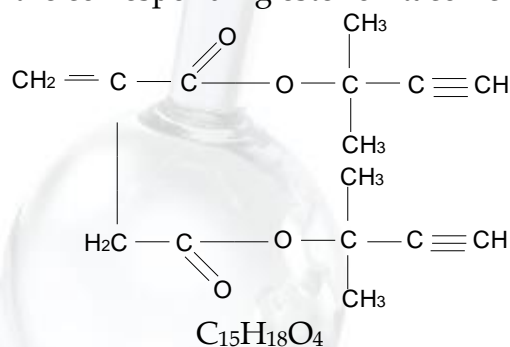


Где, R = -CH₃, R^I = -CH₃ (I), R = -CH₃, R^I = -C₂H₅ (II), R + R^I = C₃H₇,

R = -CH₃, R^I = -C₃H₇ (III), R = -CH₃, R^I = -CH₃ (IV),

General procedure: In a three-headed flask equipped with a reflux condenser, a mechanical stirrer and a dropping funnel, 2 mol of AC and 1.67 mol of triethylamine in 200 ml of absolute diethyl ether were introduced. The mixture was heated to reflux, then cooled to room temperature, and 1.58 mol of chloroanhydriditaconic acid was added with stirring over 1 hour from a dropping funnel. The ether layer was separated, and the residue was extracted with a 10% solution of sulfuric ether in 50 ml portions until the extracts ceased to become cloudy when alkalized with 5% soda solution and left overnight. Sulfur ester was distilled off, and the residue was distilled in vacuum to obtain the corresponding ester of itaconic acid. [1]

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In the IR spectrum of diacetklopovat ester of itaconic acid, an absorption band is found characteristic of valence bond-C≡C-bonds in the region of 2140 cm⁻¹, the band at 3220 cm⁻¹ is due to the stretching vibration of the ≡CH bond, and in the regions of 1645 and 1730 cm⁻¹ by vibrations -C=C- and -C(O)- bonds, respectively, with vibrations of characteristic bonds not detected.

Investigation of the process of polymerization of synthesized new monomers in bulk in the presence of the radiation initiator Co60, was carried out at a temperature of 343 K, various concentrations of the initiator, 30 r / sec, 70 r / sec and 120 r / sec were carried out at a temperature of 343 K, and the reaction duration was 1-4 hours. Moreover, in all cases, the resulting polymers, due to their solubility in their monomers, are glassy products, i.e. the polymerization of the studied esters proceeds similarly to that of conventional acrylic monomers. [1,2,3]

The kinetic curves built on the basis of the result have the usual form, characteristic of homophase radical polymerization of most vinyl monomers (Figure-1). The logarithmic dependences of the initial rate of polymerization of acetylenic monomer on the concentration of the initiator of radiation in all cases are straightforward (Figure-2). According to their slope, the

values are found and they are equal to 0.56, respectively, which indicates the course of these reactions by the free radical mechanism, mainly, with bimolecular termination of growing targets. The observed some overestimation of the values and from its theoretical value (0.50), obviously, is due to an increase in the viscosity of the system with the conversion of the monomer and, as a consequence, the rate of chain growth is somewhat hampered.

It should be noted that with an increase in the concentration of the initiator in the reaction system in all cases, the rate of polymerization is the initiation. With an increase in the polymerization time, initially, the polymer yield generally increases. However, at the end of the process, a slowdown in the formation of polymers is observed due to a decrease in the monomer concentration in the reaction system.

It can be seen from the obtained experimental data that for all studied systems, regardless of the type of monomer and solvent, the polymer yield and, accordingly, the rate of the process are increased by an increase in radiation in the initial reaction system, which is due to an increase in the yield of initiating radicals. In this case, the kinetic curves for the polymerization of all monomers have the usual form, characteristic for the course of reactions in the homogeneous phase.

Thus, the above established patterns of the effect of the concentration of the solvent and initiator on the rate of polymerization of acetylenic monomers are described by the following kinetic equations in each case:

	Н-гептане	вп-диоксаниев ЧХУ
1. ИЭДМЭК	$w = K[J]^{0.58} \cdot [M]^{1.18}$	$w = K[J]^{0.56} \cdot [M]^{1.35}$
2. ИЭМЭЭК	$w = K[J]^{0.59} \cdot [M]^{1.20}$	$w = K[J]^{1.58} \cdot [M]^{1.32}$
3. ИЭМПЭК	$w = K[J]^{1.56} \cdot [M]^{1.21}$	$w = K[J]^{1.59} \cdot [M]^{1.30}$
4. ИЭЭЦГ	$w = K[J]^{1.60} \cdot [M]^{1.23}$	$w = K[J]^{1.60} \cdot [M]^{1.22}$

The chemical polymerization of the obtained acetylenic monomers in bulk and in the medium of some organic compounds has been systematically studied. It is shown that these processes are carried out in homogeneous conditions due to the dissolution of the synthesized numbers in their monomers and the use of solvents. In this case, glassy products are formed in all cases.

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