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Synthesis and Mechanism of the Preparation of Polymeric Cationic Surface-Active Substances

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Abstract

In this paper, we for the first time for the preparation of cationic high-molecular surface-active substances (HM CSAS) with set properties developed the new ways of the complex-radical polymerization, activated by donor-acceptor interaction of cationic low-molecular surface-active substances (LM CSAS) with the acceptors of electrons - initiators of polymerization at the temperatures excluding thermal disintegration of the initiators. With application of UV-, IR-, EPR-spectroscopic methods of the research the objective laws of formation of the complex «LM CSAS - the initiator» have been established. The possible variant of the interaction of LM CSAS with peroxide was offered and the probable nature of the active centre, initiating the process of the complex - radical polymerization at moderate temperatures (room and lower) established.

Keywords: polymerization, radical, surface-active substances

Introduction

Studying the mechanism and kinetic laws of the synthesis of high-molecular surface-active substances (HM CSAS) on the basis of nitrogen - and haloid containing of low-molecular surface-active substances LM CSAS represents theoretical significance[1-3]. The properties of HM CSAS are defined by the method of their synthesis, as they are connected with the features of kinetic laws of the process and reactions mechanism[4,5]. In this connection there was a necessity for synthesis and application of such CSAS, which at the minimum concentration could provide with modified fibres demanding physical-chemical and physical-mechanical properties.

These reasons have been taken as a principle of choice CSAS to modify fibres and directed change of their complex of valuable properties. Studying the action mechanism and a role of SAS properties and their solutions has facilitated the decision of a question of their effective application for modification of fibres properties that has allowed to prove and develop the ways of increasing the CSAS efficiency. It was established that quaternary ammonium bases are the most interesting for investigation and perspective for using as modifiers of fibres of SAS class.

On the basis of the above-stated, the synthesis of LM CSAS on the base of nitrogen containing compounds with haloid containing substances discoloses wide opportunities for preparation on their basis HM CSAS with demanded structure, a structure of macromolecules, value of molecular weight, and consequently, with in advance set properties[6-10].

Materials and Methods

LM CSAS -β-methacryloilethyl-N,N-dimethylallylammoniiumbromide and β-methacryloilethyl-N,N-dimethyl-methylenecarboxyiammoniumiodide; initiators: potassium persulfate, benzoyl peroxide (BP) and dinitrilazobisizooil acids (DAA).

Methods IR-, UV-, EPR-spectroscopy.

Results and Discussion

Synthesis of LM CSAS (β -methacryloilethyl-N,N-dimethylallylammoniumbromide, β-methacryloilethyl-N,N-diethylallylammoniumjbromide, β-methacryloilethyl-N,N-dimethyl-methylenecarboxyammonium-iodide, β-methacryloilethyl-N,N-diethylmethylenecarboxyammoniumiodid, β-methacryloilethyl - N,N - dimethylpropylammoniumbromide, β-methacryloilethyl - N,N - diethylpropyl-ammoniumbromide, β-methacryloilethyl-N,N-dimethyilisopropyiloxy-ammoniumchloride, β-methacryloil-ethyl -N,N - diethyilisopropyloxyammoniumchloride, β - meth – acryloilethyl - N,N - dimethylisopropyl-oxyammoniumbromide, β-methacryloilethyl-N,N-diethyl-isopropyloxyammoniumbromide) and based on them the synthesis of HM CSAS with preservation of composition and their structure in an elementary link of macromolecules on the donor-acceptor mechanism by initiation complex radical polymerization[6-10] has been carried out.

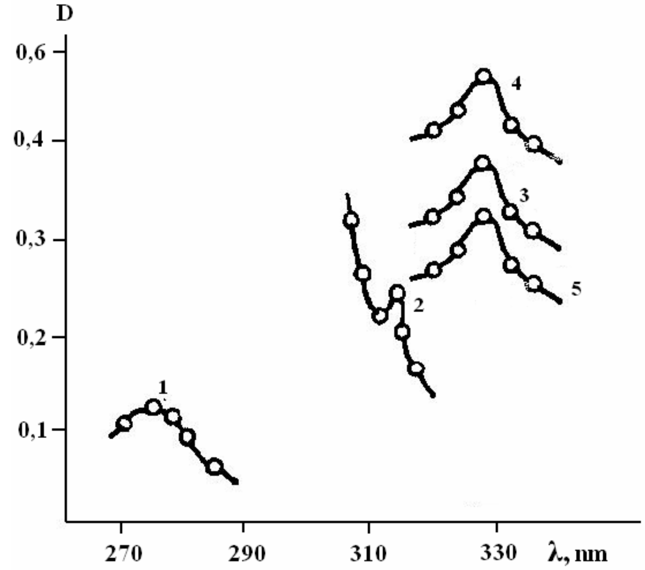


Fig. 1. Electronic UV- spectra of aqueous solutions at 293 K.

1 - potassium persulfate initiator; 2 - monomeric salt β- metakryloilethyl-N, N-dimethylallylammoniumbromide; 3- monomer salt + initiator, immediately after the fusion of their solutions; 4 – in 0.5 hours after the fusion of the solutions; 5 – in 1.5 hours after the fusion of the solutions.

For the direct proof of the formation of complex compounds in the reaction medium and the establishment of donor-acceptor character of the interaction of LM CSAS with radical initiators UV-spectroscopy method (fig. 1) has been used. The formation of the complex compounds in the reaction medium, and the study of the donor-acceptor interaction of CSAS with radical initiators the method of UV-spectroscopy was used in the wavelength range 220-500 nm. As a result, the appearance of a new absorption band shifted to longer wavelengths field compared with the absorption bands of the starting components was established. In the electronic spectra observed the appearance of new absorption bands with λ = 328 nm (fig. 1), absent in the absorption spectra of the individual components has been observed. The influence of LM CSAS on comlex formation process with potassium persulfate was established by studying colloidal-chemical properties of their aqueous solutions, which have micellar structure (critical concentration of mycellar formation is equal to 0,01 %) and possess solubilization action. The confirmation of the radical character of polymerization of the monomeric CSAS flowing at a donor-acceptor mechanism of initiation in the conditions of complex-radical polymerization is the inhibition of this process by the inhibitors of radical reactions: hydroquinone, air oxygen, diphenylpicrylhydrazyl and etc. The radicals themselves were indirectly recorded by EPR-spectra that were photographed in radiospectrometer RE-1301 in the presence of a radical "trap" of diphenylpicrylhydrazyl (Fig. 2).

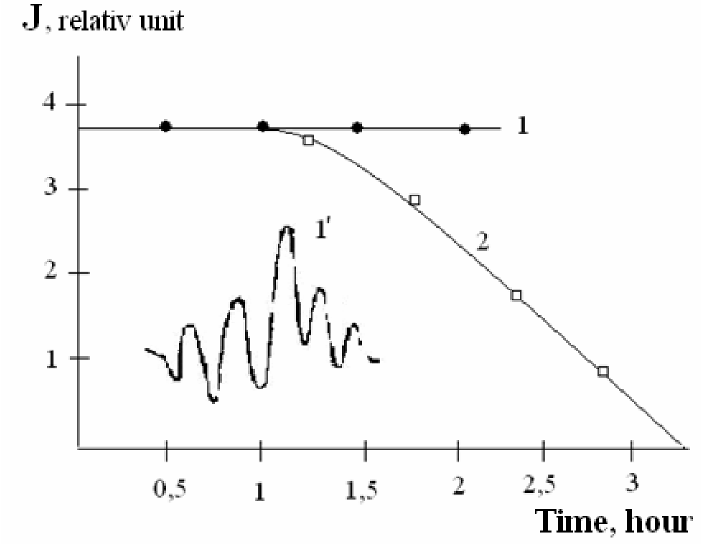
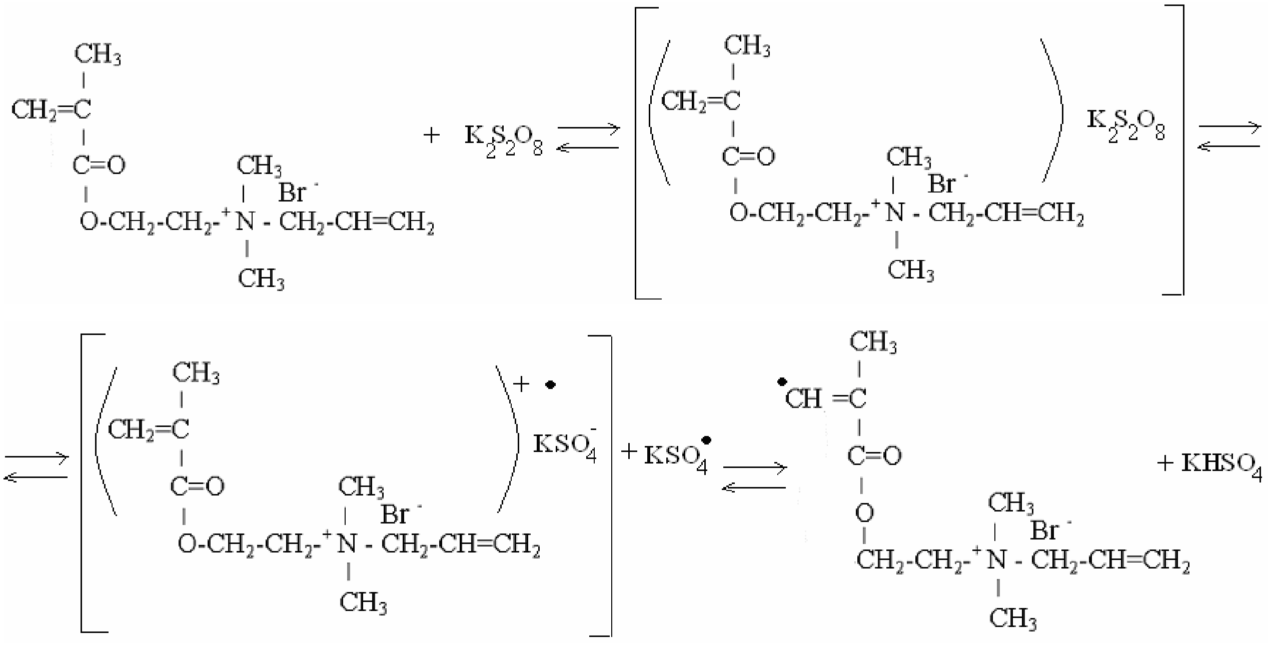


Fig. 2. The intensity change (J) of EPR signal at 293 K in a medium of dimethylformamide mol/l: β-methakryloilethyl-N, N--dimethylallylammoniumbromide = 3,5; potassium persulfate = 0,07. Diphenylpicrylhydrazyl-1; 1'-diphenylpicrylhydrazyl in dimethylformamide; 2-diphenylpicrylhydrazyl-β-methakryloilethyl-N, N-dimethyl-allylammoniumbromide + potassium persulfate.

It is experimentally established that LM CSAS on the basis of β-methacryloilethyl-N,N-dimethylallylammoniumbromide (MEDAAB) are polymerized in the presence of the initiator – potassium persulfate in aqueous medium. It was determined that the reaction order on a monomer (0,5-2,0 mol/l) and initiator ($1,10^{-3} \div 5\cdot10^{-3}$ mol/l), which has appeared equal to 1,48 and 0,5 respectively. The overestimated value of the reaction order on a monomer, in comparison with theoretical, which is equal to 1,0, specifies its participation not only in the reaction of chain growth, but also in the reaction of formation of the molecular complex, disintegration of which leads to the formation of initiating centres. The polymerization rate grows with the temperature and its dependence on reverse value of the temperature (in an interval of 283-298K) submits to Arrenius equation. The activation energy makes 53,7 kdj/mol.

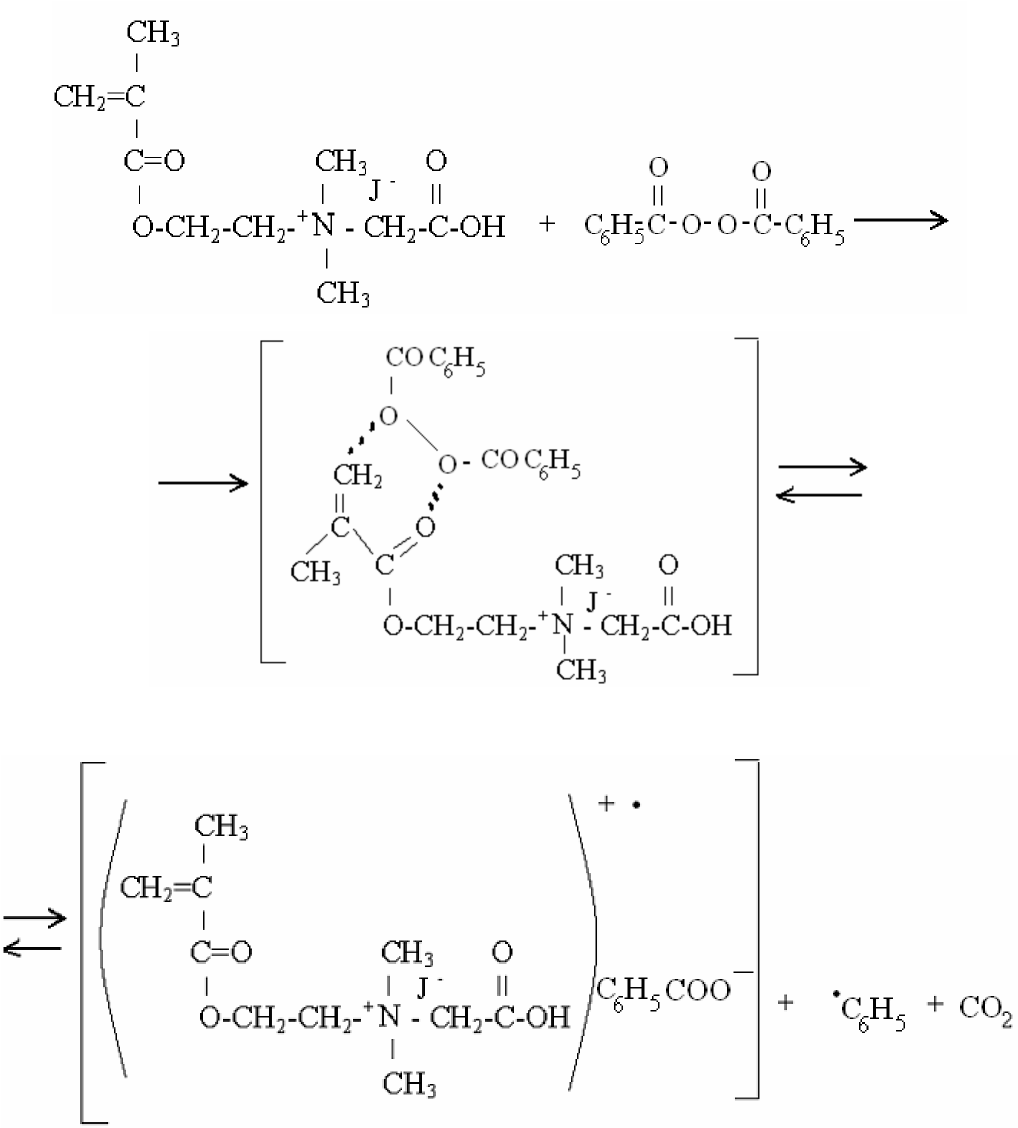
In the IR-spectra the valent vibrations of -CH$_2$ -CH = CH- groups were observed and in a monomer, and in high molecular CSAS in 1620 cm^{-1}. Polymerization took place, apparently due to the opening of double bonds of the methacrylate groups, since the absorption bands of the -C=C- groups at 1640 cm^{-1} are absent.

On the basis of data of UV-, IR-, EPR- spectroscopy and kinetic studies on the example of polymerisation of β-methacryloilethyl-N,N- dimethylallylammoniumbromide with potassium persulfate it is possible to present the reaction of their interaction by the most probable following scheme:



The role of the initiating center in the process of complex-radical polymerisation can play probably, as KSO$_4^{\bullet}$, and «monomer» radical.

The reaction of complex formations of LM CSAS and PB, disintegration with carrying electron over and formation of a free radical it is possible to present by the following scheme of 1,4-donor-acceptor of cyclic interaction:



Formed free benzoat radical can cause the complex-radical polymerization of LM CSAS at the lowered temperature.

Conclusions

For the first time for the preparation of cationic HM CSAS with set properties were developed the new ways of the complex-radical polymerization, activated by donor-acceptor interaction of cationic LM CSAS with the acceptors of electrons - initiators of polymerization at the temperatures excluding thermal disintegration of the initiators. With application of UV-, IR-, EPR-spectroscopic methods of the research the objective laws of formation of the complex «LM CSAS - the initiator» have been established, thermodynamic parameters and optimal conditions of the reaction of complex-formation determined. The possible variant of the interaction of LM CSAS with peroxide was offered and the probable nature of the active centre, initiating the process of the complex - radical polymerization at moderate temperatures (room and lower) established. It is shown that the participation of polymerizing LM CSAS in initiation act allows formation of macromolecules with the formation of HM CSAS with the stereoregular structure, containing quaternary ammonium bases.

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