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# KINETICS OF GRAFT POLYMERIZATION OF METHYL ACRYLATE ONTO HYDROXYETHYL- AND CARBOXYMETHYL CELLULOSE

## Abstract

An influence of the process condition on the grafting efficiency and molecular mass of the acrylic chains of graft copolymers of poly(methyl acrylate) with hydroxyethyl and carboxymethyl cellulose (HEC and CMC) has been studied.

The kinetics of graft polymerization of methyl acrylate onto hydroxyethyl and carboxymethyl cellulose initiated by peroxydisulfate ion in the wide region of reagent concentrations has been investigated. The reaction order with respect to the monomer is about 1, to peroxydisulfate ion and initial polymer is about zero for polymerization and grafting of methyl acrylate onto CMC and HEC. Effective activation energies are 102 and 110 kJ/mol for HEC and 78 and 80 kJ/mol for CMC in these reactions respectively.

The kinetics of the peroxydisulfate ion decomposition and the change of molecular mass of HEC and CMC in their water solutions has been investigated. The reaction order with respect to peroxydisulfate is about 1 and with respect to cellulose derivatives changes from 0.3 to zero when the cellulose ether concentration increases in the reaction of peroxydisulfate decomposition. It has been showed that the process of polymer destruction and formation of cross-linked cellulose derivatives proceeds in their water solutions in the presence of peroxydisulfate.

Graft polymerization of monomers is one of the universal and effective methods of chemical modification of polymers, natural ones in particular.

Graft copolymers of vinyl monomers and water soluble derivatives of cellulose can be obtained in a form of stable water dispersions or solutions suitable for direct applications. That gives a possibility to use them as stabilizers of emulsions and dispersions. For example, grafting of methyl acrylate onto methyl or hydroxyethyl cellulose with following hydrolysis of grafted chains gives stable products.Their emulsifying power is greater by several folds than one for bacbone cellulose ethers (Table 1).

Amphiphilio graft copolymers can reduce the adsorption strength of metals due to the Rebinder effect. Therefore they can be used as metal-cutting fluids at metal machining (Table 2). The wear of a cutting tool is significantly reduced and the surface

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quality rises at application of metal-working fluid on a base of graft copolymer of methyl methacrylate with HEC.

Amphiphilic nature of graft copolymers causes the fact that their water dispersions create films insoluble neither in water nor in organic solvents. It allows us to use them as film former. For instaance, dispersions of graft copolymers of fluor-containing monomers and carboxymethyl cellulose are good for fabrio finishing. In paarticular, graft copolymer of perfluoro-heptyl acrylate and carboxymethyl cellulose gives to a fabrio oil- and dirt-repulsive properties. Herewith the fabrios feep them even after 10 washing (Table 3).

Table 1

Emulsifying ability of cellulose ethers and their graaft copolymers

| Specimen | T, °C | Time of half – separation, s |
|---|---|---|
| Methyl cellulose | 20 | 9,8 |
| | 50 | emulsion is not formed |
| Graft copolymer of PMA with MC | 20 | 7200 |
| | 50 | 5400 |
| Hydroxyethyl cellulose | 20 | 25 |
| | 70 | emulsion is not formed |
| Graft copolymer of PMA with HEC | 20 | > 10 000 |
| | 70 | < 10 000 |

Table 2

Effect of metal-working fluid on wear of drills (steel P6M5), diameter 9.2 mm) at drilling of steel X12M. Angle rate of drilling is 59 rad/s, feed is 0.022 mm/rad (regime 1) and 0,03 mm/rad (regime 2)

| Metal-working fluid | Durability of instrument under wear, s | | Wear on back surface, m | | Surface quality, class | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 1 | 2 | 1 | 2 |
| Emulsol | 720 | 240 | 0.8 | 1.1 | 3 | 3 |
| Graft copolymer of poly (methyl Methacrylate) with | | | | | | |
| CMC | 5160 | 2280 | 0.7 | 0.7 | 4 | 4 |
| HEC | 4980 | 2160 | 0.7 | 0.7 | 4 | 4 |

Table 3

Change of properties of a fabrio treated with graft copolymer of PFHA with CMC

| Property | Change of properties after washing | | |
|---|---|---|---|
| | 0 | 5 | 10 |
| Oil resistance | 130 | 110 | 90 |
| Quality of washing, % | 94 | 89 | 87 |
| Water absorption, % | 119 | – | – |

## Experimental part

Methyl acrylate was purified by a method presented in Ref. [1] and rectified. Ammonium peroxydisulfate was recrystallized twice from water. HEC with the polymerization degree of 812 and ethylene oxide content of 32%, Na-CMC with molecular mass $3.64 \cdot 10^4$ and the substitution degree of 0.74 was used. The Process was carried out in a glass vessel under argon atmosphere at 55–75°C. Concentration of monomer was 0.12–0.98 mol/l, ammonium peroxydisulfate was 2.2–8.8 mmol/l, and cellulose ether was 5–20 g/l. The monomer conversion, S, in the samples determined by a gravimetrio method. The grafting efficiency, $\delta$, was determined by complete extraction of methyl acrylate homopolymer with acetone in Soxhlet extraction apparatus.

Formation of graft copolymers of poly(methyl acrylate) with cellulose ethers was confirmed by IR-spectroscopy investigation of products of graft polymerization (after complete extraction of methyl acrylate homopolymer by acetone and unmodified cellulose ether by water). The absorption bands of cellulose ethers (1068, 1026, 885 $cm^{-1}$) and of poly (methyl acrylate) (1732, 1160, 1198, 1256, 826 $cm^{-1}$) were bound in the products after extraction.

## Results and discussion

The investigation of an influence of the process condition on the properties of graft copolymers of poly(methyl acrylate) with hydroxyethyl- and carboxymethyl cellulose showed (Table 4), that the monomer conversion increased, grafting efficiency as well as molecular mass of polyacrylic chains decreased when the monomer/cellulose derivative ratio, initiator concentration and temperature increased. The grafting degree (GD) for all samples is high enough.

Kinetics and mechanism of monomer graft polymerization onto cellulose ethers were investigated to find optimum conditions for copolymer preparation.

The monomer conversion, determining the general polymerization rate of methyl acrylate in the presence of HEC or CMC, and its product by the grafting efficiency, $S\delta$

(characterising the strict grafting) change proportionally to time at the initial stage of kinetic curves (Fig. 1, 2). An increase in concentrations of a backbone polymer, potassium peroxydisulfate does not depend on the process rate. An increase of temperature carries out to the rise reaction rate. It is worth noting that the rates of the general polymerization process and of strict grafting of MA onto CMC and HEC are close to each other. It is evidence on the faint influence of the nature of a backbone polymer onto the reaction kinetics.

Table 4

Chemical properties of graft copolymers of poly (methyl acrylate) with hydroxyethyl cellulose

| [MA]/[HEC] by mass | $[S_2O_3^{2-}]$, % of mass HEC | T, °C | S, % | GD, % | δ, % | M.$10^{-5}$ |
|---|---|---|---|---|---|---|
| 2.0 | 10 | 30 | 94 | 160 | 85 | 2.43 |
| 2.0 | 10 | 40 | 94 | 151 | 81 | 2.28 |
| 2.0 | 10 | 50 | 95 | 124 | 65 | 2.00 |
| 2.0 | 10 | 60 | 95 | 118 | 62 | 1.66 |
| 2.0 | 10 | 70 | 96 | 114 | 60 | 1.39 |
| 2.0 | 2.5 | 60 | 151 | 151 | 99 | – |
| 2.0 | 5 | 60 | 137 | 137 | 76 | 1.66 |
| 2.0 | 10 | 60 | 118 | 118 | 62 | 1.47 |
| 2.0 | 20 | 60 | 89 | 89 | 47 | 1.33 |
| 1.0 | 10 | 60 | 92 | 92 | 99 | - |
| 2.0 | 10 | 60 | 118 | 118 | 62 | 1.66 |
| 3.0 | 10 | 60 | 112 | 112 | 39 | 2.86 |
| 4.0 | 10 | 60 | 124 | 124 | 32 | 3.94 |
| 6.0 | 10 | 60 | 136 | 136 | 23 | 4.75 |

The reaction order, calculated from the initial rates, is close to 1 with respect to monomer and to zero with respect to initiator and backbone polymer for the general polymerization process and strict grafting of MA onto HEC and CMC. Effective activation energies are 102 ±12 and 110±14 kJ/mol for the MA – HEC system, as well as 78±10 and 80±10 kJ/mol for the MA – CMC system (for the general polymerization process and strict grafting respectively). One should notice that the values of activation energy are close to each other for the general polymerization process and strict grafting.

Interaction of peroxydisulfate with polysaccharides proceeds by radical chain mechanism, to which a reaction rate decrease testifies when radical inhibitors are introduced. Initiation of this processs takes place only trough peroxydisulfate ion homolysis. The reaction rate increases when the hydroxyethyl cellulose concentration grows to

10 g/l then it reachess constaant value (Fig. 3). The rate of peroxydisulfate decomposition is less in CMC solution. The presence of carboxyle groups in the polymer macromolecule considerably decreases peroxydisulfate decomposition rate.

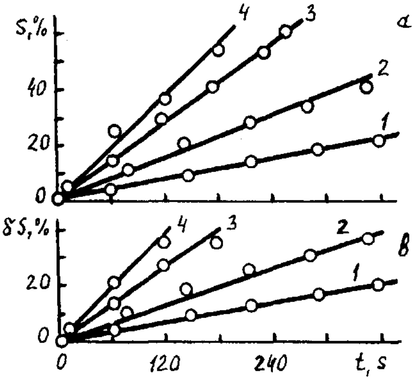

Fig. 1. Change of monomer conversion (a) and of Sδ (b) in time for methyl acrylate grafting onto HEC. The initial concentration of monomer is 0.23 mol/l, HEC 20 g/l, ammonium peroxydisulfate 4.4. mmol/l, and temperature 55 (1), 60 (2) 65 (3) and 70° C (4).

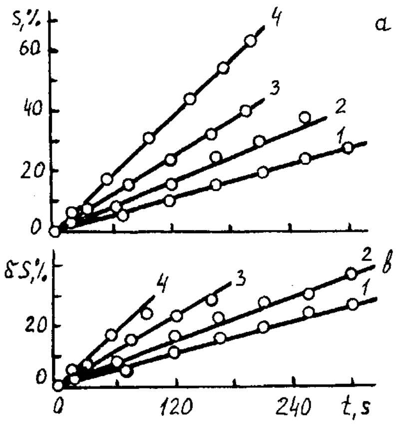

Fig. 2. Change of monomer conversion (a) and of Sδ (b) in time for methyl acrylate grafting onto CMC. The initial concentration of monomer is 0.23 mol/l, CMC 20 g/l, ammonium peroxydisulfate 4.4 mmol/l, and temperature 55 (1), 60 (2), 65 (3) and 70°C (4).

The reaction order, calculated from the initial rates, is close to 1 with respect to peroxydisulfate and changes from 0.3 (when hydroxyethyl cellulose concentration is less than 10 g/l) to zero (at the higher concentrations) with respect to hydroxyethyl cellulose. The reaction order with respect to carboxymethyl cellulose is about zero in the whole range of concentrations. Effective activation energies are 87±4 and 129±8 kJ/mol for peroxydisulfate decomposition in the presence of hydroxyethyl and carboxymethyl cellulose respectively.

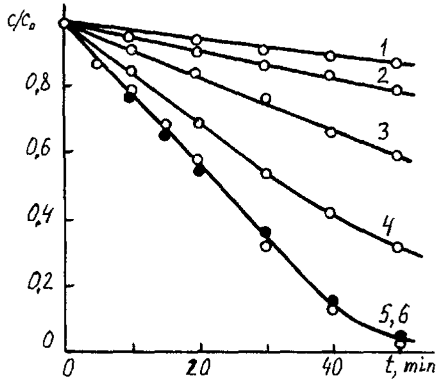

Fig. 3. Kinetic curves of ammonium peroxydisulfate decompossition in water (1) and in the presense of hydroxyethyl cellulose at initial concentration of peroxydisulfate 4.4 mmol/l, temperature 70°C and hydroxyethyl cellulose concentration 0.001 (1), 0.01 (2), 0.1 (3), 1 (4) and 3% (5).

It is necessary to note, that under peroxydisulfate action, ecomposition of polysaccharide takes place. Investigation of hydroxyethyl cellulose molecular mas dependence on reaction conversion and peroxydisulfate ion concentration showed, that the polymer decomposition process proceeds (Fig. 4). In addition to this process, the formation of cross-linked polysaccharide has been observed. At the low enough concentration of peroxydisulfate only the anomalous increase in polymer molecular mass proceeds (Fig. 4). This phenomenon may be connect to a polymer radical recombination with the formation of longer chains.

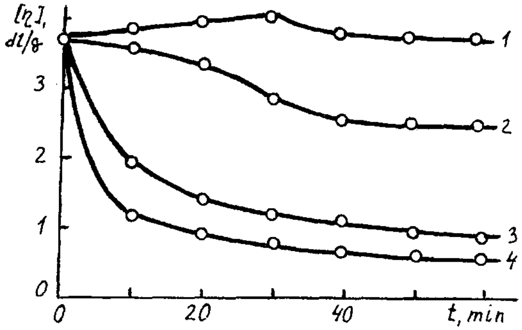

Fig. 4. Changes of intrinsic viscosity of hydroxyethyl cellulose with time at 70°C and peroxidisulfate concentration 0.044 (1), 0.22 (2), 2.2 (3) and 8.8 mol/l (4).

Therefore the process of graft polymerization of acrylic monomers onto polysaccharides includes two stages. In the first of them the homolysis of peroxydisulfate and monomer polymerization proceeds. The graft copolymer formation has been observed in this stage. Then the radical chin decomposition of peroxydisulfate and destruction of water soluble cellulose derivatives takes place.

## REFERENCES

[1] Grigoriev A.P., Laboratory Manual for Technology of Polymerizing Plastics, Vysshaya Shkola, Moscow, 1964.

## KINETYKA SZCZEPIONEJ POLIMERYZACJI AKRYLANU METYLU Z HYDROKSYETYLO- I KARBOKSYETYLOCELULOZĄ

### Streszczenie

Badano wpływ warunków procesu na efektywność szczepiania i masę cząsteczkową łańcuchów akrylowych szczepionych polimerów poli(metyloakrylanu) z hydroksyetylo- (HEC) i karboksymetylocelulozy (CMC).

Prześledzono w szerokim zakresie stężeń reagentów kinetykę szczepionej polimeryzacji akrylanu metylu z hydroksyetylo- i karboksymetylocelulozą inicjowaną jonem peroksydisiarczanowym. Zarówno w przypadku CMC jak i HEC reakcja względem monomeru jest ok. pierwszego rzędu, a względem inicjatora dla polimeryzacji jak i szczepiania jest rzędu zerowego. Efektywna energia aktywacji dla HEC wynosi 78 kJ/mol a dla CMC 80kJ/mol.

Badano kinetykę rozkładu jonu peroksydisiarczanowego i zmiany masy cząsteczkowej HEC i CMC w ich roztworach wodnych. Reakcja jest ok. pierwszego rzędu względem tego jonu a względem pochodnych celulozy zmienia się od 0,3 do zera wraz ze wzrostem stężenia pochodnej celulozy. Pokazano, że w roztworze wodnym w obecności peroksydisiarczanu zachodzi rozkład polimeru i że pochodne celulozy ulegają sieciowaniu.