Translated from *Uspekhi Khimii* 61 1002–1019 (1992) U.D.C. 541.64

The synthesis, properties, and applications of hydrophilic polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids

Z G Asadov, V S Aliev
Institute of Petrochemical Processes, Academy of Sciences of Azerbaijan

ABSTRACT. The scientific-technical and patent literature on the synthesis of hydroxyalkyl esters of acrylic and methacrylic acids by their catalytic reactions with epoxyalkanes, by the radical copolymerisation and polymerisation of presynthesised monomeric esters, and also by the chemical modification of polymerisation and copolymerisation products is surveyed. A wide variety of physicochemical properties of the polymers and copolymers based on the hydroxyalkyl esters of acrylic and methacrylic acids are described. The principal trends and prospects in the application of the high-molecular-weight products obtained in various branches of the national economy are indicated.

The bibliography includes 158 references.

Contents

I. Introduction 550
II. Synthesis of hydroxyalkyl esters of acrylic and methacrylic acids by the reaction of the monomeric acids with epoxyalkanes 550
III. Polymerisation of hydroxyalkyl esters of acrylic and methacrylic acids 551
IV. Copolymerisation of hydroxyalkyl esters of acrylic and methacrylic acids 553
V. Chemical modification of the polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids 556
VI. Properties and applications of the polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids 557

I. Introduction

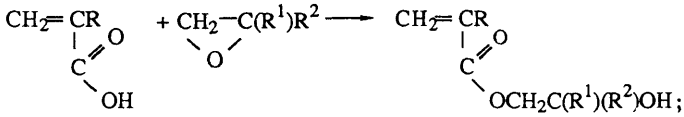
Water-soluble and hydrophilic polymers and copolymers are valuable products with unusual physicochemical characteristics. A specific feature of these compounds is the presence in their macromolecules of definite functional groups—hydroxy-, carboxy-, carbonylate, hydroxyalkyl, sulpho-, and other groups. The ratio of the hydrophilic and hydrophobic fragments in the macrochain determines the solubility in water and hydrophilicity of the polymers and copolymers. Here it is essential to bear in mind also the possibility of interchain and intrachain chemical bonds (the so called cross-links), which are formed in the synthesis of the macromolecular compounds or are introduced deliberately into the final product. They give rise to significant amendments to the physicochemical properties of the product, including a change in its solubility. These features must be taken into account in selecting approaches to the synthesis of the polymers and copolymers used to produce various materials with a specified range of physicochemical properties.

Water-soluble and hydrophilic polymers and copolymers are widely used in industry, agriculture, medicine, and science.

II. Synthesis of hydroxyalkyl esters of acrylic and methacrylic acids by the reaction of the monomeric acids with epoxyalkanes

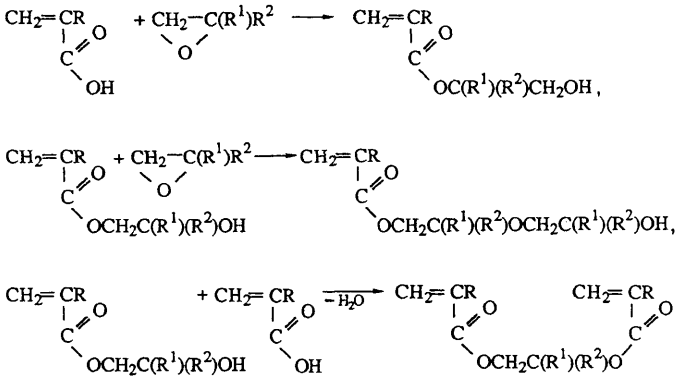
The hydroxyalkylation of acrylic (AA) and methacrylic (MAA) acids is of great applied importance because the final products of this reaction (unsaturated glycol esters) are valuable monomers from which it is possible to obtain polymeric materials with a wide variety of properties.

The addition of an epoxyalkane (EA) to AA and MAA, leading to the initiation of the formation of the hydroxyalkyl group, proceeds in accordance with the following scheme:



where R = H, CH_3, R^1 = H, CH_3, C_2H_5, R^2 = H, CH_3.

Apart from the formation of glycol monoesters, the following reactions are also possible theoretically:



The probability of each of these reactions is determined by the experimental conditions (molar ratio and concentrations of the reactants, temperature, nature of the reaction medium, etc.).

The addition of the epoxyalkane to AA and MAA in the presence of a catalyst is observed at temperatures below 100 °C. Inorganic and organic compounds of different classes have been proposed as catalysts. The weight of the catalyst is between 0.1 and 10% of that of the monomeric acid.

Among inorganic compounds, one may point to derivatives of tervalent iron: alkoxides (triethoxide, tri-δ-chlorobutoxide) and carboxylic acid salts (iron triacetate),[1] acetylacetonate and ethyl acetoacetate,[2] acrylate and methacrylate,[3] halides, $Fe(NO_3)_3$, $Fe(SCN)_3$, $Fe_2(CO_3)_3$, and $Fe_2(SO_4)_3$.[4,5] Mercury, chromium, copper, and iodine compounds are used as promoting agents in these reactions. Hydroquinone serves as a polymerisation inhibitor. In order to prevent the formation of quinone, compounds of alkali or alkaline earth metals, quaternary ammonium bases, amines, pyridine, and their salts are added. The yield of the monomeric esters exceeds 90% and their purity is 94–99%. The content of the unreacted monomeric acid is 0.2 wt.%. Hydroxyalkyl esters of AA and MAA are obtained also in the presence of other tervalent iron compounds,[6–10] for example, the hydroxide[9] and salts with aromatic carboxylic acids.[10] In the latter case, a small amount of diesters and dialkylene glycol monoacrylates and monomethacrylates is also formed.

$AlCl_3$ may be used as the catalyst of the hydroxyalkylation of AA and MAA;[11–16] $SnCl_4$ and BF_3 are unsuitable for this purpose, since they induce the polymerisation of the unsaturated acid even in the presence of an inhibitor.[11] A number of compounds of tervalent chromium (simple salts of aliphatic C_1-C_{36} acids and carbocyclic acids, coordination compounds with aliphatic or aromatic acids or *o*-hydroxyacids) have also been proposed.[17,18] When chromium is replaced by manganese and vanadium, the catalyst becomes ineffective. Chromium(III) halides[19,20] and chromium(III) salts of unsaturated aliphatic acid,[19] as well as Cr_2O_3 [19] and oxochlorochromium(III) acrylate and methacrylate[21] (the content of diesters in the products is 0.09%) have also been recommended.

Hydroxyalkyl acrylates and methacrylates (HOAA and HOAMA) can be obtained by the reaction of AA and MAA with an epoxyalkane in the presence of LiOH or $LiOH.H_2O$,[22] LiCl,[23] and lithium acrylate or methacrylate.[24] It is of interest that hydroxyalkyl methacrylates are formed with the involvement of potassium methacrylate, but potassium acrylate does not exhibit catalytic activity in the synthesis of hydroxyalkyl acrylates.[25] The use of titanium and zinc chlorides and alkoxides, their chelate compounds, and the products of their partial hydrolysis,[26] as well as vanadium compounds such as VCL_3, VCl_4, VOCl, $VOCl_3$, $V_2(SO_4)_3$, vanadyl sulphate, vanadyl acetylacetonate[27] (diesters are hardly formed as side products), and free iodine[28] has also been reported.

The esterification of AA and MAA by C_2-C_4 epoxyalkanes can be achieved under the influence for both an anion-exchange resin containing quaternary ammonium groups $[CH_2N^+(CH_3)_2C_2H_4OH]X^-$, where X^- is a univalent anion, for example the Dowex resin which is a copolymer of styrene with 8% of divinylbenzene[29–31] (the product contains 0.62% of the diglycol ester, 1.49% of the glycol diester, and 0.87% of the initial acid), as well as a cation-exchange resin of the sulphonic acid type with an aniline derivative.[32]

The hydroxyalkylation of AA and MAA is also possible in the presence of organic bases: triphenylphosphine, tributylphosphine, triethyl phosphite[33] (diacrylates and dimethacrylates are absent from the final product), cyclic and acylic compounds containing the paramagnetic nitroxy-group serving simultaneously as a polymerisation inhibitor,[34] carboxylic acid amides,[35] trialkylamines and dialkylanilines,[36–43] secondary aliphatic amines[37] (the content of diesters reaches 0.7% in the products), substituted ammonium and ammonium acrylate salts,[38] pyridine and alkylpyridines[42,44,45] and their salts with organic or inorganic acids,[43,44] quaternary pyridinium salts of the type of *N*-ethylpyridinium bromide[46] (the product does not contain appreciable amounts of diesters), and *N*-(carbamoyl-oxyalkyl)pyridinium halide or similar salts of other heterocyclic nitrogen-containing compounds[47] (high purity of the products and the absence of side products have been noted).

The hydroxyalkyl esters of AA and MAA are purified by fractional distillation,[48] where the polyalkylene glycols $HO[CH_2CH(R)O]_nH$ ($R = H, CH_3$; $n = 3-20$) may be added to prevent the formation of diesters,[49,50] or by distillation in the presence of polymerisation inhibitors (for example, hydroquinone) and various bases—alkali and alkaline earth metals, ammonia and its derivatives, amines or pyridines,[51] and hydrazine hydrate or β-hydroxyethylhydrazine.[52] In order to prevent the polymerisation of hydroxyalkyl acrylates and methacrylates during distillation, the liquid acrylate may be introduced into the mixture.[53] A procedure is available for the distillation of hydroxyalkyl esters of AA involving the addition of nitrosodiphenylamine in order to prevent their polymerisation during manufacture, transport, and storage.[54]

III. Polymerisation of hydroxyalkyl esters of acrylic and methacrylic acids

The existing publications on the polymerisation of hydroxyalkyl esters of AA and MAA are mainly devoted to processes involving the preparation of polymers of 2-hydroxyethyl methacrylate (2-HOEMA) (see, for example, the communications of Lavrov and co-workers[55–58]).

The radical polymerisation of 2-hydroxyethyl methacrylate can be achieved in bulk, in solution, and in emulsion (in organic solvents and in water). A number of procedures are used to obtain soluble polymers. For example, mixtures of dimethacrylates are removed from the aqueous solution of the monomer by their extraction with an organic solvent—preferentially hexane, heptane, and toluene. It is desirable that the polymerisation of 2-hydroxyethyl methacrylate be carried out in the presence of chain-transfer agents. The solubility of the 2-hydroxyethyl methacrylate polymer can be achieved also when the polymerisation is carried out in dilute solutions in organic solvents (benzene, chloroform) in which the monomer and the initiator dissolve, while the polymer itself does not dissolve and does not swell. The polymer is water-soluble also when the polymerisation is carried out in solvents such as dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) as well as in water (for polymerisation in water, it is recommended that an oxidation-reduction initiating system of the type of persulphate salts–ascorbic acid be used). Peroxides, hydroperoxides, and azo-compounds can serve as radical initiators for the polymerisation of 2-hydroxyethyl methacrylate.[59] Application of the method described leads to the formation of a 2-hydroxyethyl methacrylate polymer with a molecular weight between 500 and 700 000.

High-molecular-weight polymers of 2-hydroxyethyl acrylate and methacrylate can be obtained without an initiator by freezing a mixture of an aqueous solution of the monomer with a hydrophobic

solvent of the type of alkyl acetates or dialkyl ethers and by irradiation from the ionised gas of a plasma discharge.[60]

In the study of the kinetics of the polymerisation of 2-hydroxyethyl methacrylate, features close to the classical ones are mainly observed. The order of the reaction in organic solvents with respect to the radical initiator, azobisisobutyronitrile (ABIBN), was found to be half. In ethanol, the reaction order with respect to the monomer was 1.2 and in dethylene glycol 0.9. In polymerisation in water initiated by the ammonium persulphate–ascorbic acid system, the reaction order was found to be unity with respect to 2-hydroxyethyl methacrylate. The order with respect to ammonium persulphate was found to be 0.8 and that with respect to ascorbic acid was zero.

The presence in the system of chain-transfer agents affects both the rate of polymerisation of 2-hydroxyethyl methacrylate and the possibility of the manifestation of the gel effect observed in polymerisation in bulk in the absence of chain-transfer agents.[59] The yield of the polymer obtained with the aid of ABIBN and methyl azobisisobutyrate then reaches 80% (at 70 °C).[61]

In the presence of ethylene glycol dimethacrylate (EGDMA) as the cross-linking agent, 2-hydroxyethylmethacrylate forms films[62] and gel-like products[63] as a result of polymerisation in water. These swell in water and in water–dioxane mixtures. The study of the kinetics of the radical polymerisation of 2-hydroxyethyl methacrylate in bulk in the presence of 0.07–1.00% of EGDMA (using ABIBN and dicyclohexyl prooxydicarbonate as the initiator) by heat flux microcalorimetry[64] showed that, for a conversion less than 10%, the polymerisation process obeys the classical rules, while for a higher conversion of the monomer a significant self-acceleration of the process is observed, its strength depending on the content of EGDMA and 2-hydroxyethyl methacrylate. For the 0.2% content of EGDMA, the polymers formed (yield 90–96%) are completely insoluble owing to their cross-linked structure. A decrease in the EGDMA content to 0.07% makes it possible to obtain soluble polymers with a molecular weight of 315 000–792 000.

The radical polymerisation of 2-hydroxyethyl methacrylate in the polyvinylpyrrolidinone (PVP) matrix in different solvents is of interest.[65] The study of the process kinetics showed that an increase in the rate of polymerisation in the absence of highly polar electron-donating solvents is induced by the complex formation reaction between polyvinylpyrrolidinone and monomer.

The conformational characteristics of the 2-hydroxyethyl-methacrylate polymer (isotactic) were investigated by Kim and co-workers using viscometric[66,67] and fluorescence[67] methods. It was established that the chain of the 2-hydroxyethyl methacrylate polymer is more expanded in the salt solution containing ions incorporated in the water structure. In terms of their disruptive effect on the conformation of the given polymer, anions can be arranged in the sequence $SO_4^{2-} < F^- < I^- < NO_3^- < SCN^-$. The polymer conformation is more sensitive to changes in the anion than in the cation. The conformational characteristics of the isotactic 2-hydroxyethyl methacrylate polymer in water–alcohol (methanol, ethanol, propanol, isopropyl alcohol, ethylene glycol) mixtures were detected from the change in the intensity of the fluorescence of auramine introduced into the polymer solution and in the specific viscosity of the solutions. It was shown that in water the 2-hydroxyethyl methacrylate polymer has a compact structure stabilised by the hydrophobic interactions of the CH_3 groups. The structure is disrupted by alcohols. The disruption of the complex compact structure is accompanied by a decrease in the fluorescence intensity and by an increase in the specific viscosity of the solution over a narrow range of variation of the solvent composition for all alcohols other than ethylene glycol. With increase in the length of the aliphatic group of the alcohol, the compact structure is disrupted for a lower content of the latter in water. The disruptive effect of ethylene glycol can be explained by the formation of hydrogen bonds between the polar groups of the 2-hydroxyethyl methacrylate polymer and the alcohol.

The viscous properties of aqueous solutions of isotactic 2-hydroxyethyl methacrylate polymer are influenced by urea and its derivatives (thiourea, methylurea, ethylurea, 1,3-dimethylurea, and tetramethylurea, and tetramethylurea).[68] Comparison of the excess molar heat capacities of the urea or its derivatives and of the ratio of the intrinsic viscosities $[\eta_{urea}]/[\eta_{water}]$ of solutions of the 2-hydroxyethyl methacrylate polymer in water containing urea or its derivatives and in pure water respectively shows, firstly, that in aqueous solutions the isotactic polymer has the structure of a compact statistical coil and, secondly, that the addition of urea or its derivatives leads to a disruption of the compact structure of the 2-hydroxyethyl methacrylate polymer. This can be explained by the breakdown of the water structure under the influence of urea or its derivatives and by the interaction between the polymer and the additive. The temperature variation of $[\eta_{water}]$ shows that at 20 °C the isotactic 2-hydroxyethyl methacrylate polymer has the most compact conformation.

The state of water in the hydrated 2-hydroxyethyl methacrylate polymer was studied by NMR spectroscopy and differential scanning calorimetry.[69] It was shown that the onset of the mobility of water corresponds to a temperature of approximately 180 K (below which the system is a glass). In specimens with a higher water content, an appreciable proportion of mobile water freezes at 230–260 K. Near 273 K, the behaviour of water is complex and above room temperature chemical exchange processes are manifested. The equilibrium water content in the 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate polymers has been measured in distilled water and in phosphate buffer.[70] It was noted that in distilled water the equilibrium water content increases with increase in the hydrophilicity of the polymer and is almost independent of its molecular weight. In the buffer solution the degree of swelling and the amount of "frozen" water in the polymer are anomalously high, which can be explained by the ionisation of small amounts of methacrylic acid present in the polymers.

A macromonomer with two terminal COOH groups and OH side groups, having the formula $HOOCCH_2CH(COOH)S[CH_2C.(CH_3)COOCH_2CH_2OH]_nH$, was synthesised by the radical polymerisation of 2-hydroxyethyl methacrylate in tetrahydrofuran (THF) at 60 °C in the presence of thiomalic acid $HOOCCH(SH)CH_2COOH$.[71] It is used for the preparation of grafted polyamide copolymers.

The kinetics of the polymerisaiton of 2-hydroxypropyl methacrylate[39–41,72] and 2-hydroxypropyl acrylate (2-HOPA) [41,72,73] were investigated by the dilatometric method in ethanol with the process influenced by persulphate salts. In the case of 2-hydroxypropyl acrylate, the orders of the polymerisation reaction with respect to the monomer and initiator are close to the classical values (1 and 0.5), but in the case of 2-hydroxypropyl methacrylate the order with respect to the monomer is higher (1.77) and that with respect to the initiator is zero (because of its insolubility in ethanol, the persulphate is introduced in aqueous solution, which leads to the separation of the monomer and initiator phases). It was shown that the polymerisation of 2-hydroxypropyl methacrylate is described by the equation

$$1/0.77\ [M]^{0.77} = k\tau + 1/0.77\ [M]_0^{0.77}$$

where $[M]$ and $[M]_0$ are the current and initial concentations of the monomeric ester, k is the overall polymerisation rate constant, and τ is the time. The activation energy for this process was found to be 8.75 kcal mol^{-1} and the pre-exponential factor was 7.76×10^5.

In the study[73] of the effects of the nature of the reaction medium on the polymerisation of 2-hydroxypropyl acrylate at 50 °C with ammonium persulphate as the initator, it was established that the highest rate of reaction is observed in ethanol, THF, and DMSO and the lowest in acetone and DMF. The rate decreases further in the sequence water–isopropyl alcohol–methanol–1,4-dioxane, but under these conditions the final degree of conversion in methanol is much higher than in isoropyl alcohol. A lower rate of polymerisation of 2-hydroxypropyl acrylate was noted in acetonitrile.

The results of studies[73] of the kinetics of the polymerisation of 2-hydroxypropyl acrylate in ethanol–water and acetone–water binary mixtures indicate an inverse correlation between the rate of polymerisation and the volume fraction of water in the system, but in the case of the complete replacement of ethanol or acetone by water the rate of polymerisation increases. The 2-hydroxypropyl acrylate polymer is soluble in water only when its molecular weight is low.

The study[73] of the temperature variation of the polymerisation of 2-hydroxypropyl acrylate in ethanol with ammonium persulphate as the initiator at 40–70 °C showed that the rate of polymerisation increases as the temperature is reduced in the range from 40 to 65 °C. At 70 °C, the rate of polymerisation and the final degree of conversion of 2-hydroxypropyl acrylate have the minimum values in the experimental temperature range, which is probably associated with the predominance of the chain termination reaction.

The most effective initator, leading to the attainment of the optimum rates of the process and the optimum final conversion of 2-hydroxypropyl acrylate, is ammonium persulphate. Potassium persulphate exhibits a much lower initiating activity. Hydrogen peroxide occupies an intermediate position. ABIBN and benzoyl peroxide are fairly powerful initiators of the radical polymerisation of 2-hydroxypropyl acrylate. It has also been shown experimentally[73] that sodium sulphite and thiosulphate, which form redox systems with the persulphate salt, exhibit an activating affect on the polymerisation of 2-hydroxypropyl arylate.

Table 1. Rate constants for the polymerisation of 2-hydroxypropyl acrylate in ethanol (with ammonium persulphate as the initiator) at different temperatures.[73]

Constant	50 °C	55 °C	60 °C
k_i, s^{-1}	$7.24 \cdot 10^{-5}$	$11.06 \cdot 10^{-5}$	$13.85 \cdot 10^{-5}$
k_p	0.646	65.242	102.259
k_t	$5.388 \cdot 10^3$	$5.433 \cdot 10^5$	$8.531 \cdot 10^5$
k	$1.059 \cdot 10^{-3}$	$1.315 \cdot 10^{-3}$	$1.843 \cdot 10^{-3}$

2-Hydroxypropyl arylate is capable of photochemically initiated polymerisation (on irradiation with blue light). This makes it possible to employ the rotating sector method for the determination of the rate constants for the propagation (k_p) and termination (k_t) stages in the polymerisation process. These constants as well as the initation constant k_i, calculated by the inhibition method, are listed in Table 1 (k is the overall rate constant for the polymerisation of 2-hydroxypropyl acrylate).

The activation energy for the polymerisation process proved to be 10.37 kcal mol^{-1}. The Arrhenius equation assumes the following form:

$$k = 11.04 \cdot 10^7 \exp(-5220/T).$$

The activation energy for the initiation of the polymerisation of 2-hydroxypropyl acrylate with ammonium pesulphate as the initiator is 13.81 kcal mol^{-1}. The temperature variation of the initiation rate constant is described by the following equation:[73]

$$k_i = 17.69 \cdot 10^8 \exp(-6953/T).$$

IV. Copolymerisation of hydroxyalkyl esters of acrylic and methacrylic acids

Most of the published studies on the copolymerisation of the hydroxyalkyl esters of AA and MAA are devoted to the 2-hydroxyethyl methacrylate copolymers. The results of studies of its copolymerisation with a number of other methacrylate esters have been described:[74–79] methyl methacrylate (MMA),[74,79] ethyl methacrylate (EMA),[75,78] butyl methacrylate (BMA),[74,75,79] tributyltin methacrylate,[76] lauryl methacrylate,[77] and decyl methacrylate.[79] The copolymerisation is carried out in solution[74,77,79] or in bulk.[75] The solvents employed are methanol,[74,79] benzene, THF, t-butyl alcohol, and DMF.[77] The initiators used are benzoyl peroxide,[75] ABIBN,[77] and ammonium persulphate[79] (temperature 50–70 °C). With increase in the mole fraction of 2-hydroxyethyl methacrylate in the copolymer, its intrinsic viscosity also increases (the molecular weights reach one million and above[75]). There is a parallel increase in the swelling coefficient of the copolymer, its values being in the range 21.27–27.14 in the case of the copolymers with ethyl and butyl methacrylates. It was established that the introduction of up to 10% of alkyl methacrylate into the chain greatly alters the solubility and the physicomechanical properties of the polymer. The copolymers form transparent films with good adhesion to glass and metal. The copolymerisation constants (r_1 and r_2), calculated by the Kelen–Tudes, Feynman–Ross, and Ezrielev methods and from data based on the $Q-e$ scheme, are presented in Table 2.

The copolymerisation of 2-hydroxyethyl methacrylate with both 2-hydroxyethyl arylate (2-HOEA) and acrylic and methacrylic acids and their sodium or potassium salts has also been investigated.[80] Dispersion (derivatives of cellulose or anhydrosorbitol ethers served as dispersing agents) of 2-hydroxyethyl methacrylate together with an aqueous solution of the comonomer in an organic solvent immiscible with water (benzene, heptane, hexane, $CHCl_3$, CCl_4, xylene) makes it possible to obtain powdered water-soluble copolymers.

The copolymerisation of 2-hydroxyethyl methacrylate with acrylic acid has been investigated[81] in water at 20 °C in the presence of the ammonium persulphate–ascorbic acid initiating system. It was shown that, with increase in the overall concentration of the monomers from 0.4 to 1.0 M, the rate of reaction rises from 3.6×10^{-5} to 3.5×10^{-4} mol $litre^{-1}$ s^{-1}. The copolymerisation constants are 1.55 and 0.36 respectively. The best unit alternation effect in the

macrochain is observed for a 2-hydroxyethyl methacrylate mole fraction in the mixture of comonomers of 0.2–0.4.

It has been shown[82] that the rate of copolymerisation of 2-hydroxyethyl methacrylate with *N*-vinylsuccinimide increases with increase in the ester content in the initial mixture. The rate of copolymerisation in benzene is significantly higher than in DMSO and the copolymerisation constants, calculated taking into account the influence of the preterminal unit differ, which leads to different microstructures of the copolymers. According to ^{1}H NMR data the probability of the formation of the $M_1M_2M_1$ triads is greater in benzene.

Table 2. Constants for the copolymerisation of 2-hydroxyethyl methacrylate (r_1) with other monomers (r_2).

Comonomer (solvent)	r_1	r_2	Refs.
Methyl methacrylate (methanol)	0.96	0.5	[74]
	0.81±0.10	0.45±0.03	[79]
Butyl methacrylate (methanol)	0.52	0.62	[74]
	0.76±0.14	0.61±0.06	[79]
Decyl methacrylate (methanol)	0.66±0.05	2.65±0.01	[79]
Lauryl methacrylate			
(benzene)	11.2	0.7	[77]
(THF)	2	1	[77]
(t-butyl alcohol)	1.6	0.5	[77]
(DMF)	0.8	0.8	[77]
Tributyl methacrylate	2.45	0.39	[76]
Acrylic acid (water)	1.55	0.36	[81]
N-Vinylsuccinimide			
(benzene)	7.36±1.66	0.09±0.02	[82]
(DMSO)	8.5	0.05	[82]
Styrene			
(butanol, propanol, DMF)	0.59	0.53	[85]
(toluene)	1.65	0.50	[85]
Acrylamide (water)	0.98	0.14	[87]
p-Nitrophenyl acrylate (alcohol)	1.4	0.7	[96]
N-acryloyloxyethylsuccinimide (alcohols)	1.0	0.8	[96]

Lavrov et al.[83] synthesised the copolymer of 2-hydroxyethyl methacrylate with *N*-vinylamidosuccinic acid. The study of the properties of aqueous solutions of the copolymer by the viscometric titration method showed that an increase in the viscosity of the solution is observed up to a degree of ionisation $\alpha = 0.85$, which indicates the uncoiling of the macrocoil. The maximum size of the macromolecules exhibiting polyelectrolyte properties is observed at pH 7.5–8.5 ($\alpha = 0.85-0.95$). On further increase in the pH of the medium, the molecules assume a more twisted conformation.

The 2-hydroxyethyl methacrylate–N-vinyl-2-pyrrolidinone copolymer was obtained in the form of a hydrogel with the aid of ABIBN at 70 °C.[84] It was shown by optical and refractometric methods that the degree of hydration of the copolymers and their linear expansion on hydration increase in the ranges 10–80 and 5–40% respectively with increase in the content of the second comonomer units in the copolymer from 0 to 75%. The permeability of the swollen hydrogels to oxygen increases with increasing degree of hydration.

The copolymerisation constants have been determined[85] for the 2-hydroxyethyl methacrylate–styrene system in solutions in butanol, propanol, DMF, and toluene (Table 2).

The possibility of obtaining cross-linked (in the form of hydrogels) and non-cross-linked 2-hydroxyethyl methacrylate–acrylamide (AAM) copolymers by radical copolymerisation in water initiated by the ammonium persulphate–ascorbic acid system has been demonstrated.[86] Methylenebisacrylamide and triethylene glycol dimethacrylate were used as cross-linking agents. It was established that the introduction of acrylamide units into the polymer chain increases the water-absorbing properties of the product. Calculation of the probability of the distribution of the units of the comonomers from the copolymerisation constants determined by the Kelen–Tudes method[87] (Table 2) indicates a tendency towards the alternation of the units to give the ratio acrylamide : 2-hydroxyethyl methacrylate = 2 : 1.

The copolymers of 2-hydroxyethyl methacrylate with sodium 2-acrylamidomethylpropanesulphonate (2-AA-2-MPSNa) having different compositions (78 : 22, 60 : 40, 40 : 60, and 20 : 80) have been synthesised.[88] The heterogeneity of the copolymers was investigated by the isotachophoresis method — the separation of aqueous buffer solutions into series of consecutive zones in conformity with their electrophoretic mobility. Aqueous solutions of the 60 : 40 and 40 : 60 copolymers at copolymer concentrations in excess of 10% separate into two phases. The upper layer contains the copolymer enriched in 2-AAM-2-MPSNa and the lower is enriched in 2-hydroxyethyl methacrylate. The effective electrophoretic mobilities increase with increase in the mole fraction of 2-AAM-2-MPSNa to 0.5–0.6 and are almost independent of the composition of the copolymer for high contents of 2-AAM-2-MPSNa.

Polymers with a degree of polymerisation of approximately 300 and free from betaine groups have been obtained[89] by the polymerisation of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, or 2-hydroxypropyl methacrylate with methyl acrylate and *N,N*-dimethyl-*N,N*-diethylaminoethyl methacrylate in 10–20% KOH solution at 65–90 °C or in an emulsion at 50–70 °C with subsequent hydrolysis of the final product in an alkaline medium.

High-molecular-weight acrylic copolymers with $[\eta] = 12-17$, which are suitable as flocculating agents, have been synthesised[90] by the copolymerisation of hydroxyethyl acrylate or methacrylate and the vinyl monomer $CH_2=CR^1COY(CH_2)_n.N^+R^2R^3R^4X^-$ (where R^1 = H, CH_3; R^2-R^4 = alkyl; X^- = acid residue), for example, methacryloyloxyethyltrimethylammonium chloride, in a thin layer on a moving strip under the influence of UV light in the presence of non-ionic surfactants and a photoinitiator. The polymer layer is continually removed from the strip.

Copolymers of 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate with vinyl acetate (VA) have been obtained by the radiation method[91] in the presence of cross-linking agents, for example ethylene glycol.

The radical copolymerisation of 2-hydroxyethyl methacrylate monomers containing active functional groups (*p*-nitrophenyl acrylate and *N*-acryloyloxyethylsuccinimide) initiated by ABIBN has been investigated[92] in alcohol in order to produce reactive carriers for the immobilisation of proteins, enzymes, and aminoacids. The copolymerisation constants were determined by the Feynman–Ross and Ezrielev methods (Table 2).

Polymeric products with a high mechanical strength have been obtained[93] by the suspension copolymerisation of 2-hydroxyethyl

methacyrlate with the monomers $\{CH_2=CRCOO(CH_2CH_2O)_n.[CH_2CH(CH_3)O]_m\}_3P=O$ (where R = H, CH_3; m = 0–30; n = 0–3; $m + n \geqslant 1$) in 50:50 to 10:90 ratios.

The radical copolymerisation of 2-hydroxyethyl methacrylate with both *N,N'*-diethyl-*N*-(4-vinylphenylethyl)ethylenediamine and with its self-condensation product (initiated by lithium diisopropylamide in THF at 20 °C) in benzene, ethanol, and *o*-dichlorobenzene has been described.[94]

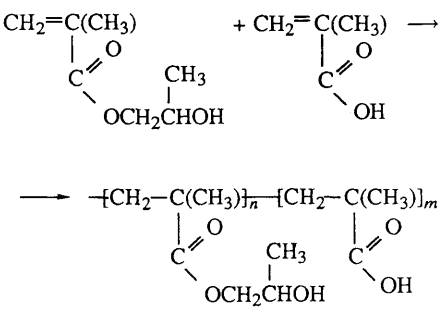
Terpolymers based on hydroxyalkyl acrylates and methacrylates (with C_6-C_{12} alkyl groups) and styrene (α- or *p*-methylstyrene) have been obtained in solution in ketones with the reaction initiated by peroxides.[95,96] Mono-, di-, or tri-alkyl acrylates and methacrylates (with C_2-C_{18} alkyl groups) [95] or acrylic (methacrylic) acid were used as the third comonomer. The copolymers are suitable for coatings and have a narrow molecular weight distribution and a molecular weight less than 4000.[96] The OH groups in the copolymer are partly esterified by treatment with natural or synthetic aliphatic acids in the presence of a catalyst.[95]

Copolymers used as current conducting salts, flocculants, and additives to cosmetic compositions have been obtained[98] by the radical copolymerisation of hydroxyalkyl arylates and methacrylates in an aqueous medium at 40–100 °C with the monomers $[R^1R^2R^3N^+CH(R^4)CH(R^5)OH]A^-$, where R^1 = C_2-C_4 alkenyl, n = 1–18, X = O or NH, R^6 = H or CH_3, R^2 = C_1-C_{18} hydroxyalkyl, R^3 = C_2-C_4 alkenyl or C_1-C_{18} alkyl, R^4, R^5 = H or C_1-C_{28} alkyl, and A = anion.

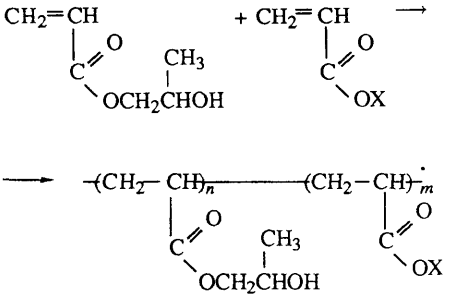
Copolymers of 2-hydroxyethyl acrylate, vinyl acetate, and ethylene, whose microstructure was investigated by ^1H and ^{13}C NMR, have also been synthesised.[98] It was shown that, for a 2-hydroxyethyl acrylate content of 5%, its units are not distributed statistically. For a vinyl acetate content of 25%, ethylene–vinyl acetate–vinyl acetate and ethylene–vinyl acetate–ethylene triads are formed in the chain, but there are no ethylene–vinyl acetate–hydroxyethyl acrylate and hydroxyethyl acrylate–ethylene–vinyl acetate triads. With increase in the molecular weight of the fractions of the copolymer with 25% of vinyl acetate, isolated by gel-permeation chromatography, the content of 2-hydroxyethylacetate also increases.

As can be seen from the data presented above, 2-hydroxyethyl methacrylate and its analogues are very active monomers in copolymerisation reactions. This is confirmed also by the Alfrey–Price parameters quoted in the literature:[81–83] Q = 1.16, e = 0.30 and Q = 0.80, e = 0.20.

The radical polymerisation of 2-hydroxypropyl methacrylate with methacrylic acid[39–41]



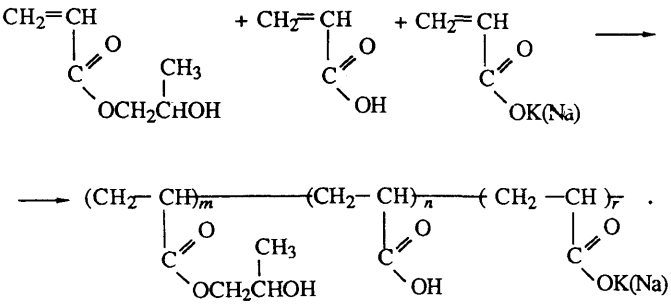
and of 2-hydroxypropyl acrylate with both acrylic acid and acrylate salts[73]



where X = H, K, or Na, has been achieved. The initiator was ammonium persulphate.

It has been shown that the highest solubility of the 2-hydroxypropyl methacrylate–methacrylic acid copolymer in water is achieved when the product is obtained in organic media, which is due to its lower molecular weight. With increase in the mole fraction of both 2-hydroxypropyl methacrylate and 2-hydroxypropyl acrylate in the copolymer, its solubility in water is impaired. The constants for the copolymerisation of 2-hydroxypropyl methacrylate and methacrylic acid proved to be 0.99 and 0.31, which indicates the higher reactivity of the ester. In the copolymerisation of 2-hydroxypropyl acrylate with acrylic acid, the difference between the reactivities of the comonomers is much greater (r_1 = 17 and r_2 = 0.02), the overall order of the reaction with respect to the comonomers being 2 and that with respect to the initiator (ammonium persulphate) being 0.7. Alkali metal acrylates (potassium and sodium acrylates) exhibit a much higher reactivity in copolymerisation with 2-hydroxypropyl acrylate than does acrylic acid. Thus the constants for the copolymerisation of 2-hydroxypropyl acrylate and potassium acrylate are 1, 10, and 0.96.

The ternary copolymers of 2-hydroxypropyl acrylate, acrylic acid, and the alkali metalacrylates indicated above have been synthesised:[73]



It is of interest that, in order to attain the best solubility of both binary and ternary copolymers involving 2-hydroxypropyl acrylate in water, it is desirable to obtain the acrylate salts *in situ* (by the reaction of acrylic acid and alkali), without isolating them from aqueous solution, to make them undergo the polymerisation reaction initiated by ammonium persulphate.

There have been a number of studies on the graft polymerisation of hydroxyalkyl esters of acrylic and methacrylic acids. Graft copolymers based on 2-hydroxyethyl methacrylate and poly(vinyl

alcohol) (PVA) have been obtained[99] in DMSO using hydroperoxides and azo-initiators. The process characteristics indicate a matrix reaction mechanism. The activating effect of the hydrogen-bonded complex between 2-hydroxyethyl methacrylate, the initiator, and the OH groups of PVA on the course of the reaction has been demonstrated.[100]

The graft copolymerisation of 2-hydroxyethyl methacrylate (in DM using ABIBN) on unsaturated polyurethane, obtained from poly(ethylene glycol) (M = 1500), methylenebis-4-phenylene isocyanate, *cis*-but-2-ene-1,4-diol, and butane-1,4-diol (in a mixture of DMSO with 4-methyl-2-pentanone as the solvent) has been carried out.[101] 2-Hydroxyethyl methacrylate can be grafted also on a polyurethane in the form of an emulsion (with t-butyl-hydroperoxide as the initiator)[102] or a film (under the influence of γ-irradiation).[103] In the latter case, the degree of grafting increases with increase in the swelling time of the film. 2-Hydroxyethyl methacrylate is grafted with an induction period of 0.5–1 h.

Studies on the photografting of 2-hydroxyethyl methacrylate on polyvinylpyrrolidinone (PVP) have been carried out.[104–107] The component ratio was 70–95:30–5. The photosensitiser was benzoyl peroxide. With increase in the PVP content, the degree of conversion of 2-hydroxyethyl methacrylate and the maximum rate of its polymerisation diminish. At the same time, the gel formation time is reduced. On irradiation with UV light, the compositions harden in a thin layer, which makes it possible to obtain hydrophilic coatings and films with valuable properties. The formation of highly permeable copolymers with a network structure has been established. 2-Hydroxyethyl methacrylate can be grafted to PVP also electrochemically.[108] An initiator-free polymerisation of 2-hydroxyethyl acrylate and methacrylate in the presence of 10–40% of PVP (molecular weight 12000) at 50–80 °C has also been described.[109] The formation of the graft copolymer is observed at a temperature as low as 50–60 °C, while homopolymerisation of the ester does not occur under analogous conditions. The yield of the copolymer and the content of the gel-fraction in the system increase with increase in temperature and with decrease in the content of PVP in the initial mixture. The rate of polymerisation increases with increasing PVP content. Dilution of the mixture of the ester and PVP with hydroxylated solvents (water, cyclohexanol, ethanol, ethylene glycol, and diethylene glycol) increases the rate of polymerisation compared with polymerisation in bulk.

Chinese investigators have achieved[110] the graft copolymerisation of 2-hydroxyethyl methacrylate on polyethylene membranes initiated by ^{60}Co γ-rays in ethanol solution at 25 °C. The initial rate of grafting was proportional to the ester concentration and the irradiation intensity raised to powers of 1.0 and 0.5 respectively. The apparent activation energy in the range 25–66 °C and the frequency factory for the graft copolymerisation are 8.0 kcal mol^{-1} and 1.505 × 10^7 respectively. The dependence of the apparent grafting rate constant k on the absolute temperature is described by the equation

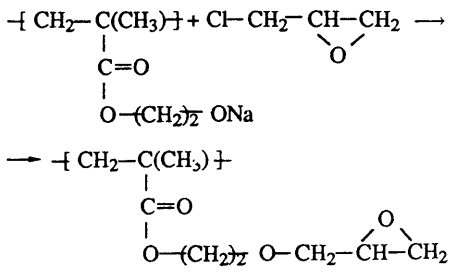
$$\ln k = 16.5269 - 4026(1/T).$$

It is suggested[111] that macroporous sorbents can be obtained by the polymerisation of 2-hydroxyethyl methacrylate initiated by ABIBN at 60–110 °C (or thermally at 100–150 °C or by exposure to radiation) in the presence of a copolymer of 2-hydroxyalkyl methacrylate (C_2–C_4 alkyl group) and a polyvinyl monomer, for example, C_2–C_4 alkylene dimethacrylate, as the carrier.

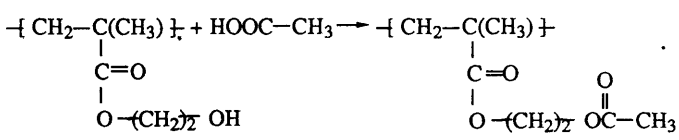
Gel-free hydroxylated graft copolymers, ensuring an effective distribution of metallic pigments without additives, are obtained[112] by the copolymerisation of monomers containing hydroxy-groups (2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, and 2-hydroxypropyl methacrylate) and carboxy-groups (monoesters of maleic fumaric acids, acrylic acid, and methacrylic acid) in the presence of an acrylic polymer contaning ethoxy-groups, the ratio of the numbers of COOH groups in the monomer and of the epoxy-groups in the acrylic polymer ranging from 1:0.5 to 0.5:1. Grafting occurs as a result of the condensation fo the epoxy- and carboxy-groups.

V. Chemical modification of the polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids

One of the methods for the chemical modification of 2-hydroxyethyl methacrylate polymers involves the carrying out of polymer-analogue transformations via the hydroxy- or ester groups. The course of the reaction is inferred from the results of elemental and functional as well as IR spectroscopic analyses. The hydroxy-group in the 2-hydroxyethyl methacrylate units can react with alkali metals to form alkoxides and with acids and acid anhydrides to form esters.[113,114] When the 2-hydroxyethyl methacrylate units interact with maleic anhydride, ethylene glycol methacrylate maleates are formed.[115] The reaction with thionyl chloride leads to 2-chloroethyl methacrylate units. The reaction with phosgene can yield 2-chlorocarbonyloxyethyl methacrylate fragments. 2-Hydroxyethyl methacrylate oligomers react with diisocyanates to form polyurethanes.[115] Glycidyl ethers have been obtained by the reaction of the sodium alkoxide derived from the 2-hydroxyethyl methacrylate units with epichlorohydrin:[116]



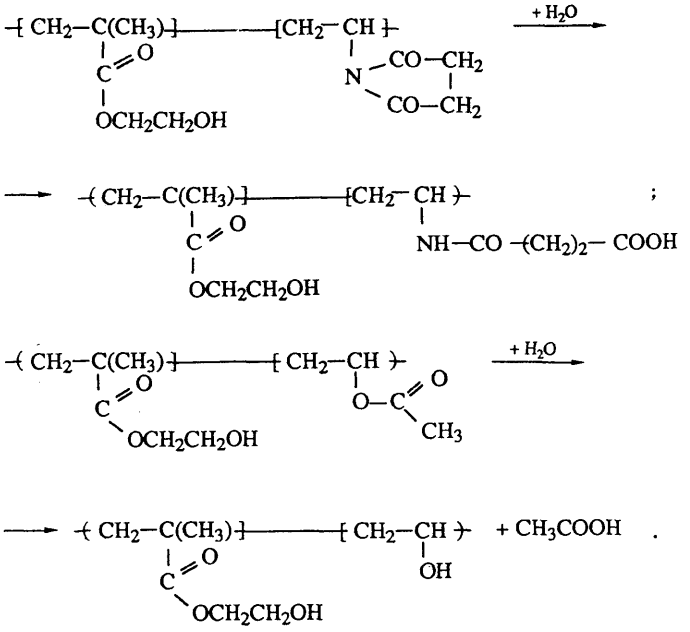
2-Hydroxyethyl methacrylate polymers enter into the acetal formation reaction involving the hydroxy-group. It has been suggested that this reaction be carried out with acetic acid in pyridine:[114]



The ester group in the 2-hydroxyethyl methacrylate units is very resistant to the action of hydrolysing agents. Alkaline hydrolysis of polymeric 2-hydroxyethyl methacrylate gels proceeds at a low rate only above 100 °C and acid hydrolysis with sulphuric acid under the

same conditions is slower still.[114] The possibility of hydrolysis at temperatures below 100 °C appears only when a non-cross-linked polymeric 2-hydroxyethyl methacrylate is used. In this case, the reaction is carried out in water (heterogeneous hydrolysis) or in a DMSO–water mixture (homogeneous hydrolysis) at 60–80 °C.[117,118] The kinetics of the alkaline hydrolysis of the polymer obey rules governing second-order reactions. In a heterogeneous medium, the hydrolysis is appreciably slower. At 20 °C, the 2-hydroxyethyl methacrylate units in the chain are not hydrolysed in either homogeneous or heterogeneous media.[117]

The *N*-vinylsuccinimide (VSI) and vinyl acetate units differ appreciably in their hydrolytic stability from the 2-hydroxyethyl methacrylate units,[117,119] which creates conditions for specific hydrolysis involving the vinylsuccinimide and vinyl acetate units in copolymers of 2-hydroxyethyl methacrylate with vinylsuccinimide and vinyl acetate, in which 2-hydroxyethyl methacrylate units are retained. The reaction results in the formation of copolymers of 2-hydroxyethyl methacrylate with *N*-vinylamidosuccinimic acid[117,118] and vinyl alcohol:[119]

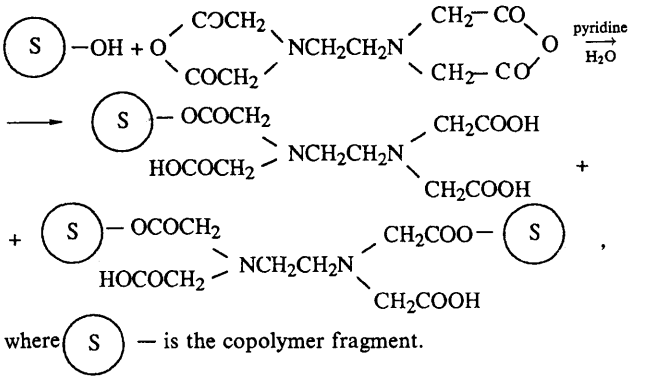


The degree of reaction involving the vinyl succinimide or vinyl acetate units is affected by the structure of the macrochain. The high reactivity of 2-hydroxyethyl methacrylate in copolymerisation with vinyl succinimide[120] and vinyl acetate[121] leads to single vinyl succinimide or vinyl acetate units separated by several 2-hydroxyethyl methacrylate units, which facilitates the interaction of the vinylsuccinimide or vinyl acetate units with the OH^- ion and permits their complete hydrolysis.

2-Hydroxyethyl methacrylate polymers can react with amines (ethanolamine, aniline, hydroxylamine), but the reaction is very slow even at 100 °C. The reaction with hydrazine proceeds most effectively.[114]

The reaction of the copolymer of 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate with the organosilicon compounds $(XR_m)_nSiR_{4-n}$, where X = NH_2, CO, COOH, HCO, etc., R and R′ = alkyl, n = 0–20, n = 1–3, has been described.[122]

By treating the copolymer of 2-hydroxyethyl methacrylate and ethylene glycol dimethyacrylate with dianhydride-complexones, it is possible to obtain chelating macromolecular products:[123]

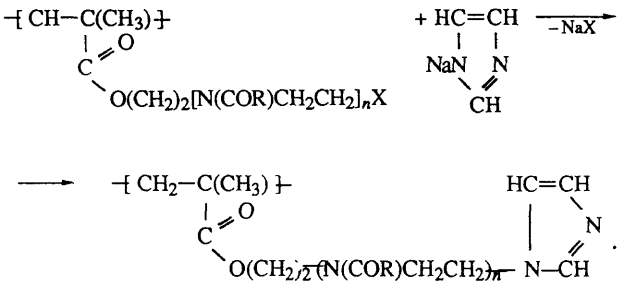


where (S) — is the copolymer fragment.

The copolymer of 2-hydroxyethyl methacrylate with 2.5% of methyl acrylate has been synthesised[124] and the interaction of gels of this copolymer with calcium ions has been shown that 2590 μg of calcium ions is absorbed per gramme of the gel at pH 8.5, while at 5.5 the gel collapses, which promotes the removal of calcium ions.

When the OH groups in the 2-hydroxyethyl methacrylate polymer are replaced by halogens (Br, Cl) and the product interacts with 2-R-oxazoline at 80–120 °C, polar graft copolymers are formed[123,125] with the units $-CH_2C(CH_3)COOCH_2CH_2.[N(COR)CH_2CH_2]_nX$, where R = H, C_1–C_3 alkyl, or phenyl, X = Br or Cl, and n = 1–20.

On treatment with sodioimidazole in methanol, THF, or DMF, the above haloderivatives of the polymeric 2-hydroxyethyl methacrylate give rise[123,126] to a product containing 0.9 mmol g^{-1} of imidazole groups:



Reactions in an aqueous medium on thin films of the cross-linked gel of the copolymer of 2-hydroxyethyl methacrylate with 2-isopropenylanthraquinone have been investigated[127] by UV and fluorescence spectroscopy. It was shown that fragments of anthrahydroquinone and of its tautomer (oxanthrone) are formed simultaneously on irradiation with near UV light.

VI. Properties and applications of the polymers and copolymers of hydroxyalkyl esters of acrylic and methacrylic acids

Polymers based on 2-hydroxyethyl methacrylate have many valuable properties: they are non-toxic, biologically compatible, and transparent and they adhere effectively to various substrates.

They are therefore recommended for use in the preparation of contact lenses, hydrogels for different purposes, membranes, films, adhesives, coatings, etc.[115,128–131]

The copolymers of 2-hydroxyethyl methacrylate with acrylic and methacrylic acids, methyl, butyl, and 2-hydroxypropyl methacrylates, as well as *N*-vinylpyrrolidinone,[132] N-1-(2-pyrrolidinonyl)ethylacrylamide,[133] styrene, and ethyl vinyl malonate are used for the manufacture of contact lenses.[115,129] Multicomponent copolymerisation is usually carried out in special moulds using a cross-linking agent (ethylene glycol dimethacrylate, etc.).[130,134]

Hydrophilic gels based on the 2-hydroxyethyl methacrylate polymers are used as carriers for physiologically active compounds,[135] the immobilisation of enzymes,[136,139] medicinal drugs,[140–143] and antigens and immunogenic substances,[130] for the preservation of enzymes and aromatic essential oils,[130] and in the manufacture of ion-exchange resins for the separation of biologically active substances.[130]

It has been established that the activity of immobilised enzymes depends on the gel structure. The introduction of a hydrophilic monomer into the polymeric 2-hydroxyethyl methacrylate gel increases appreciably the activity of the cells by virtue of the formation of a more porous gel structure, while the addition of a hydrophobic monomer lowers the activity of the cells immobilised in the gel as a result of the formation of a more rigid and finely porous gel structure.[138]

Ternary copolymers of 2-hydroxyethyl methacrylate, methyl methacrylamidoglycolate, and methyl methacrylate, deposited on a support, can be used[144] to eliminate specific pathological effectors from biological liquids of patients. These copolymers may contain covalently bound biologically active compounds capable of adsorbing the effectors.

The copolymers of 2-hydroxyethyl methacrylate with methyl methacrylate,[145,146] acrylamide,[147] and methyl acrylate[148,149] swell effectively in water. Thus the swellability of the 2-hydroxyethyl methacrylate–methyl acrylate copolymer in alkaline solutions reaches 3600% relative to the volume in an acid solution.[148]

2-Hydroxyethyl methacrylate-based gels are used to prepare implant for example, urinary bladder prostheses,[150] and catheters.[151] Membranes permeable to salts,[152–155] sugars,[152,154] urea,[154,155] dextran,[154] etc. have been developed on the basis of 2-hydroxyethyl methacrylate homopolymers and copolymers partly cross-linked with the aid of ethylene glycol dimethacrylate. Antithrombogens can be obtained by grafting 2-hydroxyethyl methacrylate on polystyrene, polyethylene, polytetrafluoroethylene, polyurethanes, PVA, and collagen.[130]

The copolymer of 2-hydroxyethyl methacrylate, methyl methacrylate, as well as sodium alginate can be used for the microencapsulation of immobilised cells,[156] while the copolymer of 2-hydroxyalkyl, acrylate and alkyl acrylate or methacrylate can be used for the microencapsulation of medicinal preparations.[157] The high capacity of 2-hydroxyethyl methacrylate polymers and copolymers for adhesion to various supports has led to its use for the preparation of coatings and adhesives.[130] The copolymers with methyl and butyl methacrylates, acrylic and methacrylic acid, etc. are used as aqueous compositions, solutions, and powdered compositions. 2-Hydroxyethyl methacrylate polymers and copolymers are employed in the preparation of transparent materials with a satisfactory wear resistance, hardness, and resistance to the appearance of turbidity,[130] and also for the preparation of compositions susceptible to thermal hardening[130] and photohardening.[158]

The copolymers of 2-hydroxypropyl methacrylate with methyl acrylate,[39,40] 2-hydroxypropyl acrylate, and potassium and sodium arylates as well as ternary copolymers of 2-hydroxypropyl acrylate with the above acrylate salts and acrylic acid[73] exhibit effective petroleum displacing properties. The copolymers of 2-hydroxypropyl acrylate with both potassium acrylate and acrylic acid exhibit bactericidal properties in relation to sulphate reducing bacteria evolving hydrogen sulphide, which stimulates the corrosion of metallic equipment in petroleum deposits.[73] In addition, the 2-hydroxypropyl acrylate–acrylic acid copolymer is an effective insulating agent, which to a large extent prevents the losses of drilling solutions and this increases the rate of drilling of petroleum and gas bore-holes.[73]

The hydroxyalkyl esters of acrylic and methacrylic acids are extremely promising and interesting monomers. A convenient method for the synthesis of these substances is believed to be the catalytic interaction of acrylic and methacrylic acids with the corresponding epoxyalkane. Homopolymers and copolymers with a wide range of exceptionally valuable properties can be synthesised from these esters. The homopolymers are obtained by the radical polymerisation of the hydroxyalkyl esters of acrylic and methacrylic acids, while the copolymers are obtained by the radical copolymerisation of the esters with monomers of different nature or by the chemical modification of homopolymers and copolymers. As a result of the above chemical reactions, it is possible to synthesise specifically high-molecular-weight compounds containing in their chains functional groups of the same or several different types. Depending on the chosen method of synthesis, there are then extensive possibilities for the regulation of the microstructure of the copolymers, i.e. of the nature of the alternation of the comonomer units in the chain.

Most of the studies published in this field have been devoted to the synthesis and applications of the polymers and copolymers of the esters synthesised by the reaction of methacrylic acid with epoxyethane. However, bearing in mind the comparative scarcity of epoxyethane and the much greater amounts of epoxypropane available as the starting material as well as certain difficulties involved in work with epoxyethane (its virtually gaseous state, explosive nature, high toxicity, and lower reactivity as a consequence of its symmetrical structure compared with hydroxypropane, which is an asymmetric epoxy-derivative), one may expect a growth of interest in the immediate future in the synthesis and application of the polymers and copolymers of the hydroxypropyl esters of acrylic and methacrylic acids. The results of studies included in this review and carried out at the Institute of Petrochemical processes of the Azerbaijan Academy of Sciences by the present authors and their co-workers are consistent with such forecasts.

References

1. Th Volker, H Walter, BRD P. 1 147 938
2. H Ito, K Kimura, Japanese P. 26 606; *Ref. Zh. Khim.*, 1970, 1N85P
3. W Gruber, BRD P. 1 255 104
4. M Murayama, US P. 3 441 599
5. M Murayama, US P. 1 137 071
6. M Murayama, Japanese P. 8970; *Ref. Zh. Khim.*, 1971, 7N91P
7. M Murayama, K Abe, Japanese P. 14 087; *Ref. Zh. Khim.*, 1973, 14N85P
8. M Murayama, BRD P. 1 568 838

9. T Matsuda, S Takamatsu, Japanese Appl. 54-39 008; *Ref. Zh. Khim.*, 1980, 6N61P
10. N Simizu, H Taiki, S Matsumoto, Japanese P. 56-161 349; *Ref. Zh. Khim.*, 1983, 8N59P
11. H J Wright, J F Bremmer, Australian P. 280 288
12. H J Wright, J F Bremmer, B. P. 1 066 086
13. H J Wright, J F Bremmer, US P. 3 150 167
14. H J Wright, J F Bremmer, French P. 1 390 843
15. H J Wright, J F Bremmer, Dutch P. 128 262
16. R L Routon, US P. 3 441 598
17. Y Kanbara, Japanese Appl. 61-27 945; *Ref. Zh. Khim.*, 1987, 2N42P
18. R Steckler, US P. 3 875 211
19. S Nezu, A Miyamoto, A Aozima, Japanese Appl. 57-38 747; *Ref. Zh. Khim.*, 1983, 8N58P
20. W Kunze, H Brachel, H Gattner, BRD P. 1 518 642
21. A A Gololobova, A P Sineokov, Z S Salakhetdinov, et al. USSR P. 505 627; *Ref. Zh. Khim.*, 1977, 3N80P
22. Y Tanizaki, Y Kubo, Japanese P. 21608; *Ref. Zh. Khim.*, 1972, 16N57P
23. Th H Cour, US P. 3 174 995
24. Y Tanizaki, Y Kubo, Japanese P. 47-51 338; *Ref. Zh. Khim.*, 1974, 12N75P
25. J-F Nemec, E L Wolffe, Sh N Lewis, US P. 3 314 983
26. H Ito, K Kimura, Japanese P. 2686; *Ref. Zh. Khim.*, 1970, 5N99P
27. A Itoi, M Kawamata, T Ono, et al., Japanese Appl. 56-87 537; *Ref. Zh. Khim.*, 1982, 10456P
28. N Murayama, Japanese P. 12 643; *Ref. Zh. Khim.*, 1968, 19N74P
29. H S R Bearden, Dutch P. 136 048
30. H S R Bearden, French P. 1 357 423
31. H S R Bearden, B. P. 1 003 346
32. Y Hamamoto, Japanese P. 17 682; *Ref. Zh. Khim.*, 1971, 12N78P
33. C Suling, H Wilms, E Roos, BRD P. 1 568 487
34. Kh-M A Brikenshtein, A A Berlin, A A Radugina, et al., USSR P. 749 823; *Ref. Zh. Khim.*, 1981, 7N44P
35. F Meier, N V Kutepow, BRD P. 1 248 036
36. W Gruber, H Walter, BRD Appl. 2 345 394; *Ref. Zh. Khim.*, 1975, 22N74P
37. Y Takayama, S Saito, Japanese P. 685; *Ref. Zh. Khim.*, 1970, 6N21P
38. H Ito, K Kimura, Japanese P. 27 083; *Ref. Zh. Khim.*, 1971, 15N94P
39. A Yu Yusubov, Candidate's Thesis in Chemical Sciences, Institute of Petrochemical Processes, Academy of Sciences of the Azerbaijan SSR, Baku, 1985, 149 pp
40. V S Aliev, Z G Asadov, A Yu Yusupov, et al. *Azerb. Khim. Zh.*, 1986, (2) 55–60
41. V S Aliyev, Z G Asadov, A Yu Yusubov, et al. *MACRO'87: 31st IUPAC Macromolecular Symposium: Abstracts of Papers, Microsymposium 1,* Merseburg, 1987, p. 117
42. A Yu Yusubov, A D Agazade, G A Akhmedova, Z G Asadov *Khimiya i Tekhnologiya Neftekhimicheskogo Sinteza i Vysokomolekulyarnykh Soedinenii* (The Chemistry and Technology of Petrochemical Synthesis and High-Molecular-Weight Compounds), Baku, 1988. Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 13.01.89, No. 326-V89
43. E Chadwick, B.P. 970 202
44. A J Simpson, B. P. 998 394
45. A Obami, S I Mekhtiev, P D Shikhalizade, et al. *Azerb. Khim. Zh.*, 1984, (4) 21–24
46. I Girvan, M A John, B. P. 1 096 035
47. R Dowbenko, R M Christenson, US P. 3 431 294
48. E G Stepanov, B A Saraev, V A Podgornova, et al. *Promyshlennost' Sinteticheskogo Kauchuka,* 1975, (6) 5–7
49. M Murayama, G Abe, Japanese P. 41 524; *Ref. Zh. Khim.*, 1972, 1N63P
50. M Murayama, K Abe, US P. 3 709 929
51. M Murayama, Japanese P. 8971; *Ref. Zh. Khim.*, 1971, 7N92P
52. S Suzuki, S Miura, H Tatemichi, Japanese P. 4850; *Ref. Zh. Khim.*, 1967, 24N77P
53. Y Kanbara, S Asano, V Isozaki, et al., Japanese Patent Application 63-41 441; *Ref. Zh. Khim.*, 1988, 7N27P
54. N Ito, K Suzuki, Japanese P. 44-76 893; *Ref. Zh. Khim.*, 1980, 6N59P
55. N A Lavrov *Khimicheskaya Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties, and Applications of Plastics), Leningrad, 1989, pp. 77–84
56. N A Lavrov *Khimicheskaya Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties, and Applications of Plastics), Leningrad, 1984, pp. 17–21
57. N A Lavrov, A F Nikolaev, N A Astaf'eva, USSR P.1 353 780; *Byul. Izobret.*, 1987, (43)
58. N A Lavrov, A F Nikolaev *Zh. Prikl. Khim.*, 1986, **59**(11) 2691–2693
59. T Mulavasic, U Osredkar, I Anzur, et al. *Vestn. Sloven. Kem Drus.*, 1986, **33**(2) 123–132
60. Y Osada, T Yamamoto, Y Kondo, Japanese Appl. 59-202 204; *Ref. Zh. Khim.*, 1986, 3S426P
61. W T K Stevenson, R A Evangelista, R L Broughton, et al. *J. Appl. Polym. Sci.*, 1987, **34**(1) 56–83
62. N A Peppas, H J Moynihan, L M Lucht *J. Biomed. Mater. Res.*, 1985, **19**(4) 397–411
63. Th P Davis, M B Huglin *Makromol. Chem. Rapid Commun.*, 1988, **9**(1) 39–43
64. D I Val'dman, A B Kochnov, A I Val'dman, et al. *Vsesoyuznaya Konferentsiya "Radikal'naya Polimerizatsiya": Tezisy Dokladov, Gor'kii* (All-Union Conference on "Radical Polymerisation". Abstracts of Reports, Gorky), Gorky, 1989, p. 142
65. O V Suberlyak, V I Skorokhodov, A I Soshko *Kinetics of the Polymerisation of 2-Hydroxyethyl Methacrylate in the Presence of Polyvinylpyrrolidinone,* Kiev, 1985, 8 pp. Article Deposited at UkrNIINTI, 30.05.85, No. 1166
66. W G Kim, M S Jhon *J. Polym. Sci.*, 1988, **A26**(3) 859–864
67. W G Kim, S H Jeon, M S Jhon *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **A25**(2) 467–474
68. S H Jeon, M S Jhon *J. Polym. Sci.*, 1989, **A27**(1) 237–244
69. G Smyth, F X Quinn, V J McBrierty *Macromolecules,* 1988, **21**(11) 3198–3204
70. W T Stevenson, M V Sefton *J. Appl. Polym. Sci.*, 1988, **36**(7) 1541–1553
71. J Chujo, H Kobayashi, Y Yamashita *Polym. Commun.*, 1984, **25**(9) 278–280

72. G A Akhmedov, A Yu Yusubov, Z G Asadov *Khimiya i Tekhnologiya Neftekhimicheskogo Sintesa i Vysokomolekulyarnykh Soedinenii* (The Chemistry and Technology of Petrochemical Synthesis and High-Molecular-Weight Compounds), Baku, 1988. Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 13.01.89, No. 326-V89
73. G A Akhmedova, Candidate's Thesis in Chemical Sciences, Institute of Petrochemical Processes, Academy of Sciences of the Azerbaijan Republic, Baku, 1991, 203 pp
74. A V Tkachev, V A Tverskoi *Copolymerisation of Hydroxyethyl Methacrylate with Methacrylic Monomers,* Cherkassy, 1987, 2 pp. Article Deposited at the ONIITEKhIM, 13.11.87, No. 1243-KhP87
75. M S Choudhary, I K Varma *J. Polym. Sci., Polym. Chem. Ed.,* 1985, **23**(7) 1917–1929
76. J R Dharia, C P Pathak, G N Babu, S K Gupta *J. Polym. Sci.,* 1988, **A26**(2) 595–599
77. R Ito, K Uchida, T Kitano, E Yamada, T Matsumoto *Polym. J.,* 1985, **17**(6) 761–766
78. D Briggs, B D Rather *Polym. Commun.,* 1988, **29**(11) 6–8
79. A V Tkachev, V A Tverskoi *Vsesoyuznaya Konferentsiya "Radikal'naya Polimerizatsiya". Tezisy Dokladov, Gor'kii* (All-Union Conference on "Radical Polymerisation". Abstracts of Reports, Gorky), Gorky, 1989, p. 36
80. T Atano, S Kanefusa, S Kadovni, Japanese Appl. 59-135 201; *Ref. Zh. Khim.,* 1985, 13S373P
81. N A Lavrov, A F Nikolaev, T S Bocharova *Zh. Prikl. Khim.,* 1989, **62**(10) 2401–2403
82. N A Lavrov, A F Nikolaev *Zh. Prikl. Khim.,* 1988, **61**(7) 1648–1650
83. N A Lavrov, A F Nikolaev, V M Chudnova *Zh. Prikl. Khim.,* 1988, **61**(7) 1646–1648
84. G Kossmehl, J Volkheimer, H Schafer *Makromol. Chem.,* 1989, **190**(6) 1253–1262
85. J Lebduška, J Snuparekml, K Kaspar *Chem. Prum.,* 1986, **36**(9) 472–475
86. N A Lavrov, N M Grinberg *Khimicheskaya Tekhnologiya Svoistva i Primenenie Plastmass* (Chemical Technology, Properties and Applications of Plastics), Leningrad, 1988, pp. 37–40
87. V Konsulov, D Kirova, N Grozeva *Khimiya Industriya,* 1987, **59**(5) 216–218
88. L R Whitlock, L M Wheeler *J. Chromatogr.,* 1986, **368**(1) 125–134
89. R P Foss, US P. 4 749 762
90. A Yada, Sh Matsumoto, Y Kawamori, Y Adachi, US P. 4 762 862
91. M S Ramakrishna, D D Deshpande, G N Babu *Angew. Makromol. Chem.,* 1985, **130** 171–178
92. N A Lisovtseva, G F Zvereva, G V Dubinkina *Vsesoyuznaya Konferentsiya "Radikal'naya Polimerizatsiya". Tezisy Dokladov, Gor'kii* (All-Union Conference on "Radical Polymersiation". Abstracts of Reports, Gorky), Gorky, 1989, p. 19
93. S Tani, K Kogo, Y Nodzaki, K Osima, Japanese Appl. 198 606; *Ref. Zh. Khim.,* 1990, 6S557P
94. Y Nabeshima, T Tsuruta *Makromol. Chem.,* 1989, **190**(7) 1635–1647
95. D Briche, D Guymord, Ph Persisse, J P Pouget, French Appl. 2 601 023; *Ref. Zh. Khim.,* 1989, 7S620P
96. V R Kamath, US P. 4 777 280
97. H-H Goeretz, A Oftring, F Voget, BRD Appl. 3 725 449; *Ref. Zh. Khim.,* 1989, 22S556P
98. M F Grenier-Loustalot, M Audenaert, J Boutillier, D Lecacheux *Eur. Polym. J.,* 1989, **25**(4) 411–418
99. O S Zaikina, S M Romaniv *Vtoraya Konferentsiya Molodykh Uchenykh Khimicheskikh Fakul'tetov RPI i LGU, Riga* (The 2nd Conference of Young Scientists from the Faculties of Chemistry at the Riga Polytechnic Institute and Leningrad State University, Riga), Riga, 1987, p. 68
100. O V Suberlyak, O S Zaikina, S M Romaniv *Kompozitsionnye Polimernye Materialy,* Kiev, 1989, (41) 51–54
101. S H O Egbow *Angew. Makromol. Chem.,* 1987, **148**(2329) 79–86
102. O Murai, T Sakai, Japanese Appl. 1 110 506; *Ref. Zh. Khim.,* 1990, 6S562P
103. B Yansen, G Ellinghorst *J. Biomed. Mater. Res.,* 1985, **19**(9) 1085–1099
104. O V Suberlyak, M L Sheketa, A I Soshko *Photopolymerisation of Liquid Compositions Based on 2-Hydroxyethyl Methacrylate and Polyvinylpyrrolidinone,* Kiev, 1985, 7pp. Article Deposited at UkrNIINTI, 23.08.85, No. 1515
105. L Sheketa, B I Bardak *Materialy 3-i Konferentsii Molodykh Uchenykh Khimiko-Tekhnologicheskogo Fakul'teta RPI, Riga* (Proceedings of the 3rd Conference of Young Scientists at the Faculty of Chemical Engineering of the Riga Polytechnic Institute, Riga), Riga, 1989, p. 78
106. O V Suberlyak, M L Sheketa *Plast. Massy,* 1989, (8) 15–17
107. O V Suberlyak, M L Sheketa, A I Soshko *Zh. Prikl. Khim.,* 1988, **61**(8) 1877–1880
108. M S Kurilo, M M Tsyunok, M M Blazhkivskii *Vestn. L'vov Politekh. Inst.,* 1989, (231) 31–33
109. O V Suberlyak, M Sh Poretskaya, G M Yaremko *Ukr. Khim. Zh.,* 1988, **54**(10) 1109–1111
110. Fang Yue-e, Shi Tianyi, Wang Wenfeng, Shi Fang *J. Appl. Polym. Sci.,* 1989, **38**(5) 821–828
111. J Coupek, S Vozka, A Frydrychova, V Smigol, Czech. P. 260 852; *Ref. Zh. Khim.,* 1990, 4S667P
112. K Das Suryya, S Porter, R Dowbenko, EEC Appl. 0 307 504; *Ref. Zh. Khim.,* 1990, 4S666P
113. N A Lavrov *Khimicheskaya Tekhnologiya Svoistva i Primenenie Plastmass* (Chemical Technology, Properties and Applications of Plastics), Leningrad, 1988, pp. 32–37
114. S Sevcik, J Stamberg, P Schmidt *J. Polym. Sci. C,* 1967, (16) 821–831
115. N A Lavrov, A F Nikolaev *Plast. Massy,* 1984, (8) 55–57
116. F Ibragimov, T I Usmanov, T G Gafurov *Vysokomol. Soedin., Ser. A,* 1970, **12**(11) 2621–2624
117. N A Lavrov, V M Chudnova, A F Nikolaev *Zh. Prikl. Khim.,* 1986, **59**(7) 1554–1558
118. A F Nikolaev, N A Lavrov, S G Bondarenko, V Bondarenko, USSR P. 891 689; *Otkrytiya. Izobreteniya,* 1981, (47) 111
119. N A Lavrov, A F Nikolaev, Yu V Solomatin *Zh. Prikl. Khim.,* 1987, **60**(11) 2616–2618
120. N A Lavrov, V M Bondarenko, A F Nikolaev, S N Sautin *Vysokomol. Soedin.,* 1981, **23** 142–144
121. N A Lavrov, A F Nikolaev, Yu V Solomatin *Zh. Prikl. Khim.,* 1987, **60**(1) 167–170
122. W Schössler, J Coupek, F Hiepe DDR P. 256 720; *Ref. Zh. Khim.,* 1988, 22S569P

123. J Kahovec, M Jelinkova, J ACoupek *Polym. Bull.*, 1987, **18**(6) 495–499
124. M R Van de Mark, N D Lian, M Brandon, E C Eckstein *J. Polym. Sci.*, 1987, **C25**(8) 327–330
125. J Kahovec, M Jelinkova, J A Coupek, Czech. P. 253 004; *Ref. Zh. Khim.*, 1989, 13S512P
126. M Jelinkova, J Kahovec, J A Coupek, Czech. P. 251 117; *Ref. Zh. Khim.*, 1989, 3S669P
127. Y Takahashi, V Foyle, J E Guillet, *IUPAC 32nd Int. Symp. Macromol. Kyoto, Prepr-Kyoto*, 1988, p. 185
128. N A Lavrov, A F Nikolaev *Plast. Massy*, 1984, (4) 10–12
129. O Wichterle, D Lim *Nature*, 1960, **185** 117
130. N A Lavrov *Khimicheskaya Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties, and Applications of Plastics), Leningrad, 1987, pp. 26–36
131. N A Lavrov *Khimicheskaya Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties, and Applications of Plastics), Leningrad, 1989, pp. 77–84
132. S G Starodubtsev, O K Boiko, N P Pavlova, V A Kabanov *Plast. Massy*, 1985, (1) 30–33
133. J Vacik, B Obereigner, D Souckova, J Kudelkova, K Smetana *IUPAC 32-nd Int. Symp. Macromol. Kyoto, Prepr.-Kyoto*, 1988, p. 591
134. O V Suberlyak, O S Zaikina, I G Tkhir, A I Soshko *Plast. Massy*, 1985, (11) 27–29
135. H Singh, P Vasudeva, A R Pay *J. Sci. Ind. Res.*, 1980, **39**(3) 162–171
136. P Yoshida, M Kumakura, I Kaetsu *J. Macromol. Sci. A. Chem.*, 1980, **14**(4) 555–569
137. M Kumakura, I Kaetsu *J. Polym. Sci., Polym. Lett. Ed.*, 1983, **21**(8) 609–613
138. M Kumakura, I Kaetsu *J. Appl. Polym. Sci.*, 1983, **28**(12) 3759–3765
139. M Kumakura, I Kaetsu *J. Dispers. Sci. Technol.*, 1983, **34**(2) 147–159
140. K F Mueller, W R Good *AIChE Symp. Sec.*, 1981, **77**(206) 42–51
141. J M Collett, D Attwood, J M Wodd *Am. Chem. Soc., Polym. Prepr.*, 1983, **24**(1) 62–63
142. N M Franson, N A Peppas *Am. Chem. Soc., Polym. Prepr.*, 1983, **24**(1) 53–54
143. J Kopecek *Abstracts of Papers, 194th American Chemical Society National Meeting*, New Orleans, 1987, p. 753
144. J H Me Jain, R D Jarrett, US P. 4 737 544
145. C Migliaresi. L Nicodemo, L Nicolais, P Passerini *J. Biomed. Mater. Res.*, 1984, **18**(2) 137–146
146. C Migliaresi, L Nicodemo, L Nicolais, P Passerini *Polymer*, 1984, **25**(3) 686–689
147. N A Lavrov, F A Kuz'mina, M V Vinogradov *Khimicheskayo Tekhnologiya, Svoistva i Primenenie Plastmass* (Chemical Technology, Properties and Applications of Plastics), Leningrad, 1988, pp. 148–151
148. L Pinchuk, E C Eckstein, M R Van de Mark *J. Appl. Polym. Sci.*, 1984, **29**(5) 1749–1760
149. J Verhoeven, R Scheffer, J A Bowstra, H E Junginger *Polymer*, 1989, **30**(10) 1946–1950
150. L Pinchuk, E C Eckstein *J. Biomed. Mater. Res.*, 1981, **15**(2) 183–189
151. K Ito, Y Masuda, T Shintani *Polym. J.*, 1983, **15**(8) 557–583
152. M F Refogo, F L Leong *IUPAC 28th Macromolecular Symposium. S. I.*, Amherst, 1982, p. 725
153. I G Tkhir, O V Suberlyak, V P Stadnik, A I Soshko *Zh. Prikl. Khim.*, 1983, **56**(10) 2250–2254
154. S Wisniewski, Wan Kim Sung *J. Membr. Sci.*, 1980, **6**(3) 299–308
155. S C Yoon, M S Jhon *J. Appl. Polym. Sci.*, 1982, **27**(12) 4661–4668
156. E V Lamberti, R Evangelista, M A Wheatley, et al. *Polym. Biometer. Proc. Symp.*, New York–London, 1984, pp. 39–50
157. T Fukuda, I Takeuchi, I Fukumori, Japanese Appl. 1 113 322; *Ref. Zh. Khim.*, 1990, 5S566P
158. H Ahne, W Plundrich, BRD Appl. 3 630 954; *Ref. Zh. Khim.*, 1989, 3S668P