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Synthesis and characterization of novel linear and crosslinked polyelectrolytes derived from the acetoacetic ester and acrylic acid

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Summary

Novel linear and crosslinked polyelectrolytes based on acetoacetic ester and acrylic acid were synthesized for the first time via Michael addition reaction followed by radical polymerization. The structure and properties of polyelectrolytes were characterized by FTIR, Raman and NMR spectroscopy, TGA, DSC, GPC, viscometry and potentiometric titration. Considerable influence of water content on the swelling rate of hydrogels was established. The swelling-deswelling properties of hydrogels were studied in dependence of pH, ionic strength and in water-organic solvent mixtures.

Introduction

Involvement of new monomers into polymerization reaction with formation of polyelectrolytes is of great interest [1]. Earlier [2-4] we have shown that ethyl 3-aminocrotonate and its alkyl derivatives are able to be involved into Michael addition reaction with formation of intermediate betaine type monomers upon addition of unsaturated carboxylic acids. The latter were polymerized by radical-initiated polymerization in bulk, water, and water-organic solvents and as a result a series of linear and crosslinkled polybetaines were obtained. It was marked that the specific feature of mixture of ethyl 3-aminocrotonate and unsaturated carboxylic acids is that the polymerization process in bulk occurs exothermically even at room temperature and without adding of an initiator. The kinetics and mechanism of polymerization of intermediate betaine type monomers were evaluated.

In the present communication we report for the first time on polymerization of acetoacetic ester proceeding in the presence of acrylic acid via Michael reaction. Some physico-chemical properties of novel linear and crosslinked polyelectrolytes are described.

Experimental

Materials

Acetoacetic ester (ethyl acetoacetate) (99%), acrylic acid (99.5%), initiator azoisobutyronitrile (AIBN) and crosslinking agent N,N'-methylenbisacrylamide (MBAA) were purchased from Aldrich. Acrylic acid was purified by distillation under the low pressure and kept in refrigerator. Reagent grade solvents acetone, ethanol, DMF, DMSO purchased from Aldrich were used. 0.1N HCl and 0.1N KOH were used for potentiometric titration. Ionic strength of the solution was adjusted by reagent grade KCl.

Methods

FT-IR and Raman spectra were recorded using a Perkin Elmer Spectrum GX. The thermal stability of polymers was determined with Thermal Analyst, TA Instrument 2100. The temperature range was from 20 to 800 °C and the heating rate was 10 $°C \cdot min^{-1}$ in nitrogen atmosphere. DSC measurement was carried out with the help of TA 2010. The temperature range was from 30 to 350 °C and the heating rate was 10 °C/min in nitrogen atmosphere. ^1H NMR spectra were obtained in D_2O at room temperature with the help of JEOL JNM-LA 300 WB FT-NMR. Molecular masses of were determined by using of gel permeation chromatography (Waters 1525 Binary HPLC pump, Waters 2414 RI Detector). Waters ultrahydrogel 120, 250, 500 and 0.1M $NaNO_3$ aqueous solution were used as columns and mobile phase respectively. The column temperature was 45^oC and flow rate was 0.8 mL/min. The injected volume of each sample was 100μL. Molecular masses were determined by calibration curve obtained from pullulan (polysaccharide) kit (Shodex, Japan) during 60 min. The refraction index detector's temperature was kept at 35 ^oC. Potentiometric titration was carried out on the pH/conductivity meter "Mettler Toledo MPC 227" (Switzerland) at room temperature. The viscosity of polymer solutions was measured by Ubbelohde viscometer at 25 ± 0.1 °C.

Polymer synthesis

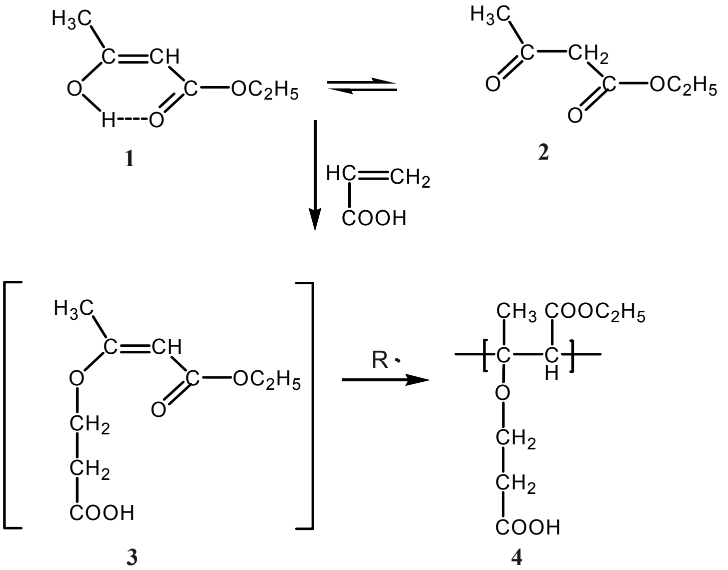
Equimolar monomer mixture of AAE (0.5 mol, 1.8 mL) and AA (0.5 mol, 1.2 mL) containing AIBN ($5 \cdot 10^{-3}$ $mol \cdot L^{-1}$) was bubbled by nitrogen gas during 5 min to remove the dissolved oxygen and the polymerization reaction was carried out at 70 °C during 15 min. The radical polymerization of equimolar monomer mixture (0.5 mol of AAE and 0.5 mol of AA) was also carried out in the presence of 0.28; 0.6; 0.83; 1.39; 1.94 and 2.78 mol of water in monomer mixture. The obtained polymers were purified by two-fold precipitation from aqueous solution into acetone. The crosslinked polymers were synthesized in the same conditions as linear one but in the presence of 0.6; 1.67; 2.78 and 5.55 mol of water and $5 \cdot 10^{-3}$ $mol \cdot L^{-1}$ MBAA. Gel samples were washed by distilled water during 1 week to remove the sol fraction.

Equilibrium swelling measurements

Swelling degree of gels α (in g/g) was calculated according to the formula: $\alpha = (m - m_o)/m_o$, where m and m_o are the masses of swollen and dried gels respectively. The swelling degree (g/g) of hydrogels in the mixtures of different solvents (water–ethanol, water-acetone, water-DMF an water-DMSO) was determined gravimetrically by measurement of the mass of mixture-swollen and dried gels and calculated according to the formula: $\alpha_{wo} = (m_{\mathrm{wo}} - m_0)/m_0$, (where α_{wo} is the swelling degree in water-organic solvent mixtures, m_{wo} is the mass of gel in water-organic solvent mixtures and m_0 is the mass of dried gel). The swelling rate was expressed as $q = W_s / W_d$, where W_s is the weight of swollen hydrogel W_d, is the weight of initially dried hydrogel. The swelling rate was expressed as $kt^n = M_t / M_\infty$, where k is the swelling rate constant, n is a characteristic exponent describing the mode of the penetrant (water) transport mechanism, t is the absorption time, M_t is the mass of water absorbed at time t, M_∞ is the mass of water absorbed at infinite t_∞. The constants k and n were calculated from the slopes and intercepts of the plots of $\ln(M_t/M_\infty)$ versus $\ln t$ [5].

Results and discussion

It is well known [6] that acetoacetic ester (AAE) exists in enol (**1**) and keto (**2**) tautomeric forms (Scheme 1).



Scheme 1. Acetoacetic ester in enol (**1**) and keto (**2**) tautomeric forms and formation of intermediate 3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester (**3**) and final polymer product poly[3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester] (**4**)

This is confirmed by appearance of two peaks from C=O bonds replaced at 1712 and 1737 cm^{-1} (Table 1). Stretching vibrations of C=C bonds corresponding to *cis*- and *trans*-isomers of **1** appear at 1633 and 1650 cm^{-1}. Intensive peaks at 1039 and 1148 cm^{-1} are responsible for C-O-C groups. Very small peaks of hydrogen-bonded OH groups are observed at 3441 and 3556 cm^{-1}. It should be mentioned that AAE itself does not polymerize due to stabilization of enol form via conjugation of C=C and C=O bonds and additional formation of intramolecular hydrogen bonds. Addition of AA to AAE leads to formation of intermediate product 3-(2-carboxyethoxy)-but-2-

enoic acid ethyl ester **3** due to migration of hydrogen atoms from the enol tautomeric form to α-carbon atoms of AA. The intermediate product **3** is able to polymerize fast to final product poly[(3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester)] **4** upon the addition of initiator.

As seen from Table 1 the FT-IR spectra of **4** show disappearance of C=C bonds at 1633 and 1650 cm^{-1}. Hydrogen-bonded OH groups of COOH as broad lines appear at 3452 cm^{-1}. The intensive and broad peak at 1697 cm^{-1} belongs to stretching vibrations of C=O groups. Asymmetric vibration of carboxylic groups is appeared at 1450 cm^{-1}.

Table 1. FT-IR spectra of **1** and **4**

Functional groups	Frequency, cm^{-1}	
	1	**4**
ν (OH)	3556	3452
	3441	
ν (CH)	2985	2928
ν (C=O)	1737	1697
	1712	-
ν (C=C)	1650	-
	1633	-
ν (COO$^-$)	-	1450
ν COC	1148	1157
	1039	1037

Figure 1 shows the ^{1}H NMR spectra of **4** together with assignments of functional groups.

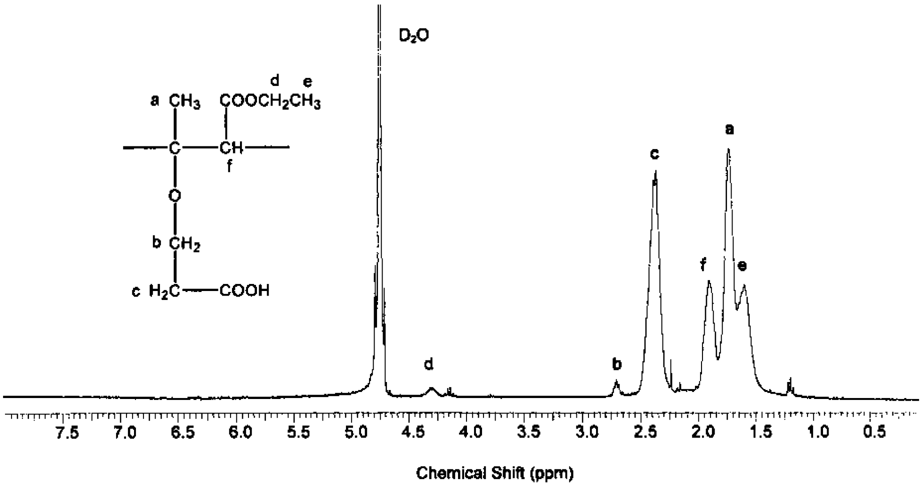


Figure 1. ^{1}H NMR spectra of poly[3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester] in D_2O

Thus FTIR and ^{1}H NMR spectra confirm the formation of polymer with structure **4**. The chromatogram and the molecular weight distribution of linear polymer are shown in Figs. 2 and 3. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) are equal to $M_n = 5.6 \cdot 10^5$, $M_w = 8 \cdot 10^5$, PDI = 1.42.

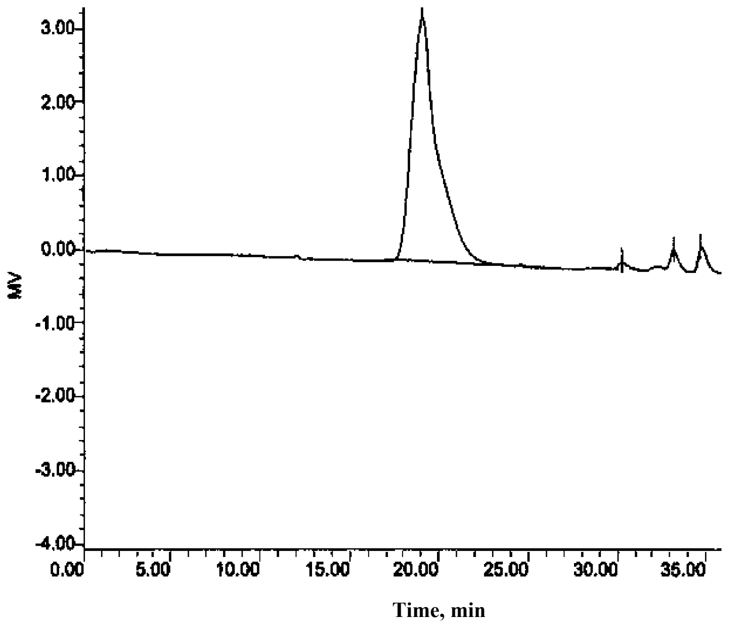


Figure 2. Chromatogram of poly[3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester]

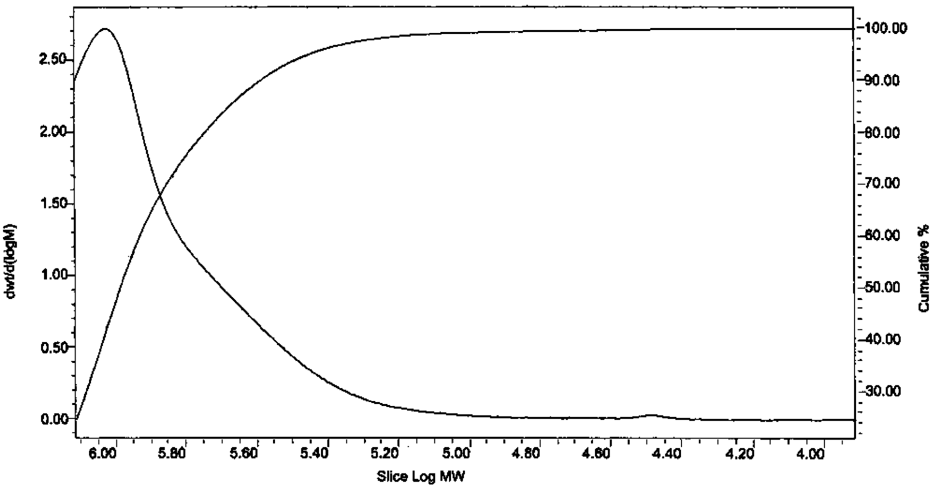


Figure 3. Molecular weight distribution of poly[3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester]

DSC trace exhibits the glass transition temperature at 220 °C (Fig. 4). TGA data show the three well-defined bends that correspond to water evaporation, melting and decomposition at 100, 250 and 393 °C respectively (Fig. 5).

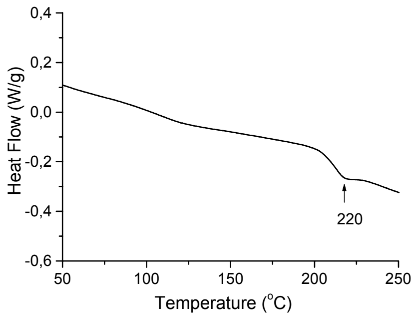


Figure 4. TGA curve of linear poly[(3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester)]

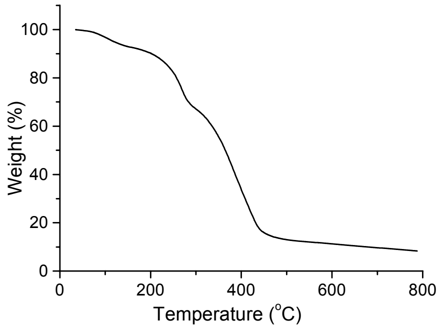


Figure 5. DSC curve of linear poly[(3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester)]

The direct and back potentiometric titration data confirm the presence of ionizable carboxylic groups. The pK_a of carboxylic groups determined from the Henderson-Hasslebalch equation in 0.1 N KCl is equal to 4.6 and close to those of poly(carboxylic acid)s. In aqueous solution **4** shows polyelectrolyte anomaly that disappears upon addition of neutral salt.

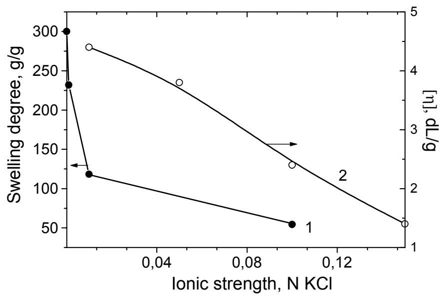


Figure 6. Dependence of the intrinsic viscosity of linear (1) and swelling degree of crosslinked (2) poly[(3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester)] on the ionic strength

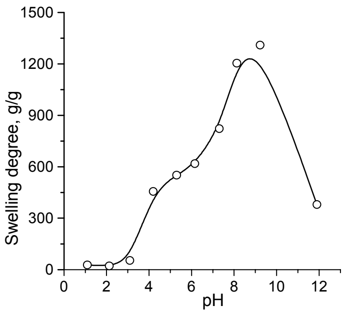


Figure 7. Dependence of the swelling degree of crosslinked poly[(3-(2-carboxyethoxy)-but-2- enoic acid ethyl ester)] on pH of outer solution

Increasing of salt concentration leads to decreasing of the intrinsic viscosity of linear and swelling degree of crosslinked **4** due to screening of charged groups of polyelectrolyte chains by low-molecular weight electrolytes (Fig. 6). The dependence of swelling degree of crosslinked poly[(3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester)] on pH passes through a maximum at pH ≈ 9 because of ionization of carboxylic groups (Fig. 7). A further decrease of the swelling degree is attributed to an increase of the ionic strength, caused by the excess amount of NaOH. The time dependent swelling behavior of crosslinked **4** synthesized at various amounts of added water is represented in Fig. 8. Both swelling rate *q* and the swelling constant *k* increase with increasing of water content in reaction mixture. This is probably due to participation of water molecules in formation of hydrogen bonds within the network structure. The constants *k* and *n* calculated from the slopes and intercepts of the plots of $\ln(M_t/M_\infty)$ versus ln *t* are given in Table 2.

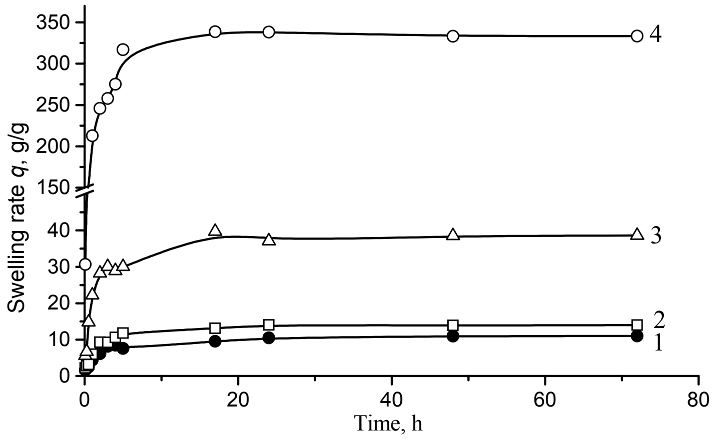


Figure 8. Swelling rate *q* of crosslinked poly[3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester] at 0.6 (1); 1.67 (2); 2.78 (3) and 5.55 mol (4) of added water to monomer mixture

Table 2. The values of *n* and *k* for hydrogels synthesized in the presence of various amounts of water

Water content, vol.%	*n*	*k*
10	0.37	0.12
30	0,40	0.11
50	0,44	0.12
100	0,55	0.08

The values of $n = 0.55$ is close to Fickian diffusion (n=0.5) while $n < 0.5$ indicates to non-Fickian or anomalous transport.

Significantly collapsing of hydrogels due to poor thermodynamic quality of solvents with respect to carboxylic groups of **4** is observed in acetone, ethanol and DMF (Fig. 9). For all water-organic solvent mixtures the continuous collapsing of hydrogels takes place. These results confirm the universal behavior of hydrogels with respect to thermodynamic quality of solvents.

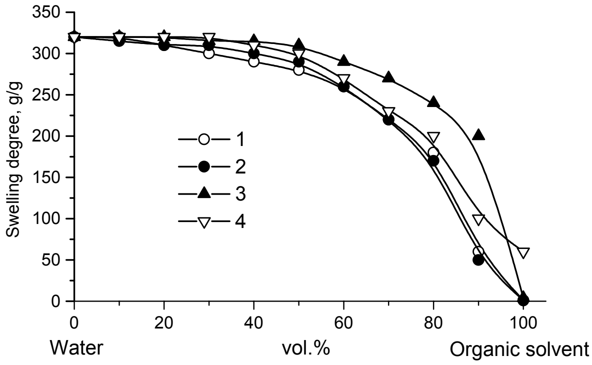


Figure 9. Swelling-deswelling behavior of crosslinked **4** in water-acetone (1), water-ethanol (2), water-DMF (3) and water-DMSO (4) mixtures

Conclusions

Addition of acrylic acid to acetoacetic ester leads to formation of intermediate monomer product 3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester due to migration of hydrogen atoms from the enol tautomeric form to α-carbon atoms of acrylic acid. FT-IR and NMR spectra confirm the structure of novel polymer. In pure water poly[3-(2-carboxyethoxy)-but-2-enoic acid ethyl ester] exhibits the polyelectrolyte anomaly that disappears in salt containing solution. The pK_a of carboxylic groups determined in 0.1 N KCl is equal to 4.6 and close to those of poly(carboxylic acid)s. Considerably increasing of swelling degree of hydrogels upon addition of water into reaction mixture is probably due to participation of water molecules in formation of hydrogen bonds within the network structure. Water absorption mechanism of hydrogels is described by Fickian and non-Fickian diffusion. Hydrogels are in collapsed state in organic solvents.

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