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Complexation of new linear copolymers based on ethyl acrylate

Abstract. The processes of complexation of diphilic macromolecules with high molecular acids in recent years have moved into a separate and rapidly developing direction of the chemistry of polymers. Of particular interest are complexes based on nonionic thermosensitive copolymers and polycarboxylic acids, which acquire properties significantly different from those of the original components. In this regard, studies related to the establishment of complex-forming and surface-active behavior of non-ionic polymers with thermoregulated characteristics, acquires a particular urgency, both scientifically and in practice.

In the preparation of copolymers of a linear structure by the radical polymerization method, the samples were crosslinked after traditional planting and drying, and for this reason the method for the first time used the method of removal from unreacted monomers and oligomers by a dialysis membrane and dried samples by the lyophilic dryer.

The study also investigated the establishment of the main regularities of synthesis and intermacromolecular reactions of heat-sensitive, proton acceptor copolymers based on 2-hydroxyethyl acrylate (HEA) and ethyl acrylate (EA) with proton-donor polycarboxylic acids. Using the turbidimetry method, it was possible to show that the mutual transition of the hydrophobic complex-hydrophilic associate can be initiated not only by changing the pH, but also by varying the concentration of the solution. A whole layer of new interesting data has been obtained on the features of the effect of complexation on the thermosensitive properties of diphilic macromolecules. The set of the obtained data allowed to describe in more detail and demonstrate the scheme of mutual transitions hydrophobic complex-hydrophilic associate-noninteracting macromolecule depending on pH.

Key words: Radical copolymerization, 2-hydroxyethylacrylate, ethylacrylate, polyacrylic acid, interpolymer complexes.

Introduction

During the last several decades, there has been an intensive study of the issues concerning intermacromolecular interactions underlying the changes in the physicochemical characteristics and behavior of polymer systems. To date, there is a fairly large number of publications devoted to this area, which points to the special significance of products of interactions-IPC [1-4]. IPC are insoluble high-molecular structures formed due to the association of repeating units of various macromolecular chains. That is, macromolecules interact with each other through the forces of physical nature of a different nature and intensity. These links are most often Van der Waals forces, hydrogen bonds, hydrophobic and electrostatic interactions [1; 2]. In addition, such an interaction is accompanied by a change in the conformations of the links and individual segments of the macromolecular chain. Chemical and steric complementarity is a condition for effective interaction of polymers with the formation of IPC [2]. Complementary are such macromolecules, the functional groups of which can interact in a specific way, and the structure of these molecules should not create obstacles for the formation of the number of bonds necessary for the stability of the complex. By the type of dominant interaction, IPC are divided into stereocomplexes, polyelectrolyte complexes and complexes formed by hydrogen bonds [1; 5].

It should be noted that polycomplexes are formed in acidic media, therefore, the stability of the complex is highly dependent on pH as well as ionic strength. In addition, complexation is stabilized by cooperative nature, hydrophobic interactions, and is usually enhanced by decreasing ambient temperature [2; 6].

The interaction of polymeric acids with proton-acceptor nonionic polymers leads to the formation of polycomplexes stabilized by hydrogen bonds with precipitation. In this case, IPC have a strictly defined composition and their physicochemical, mechanical and other properties in most cases do not depend on the properties of the initial components of the components. Such IPC are of considerable interest from a practical point of view. The products of intermolecular interaction through hydrogen bonds are already widely used as medical materials [7-9], biomaterials [10], emulsifiers [11], sorbents for the recovery of heavy metals [12], etc. In this regard, the expansion of the range of IPC with the use of available polymers, as well as the creation of new composite materials on their basis, is a very urgent task.

The composition of IPC stabilized by hydrogen bonds can be determined by the number of proton acceptor centers in the non-ionic polymer. Thus, as the oxygen content of the non-ionic polymer increases, the number of polycarboxylic acid units bound to the polycomplex increases. For most systems in dilute solutions, the formation of complexes of stoichiometric composition is characteristic [1].

For the new copolymers (CPL) based on HEA and EA, the processes of their complexation with polycarboxylic acids were first studied. The critical value of complexation (pH_c) was fruitfully used as a criterion for the complexing ability of systems, which made it possible to establish a number of regularities on the influence of factors of different nature on the stability of the generated IPC. When studying the complexation of linear copolymers of HEA-EA with linear polyacrylic acid in solutions, the formation of polycomplexes of stoichiometric composition stabilized by hydrogen bonds and hydrophobic interactions has been established. As the basic physicochemical methods of investigation, we used: IR spectroscopy with Fourier transducer, UV spectroscopy, turbidimetry.

Materials and methods

2-hydroxyethylacrylate (HEA) (Sigma Aldrich (UK)) contained 96% of basic product. It was purified by double vacuum distillation in argon flow (b.p.=91^0/12 mm. sec., n_D^{20}=1.4500).

Ethylacrylate (EA) (Fisher Scientific (UK)) contained 96% of basic product. It was washed by 10 % water KOH solution from inhibitor, was dried above potash and was purified by double vacuum distillation (b.p.=99^0C, T_i=71^0C, n_D^{20}=0,9405).

Polyacrylic acid (PAA) with a molecular mass of 250000 (Sigma-Aldrich Co. (the USA)) was used without additional purification.

Azo-bis-iso-butyric acid dinitrile (ABAD) of "c" grade (Acros (the USA)) was twice recrystallized from absolute methanol, m.p.=103^oC.

Ethanol (absolute with m.p.=78^oC/760 mm. Hg, n_D^{20}=1.3612-1.3618) was produced by Sigma-Aldrich Co." (USA).

The solutions of isopoly acid were prepared by mixing the solutions of starting components. They were allowed to stand for 5 minutes. The measurements were made.

To prepare solutions distilled water was used.

Synthesis of HEA-EA copolymers of linear and grid-typed structure

Water-soluble linear (co) polymers of PHEEA, PEA, HEA-EA of composition 90:10%; 80:20%; 70:30%; were synthesized using the method of radical copolymerization of a 50% solution of a mixture of HEA-EA of various compositions in an ethanol solvent at 60°C. Copolymerization was carried out in the ampoules of molybdenum glass. The content of ampoules was blown off by argon for 20 minutes to remove oxygen from reaction mixture. The substance radical polymerization of liner EA and HEA monomers was initiated by thermal decomposition of azo-bis-iso-butyric acid dinitrile. The resulting linear copolymers were poured into the dialysis membrane to purify from unreated monomers. The samples obtained were dried by liophylization up to a constant weight and then aqueous solutions were prepared.

Physico–chemical methods of investigation of polymers and their intermolecular complexes.

IR spectra of initial samples of polymers and their interpolymer complexes (IPK) were recorded on a spectrophotometer (Perkin-Elmer FTIR Spectrum Two (UK)) in the region of 400-4000 cm^{-1}. Samples were prepared in the form of tablets with KBr.

The optical density of solutions of polymers and their interpolymer complexes (IPC) were determined on the UV spectrophotometer (Shimadzu UV / VIS-2401 PC (Japan)) at a wavelength of 400 nm.

pH of polymer solutions and their mixtures were determined at a constant temperature of 25°C on the digital ionomer (Hanna Instrument pH 211 meter (Hanna Ltd., Portugal)) with a precision of +0.01 units of pH.

pH of the solutions were regulated by adding small amounts of 0.1 M HCl and 0.1 M NaOH

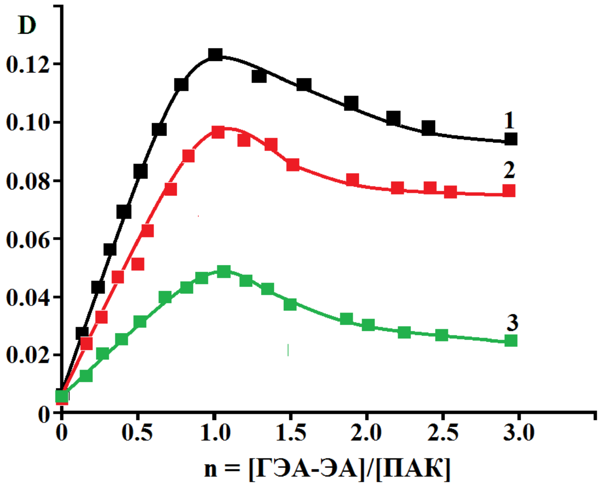
Liophylization. The samples were liophylized using Heto PowerDry® LL3000 connected to rotor lubricating pump (Edwards RV3) at -53°C.

The dialysis membranes (molecular mass of 12-14 kDa) were supplied by MediCell International Ltd company (UK).

Results and discussion

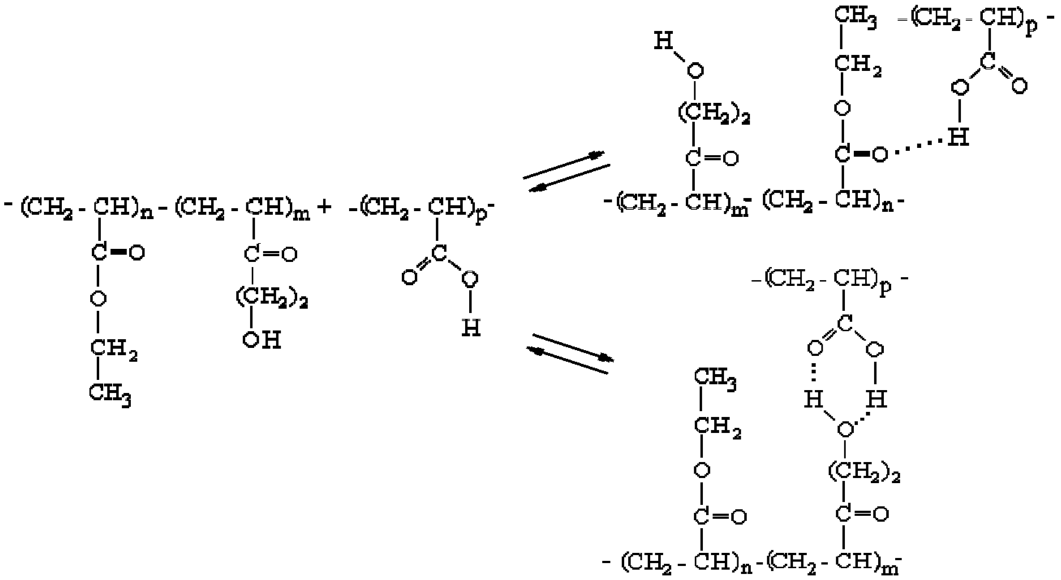
A special class is the IPC formed by polycarboxylic acids with non-ionic polymers and stabilized by the hydrogen bond system. IPC possess a unique set of physico-chemical properties, different from those of the initial components.

In the present paper the complex formation of HEA-EA copolymer with polyacrylic acid (PAA) in aqueous solutions was studied using turbidimetry. The addition of the solutions of HEA-EA copolymers to PAA solutions is accompanied by increasing optical density which evidences the formation of hydrogen bonds formed by the system with the involvement of PAA carboxyl groups with hydroxyl and carbonyl groups of HEA-EA components in isopoly acid system (Figure 1, Scheme 1) [13, 14]. The curbes of turbidimetric titration obtained evidences stoichiometricity of the composition of polycomplexes.



IMM [HEA]:[EA]=70:30 (1); 80:20 (2) mol.%;
PHEA(3); T=298 K;
MM (PAA)=250000; [HEA:EA]= [PAA]=0,01 M

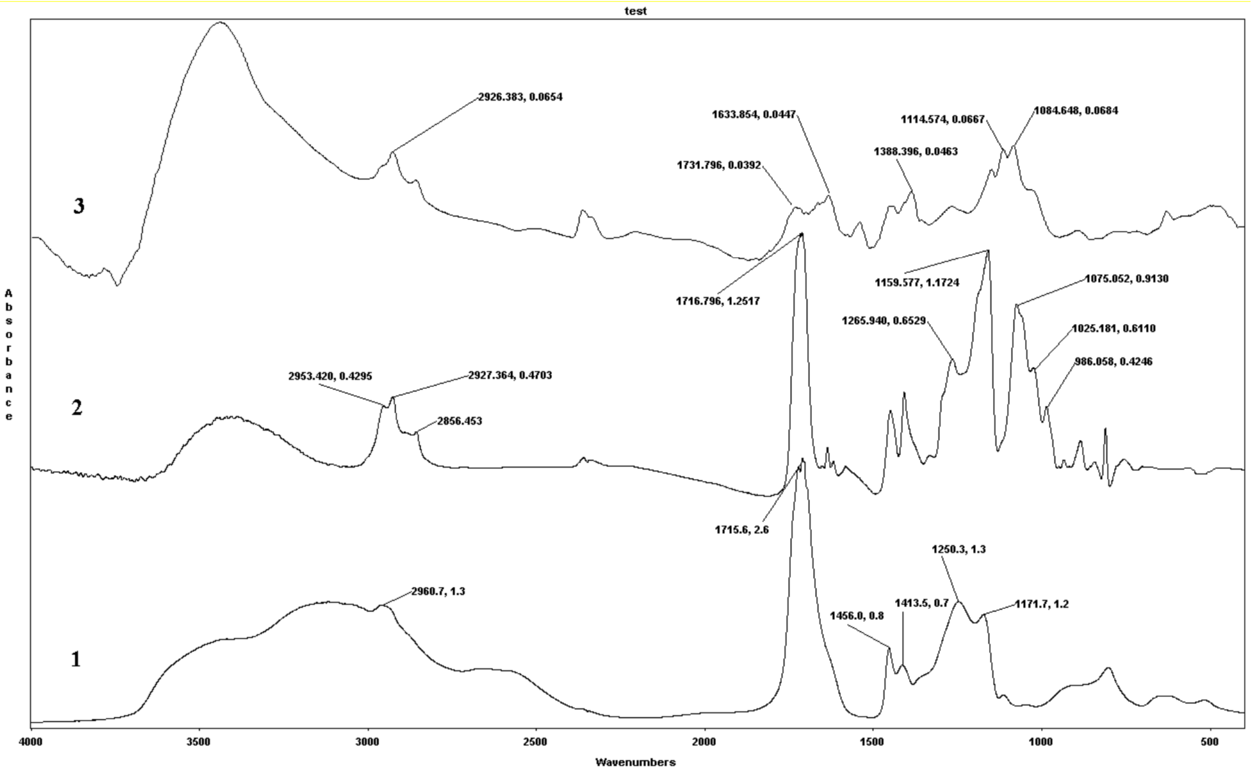
Figure 1 – Turbidimetric titration of PAA solution with solutions of copolymers HEA-EA



Scheme 1 – Scheme of interaction of linear copolymers based on HEA-EA with PAA

To confirm the formation of a hydrogen bond between the interacting polymers, IR spectra of polycomplexes and initial polymer components were recorded.

Figure 2 shows the IR spectra of the CPL HEA-EA, PAA and IPC on their basis. It can be seen from these figures that the characteristic bands in the IPC spectra are clearly related to the initial polymer components. In this case, a shift to the short-wavelength region (λ= 1731.7 cm^{-1}) is observed for the band belonging to the valence vibrations of the carbonyl group of PAA (λ = 1715.6 cm^{-1}), which is obviously due to the formation of a hydrogen bond between C = O carboxyl PAA and hydroxyl group of monomer units of HEA. Complexation of polymers by hydrogen bonding in aqueous solutions is accompanied by compacting of macromolecules with the precipitation of IPC.



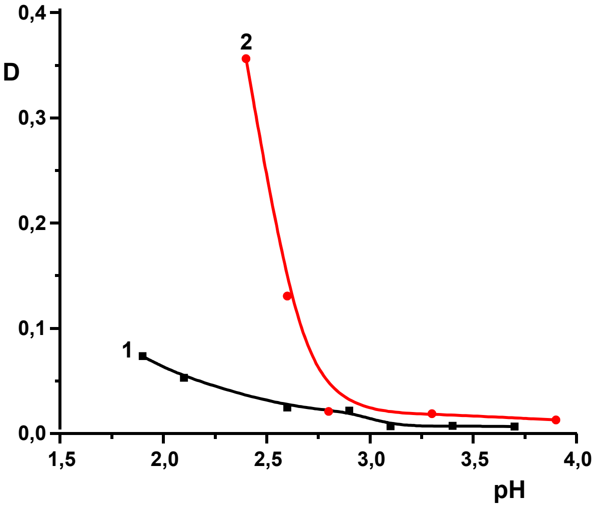
IR spectra: PAA (1); CPL HEA-EA (2); complex CPL HEA-EA – PAA (3).

Figure 2 – IR spectra of PAA, CPL HEA-EA и HEA-EA copolymers with PAA

The processes of formation of IPCs are characterized by critical phenomena. Significant changes in various parameters of the environment depend on the properties of the system. In addition, to form a polymer-polymer complex, the polymer must have a minimum critical size of functional groups in order to provide the required level of hydrogen bonding density between complementary macromolecules.

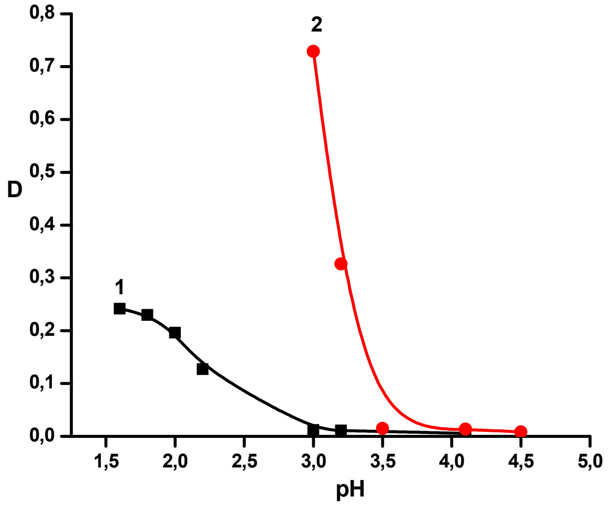
The critical pH of complex formation depends on the nature, concentration and ionic strength of the macromolecules that act, as well as the presence of various substances in the solution. The critical pH_c value is used as a quantitative criterion for the complex formation ability of a polycarboxylic acid-nonionic polymer system, in aqueous solutions. Its increase indicates that the interpolymer complex formation of macromolecules is enhanced. The cooperative nature of the process and, consequently, a sharp increase in the turbidity of the medium is observed below the critical pH of complexation (pH_c), first mentioned in the works of Tsuchida et al. [15] and a certain gravimetric method from the analysis of dry IPC samples of some polycarboxylic acids with polyethylene oxide.

For the quantitative evaluation of the complexing ability of HEA-EA copolymers with PAA we determined critical pH of complex formation (pH_c) (Figure 3-4). The sharp increase in optical density was found to be observed for the mixtures of the solutions of HEA-EA copolymers with PAA when reaching $pH_{c.}$ It evidences the complex formation between polymers. At that when HEA content increases in the copolymer composition the value pH_c shifts to the region of lower values (from 2.8 to 3.2) which evidences the decrease in the system complexing ability conditioned by decreasing the contribution of hydrophobic interactions of EA components to the stabilization of polycomplexes. If the component of ethyl acrylate is increased in the copolymer, then the pH_c increases. This increases the process of the complex and creates high-strength complexes. (figure 5). The data obtained are well-agreed with the results of the paper [16-18].



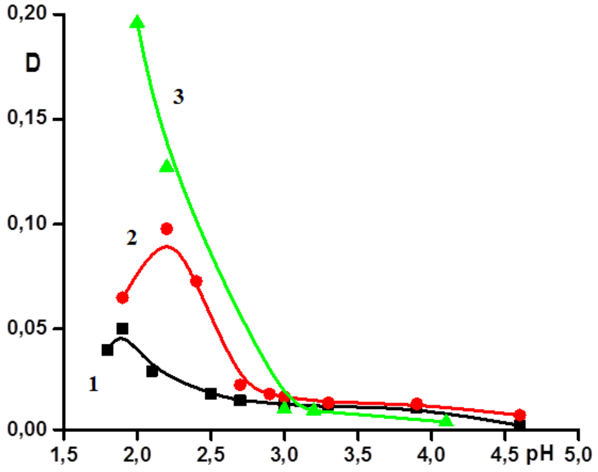
IMM [HEA]:[EA]=90:10 mol.%;
[PAA]=[HEA-EA]= 0.01 (1); 0.05% (2);
MM (PAA)=250000; [PAA]/[HEA-EA]=1:1

Figure 3 – Dependence of the optical density of aqueous solutions of mixtures CPL [HEA-EA]/ [PAA] on pH



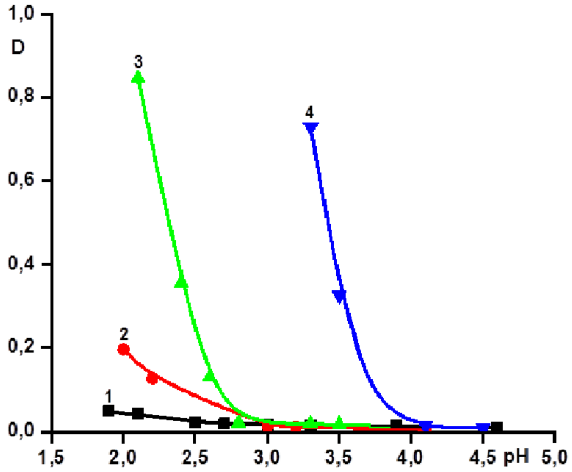
IMM [HEA]:[EA]=80:20 mol.%;
[PAA]=[HEA-EA]= 0.01 (1); 0.05% (2);
MM (PAA) = 250000; [PAA]/ [HEA-EA]= 1:1

Figure 4 – Dependence of the optical density of aqueous solutions of mixtures CPL [HEA-EA]/ [PAA] on pH



PHEA(1); IMM [HEA]:[EA]=90:10 (2); 80:20 (3) mol.%;
MM (PAA)=250000;
[PAA]/[HEA-EA]=1:1. [HEA-EA]=0.01%

Figure 5 – Dependence of the optical density of aqueous solutions of mixtures CPL [HEA-EA]/ [PAA] on pH



IMM [HEA]:[EA]=80:20 mol.%;
MM (PAA)=2000 (1); 100000 (2); 250000 (3); 750000 (4);
CPL [HEA-EA]/ [PAA]=1/1; [HEA-EA]= [PAA]=0.01%

Figure 6 – Dependence of the optical density of aqueous solutions of mixtures CPL [HEA-EA]/ [PAA] on pH

In the paper the influence of the molecular mass of polyacrylic acid on the interaction in HEA-EA copolymers–polycarboxylic acid was studied (Figure 6). The formation of isopoly was shown not be observed in the solution of copolymers when adding PAA with a macromolecule of 2000 which is well-agreed with the ideas of existing the lower limit of macrochain length during isopoly acid formation [17; 18]. When PAA macromolecule grows in the range of 100000-750000 the critical value of complex formation increases. This can be explained by an increase in the proportion of non-ionized carboxyl groups, an increase in the effect of cooperativity, and an increase in the length of the macrochain, a decrease in the degree of ionization of the polyacid, and the formation of hydrogen bonds with nonionic polymers.

Conclusion

For the first time, complex formation of linear HEA-EA copolymer with linear PAA in the solutions was studied, the formation of polycomplxes stabilized by hydrogen bonds and hydrophobic interactions was identified. The efficiency of complex formation was shown to increase with rising the content of ethylacrylate in the composition of copolymers and PAA macromolecule mass.

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