Introduction It is well known that Polyacrylamide flocculants in non-ionic, cationic and anionic form are widely used in wastewater treatment [1]. The flocculation performance of flocculants depends on the chemical nature of flocculants, their molecular weight, the suspension solid content in the wastewater, etc [2]. The solution properties of polymer-flocculant influence the flocculation process, namely, the more expanded polymer chain, the better its flocculation ability. The shape of polymer chain in solution mainly depends on the concentration of the linear polymer in solution for given polymer/solvent system [3]. But for polymers of non-linear architecture the number of variable parameters become overwhelmingly large, namely, initial polymer architecture, average degree of polymerization, solubility properties, changing the solvent composition, distance between grafts, nature and flexibility of backbone and grafts, etc [4-7]. All these factors can influence the formation of nanostructure, determining the final properties of such compounds. It was pointed by Singh [8-10] that graft copolymers based on polysaccharide and polyacrylamide exhibit much better flocculation characteristics than the conventional polysaccharide and synthetic polymer-based flocculants. Obviously, these systems should be very interesting due to possibility to obtain samples having various internal molecular structures with partially hydrolysed grafted PAA chains, which can trapped the metal ion during flocculation process [11-12]. However until now the influence of the intramolecular structure of anionic branched polymers on their efficiency to capture the metal ions has not been investigated. Experimental Polymer sample Ceric-ion-induced redox initiation method has been used for the synthesis of the graft copolymers Dextran-graft-Polyacrylamide (Figure.1) [13, 14]. Dextrans with different molecular weights were purchased from Serva (Sweden) whose characteristics given by the manufacturer are Mw= 2x104 (designated as D20 throughout) and Mw= 7x104 (designated as D70 throughout). Cerium (IV) ammonium nitrate (CAN) from Aldrich was used as initiator. Acrylamide monomer was obtained from Reanal (Hungary). Fig. 1 - Fragment of D-g-PAA macromolecule For these copolymers the ratio of molar concentrations of CAN and dextran was kept constant as in [13, 14] for obtaining copolymers with the same number of grafts, but the amount of initiator was increased twice in the aim to obtaining more long grafts. Gel-exclusive chromatography (SEC), static light scattering (LS) and viscometry were used for graft copolymers molecular parameter estimation, namely Mn, Mw, Mw/Mn, radius of geration Rz and second virial coefficient A2 (Table.1). Experimental methods Alkaline hydrolysis Alkaline hydrolysis of graft copolymers samples was performed as follows: 2 g of D-g-PAA was dissolved in 200 cc of distilled water then required amount of NaOH was added to it. The mixture was placed in a thermostated water bath at 50° C. At the end of the required reaction time (in 15, 30 and 60 min) the probes were precipitated by acetone and freeze-dried. Potentiometry The potentiomatric titration were performed using a pH meter pH-340 (Russia) using combined glass electrode. We use as titrant HCl (0,2 N), polymer concentration was 0.2g/dl. The measurements were made at 25 °C under nitrogen, with constant stirring. Viscosimetry The viscosity of the polymer solution was measured with capillary viscometer of the Ostvald type using capillary of 0.56 mm i.d. the apparatus was thermostated at 25°C. FTIR spectroscopy The FT-IR spectra were obtained by Spectrophotometer Nicolet NEXUS-475 (USA) in the range 4000-400cm-1 using of thin copolymer films (l = 6-9 mm). The films were cast from aqueous solutions. Results and discussion The results of D-g-PAA samples characterisation are presented in the Table1. Table1 - Graft copolymers molecular parameters determined by SEC, LS and viscometry methods Sample Mw (SEC) Mw/Mn (SEC) Rz, nm (SEC) Mw (LS) A2, cm3/g (LS) Rz, nm (LS) [h], dl/g D20-g-PAA 5,2´106 1,81 167 5,6 5,3´10-4 182 6,8 D70-g-PAA 4,2´106 1,65 162 4,7 3,7´10-4 168 6,8 The values of the weight-averaged molecular weights are in rather good agreement with those derived from light scattering. Also, SEC indicates that these samples possess relatively low molecular weight polydispersity. The second virial coefficient value A2 and the form of Zimm-plots testify that D-g-PAA samples dispersed to individual molecules in water solution. The dependence of reduced viscosity on concentration (Figure 2) is typical for nonionic polymer. Fig. 2 - Dependence of reduced viscosity on the concentration for D20-g-PAA (1) and D70-g-PAA (2) For samples saponification the alkaline hydrolysis was used. During hydrolysis the -CONH2 groups of PAM chains are converted to the -COOH groups according to scheme: FTIR spectra for nonionic and modified sample of D20-g-PAA are presented in the Figure 3. The drastic change in the spectra of nonionic and modified samples is observed in the Amide1 (1650-1660 cm-1, CO stretching) and Amide 2 (1615 cm-1, NH bending) region. For D-g-PAA saponified samples the additional peak at 1570 cm-1 (COO-, stretching) appears. This indicates that under saponification condition the part of acrylamide moiety is converted into acrylate. Fig. 3 - FTIR spectra of nonionic (1) and modified (2) D20-g-PAA samples Figures 4 (a, b) show the dependence of degree of H+ ions absorbance (s) on pH value for different time of samples saponification. The process of alkaline hydrolysis differs in time for D20-g-PAA and D70-g-PAA. For D20-g-PAA the degree of H+ ions absorption achieves maximum in 30 min and don’t change after. For D70-g-PAA the value of absorption degree increases in 30 min too. It our opinion it dials with the different initial molecular structure of nonionic copolymers as the degree of conversion during process of saponification depends on the accessibility for saponifier the functional groups, which can be hydrolyzed. Thus, the density of macrocoil conditions the velocity of diffusion of saponifier. The intramolecular structure of D-g-PAA copolymers defined the mutual position of grafted polyacrylamide chains on dextran backbonds and their conformation in solution. According to the synthesis conditions the number the grafts in these copolymers should be the same. Obviously that for D20-g-PAA the grafted chains have more extended conformation as value d between grafts near tethering point (Figure5) is smaller in 3.5 time (70000/20000=3.5) as well as the value of r far from this point [14]. Schematically the space available to one graft is a cone whose solid angle is related to the distance between adjacent grafts, namely as the larger the distance, the larger is the cone solid angle (Fig.5). We investigated the ability of modified graft copolymers to absorb polyvalent metal ions (Ni2+, Co2+, Al3+) by viscometry method. We used nickel, cobalt and aluminum chlorides. Figures 6, 7 and 8 show the dependences of reduced viscosity on Ni2+ and Co2+ ions concentration. It is seen that the dependences have similar character for copolymer samples, hydrolyzed 15 and 30 min (Fig.6). The drastic change in reduced viscosity is observed at low concentration of metal ions, the precipitation occurs when their concentration become bigger 0.06 mol/l. Obviously, it dials with the intramolecular complexation between carboxilic groups of partially Fig. 4 - Dependence of H+ absorbance degree on pH for modified D20-g-PAA samples (a) and D70-PAA (b) in 15, 30, 60 min of alkaline hydrolysis Fig. 5 - Fragment of D-g-PAA macromolecule near tethering point hydrolysed PAA-chains and Ni2+ and Co2+ ions. As results, the macrocoils compactization occurs. Increase in polymer concentration don’t influence significantly on the metal ions adsorption (Fig. 8). The precipitation process is observed when the intramolecular complex formation begins (Figures 6-8). For D-g-PAA samples modified 60 min the precipitation is observed within all investigated region of metal ions concentration as well as for system Al3+/D-g-PAA of different hydrolysis degree. The increasing in polymer concentration doesn’t influence significantly on the metal ions adsorption (Figure 8). The increase in the distance between grafts for D20-PAA and D70-g-PAA doesn’t influence drastically on the process of Ni2+ and Co2+ trapping (Fig. 8). Fig. 6 - Dependence of reduced viscosity on concentration CoCl2 for modified D20-g-PAA samples Fig. 7 - Dependence of reduced viscosity on concentration NiCl2 for modified D70-g-PAA samples (time of hydrolysis 30 min) Fig. 8 - Dependence of reduced viscosity on concentration NiCl2 for modified D20-g-PAA and D70-g-PAA samples (time of hydrolysis 30 min) Fig. 9 - Dependence of reduced viscosity on concentration AlCl3 for modified D20-g-PAA and D70-g-PAA samples (time of hydrolysis 15, 30 and 60 min) Concluding remarks Thus, the alkaline hydrolysis of graft copolymers Dextran-g-Polyacrylamide with different length of main polysaccharide chain and long grafts has been investigated. It was shown that intramolecular structure namely the conformation of copolymers the grafted polyacrylamide chains influences on the kinetics of hydrolysis and on the degree of amide groups conversion. It was established that the modified samples are highly efficient compounds for removal metal ions from water medium therefore they can be used in the water treatment processes for removal metal ions from water medium. The difference in the internal molecular structure of branched polymers D-g-PAA doesn’t drastically influence on the process of metal ions trapping.