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Synthesis and Characterization of Poly(Acrylamide-*Co*-Acrylic Acid) Flocculant Obtained by Electron Beam Irradiation

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The goal of the paper was to prepare a class of flocculants by free-radical copolymerization of acrylamide with acrylic acid in aqueous solutions in the presence/absence of potassium persulphate as initiator. Reaction medium was submitted to electron beam treatment of 0.6 to 1.5 kGy in atmospheric conditions and at room temperature. Because of the complexity of reaction mechanisms involved in radio-induced polymerization, was necessary to establish the connection between absorbed dose and initiator concentration, both of them very important in free radical production. Unlike the conversion coefficient and residual monomer concentration, intrinsic viscosity and Huggin's constant are sensitive to the initiator concentration variation for all used irradiation doses. The copolymerization was confirmed by FTIR measurements. The flocculation characteristics were evaluated in 0.2 wt % kaolin suspension at room temperature using different polymer dosages between 0 to 10 ppm. High flocculation efficiency was obtained using the polymer having high values of intrinsic viscosity, molecular weight and radius of gyration.

Keywords: *poly(acrylamide-co-acrylic acid), synthesis, absorbed dose, flocculation, FTIR*

1. Introduction

Pure water is an essential requirement for the survival of human beings. To meet the requirements of potable, industrial and agricultural water, the immediate need is to treat wastewater, which contains both dissolved and suspended particles. These effluents are highly undesirable and unsafe. The removal of contaminants from wastewater is a must before they can be reused[1]. The removal can be accomplished by gravitation (very slow), by coagulation (dependent on electric charge situation) and by flocculation (not dependent on electric charges and the fastest)[2]. Coagulation is one of the most important physicochemical operations used in water, and wastewater treatment and can be achieved by chemical and electrical means[3]. Coagulation and flocculation occur in successive steps intended to overcome the forces stabilizing the suspended particles, allowing particle collision and growth of floc. Coagulation has been defined as the addition of a positively charged ion of metal salt or catalytic polyelectrolyte that results in particle destabilization and charge neutralization. Coagulation targets the colloid particles of size 10^{-7} to 10^{-14} cm in diameter. The colloid particles exhibit Brownian movement through the water; their surface is negatively charged so they repel one another, and they form a stable dispersed suspension[4]. If colloid particles or ions of positive electric charge are added it neutralizes the electric negative charge. Flocculation refers to the successful collision that occurs when destabilized particles are driven toward each other by the hydraulic shear force in the rapid mix and flocculation basin. It agglomerates of a few colloids then quickly bridge together to form microflocs which is turned into visible floc masses[5]. Coagulation happens by the addition in the water to be treated of inorganic salts, based on aluminium or iron (aluminium sulfate - alum, ferric sulfate, ferric chloride, ferrous sulfate, and sodium aluminate) while flocculation happens by the addition of organic polymers.

Polymers have been utilized in coagulation/flocculation processes for water purification for at least four decades. Some of the advantages of them use are the following: lower coagulant dose requirements, a smaller volume of sludge, a smaller increase in the ionic load of the treated water, reduced level of aluminium in treated water, cost savings[6].

Polymers used in water treatment are water soluble and are broadly characterized by their ionic nature: cationic, anionic and non-ionic. Usually, but not always, cationic polymers possess quaternary ammonium groups that have a formal positive charge irrespective of pH (poly(diallyldimethyl ammonium chloride) or cationic polyacrylamides). Anionic polymers contain weakly acidic carboxylic acid groups, so the charge density depends on pH (anionic polyacrylamides). Synthetic polymers often described as non-ionic actually contain some 1-3% of anionic groups, as in the case of polyacrylamide where they arise from hydrolysis of the amide groups under the preparative conditions employed[6]. Mechanisms of flocculation of particles by polymers can be described by the polymer bridging, charge neutralization including "electrostatic patch" effects and depletion flocculation. The last one which depends on the presence

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of free unabsorbed polymer is not significant in water treatment practice[6].

The extensive use of polymers as flocculants is due to their distinct characteristic attributes: are convenient to use and they not affect the pH of the medium, they are used in small quantities (1-5ppm) unlike the inorganic salts and, in the most cases, the flocs formed during flocculation by organic polymers are bigger and stronger than during coagulation with inorganic salts. Moreover, large tonnage use of inorganic compounds produces higher volumes of sludge. Among polymeric flocculants, the synthetic polymers can be tailor made by controlling molecular weight, molecular weight distribution, the structure of polymers and the nature and percentage of ionic groups[5,6].

During the last 30 years, the production of polymeric flocculants has rapidly increased. Radiation research in the field of polyelectrolytes chemistry was first developed using ^{60}Co sources[7]. In the authors of the present work laboratory, the flocculants based on acrylamide and acrylic acid, have been synthesized by electron beam irradiation[8-10]. Polyacrylamide based flocculants, which are used in the flocculation process, are high molecular weight compounds that are soluble in water and have major advantages such as flexibility and effectiveness in treating wastewater[11]. The performances of polyacrylamide as flocculant are superior, compared with those of organic and inorganic coagulants, in terms of lower utilization dosages and lower volumes of sludge. Also, their effectiveness is only slightly influenced by the pH level of water to be treated[11]. Based on studies, some experimentalists have established which are the major advantages of radiation induced polymerization processes: very easy to manipulate the molecular weight, from low to very high, by simply changing the feed composition as well as the composition of the product by incorporating different monomers; higher conversion efficiency (near 100%); very low residual monomer contents; no production of waste matter or evolution of noxious gases; no production of hazardous effluents; very clean process[8-10]. The processing of materials by irradiation with accelerated electrons removes many drawbacks of conventional technology, because ionizing radiation initiates polymerization without thermal input from the outside, due to free radicals that are formed at the interaction of these rays with monomers and especially with the solvent (water in this case) in which these monomers are found. So a good solution is to use ionizing radiation to produce polymer materials, especially using accelerated electron beams which actually direct all their energy in the volume of irradiated monomer solutions. The research line of the authors of the present work laboratory is to done the processing of materials for research and industrial applications especially for polymerization, cross-linking or monomers grafting onto polymers, by electron beam irradiation (EB)[12-17].

In this paper, physico-chemical characteristics of polymeric materials (flocculants) obtained by electron beam irradiation, are presented. The paper also presents the results of the flocculation studies in order to demonstrate the flocculation efficiency of the polyelectrolyte. One possible mechanism for the reaction acrylamide and acrylic acid is also proposed.

2. Experimental

2.1. Materials

The materials used for flocculants obtaining were**:** acrylamide – AMD (molar mass 71.08 g/mol; density 1.13 g/cm^3; solubility in water 2.04 kg/L at 25 °C); acrylic acid – AA (molar mass 72.06 g/mol; density 1.051 g/cm^3;solubility in water: miscible) and potassium persulphate – PP (molar mass 270.322 g/mol; density 2.477 g/cm^3; solubility in water 1.75 g/100 mL at 0 °C). All reagents listed above were of 99% purity and have been acquired from LACHEMA, Germany, and used directly, without purification. Other chemicals used in this study for physico-chemical characterization of the flocculants were of analytical grade.

2.2. Experimental installations and polymer preparation

Experiments were carried out with an experimental installation consisting mainly of the following units: an electron linear accelerator of 6.23 MeV energy and 75 mA peak current of the EB (ALIN-10 from National Institute for Laser, Plasma and Radiation Physics) and an irradiation chamber containing the samples of monomer solution. The ALIN-10 accelerator is a travelling-wave type, operating at a wavelength of 10 cm and having 164 W maximum output power. The accelerating structure is a disk-loaded tube operating in the π/2 mode. The optimum values of the EB peak current I_{EB} and EB energy E_{EB} to produce maximum output power P_{EB} for a fixed pulse duration τ_{EB} and repetition frequency f_{EB} are as follows:

E_{EB}= 6.23 MeV
I_{EB} =75 mA
P_{EB} = 164 W (f_{EB} = 100 Hz, τ_{EB} = 3.5 μs)

The EB effects are related to the absorbed dose (D) and absorbed dose rate (D*). The absorbed dose is the major parameter in the accelerated electron radiation[18]. The polymerization and copolymerization process performances are provided by the strict control of this parameter[15,18]. The relation defining the absorbed dose is:

$$D = \frac{d\varepsilon}{dm} \tag{1}$$

where *dε* is the mean energy given up by the ionizing radiation to the mass amounts *dm* of the substance interacting with this ionizing radiation.*dm* is emphasized to be very low but not so low that the mean energy *dε* given up by the radiation would undergo a significant fluctuation.

Absorbed dose is measured in Joule/kg. The SI unit measure for the absorbed dose is the gray (Gy):

$$1\ Gy = 1\ Joule / kg \tag{2}$$

Electron beam dose rate was fixed at 2 kGy/min in order to accumulate doses between 0.6 and 1.6 kGy. The thickness of 2.5 cm of the irradiated samples was established in accordance with the samples densities (of about 1 g/cm^3 in our case) and EB energy. Each sample was irradiated in polypropylene glasses in atmospheric conditions and at room temperature of 25 °C. For the irradiation, were prepared seven different types of aqueous solutions based on acrylamide and acrylic acid. Table 1 represents reaction conditions to synthesize the flocculants.

2.3. Polymer characterization

2.3.1. Physico-chemical characteristics

In order to determine the conversion coefficient (C_c) and the residual monomer concentration (M_r), 2 grams from each of the polymers were placed in 200 ml distilled water for 24 hours and then every sample was stirred for 1 hour at 400 rpm to ensure a very well mixing. The conversion coefficient and the residual monomer concentration were determined by titrimetric method. In this method, bromine reacts with the double bond of residual monomer[19,20]. After complete dissolution in water, the polymers were treated excessively with a bromide-bromate solution and the bromine excess was determined by means of the iodatometry method in presence of sodium thiosulphate solution (1 M).

The intrinsic viscosity ($\eta_{intr.}$) and the Huggins' constant (k_H) were determined by the viscosimetry method, using the Hoppler type BH-2[21].The principle of falling-ball viscosimeters is based on the fact that the viscosity of liquid modifies the speed of ball falling through this liquid. The time of fall of the ball through the polymeric solution was measured for five different concentrations of it. As a solvent, sodium nitrate 1 M was used and the working temperature was 30°C. Using the time of fall of the ball through the polymeric solution (t) and the time of fall of the ball through the solvent (t_0) the relative viscosity ($\eta_{rel} = t / t_0$) was obtained. Specific viscosity was calculated from the relation, $\eta_{sp} = (\eta_{rel.} - 1)$. Reduced viscosity was determined using the relation $\eta_{red} = (\eta_{sp}/c)$, where *c* is the polymer concentration (g/dL). From the graphical representation of the η_{red} as a function of the copolymer concentration, by extrapolation, was obtained the intrinsic viscosity η_{intr} and tgα. Linearity constant was determined from the following relation: $k_{H} = \text{tg}\ \alpha/[\eta_{intr}]^2$. Intrinsic viscosity is a measure of the hydrodynamic volume occupied by the individual polymer molecules in isolation[22]. In dilute solutions, the polymer chains are separate and the $[\eta_{intr}]$ of a polymer in solution depends only on the dimensions of the polymer chain. Because $[\eta_{intr}]$ indicates the hydrodynamic volume of the polymer molecule and is related to the molecular weight, it provides deep insights on the molecular characteristics[23]. From the Mark-Houwink equation the relationship among the molecular weight and viscosity are given below:

$$[\eta] = K*[Mwa] \tag{3}$$

where [η] is the intrinsic viscosity (dL/g), M_w is molecular weight (g/mol), K and *a* are constants for a particular polymer – solvent system (K and *a* are $3.73*10^{-4}$ and 0.66 in 1 M aqueous sodium nitrate at 30 °C)[21,24].

Radius of gyrations is a parameter which characterizes the size of a particle of any shape. As the radius of gyration will be higher, the molecular dimension of the polymer will be much higher and that will affect synergistically the flocculation characteristics[25]. Radius of gyration was determined by the following relation[26,27]:

$$R_g = 0.0147 * M_w^{0.59} \tag{4}$$

2.3.2. FTIR analysis

In order to obtain spectral information regarding the polyelectrolyte chemical structure, a FTIR spectrophotometer – JASCO FT/IR 4200 was used by ATR measurement method. Samples spectra are the average of 30 scans realized in absorption, in the range of 4000 – 600 cm^{-1}, with a resolution of 4 cm^{-1}.

2.4. Flocculation studies

Flocculation studies were carried out on kaolin suspension (0.2 wt %), at room temperature (20-25 °C) using the standard Jar test apparatus (Velp FC 6S, Italia). The jar test apparatus consists of 6 stirrer blades connected to a variable speed (0-100 rpm) motor through a gear system. In each beaker, 500 mL of kaolin suspension was taken and placed on the flocculator dipping the stirrer blades in the suspension. Under a slow stirring condition, the polymer solution was added by means of a pipette in order to determine the polymer concentration influence (1-10 ppm). Immediately after addition of polymer solution, the suspensions were stirred at a constant speed of 60 rpm for 15 min, and then allowed to sediment for 15 min. Clear supernatant was drawn from the top layer (up to depth 1-2 cm) and its transmittance was measured at 620 nm using a Cary Bio-100 UV-VIS spectrophotometer.

3. Results and Discution

3.1. Physico-chemical properties

The characteristics of poly(acrylamide-*co*-acrylic acid) flocculants are influenced by the following factors: chemical composition of the solutions to be irradiated and absorbed dose level[28-30]. Electron beam induced copolymerization reaction, under proper irradiation conditions and for fixed

Table 1. Flocculants synthesis details.

Flocculant	Amount of chemicals (mol/L)					Irradiation dose (kGy)
	AMD	AA	PP	FS	HS	
F1-1..... F1-6	5	0.5	0	1.1 x 10^{-3}	0.5	0.6; 0.8; 1.2; 1.4; 1.5; 1.6;
F2-1..... F2-6	5	0.5	0.75 x 10^{-4}	1.1 x 10^{-3}	0.5	
F3-1..... F3-6	5	0.5	1.5 x 10^{-4}	1.1 x 10^{-3}	0.5	
F4-1..... F4-6	5	0.5	3 x 10^{-4}	1.1 x 10^{-3}	0.5	
F5-1..... F5-6	5	0.5	4 x 10^{-4}	1.1 x 10^{-3}	0.5	
F6-1..... F6-6	5	0.5	5 x 10^{-4}	1.1 x 10^{-3}	0.5	
F7-1..... F7-6	5	0.5	6 x 10^{-4}	1.1 x 10^{-3}	0.5	

chemical composition of the monomer mixtures to be irradiated, gives higher conversion efficiency (near 100%) and lower residual monomer concentration (under 0.01%) than classical copolymerization (by heating). In radiation copolymerization/polymerization, a completely "inert" reactant does not exist. Any substance when added to a monomer absorbs the radiation energy, resulting in various secondary processes, which finally lead to an additional production of free radicals. Indeed, due to water presence in the EB irradiated system, our experiments show that the role of the radicals originated from irradiated water is predominant compared to the radicals which come directly from the monomer irradiation. Thus, irradiated water radicals facilitate the copolymerization process and decrease the required absorbed dose level. The main function of the ionizing radiation in a radiation-initiated polymerization is limited to the primary events. The initiation step leads to the production of free radicals and the subsequent steps of propagation, termination and chain transfer proceed as in a chemically catalyzed process. Because of the complexity of reaction mechanisms which are happening in case of copolymerization process induced by irradiation we tried to establish a connection between EB absorbed dose and initiator concentration (PP), both of them very important in free radical production. The results presented in Figures 1-4 show that the polymerization process is complete at a low EB absorbed dose rates and using a very small initiator concentration. In that case, the principal source of free radicals is water used as solvent in monomer mixture. Conversion coefficient is the first parameter characterized and it is required to be higher than 95%, because a high conversion coefficient is equivalent with high monomer transformation efficiency in polymerization process and a substantial reduction of residual monomer concentration. From the results obtained it is observed that conversion coefficient increases slowly with the amount of initiator increase (Figure 1). Can be noticed that, for samples that contain a small amount of initiator (0.75 × 10^{-4}mol/L),

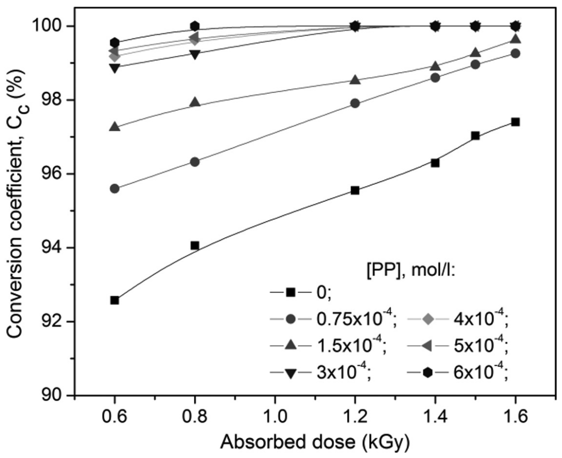

Figure 1. The effect of initiator concentration and EB absorbed dose on conversion coefficient (C_C).

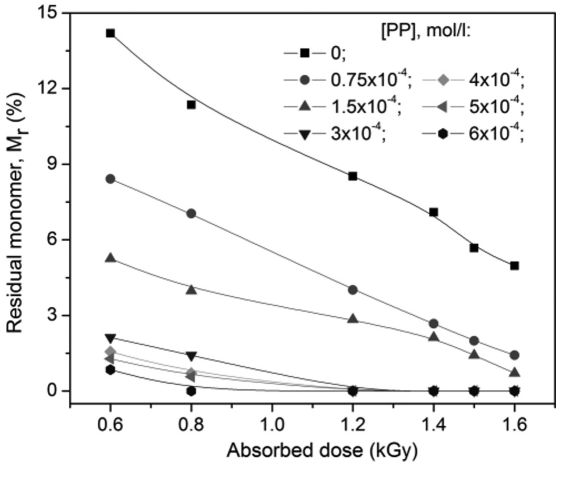

Figure 2. The effect of initiator concentration and EB absorbed dose on residual monomer content (M_r).

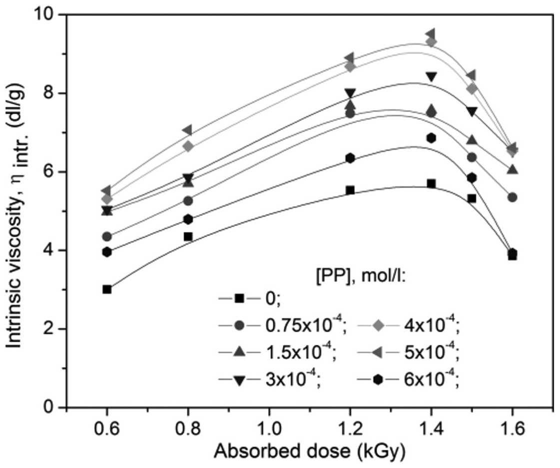

Figure 3. The effect of initiator concentration and EB absorbed dose on intrinsic viscosity ($\eta_{intr.}$).

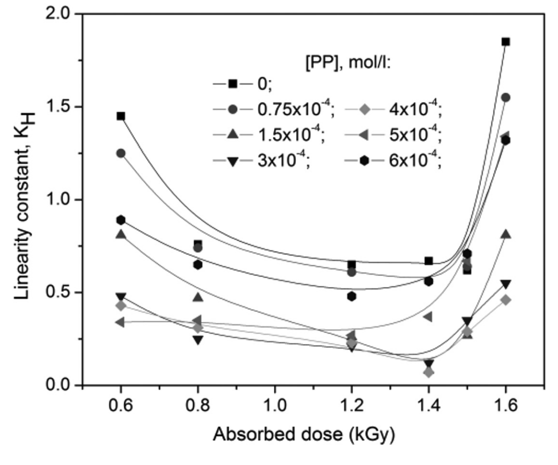

Figure 4. The effect of initiator concentration and EB absorbed dose on linearity constant (k_H).

even at the lowest irradiation dose (0.6 kGy), conversion coefficient is over 95%. Simultaneously with the conversion coefficient increasing, residual monomer decreases with amount of initiator and absorbed dose increase (Figure 2).

For the intrinsic viscosity, η_{INTR} , we expected to obtain values over 6 dl/g, which means liniar polymer, whitout ramifications and with water solubility. Regarding the linearity constant, k_H, we aim to obtain values below 1 because only in this case is ensured solubility and a good flocculation of the polymer. Unlike the conversion coefficient C_c and residual monomer concentration M_r, intrinsic viscosity η_{intr} and Huggin's constant k_H remain sensitive to the initiator concentration variation for all used irradiation doses (Figures 3 and 4). Usually, the intrinsic viscosity η_{intr} increases rapidly with initiator concentration increasing, reaches a maximum and then decreases rapidly at lower irradiation doses and slower at higher irradiation doses.

Intrinsic viscosity of a polymer is indicative of its hydrodynamic volume in solution, which depends on its molecular weight, structure and nature of the solvent as well as the temperature of the medium. For two polymers with approximately similar molecular weight, the branched polymer has lower hydrodynamic volume compared to its linear counterpart and thus has lower intrinsic viscosity value. Furthermore, the longer the branching the higher is the intrinsic viscosity and vice versa[31]. The intrinsec viscosity of a polymer is dependent on its molecular weight and chain dimension[32,33]. In dilute solutions, the polymer chains are separate, so intrinsic viscosity of a polymer in solution depends only on the dimensions of the polymer chain and on the molecular weight[23,32]. Huggin's constant k_H, follows exactly the variation of intrinsic viscosity. Thus, it rises and falls with practically the same rate that intrinsic viscosity η_{intr}, falls and rises, depending on the initiator concentration. We can say that, by getting high values for the intrinsic viscosity $\eta_{intr,}$ are obtained minimum values for the linearity constant k_H. The measured values of Huggin's constant k_H are well below 1 even for low values of intrinsic viscosity η_{intr}, and that is a very important result because polyelectrolytes efficiency is assured by their linearity, i.e. by $k_H<1$.

3.2. FTIR study

Fourier transform infrared spectroscopy is one of the most widely employed techniques for analyzing polymeric materials. The spectra of polymeric flocculants obtained at 1.4 kGy in the range of the 4000-650 cm^{-1} are depicted in Figures 5 and 6**.** We have chosen to represent the FTIR of these samples because it exhibits the best results for all four characteristics: conversion coefficient, residual monomer content, intrinsic viscosity and linearity constant.

The FTIR spectra confirm the formation of copolymer of acrylamide and acrylic acid as is evident from bands that appeared in the range of 3100–3500 cm^{-1} (O–H and N–H stretching)[34]. The absorption located in the regions 3350-3330 cm^{-1} and 3200-3185 cm^{-1} corresponds to the asymmetric and symmetric NH_2 stretching vibrations from acrylamide[35,36]. On the other hand, the broad absorption bands from 3400 cm^{-1} to 2950 cm^{-1} can be assigned to the –OH from the carboxylic group[37]. The methylene group vibrations are used to monitor the extent of polymerization.

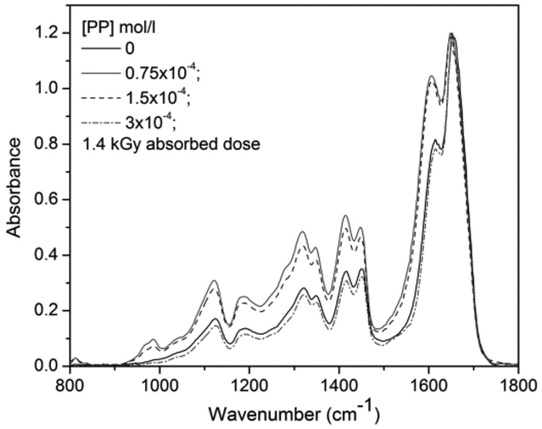

Figure 5. FTIR spectra of samples obtained at 1.4 kGy in range of 650-1800 cm^{-1}.

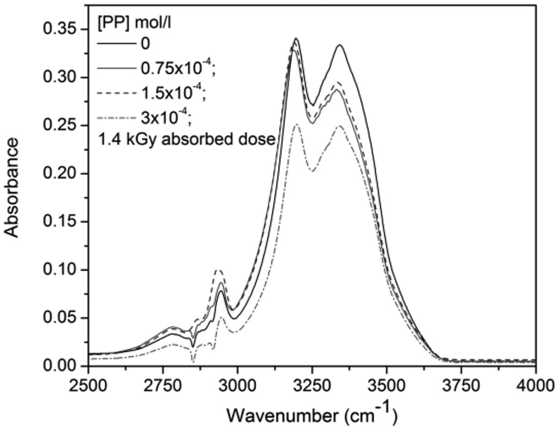

Figure 6. FTIR spectra of samples obtained at 1.4 kGy in range of 2000-4000 cm^{-1}.

The intensity bands appearing in the regions 2950-2940 cm^{-1} and 2915-2900 cm^{-1} are assigned to both asymmetric and symmetric CH_2 stretching vibrations. In addition, the absorption band in the region 2790-2770 cm^{-1} is assigned to CH stretching vibration of polymer backbone. The shoulder in the same region also suggests the presence of COOH in copolymers. At 1653-1645 cm^{-1}, a stretching of the C=O group from the AMD and AA unit appears in all spectra. At this wave number there is also the OH angular deformation from water, which explains the existence of this band in the polyacrylate spectrum[35]. The characteristic peak which appeared in the range of 1620-1600 cm^{-1} is due to the NH_2 bending from AMD. The absorption band in the region 1455-1445 cm^{-1}, is assigned to CH_2 stretching vibration. The absorption located in the regions 1450-1410 cm^{-1} has been assigned to C-N stretchingvibrations[35,36]. Bands at 1560 and 1406-1410 cm^{-1} are due to the symmetric and asymmetric stretching of $COO^{-}$of acrylate (acrylic acid neutralized with NaOH)[34]. The presence of adsorbed water can be seen by the band at 3300 cm^{-1} in all spectra.

3.3. Flocculation studies

When flocculant is added in water which requires treatment, an interface is formed. Above it is the supernatant liquid while below is the suspension containing the contaminants. Under the action of the flocculating agent, that is along with the progress of the flocculation process, that interface descends, until all contaminants are settled at the bottom[2]. The most important characteristics of polymeric flocculants are molecular weight and radius of gyration[2,38]. Conventionally, polymers are regarded as having, low, medium or high M_w, corresponding to M_w values in the ranges: $<10^5$, 10^5–10^6 and $>10^6$, respectively[38]. Radius of gyrations is a parameter which characterizes the size of a particle of any shape. The higher the radius of gyration larger will be the polymer dimensions, affecting the flocculation characteristics synergistically[31]. The molecular weight and radius of gyrations are represented in Figures 7 and 8.

For flocculation tests were chosen the copolymers obtained at 1.4k Gy absorbed dose, because it exhibits the best results for all four characteristics: conversion coefficient, residual monomer content, intrinsic viscosity, linearity constant, molecular weight and radius of gyrations. The flocculation tests were performed at different polymer dosages, which varied from 0 to 10 ppm at the measured pH of 7. The flocculation performance is explained in terms of transmittance of the supernatant liquid versus polymer concentration. It was obtained a higher flocculation efficiency from the polymer with higher intrinsic viscosity and therefore with higher molecular weight and radius of gyrations (Figure 9). Flocculation efficiency increased for copolymers with higher viscosity is due to higher affinity for contaminants, which can be explained by a greater spreading of the polymer chains in contaminated water.

In Figure 9 is observed that the flocculation efficiency increased with increasing flocculant dosage for all flocculants and reached the maximum at 5 and 6 ppm dosage. After 6 ppm dosage, the flocculation efficiency decreases. At low polymer dosages, the settling rates were low due to insufficient polymer available for bridging particles together and the flocs were not large enough to provide adequate settling rates. As the polymer concentration increased, more particles were bridged and bigger flocs were obtained, hence a significant increase in the settling rates resulted[39]. It is well known that bridging is one of the major flocculation mechanisms of polymeric flocculants. The mechanism is favored when the polymers has a long chain. In order to create effective bridges, there must be sufficient polymeric chains, which are able to extend far enough to facilitate the attachment of other particles[31]. From the experiments is observed the effectiveness of polymers as the bridging flocculants depends greatly on their properties: molecular weight and thus the intrinsic viscosity. The molecular weight directly influences the effective size of molecules in solution and in the adsorbed state. Polymers with higher molecular weight are found to be more effective flocculants[39].

3.4. Reaction mechanisms

The advantage of radio-induced copolymerization is that radicals can be formed by decomposition of all reactants (initiator, solvent, and monomers) present in the system.

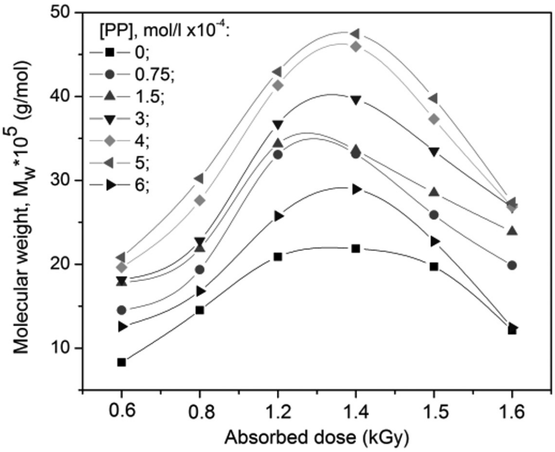

Figure 7. The effect of initiator concentration and EB absorbed dose on molecular weight (M_w).

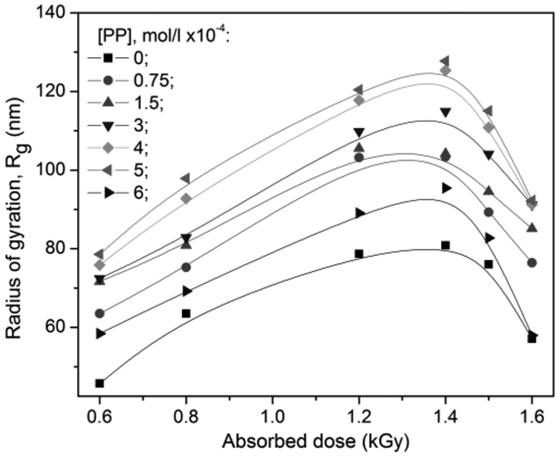

Figure 8. The effect of initiator concentration and EB absorbed dose on radius of gyration (R_g).

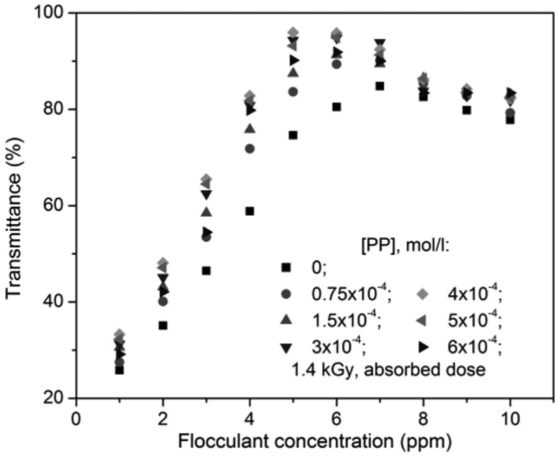

Figure 9. Flocculation performance as a measure of light transmission for different concentrations of flocculants obtained at 1.4 kGy.

The main function of ionizing radiation with accelerated electrons is to achieve the first step of the polymerization process: the initiation phase leading to free radical formation and to some specific side effects. The next polymerization phases, propagation, completion and the chain transfer process, take place almost identically to classic polymerization processes. Potassium persulphate on its own or in redox systems is one of the water soluble initiators, frequently used in polymerization and copolymerization processes of acrylamide. In accelerated electron field, it is considered that takes place the mechanism of potassium persulphate decomposition presented in Figure 10a. If surrounding water molecules make up a potential barrier against separation of free radicals by diffusion, the latter remain isolated as in a cage (cage effect). This facilitates their destruction by recombination. Thus, in the general scheme of radical formation from initiator, reactions determined by this cage effect are considered to take place (Figure 10b).Water is an extremely important environment in the specific case of the polymerization process. When a high kinetic energy electron covers a water layer, it gradually loses energy by Coulomb interaction with molecules in the environment[21,40,41]. These interactions result in ionizations and excitations of water molecules. The water ionizing process is thus simply treated, obtaining H_2O^+ and e^-, which further undergoes a neutralization process obtaining a highly excited water molecule, which will dissociate into radicals (Figure 10c). Radicals, precursors of the copolymerization reaction can also form due to the interaction of accelerated electrons with the two monomers, acrylamide and acrylic acid (Figure 10 d, e), forming, in the first phase, two excited states**.**

Based on the obtained results and existing literature studies[42,43], is proposed a possible mechanism for the copolymerization of acrylamide and acrylic acid by electron beam irradiation in Figures 11 and 12.The reaction mechanism is the same in the presence of "initial radicals" formed from water or initiator, the only difference is in the stage of initiation when free radicals, precursors of copolymerization reaction, are formed. The possible reaction mechanisms are presented in Figure 11.

In absence of initiator, when acrylamide and acrylic acid are exposed together to ionizing radiation (electron beam), one double bond (from AMD or AA) was broken and free radicals are formed[43]. These free radicals react with each other and a copolymeric AMD/AA flocculant is produced. Figure 12 show the possible copolymerization mechanism by which one of the excited states obtained from AMD turns into radicals and thus participates to the propagation reaction, and further to obtaining the final product. Ionizing radiation produces an excitation of polymer molecules in the vicinity of the impinging radiation. The energies associated with the excitation depend on the absorbed dose of electrons. The interaction results in formation of free radicals formed by dissociation of molecules in the excited state or by interaction of molecular ions[15-20]. The free radicals or molecular ions can react by connecting the polymer chains directly or initiating reactions. In the case of acrylic acid, schemes are identical.

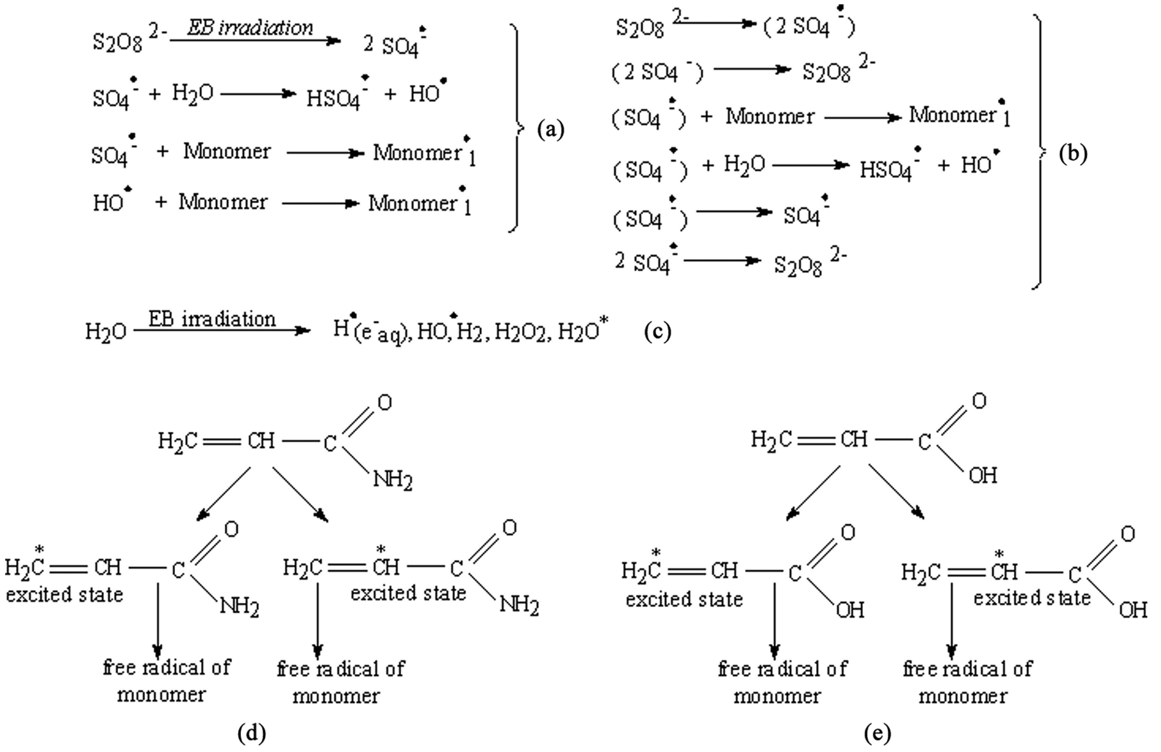

Figure 10. Possible mechanism for obtaining radicals by electron beam irradiation: (a) and (b) from initiator, potassium persulphate; (c) from water; (d) from acrylamide; (e) from acrylic acid.

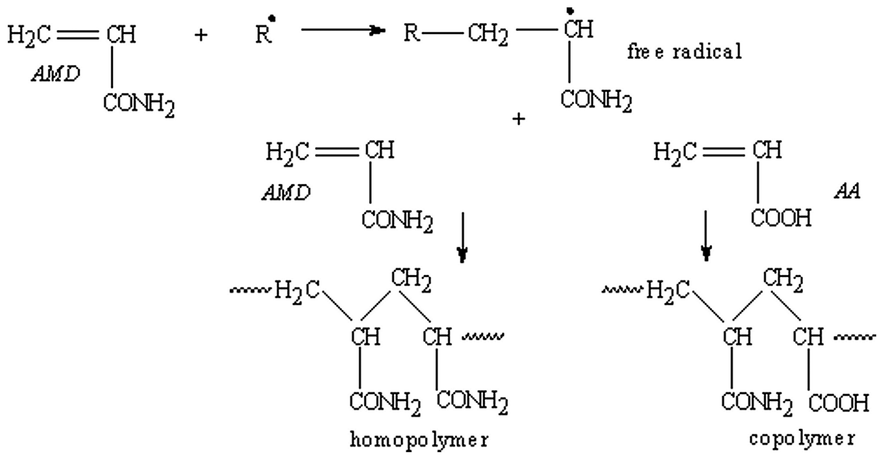

Figure 11. Possible mechanism for obtaining of poly(acrylamide-*co*-acrylic acid) in presence of “initial radicals” formed from water or initiator.

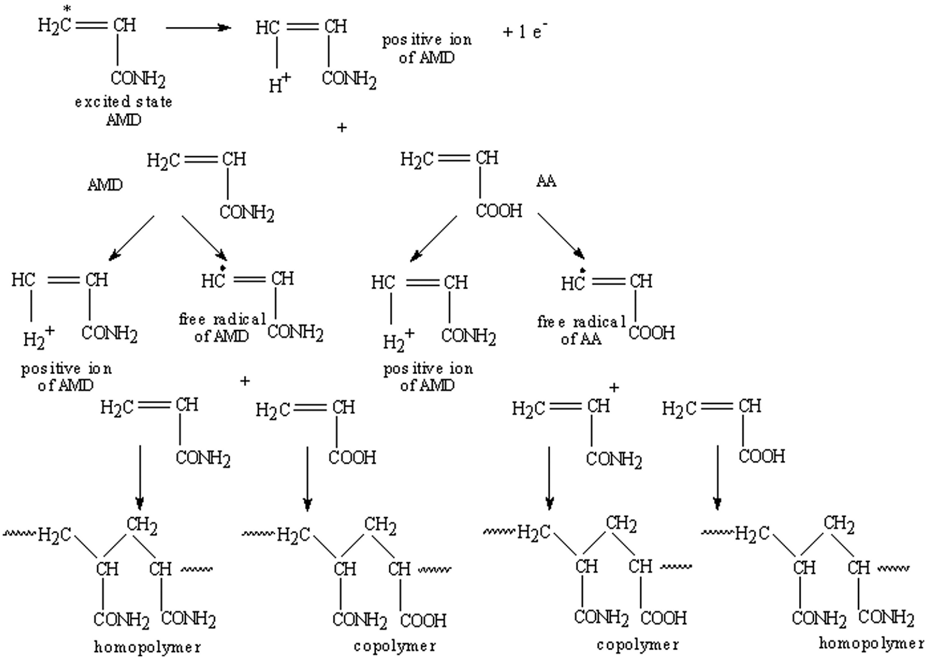

Figure 12. Possible copolymerization mechanism of acrylamide and acrylic acid.

4. Conclusions

In this study, we synthesized poly(acrylamide-*co*-acrylic acid) flocculants in aqueous solutions in the presence or absence of potassium persulphate by electron beam irradiation in atmospheric conditions and at room temperature of 25 °C. The experimental results show that physico-chemical characteristics (conversion coefficient, residual monomer content, intrinsic viscosity, linearity constant, molecular weight and radius of gyration) increase with increasing of the absorbed dose and amount of initiator. The best results were obtained at 1.4 kGy absorbed dose and 5×10^{-4} mol/L amount of initiator. Also, the flocculants obtained at 1.4 kGy was characterized by FTIR and copolymerization was confirmed. The flocculation tests were performed at different polymer dosages, which varied from 0 to 10 ppm. The experimental results show that the higher flocculation efficiency is obtained from the polymer with higher intrinsic viscosity and therefore, with higher molecular weight and radius of gyrations. We proposed some possible reaction mechanisms for obtaining radicals by electron beam irradiation of poly(acrylamide-*co*-acrylic acid) in presence of “initial radicals” formed from water or initiator, and for copolymerization of acrylamide and acrylic acid. It can be concluded that, for obtaining flocculants with a given chemical composition by electron beam irradiation, there is an optimal EB absorbed dose where the physico-chemical characteristics reach maximum values and the flocculation efficiency is increased.

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