Synthesis of New Flocculant Materials by Copolymerization of Acrylamide and Acrylic Acid by Electron Beam Irradiation

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Radiation-induced polymerization can produce a wide variety of water-soluble polyelectrolytes which are used to increase the performance of the waste water treatment. The main goal of this study was to investigate the influence of the radiation dose (D), initiator concentration [I], sodium chloride concentration, total monomer concentration [TMC] and monomer ratio (R) on the physical and chemical properties of the acrylamide – acrylic acid based polyelectrolites, obtained by copolymerization in accelerated electron beam fields. In accordance with the established purposes, the polyelectrolyte must have high conversion coefficient (CC > 95%), low residual monomer content (M_r < 0.01), high intrinsic viscosity (η_{intr} > 7 dL/g), low linearity coefficient (k_H < 0.4) and a very good solubility in water. The experiments were performed using a linear accelerator facility (ALIN-10, built in NILPRP Accelerators Laboratory, Bucharest) of 6.23 MeV at irradiation doses between 0.9 kGy and 1.8 kGy at room temperature and ambient pressure. The best results were obtained at 1.5 kGy.

Keywords: acrylamide, acrylic acid, ionizing radiation, polyelectrolytes

Polyelectrolytes are water-soluble polymers or copolymers carrying ionic charge along the polymer chain. The solid - liquid separating efficiency makes these polyelectrolytes a unique class of polymers which find extensive application in potable water, industrial raw and processed water, municipal sewage treatment, mineral processing and metallurgy, oil drilling and recovery, etc [1-3]. During the last 30 years, the production of polymeric flocculants has increased rapidly. Radiation research in the field of polyelectrolytes chemistry was developed using ^{60}Co sources at first [4]. Due to the ever growing ecological problems we have chosen to develop new acrylamide copolymers. Radiation technology was developed at a semi-industrial scale with electron beam (EB) sources at the National Institute for Lasers, Plasma and Radiation Physics, Accelerators Laboratory–Bucharest [5-10]. The major advantages of radiation induced polymerization processes are: (1) easy manipulation of 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; (2) precise control of charge density as the monomer feed composition is controlled at the initial stages only; (3) precise control of molecular weight distribution; (4) no flammable and toxic solvents used; (5) no production of waste matter or evolution of noxious gases; (6) no production of hazardous effluents; (7) very low monomer contents; (8) very clean process.

Experimental part

Materials

Acrylamide (AMD) (min 99 % purity, molar mass 71.08 g/mol, density 1.13 g/cm^3, solubility in water 2.04 kg/L at 25 °C) and acrylic acid (AA) (min 99 % purity, molar mass 72.06 g/mol, density 1.051 g/cm^3, solubility in water: miscible, viscosity 1,3 cP at 20 °C) monomers, potassium persulfate (I) (min 99 % purity, molar mass 270.322 g/mol , density 2.477 g/cm^3, solubility in water 5.29 g/100 mL at 20°C), sodium hydroxide (NaOH) (min 99 % purity, molar mass 39.997 g/mol, density 2.130 g/cm^3, solubility in water 1260 g/L at 20°C) and sodium chloride (NaCl) (min 99 % purity, molar mass 58.443 g/mol, density 2.165 g/cm^3, solubility in water 359g/L at 25°C), were obtained from LACHEMA, Germany, and used directly, without purification.

Sample preparation

Preparation of polyelectrolytes is based on co-polymerization by EB irradiation of the aqueous solutions containing appropriate mixtures of acrylamide (AMD) and acrylic acid (AA) monomers and certain agents, to mitigate cross-linking of the polymer structure, and initiators (potassium persulfate) to optimize the monomer conversion process. The thickness of the irradiated samples (monomer aqueous solutions) was 23 mm. The aqueous solutions irradiated to produce acrylamide-acrylic acid copolymers have typical chemical compositions shown in table 1.

Installations, methods and sample irradiation

The characteristics of the acrylamide–acrylic acid copolymers are influenced by the following factors: chemical composition of the solutions to be irradiated, absorbed dose (D = energy quantity per unit mass in Gy or J/kg) and absorbed dose rate (D^* = energy quantity per unit mass and unit time in Gy/s or J/kg/s). Under proper irradiation conditions and for fixed chemical composition of the monomer mixtures to be irradiated, electron beam (EB)-induced polymerization, results in higher conversion efficiency (near 100 %) and lower residual monomer concentration (under 0.01 %) than classical polymerization of the acrylamide–acrylic acid aqueous solutions. EB-induced polymerization involves the Coulomb interaction between the accelerated electrons and the atoms or molecules in the irradiated medium. These interactions generate reactive ions, excited states and radicals to drive

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Table 1
TYPICAL CHEMICAL COMPOSITION OF THE AQUEOUS SOLUTIONS

Chemical composition	Characteristics
Total monomer concentration [TMC]	10% - 60%
Monomer ratio in terms of percentage, R = AMD/AA	70/30 – 95/5
Initiator, potassium persulfate [I]	0.002%-0.016%
NaC1 concentration	0 -8%

the chemical reactions. Polymerization is induced by ionizing radiation almost the same way as free radical addition polymerization. The initiation step in both reactions requires the admittance of some additional energy. Regarding the ionizing polymerization this energy is provided by the radiation field. The main function of the ionizing radiation in a radiation–initiated polymerization is limited to the primary events, the initiation step, which leads to the production of free radicals and to a few specific secondary effects. The subsequent steps of propagation, termination and chain transfer are similar to the ones in a chemically catalyzed process. Electron beam (EB) irradiations were carried out using ALIN-10, a linear electron accelerator. For constant pulse duration (τ_{EB} = 3.5 μs) and repetition frequency (f_{EB} = 100 Hz), the optimum values of the EB peak current I_{EB} and EB energy E_{EB} required to produce the maximum output power P_{EB} are: E_{EB} = 6.23 MeV; I_{EB} = 75 mA; P_{EB} = 164 W.

Laboratory tests

Our interest was focused on the basic optimization of the important characteristics in waste water treatment, such as conversion coefficient (*CC*), residual monomer concentration (M_r), intrinsic viscosity (η_{intr}) or average molecular weight (M_w) and a linearity coefficient given by the Huggins' constant (k_H).

The conversion coefficient (*CC*) and the residual monomer concentration (M_r) are determined based on the bromation reaction of the double-bond. After being dissolved in water, the copolymer AMD/AA is treated excessively, with a bromide-bromate solution, and the bromine excess is determined by means of a iodatometry method. The percent of residual monomer M_r is determined using the following mathematical equation:

$$M_r(\%) = \frac{(V_{CS} - V_{COS}) * N * 3.554}{M_{CO}} \qquad (1)$$

where:

- V_{CS} represents the volume of the $Na_2S_2O_3$ solution used for the standard titration (mL);
- V_{COS} represents the volume of the $Na_2S_2O_3$ used for the sample titration (mL);
- M_{CO} represents the sample mass of the analyzed copolimer (g);
-*N* represents the normality of the $Na_2S_2O_3$ solution.

The conversion coefficient *CC* is determined based on the relations: (2)

$$CC(\%) = 100 * (TCC - M_r)/TCC$$

$$TCC(\%) = (M_{CO} * TMC)/400 \qquad (3)$$

where:

- M_{CO} represents the AMD/AA copolymer quantity analyzed after being dissolved in 400 mL of distillate water;
-*TMC* is the total monomer concentration in the irradiated solution.
- *TCC* is the theoretical copolymer concentration;

The intrinsic viscosity (η_{intr}) and the Huggins' constant (k_H) are determined through the viscosimetry method, using a Hoppler BH-2. Sodium nitrate was used as a solvent 1N ($NaNO_3$) and the working temperature was 30°C.

η_{intr} is determined using the relations:

Relative viscosity, η_{rel} is given by:

$$\eta_{rel.} = t_{CO} / t_{CS} \qquad (4)$$

where:

t_{CO} is the falling-time of the ball through the copolymer solution

t_{CS} is the falling-time of the ball through the standard solution;

Specific viscosity, $\eta_{spc.}$

$$\eta_{spc.} = \eta_{rel.} - 1 \qquad (5)$$

Reduced viscosity, $\eta_{red.}$.

$$\eta_{red.} = \eta_{spc.} / c_{CO} \qquad (6)$$

c_{CO} = copolimer solution concentration (%).

Intrinsic viscosity η_{intr} and *tg* α are obtained from the graphical representation (shown in fig. 1) of the reduced viscosity as a function of the copolymer concentration, through extrapolation. Then, the linearity constant can be determined knowing that:

$$k_H = \frac{tg.\alpha}{(\eta_{int\,r.})^2} \qquad (7)$$

Results and discussion

Influence of sodium chloride concentration [NaCl], in EB irradiation

Experiments proved that high irradiation absorbed doses are necessary for high conversion coefficients (*CC*), because monomer conversion is the first important parameter of the obtained polymeric material. High

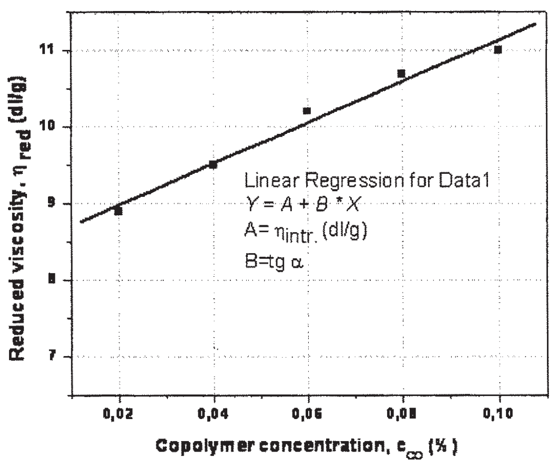

Fig. 1. The reduced viscosity as a function of the copolymer concentration

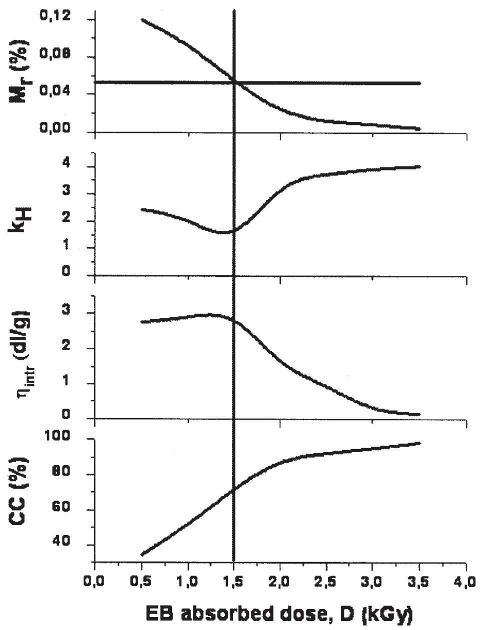

Fig. 2. The effect of the EB absorbed dose on *CC*, $\eta_{intr.}$, k_H and M_r for samples with [TMC] = 40%, [I] = 0.005%, [NaCl] = 0%;

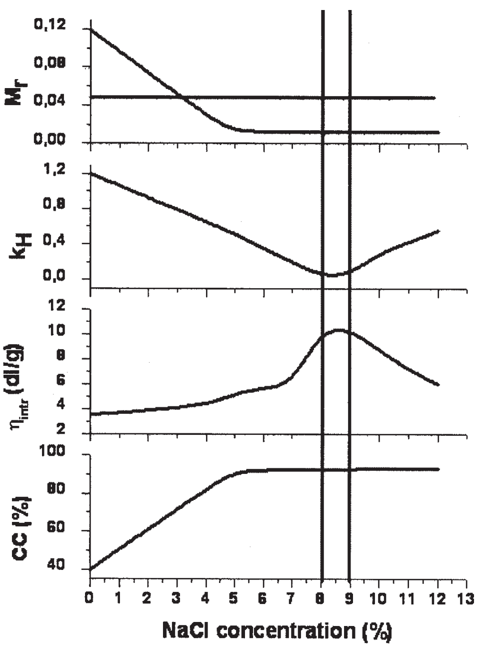

Fig. 3. The effect of the NaCl concentration and the EB absorbed dose of 1.5 kGy on *CC*, $\eta_{intr.}$, k_H and M_r for samples with [TMC] = 40%, [I] = 0.005%

conversion coefficients indicate a high efficiency of monomers utilization and a substantial decrease of residual monomer concentration, which is a very important aspect, taking into account the well known toxicity of the acrylamide monomer. In accordance with the radiation induced polymerization particularities, the conversion coefficient is influenced, by the following factors: electron beam absorbed dose, electron beam absorbed dose rate and chemical composition.

High level of electron beam absorbed dose substantially increases the conversion coefficient but decreases the intrinsic viscosity. Low electron beam absorbed dose rate increases both the conversion coefficient and the intrinsic viscosity because the dose is accumulated in relatively high times.

Figure 2 shows that irradiation doses higher than 30 Gy are required in order to obtain values of *CC* over 95 %. But the increase of the conversion coefficient is always followed by a dramatic decrease of the intrinsic viscosity, because high irradiation doses affect polymerization mechanisms in the following way: polymer chains suffer formation-fragmentation processes which lead to low molecular weight structures, most of them water insoluble (with k_H values higher than the unit), and therefore unsuitable for the purpose. As we will further show, it is almost impossible to act on the initiator concentration [I] in order to increase the conversion coefficient without having a negative influence on the intrinsic viscosity. For this reason, we decided to introduce an additional chemical agent, sodium chloride (NaCl), chemically neutral, stable and easy to find. So, the adding of the sodium chloride to the chemical composition of the monomer solution allows the reduction of the irradiation dose and this increases the electron beam efficiency and the initiation speed along with the fast consumption of the free radicals in the presence of metallic ions (sodium in this case).

The results presented in figure 3 demonstrate the necessity of sodium chloride introduction in the monomer solution to be irradiated. These results helped us identify the optimum value range of sodium chloride concentration. In order to establish the optimum concentration, we studied its effect on the conversion coefficient (*CC*), the intrinsic viscosity (η_{intr}), the Huggin's constant (k_H) and the residual monomer concentration (M_r). Of all these parameters, the intrinsic viscosity (η_{intr}) is the most sensitive to the variation of the sodium chloride concentration and it even presents critical values. As a consequence, k_H depends on the sodium chloride concentration in the same manner. *CC* and M_r, parameters which are dependent on each other, increase very fast with the growth of sodium chloride concentration, reach a maximum and then become constant. High values of M_r, superior to the limits accepted by specific regulations, were obtained at low sodium chloride concentrations. Increasing the sodium chloride concentration, the value of M_r decreases under the accepted limit, which is a very useful result in the optimization of the acrylamide concentration.

Based on the influence of the sodium chloride concentration studies, we want to point out the following important conclusions.

Irradiated monomers solutions with no sodium chloride in their chemical composition have a conversion coefficient that decreases under 80%, which means that the M_r of AMD is higher than 0.05%, which is in total disagreement with "Environmental Health Criteria-49-Acrylamide".

Adding sodium chloride and increasing its concentration up to 4% leads to the growth of the conversion coefficient but does not improve other studied parameters. Only for a well-established chemical composition and under proper irradiation conditions a sodium chloride concentration of 8% confers adequate values for the studied parameters. Further on, we will refer to the 8% sodium chloride concentration, as the optimum percentage for our purpose.

Influence of total monomer concentration [TMC] and monomer ratio R, in EB irradiation

The influence of [TMC] and R on the characteristics of the obtained copolymer correlated with the absorbed dose (D) was studied during the experiments regarding the chemical composition optimization. The results are presented in figures 4 and 5 and we can point out the following important conclusions.

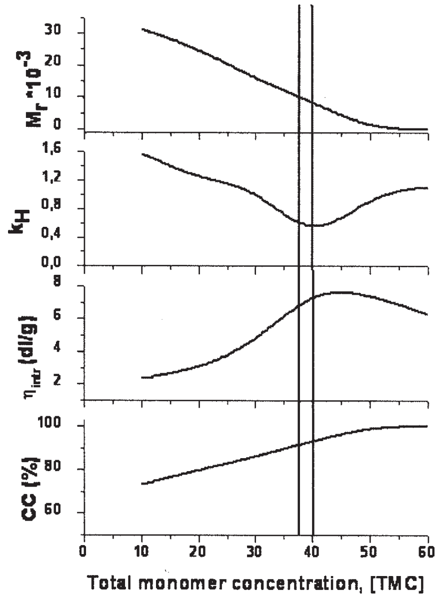

Fig. 4. The effect of the total monomer concentration, [TMC] and the EB absorbed dose of 1.5 kGy on *CC*, $\eta_{intr.}$, k_H and M_r for samples with [I] = 0.005%, [NaCl] = 8%

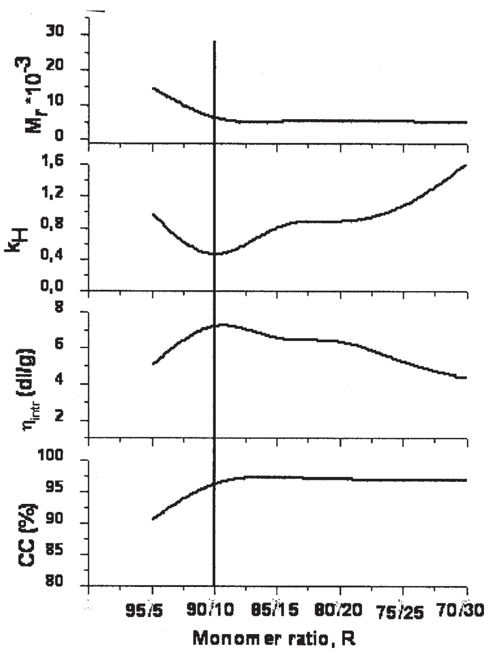

Fig. 5. The effect of the monomer ratio, R and the EB absorbed dose of 1.5 kGy on *CC*, $\eta_{intr.}$, k_H and M_r for samples with [I] = 0.005%, [NaCl] = 8%, [TMC] = 40%;

Figure 4 shows that for low [TMC] values (10 to 30 %), the conversion coefficients are under 85 % and the linearity of the obtained polymer is also poor (k_H between 1 and 1.6), which is in accordance with our purposes. This can be explained by the fact that short copolymer chains are formed during polymerization. For a [TMC] of 60%, one can observe an increase of the *CC* up to 100 %, and also a slight decrease of the η_{intr}. This phenomenon is explained by the fact that a series of secondary reactions, such as the transfer chain with the system monomers, with the solvent or even with the obtained copolymer appear at this concentration. A partly cross linked copolymer is obtained through all these chemical reactions. The synthesized copolymer had physico-chemical characteristics similar to the ones we were hoping for (*CC* > 85%, η_{intr} > 6.5 dLg, k_H < 0.8, M_r < $1*10^{-3}$%), for [TMC] concentrations between 38 to 40 % and an absorbed dose of 1.5 kGy. This is why we decided to establish the 40% value of the [TMC] as the optimum value.

(R) is also a very important parameter. One can observe in figure 5 that while CC > 85 %, the other parameters values are not so good comparing to our goal (η_{intr} < 6.5 dL/g, k_H > 0.8, M_r > $1*10^{-3}$%), for a monomer ratio AMD/AA of 95/5. The experiments have shown that the optimum monomer ratio (R) for AMD/AA is 90/10.

Influence of initiator concentration [I], in EB irradiation

In radiation-initiated polymerization, a completely "inert" solvent does not exist. Any substance when added to a monomer absorbs the radiation energy, and this, results in various secondary processes, which finally lead to an additional production of free radicals. Indeed, our experiments show that due to water presence in the EB irradiated system, the role of the radicals originating in the irradiated water is predominantly than of the radicals which come directly from the monomer irradiation. Thus, the irradiated water radicals ease the polymerization process and decrease the required absorbed dose level for acrylamide-acrylic acid copolymers. Taking into account the complexity of reaction mechanisms which are happening in radiation induced polymerization, we tried to establish a connection between the EB absorbed dose and the initiator concentration [I], both of them very important in free radical production. The experiments show that the polymerization process is complete at low EB absorbed dose rates and using a very small initiator concentration. In this case the principal source of free radicals is water, used as solvent in monomer mixture. Previous experiments have shown that the values of the physico-chemical parameters can be very close to the ones we wanted from the very beginning for [TMC] = 40%, [NaCl] = 8% and R(AMD/AA) = 90/10 but we consider that these values can be improved if we optimize the initiator concentration [I]. The results are presented in figures 6-9 and show the following aspects.

In figure 6 one can see that all the samples irradiated with doses between 1.2 kGy and 1.8 kGy have a *CC* > 95 %, except one corresponding to a 0.9 kGy absorbed dose ([I] = 0.002 %). According to the mathematical equations (1-3) the greater the CC, the smaller the M_r is and so a M_r = 0 corresponds to a *CC* = 100 % (as shown in fig. 7).

Figure 8 shows that η_{intr} presents values greater than 8.5 dL/g while the initiator concentration was between 0.0075 % and 0.014 % and the absorbed dose was 1.5 kGy. These results are in accordance with the ones in figure 9

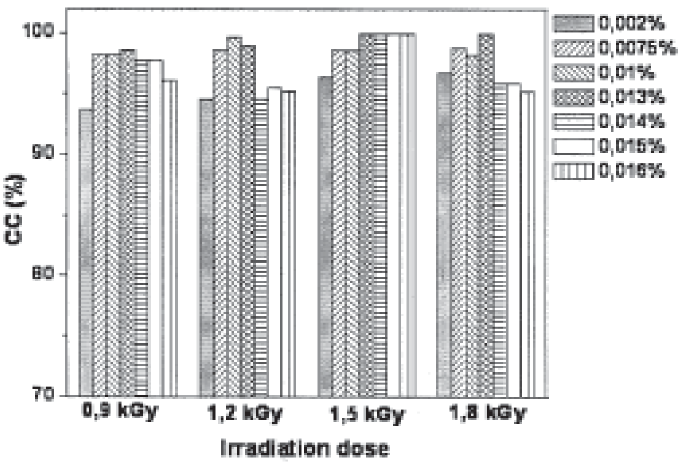

Fig. 6. The effect of the initiator concentration and the EB absorbed dose on the conversion coefficient, *CC*, for samples with [TMC] = 40%, [NaCl] = 8%.

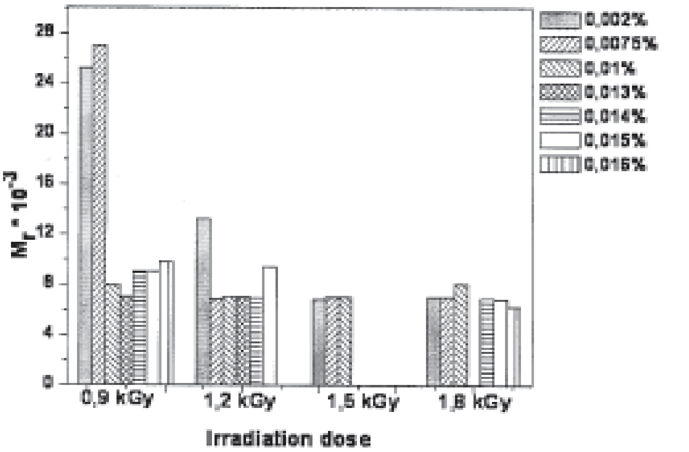

Fig. 7. The effect of the initiator concentration and the EB absorbed dose on the residual monomer content, M_r, for samples with [TMC] = 40%, [NaCl] = 8%.

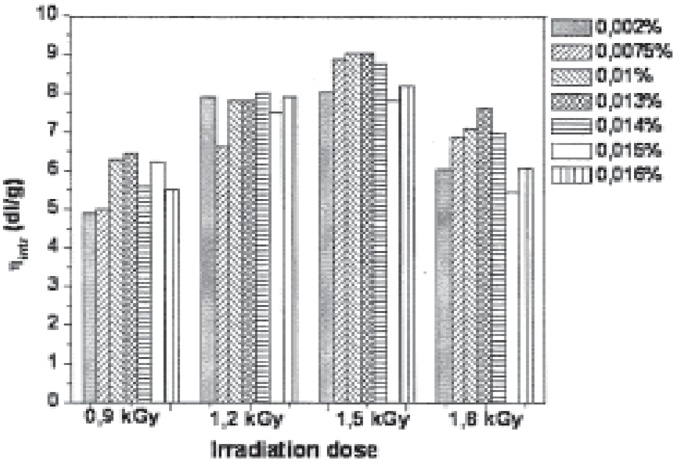

Fig. 8. The effect of the initiator concentration and the EB absorbed dose on the intrinsic viscosity, η_{intr}, for samples with [TMC] = 40%, [NaCl] = 8%.

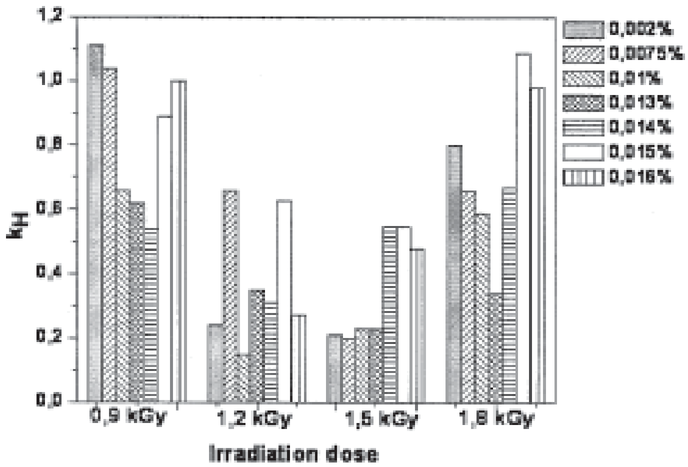

Fig. 9. The effect of the initiator concentration and the EB absorbed dose on the linearity constant, k_H, for samples with [TMC] = 40%, [NaCl] = 8%.

which show that the k_H parameter has the lowest values under the same conditions. The obtained polymer has linear chains and dissolves very well in water, which is necessary because flocculent polyelectrolytes are used for waste-water treatment as aqueous solutions.

A possible explanation for the increase of viscosity with the increase of the initiator concentration [I] can be given: a sufficiently high quantity of free radicals is formed in the reaction medium, that makes it possible to obtain a linear AMD-AA copolymer without branches on its chain, for an optimum value of the initiator concentration. In this case AMD and AA polymerize only through the –C–C– type of bonds instead of double bonds. If $[I] > [I]_{optim}$ then radicals can appear on the AMD chain for the amide group, as well as on the AA chain for the carboxylic group which creates linear bonds of AMD-AA and so a cross linking phenomenon is produced (corresponding to low values of η_{intr}) that results in lowering the water solubility of the AMD-AA copolymer.

From the comparative analysis of the figures 6 to 9 one can see that there are an optimum absorbed dose D_{optim} = 1.5 kGy and an optimum initiator concentration $[I]_{optim}$ = 0.013 % for which the obtained copolymer has a conversion coefficient of 100%, an intrinsic viscosity greater than 9 dL/g, a linearity coefficient lower than 0.25 and the residual monomer equal to 0.

Conclusions

Radio-induced polymerization is characterized by clearly different features than classic polymerization due to the initial phase. During this phase, in radio-induced polymerization, free radical generation is the result of mechanisms specific to the interaction of ionizing radiations with the substance.

Experiments have shown that, for a given chemical composition, there are an optimum absorbed dose and an optimum initiator concentration for which the copolymer obtained through irradiation in an accelerated electron field has a conversion coefficient, CC, of 100%, an intrinsic viscosity, η_{intr}, greater than 9 dL/g, a linearity coefficient, k_H, and 0 residual monomer, M_r. For an absorbed dose lower than the optimum absorbed dose D_{optim} = 1.5 kGy, the quantity of free radicals is insufficient which cannot assure a conversion, CC, greater than 85% and a residual monomer close to $1*10^{-3}$ %, regardless of the quantity of initiator used in experiments. The cross linking reactions prevail, the polymer is no longer linear, the intrinsic viscosity decreases as the linearity coefficient increases, for an absorbed dose greater than the optimum absorbed dose regardless of the presence or absence of the initiator.

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