



Preparation of polyelectrolytes for wastewater treatment

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Abstract

Liquid-phase polymerisation of acrylamide-acrylic acid to form polyelectrolytes used in wastewater cleaning was examined using accelerated electron beam and microwave irradiation methods. Polymerisation was carried out in aqueous solutions at temperatures $\sim 60^\circ\text{C}$. Monomers total concentration was established at 40% (36% acrylamide and 4% acrylic acid). Only using the features of simultaneous radiation–induction and microwave heating can result in the formation of linear polymer chains with good water solubility and low residual monomer concentration. The flocculation capacity of the obtained polymers was tested using two wastewaters, one sampled from a slaughterhouse and the other from a vegetable oil plant. Quality indicators such as total suspended matters (TSM), chemical oxygen demand (COD), biological oxygen demand (BOD) and fat, oils and grease (FOG) were measured before and after the treatment with polymeric flocculants and compared with the results obtained in classical treatment with $\text{Al}_2(\text{SO}_4)_3$. It was found that the combined treatment with polymers and $\text{Al}_2(\text{SO}_4)_3$ increases the degree of purification of both wastewaters up to 99%. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Water must be considered a resource that must be conserved. Before being discharged, water must be purified.

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Nomenclature

a	parameter in Eq. (1) (dimensionless); for acrylamide copolymers $a = 0.57$
C	polymer concentration (%)
CC	conversion coefficient of monomer to polymer (%)
D	total absorbed dose (Gy)
D^*	total absorbed dose rate (Gy/s)
E_{EB}	electron beam energy (eV)
k_H	Huggins' constant (dimensionless)
K	parameter in Eq. (1) (dimensionless); for acrylamide copolymers $K = 1.34 \times 10^{-3}$
M_W	polymer molecular weight (amu)
P_{MW}	microwave power (W)
R_m	residual monomer concentration (%)

Greek letters

α	angle made by plotting η_{red} versus C
η	intrinsic viscosity (dl/g)
η_{red}	reduced viscosity (dl/g)
η_{rel}	relative viscosity (dl/g)
η_{sp}	specific viscosity (dl/g)

The goal is to discharge water with chemical–physical and biological characteristics that will not have a detrimental impact on the environment, or better yet, that can be reused. Wastewater treatment consists of applying known technology to improve or upgrade the quality of a wastewater. Physico-chemical methods, which play a considerable role in treating process wastewaters, are used both on their own and in combination with mechanical, chemical and biological methods. Physico-chemical methods are being increasingly used for the preliminary treatment of wastewater before its biochemical purification. This is due to stricter requirements in regard to the degree of purification of wastewater and the need to remove all organic admixtures before it is discharged. The coarsely dispersed particles are easily removed by mechanical treatment although finely dispersed particles and colloid particles remain. To remove them, coagulation methods are needed. The particles in a colloid system agglomerate to form larger particle aggregates which are settled out and removed mechanically from the wastewater. One of the forms of coagulation is flocculation, in which the small suspended particles form loose accumulations of flocs which settle out easily under the influence of specially added substances (flocculants). The use of flocculants that increase the density and the solidity of the flocs formed reduces the consumption of coagulants and increases the reliability of the work and the throughput capacity of the treatment plant. The rate and effectiveness of the flocculation process depends on the composition of the wastewater, its temperature, the rate of mixing, and the order in which coagulants and flocculants are introduced into the wastewater. When dissolved in wastewater, flocculants may be in a non-ionised or ionised state. If they are ionised, they are called soluble polyelectrolytes.

Depending on the composition of the polar groups, flocculants can be non-ionogenic, cationic, anionic and amphoteric polymers. The obtaining of tough polymeric flocculants has been the subject of many studies in the past decades. An alternative and innovative way to conventionally initiated polymerisation reactions (heat sensitive peroxide, redox systems, etc.) can be the use of ionising radiation, like gamma photons or accelerated electrons. Some significant advantages can be ascribed to this polymerisation route both in terms of purity of the final products and polymerisation temperature and initiation rate range of operation [1].

In this work, the polymerisation of acrylamide and of acrylic acid using ionising (electron beams) and non-ionising (microwave) irradiation has been investigated. The aim is to investigate the possibility to favour the formation of polyelectrolytes suitable for wastewaters treatment.

Previous work carried out in our laboratory has shown that electron beams and microwave energies can be applied as the energy source for the polymerisation of acrylamide, acrylic acid, and vinyl acetate in aqueous solutions [2]. Since then we have focused our attention on finding improved irradiation conditions and a better chemical composition of the solutions to be irradiated for increasing the final parameters of the copolymer with regards to water solubility, average molecular weight, residual monomer concentration and efficiency on wastewater cleaning processes as well as to the electrical energy reduction and so, the technological cost.

2. Experimental

2.1. Materials

The synthesis of the acrylamide–acrylic acid copolymer (denoted throughout the text as polymer PA) was carried out by irradiating aqueous solutions of appropriate acrylamide and acrylic acid quantities. Complexing agents (CX) for the impurities inhibition, chain transfer agents (CT) for the crossed-link structure inhibition and initiators (INI) for the monomer conversion optimisation have been also added to the initial solution of monomers. A typical chemical composition of the aqueous stock solution used for polymerisation is given in Table 1.

Table 1
Typical recipe for irradiation-induced copolymerisation of acrylamide and acrylic acid

	Material	Weight ratio (%)
Monomer	Acrylamide	36
	Acrylic acid	4
Complexing agents (CX)	Ethylenediaminetetraacetic acid (EDTA)	0.005–0.1
Chain transfer agent (CT)	Sodium formate	0.005–0.1
Initiator (INI)	Sodium persulfate	0.005–0.8
Dispersion media	Distilled water	~60

2.2. Characterisation

The copolymer properties were studied through the following parameters:

- Conversion coefficient (CC) of the monomers to copolymer by bromine addition to the double olefin bond as described by Mendham et al. [3]. The reactant, bromine, is generated in situ through reaction between 0.1 N KBr/KBrO₃ and 18% HCl. Unreacted Br₂ is measured by titration with 0.1 N Na₂S₂O₃ in the presence of 1% starch solution.
- Average molecular weight (M_W) or intrinsic viscosity (η).
- Chain linearity coefficient given by Huggin's constant (k_H).

According to Flory [4], the values of η , M_W , and k_H can be calculated from Mark–Houwink–Sakurada equations for a polymer in aqueous solution of 1 N NaNO₃ at 30 °C and pH = 7:

$$\eta_{\text{red}} = \eta + C \times \text{tg}\alpha, \quad \eta_{\text{red}} = \frac{\eta_{\text{sp}}}{C} = \frac{\eta_{\text{rel}} - 1}{C}, \quad \text{tg}\alpha = \frac{\Delta\eta_{\text{red}}}{\Delta C},$$

$$k_H = \frac{\text{tg}\alpha}{\eta^2}, \quad \eta = KM_W^a \quad (1)$$

where η_{rel} is established from measurements with a Hoppler viscosimeter BH-2.

The irradiation of the samples was carried out in Pyrex flasks containing ca. 75 ml monomer solution.

2.3. Irradiation system

The irradiation system consists of an electron beam accelerator (ALID-7 of 5.5 MeV and 670 W output power) and a microwave multimode cavity operated at 2.45 GHz and variable power, up to 850 W. The irradiation system shown in Fig. 1 has been described in detail elsewhere, by Radoiu et al. [5]; the originality of this system consists of its three possible

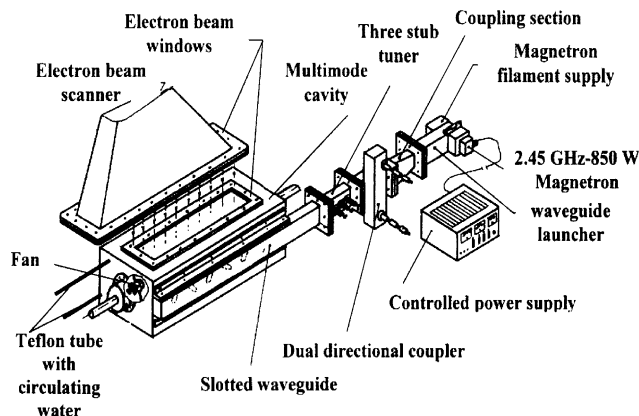


Fig. 1. Schematic drawing of the irradiation system.

operational modes: irradiation with electron beams (EB) only, with microwaves (MW) only, and with simultaneous microwaves and electron beams (MW + EB).

2.4. Wastewater sample

Wastewater samples were collected from the Slaughter House, INCAF, Ploiesti and the Vegetable Oil Plant, Solaris, Bucharest.

Quality parameters such as total suspended matters (TSM), chemical oxygen demand (COD), biological oxygen demand (BOD) and fat, oils and grease (FOG) were measured to investigate the effect of the polymer addition on the degree of purification of wastewater.

The analysis of the impure water was carried out in parallel with a blank determination on pure, double-distilled water [3,16]. The total chemical oxygen demand (COD) is a measure of the total quantity of oxygen required to oxidise all organic material into carbon dioxide and water; it was measured by the dichromate COD test. A 2-h reflux with concentrated sulphuric acid and potassium dichromate with silver sulphate and mercuric sulphate catalysts is adequate for complete oxidation of all but a few aromatic organic compounds. The 5-day, 20 °C, biochemical oxygen demand (BOD₅) has been also used for evaluating BOD in wastewaters. BOD₅ is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions. The total suspended solids (TSS) content was determined by dry ashing at 105 °C and UV-Vis spectrometry of suspended solid extinction (the amount of light stopped or scattered by a suspension). Fat, oil and grease (FOG) content was determined by extraction with petroleum ether.

The degree of purification RE was calculated as follows:

$$\text{RE}(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where C_i and C_f are the initial (before treatment) and final (after flocculation) concentrations of the load, respectively.

3. Results and discussion

Laboratory experimental methods and procedures in ionising (gamma radiation with Co⁶⁰ and accelerated electron beams) and non-ionising (2.45 GHz microwaves) treatments for polymeric materials obtaining have been continuously evolving [6,7]. Early experiments to demonstrate the viability of the technique and to identify and test some of the basic ideas governing the use of irradiation in monomer aqueous systems have shown that the irradiation induced polymerisation gives, in the proper irradiation conditions and for an adequate chemical composition of the monomeric solution, higher conversion coefficients (>99.9%) and lower residual monomer concentration (<0.05%) than classical polymerisation. It has also been proven that the characteristics of the PA copolymer are influenced by the chemical composition of the solution to be irradiated, absorbed dose level D , absorbed dose rate level D^* , and the nature of the energy which induces the polymerisation process.

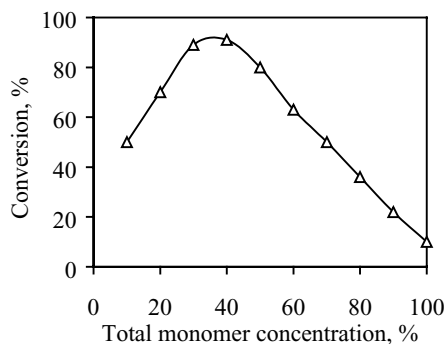


Fig. 2. Polymerisation conversion vs. total monomer concentration EB irradiation, $D = 1.9$ kGy, $CX = 0.025\%$, $CT = 0.2\%$.

3.1. Polymerisation with accelerated electron beams (EB)

In EB polymerisation the radical reaction mechanism depends on the total monomer concentration as well as on the presence of water in the system; however, the radicals originated from water radiolysis have a predominant role on the radicals produced by monomer irradiation. Fig. 2 shows the effect of initial monomer concentration on the conversion of monomer to polymer. It can be easily observed that a total monomer concentration greater than 40% leads to a decrease in reaction efficiency indicating that the water radicals facilitate the polymerisation process.

Although increasing the total absorbed dose (D) gives better reaction efficiency (conversion of monomer to polymer) and high intrinsic viscosity values, the final polymer has very poor water solubility indicating a cross-linked structure. Polymers with good chain linearity (given by k_H) and high molecular weight (given by η) are desirable because they are water-soluble and have good flocculation properties, i.e. fast gravitational sedimentation and compact sediment.

Fig. 3 shows the polymerisation conversion and molecular weight against total absorbed dose level. The dose level dependence of the conversion is represented by S-shaped curves. After a short initial period, the polymerisation rate increases until the higher conversion. This feature can be explained by the gel effect. At the early polymerisation stage, the process mainly occurs in the continuous phase, and the growing oligomers form in the continuous phase. As conversion increases, the viscosity with each particle builds up, decreasing the rate of diffusion-controlled termination, and in turn accelerating the rate of propagation, which results in the presence of the gel effect [8,9]. The polymer molecular weight (given by the intrinsic viscosity) increases with irradiation time in the early stages and then reaches a steady value, which is also indicative of the existence of the gel effect.

Fig. 3 shows a decrease in the polymer molecular weight with the irradiation time, from 93×10^5 after 10 min of irradiation to about 63×10^5 amu after 20 min. This result can be explained considering that during irradiation several processes can occur. They involve monomer polymerisation, chain branching and cross-linking and degradation of the PA polymer already formed; also, interactions among all the components are caused. A competition

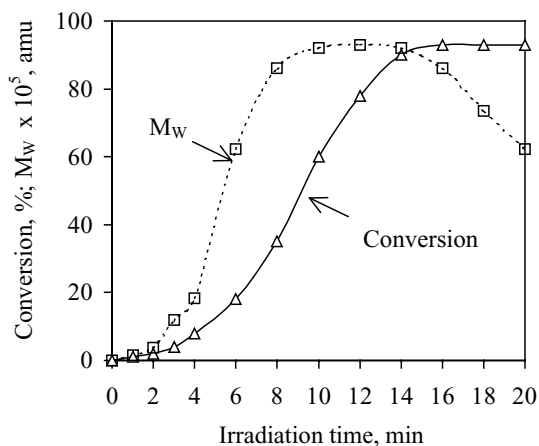


Fig. 3. Polymerisation conversion vs. irradiation time and polymer molecular weight (M_w) vs. irradiation time. Dose rate 150 Gy/min; CX = 0.025%, CT = 0.1%, INI = 0.5%.

between all these phenomena can be suggested. PA degradation determines a general decrease of its performance in wastewater cleaning, clearly attributable to the different effects of ionising radiation on the monomer, which affect the final structure of the polymer.

It is noteworthy that polymers with high molecular weight are insoluble in water. The cross-linking effect can be controlled by CT. High quantities of CT prevent the cross-linking effect but lead to lower M_w and polymer conversion values (Table 2).

3.2. Microwave polymerisation (MW)

Alongside ceramic processing, polymer chemistry forms probably the largest single discipline in microwave chemistry, and the methods used are certainly among the most developed. Polar starting materials and very often products, allow rapid and controllable syntheses, the dielectric properties themselves being an excellent indicator of reaction progress. The ability to control syntheses with high accuracy and with direct heating of the reactants has the advantage of large potential savings in energy [10].

Table 2
The effects of EB irradiation mode and chemical composition on the PA parameters

CT (%)	$M_w (\times 10^{-6}, \text{amu})$	k_H	Solubility in water
0.05	15.90	3.12	Insoluble
0.01	9.31	1.52	Insoluble
0.15	4.67	0.88	Partial soluble
0.2	3.38	0.25	Soluble
0.5	2.83	0.15	Soluble
1.0	2.41	0.08	Soluble
2.0	1.25	0.05	Soluble

Dose level, 1.9 kGy; INI, 0.5%; CX, 0.025%.

Table 3
Microwave polymerisation of acrylamide–acrylic acid aqueous solutions

Irradiation time (s)	M_W ($\times 10^{-6}$, amu)	k_H	Solubility in water
115	1.05	1.50	Partial soluble
120	2.92	0.96	Soluble
125	4.01	0.61	Soluble
130	4.50	0.52	Soluble
135	4.96	0.36	Soluble
140	3.51	3.26	Insoluble

Monomer total concentration 40% (w/w), $P_{MW} = 250$ W; INI, 0.5%; CT, 0.2%; CX, 0.025%.

The origin of microwave heating lies in the ability of the electric field to polarise the charges in the irradiated material and the inability of this polarisation to follow extremely rapid oscillations (2.45 GHz frequency) of the electric field. Therefore, the polarisation vector lags the applied electric field ensuring that the resulting current has a component in phase with the applied electric field, which results in the dissipation of power within the material. Coupled with these polarisation effects, a dielectric can be heated through direct conduction due to, for example, the redistribution of charge particles under the influence of the externally applied electric field forming conducting paths, particularly in mixtures of heterogeneous materials [11]. From the above consideration, it is clear that polar molecules can absorb microwaves resulting in a greater heating rate. Consequently, a solvent able to couple efficiently with microwaves will increase the reaction rate of the dissolved solutes, even poorly polar ones. Thus, in the microwave-induced polymerisation of acrylamide–acrylic acid solutions, due to the presence of water with strong microwave absorbance, it was expected that the polymerisation reaction rate would be much enhanced. Indeed, the use of microwave heating for acrylamide–acrylic acid aqueous solution polymerisation requires a significantly reduced time than conventional heating, about 50–100 times lower.

Due to rapid, volumetric and selective microwave transfer, the molecular weight dispersion of the polymeric material is low. Median M_W values ($(3-5) \times 10^6$ amu) but good water solubility were always obtained in microwave fields (Table 3).

3.3. Simultaneous polymerisation with accelerated electron beams and microwaves (EB + MW)

The irradiation with electron beams has been already recognised as a very effective method for material processing because it can induce chemical reactions at any temperature in solid, gas or liquid phase without using catalysts. The main disadvantage of the method is that the required doses are generally very high. In addition, the equipment involved in ionising radiation chemistry requires expensive shielding and high maintenance costs. Thus, for industrial scale processing, the problem of minimising the electricity consumption as well as the electron beam cost is especially important.

The results of simultaneous irradiation with electron beams and microwaves (EB + MW) of 40% acrylamide–acrylic acid aqueous solutions are given in Table 4. The additional use of

Table 4
 Polymerisation of acrylamide–acrylic acid solutions under simultaneous irradiation with EB and MW

Total absorbed dose (kGy)	$M_W (\times 10^{-6}, \text{amu})$	k_H	Solubility in water
0.2	2.2	0.30	Soluble
0.3	7.1	0.15	Soluble
0.4	8.9	0.09	Soluble
0.5	9.0	0.05	Soluble
0.6	8.5	0.10	Soluble
0.7	7.5	0.15	Soluble
0.8	6.7	0.19	Soluble
1.0	4.1	0.57	Soluble

Monomer concentration, 40%; INI, 0.5%; CT, 0.2%; CX, 0.025%; $P_{MW} = 250 \text{ W}$; irradiation time, 30 s.

MW energy to the EB energy results in excellent properties of the polymer, very high M_W simultaneously with low k_H and a reduction in the electron beam dose of 2–4 times.

3.4. Wastewater treatment

Methods of coagulation and flocculation are widely used for treating wastewater in many branches of the industry [12–15]. The effectiveness of the coagulation treatment depends on many factors: the type of colloid particles, their concentration and degree of dispersion, the presence in wastewater of electrolytes, and other substances. The main process for the coagulation treatment of the process wastewater is heterocoagulation—the interaction of colloid and finely dispersed particles in the wastewater with the aggregates formed when coagulants are introduced into the wastewater. Suspended particles acquire an electrostatic charge, which, in water treatment is usually negative. The charges produce repulsion between particles, which tends to stabilise the suspension. In colloidal suspensions, which have a maximum particle size of less than $2 \mu\text{m}$, this repulsion effectively prevents settling. Coagulating agents are selected to have an opposite charge to that of the suspended solids and effectively neutralise that charge. This destabilises the suspension and allows the particle to come together. Flocculating agents form bridges between particles and lead to the formation of large agglomerates, which can be removed by settlement or flotation.

Preliminary experiments comprising investigation of the flocculation capacity of PA polyelectrolyte were carried out in order to quantify parameters such as total suspended matters (TSM), chemical oxygen demand (COD), biological oxygen demand (BOD) and fat, oils and grease (FOG). High average molecular weight ($9 \times 10^6 \text{ amu}$) and low k_H (0.05) PA obtained by EB + MW treatment was employed. Two wastewaters, one from a slaughterhouse and the other from a vegetable oil plant, were tested. The coagulant (aluminium sulphate from 10% solution) and the flocculant (PA from 0.1% solution) were gradually poured into the water with 20–30 rpm stirring. The pH was fixed at 7 with $\text{Ca}(\text{OH})_2$ and the temperature of the treated water was 20°C . The results are presented in Tables 5 and 6.

The experimental data shown in Tables 5 and 6 indicate that the use of PA polyelectrolyte in combination with a classical coagulant $\text{Al}_2(\text{SO}_4)_3$ much increases the degree of purification of both wastewaters.

Table 5
Wastewater from the slaughter house INCAF, Ploiesti, Romania

Quality indicator	Level of admixture in the water (mg/l)			RE (%)	
	Before treatment	After treatment		C	C + P
		C ^a	C + P ^b		
TSS	766	496	112	33.9	85.4
BOD	1500	1050	205	30.0	86.3
COD	480	321	100	33.1	79.1
FOG	332	275	32	17.1	90.0

^a Classical treatment: 1 l wastewater + 4 ml Al₂(SO₄)₃ 10%.

^b Combined treatment: 1 l wastewater + 2 ml Al₂(SO₄)₃ 10% + 4 ml PA 0.1%.

Table 6
Wastewater from the vegetable oil plant Solaris, Bucharest, Romania

Quality indicator	Level of admixture in the water (mg/l)			RE (%)	
	Before treatment	After treatment		C	C + P
		C ^a	C + P ^b		
TSS	1020	971	50	4.8	95.1
BOD	2300	1400	298	39.1	87.0
COD	4664	2889	395	38.1	91.5
FOG	3497	82	8	97.7	99.8

^a Classical treatment: 1 l wastewater + 4 ml Al₂(SO₄)₃ 10%.

^b Combined treatment: 1 l wastewater + 2 ml Al₂(SO₄)₃ 10% + 4 ml PA 0.1%.

4. Conclusions

It has been proved that both external accelerated electron beams and microwaves can be regarded as sources for the acrylamide–acrylic acid polymerisation. The examination of the above results suggested that the combination between the ionising effects of external accelerated electron beams and the dielectric heating feature of microwaves could give new and promising results in the polymer chemistry. Expected improvements include a reduction of the total required absorbed dose of electron beam irradiation and also, an improvement of the polymer properties such as higher molecular weight and good water solubility.

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