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Dielectric heating in acrylamide solution polymerization. Comparative study

G. E. IOANID, I. NEAMTU*
"Petru Poni" Institute of Macromolecular Chemistry Grigore Ghica Voda Alley No. 41 A, RO - 700487 Iasi, Romania

Dielectric heating is a potential alternative for material processing, more energy efficient, allowing rapid and controlled processes, that applies the principles of green chemistry. In the paper there are presented a polymerization equipment with conventional / dielectric heating and the effect of the high frequency electromagnetic field presence - as source of thermal energy - during poly(acrylamide) synthesis. By using this technique, significant increase of the conversion and reaction rate are registered; some properties of the synthesized polymer are influenced, too.

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1. Introduction

Dielectric heating (DH) is the method of heating electrical non-conducting materials. It is an incredibly rapid and selective, clean and safe, versatile and energetically-convenient heating method, gaining increasing favour in 1980's and 1990's for industrial processing of numerous materials: rubbers, ceramics, textiles, minerals, wood, adhesives, some plastics and thermosetting resins, etc. In the field of polymeric materials, dielectric heating has shown a great potential, still far from being extensively used as it could, for accelerated processing of high-performance plastics, rubbers, and related composites [1-7].

The material to be heated is placed between two electrodes, to which a high frequency (HF) energy source of $10^6 - 10^7$ Hz is connected. The oscillating field passes through the material and as the field direction changes, the polarisation of individual molecules reverses rapidly, causing friction and hence heat. The higher the frequency, the greater the emitted heat in time it is. Radio frequency (RF) energy and microwave (MW) energy are both dielectric heating technologies, where electromagnetic radiation generates heat in dielectric materials. For dielectric materials heating, such as organic substances are, there are used two bands of frequency: high frequency or radiofrequency waves (1-300MHz) with admissible domains set at 13.56 and 27.12 MHz and microwaves frequency from 300 MHz to 300 GHz with admissible domains set at 896, 915 or 2450 MHz.

Electromagnetic waves possess several characteristics that provide unique features that are not available in the conventional heating of materials. Some of the key characteristics of electromagnetic waves' interactions with materials are: penetrating radiation; controllable electric field distributions; rapid heating; selective heating (differential absorption) of materials; and self-limiting reactions. These characteristics, either singly or in combination, represent opportunities and benefits not available from conventional heating methods; at the same time, there are showing dielectric heating is a way to eco-friendly, *green chemistry*.

But, the main advantage of dielectric heating is the almost instantaneous so-called "volumetric" or "in core" heating effect in an homogeneous and selective manner, arising from the fact the energy is absorbed directly into the material mass, rather than being transferred to it, *via* surface. Thus, the use of electromagnetic energy for materials processing has major potential, and real advantages over conventional heating, including: time and energy savings, rapid heating rates, uniform microstructures and hence better product performance, lower environmental impact.

Almost any type of organic reaction requiring heating or thermal conditions can be performed using electromagnetic radiation. Dielectric heating is dependent on the ability of a substance to absorb electromagnetic energy and to convert it into heat. The matrix absorbs the radiation by two mechanisms: dipole polarization and ion conduction. As the applied field oscillates, the dipoles or ions attempt to realign or reorient themselves with the alternating electric field and, in the process, energy is lost in the form of heat through molecular friction and dielectric loss. The amount of heat generated by this process is directly related to the ability of the matrix to align itself and the frequency of the applied field.

In this context, as a result of the great reactivity due to the presence of double bond and amide functional group, acrylamide is a model compound that offers distinguished theoretical information on the polymerization assisted by a high frequency electromagnetic field.

The article reports and compares acrylamide solution polymerization assisted by a high frequency electromagnetic field of 27.12 MHz with the reaction realized by conventional heating. The effects of the presence of HF field are interpreted in terms of process kinetic and of some characteristics of polyacrylamide synthesized by this method.

2. Experimental

2.1. Materials

Acrylamide (Merck, Darmstadt,Germany) as the monomer is radical polymerized in solution of distilled water, ethylene glycol (EG) and glycerol (Gl), at 0.7 M × l $^{-1}$ concentration. Potassium peroxydisulphate (Merck, Darmstadt, Germany) in 0.028 M × l $^{-1}$ concentration was used to initiate polymerization at 70 ^{o} C for 50 min, at atmospheric pressure and constant stirring. All reactants are analytical reagents grade and are used as received.

The reactions are conducted with conventional heating (C) and assisted by a high frequency electromagnetic field (DH), strictly in the conditions mentioned in Table 1.

Table 1. Conventional (C) and high frequency (DH) assistedpolymerization of acrylamide.

Reaction conditions	C	DH
Temperature, ^{o}C	70	70
Reaction time, min	50	50
Agitation, rot/min	150	150
Distance between electro-des ,mm	-	50
Frequency, MHz	-	27.12
Tension, kV/cm	-	0.2
Irradiation power, Watt	-	60

2.2. Experimental set-up

Poly(acrylamide) synthesis is performed in the installation designed and realized in our laboratory and shown in Fig. 1; it allows the concomitant realization of dielectric (DH) and conventional (C) heating techniques.

The system is composed of two thermoresistent glass reaction vessels A and B of cylindrical shape and thermal isolated, two semi cylindrical shaped copper electrodes 4 placed on the exterior walls of the reactor A and connected to the high frequency power generator operating at 27.12 MHz and a complex ensemble for temperature equalization and control in the two reaction vessels (temperature transducer with thermistor, rotary pump for cooling water circulation, coils, cooling vessel, electrovalve, rotating mechanical stirrers, command - control device). The temperature obtained by dielectric heating of the reaction medium in vessel A is transferred into vessel B by auxiliary circuit for thermal transfer; thus, temperature increase into the two reaction vessels is realized with the same gradient.

The reaction components are charged into the reaction vessels and the experiments are started at the parameters mentioned in Table 1.

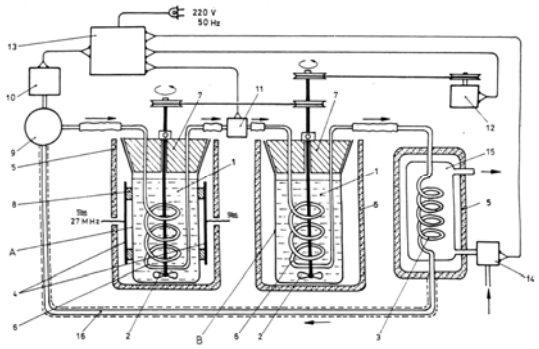

Fig. 1. Schematic diagram of the installation with dielectric and conventional heating : A, B reaction vessels; 1-reaction medium; 2- rotating mechanical stirrer; 3-cooling coil; 4-copper electrodes connected to HF generator; 5-thermal isolation; 6-thermal transfer coil; 7-bell ; 8-teflon ring; 9 - rotary pump; 10-driving motor for rotary pump; 11-temperature transducer with thermistor; 12- driving motor for stirrers; 13-command - control device; 14-electrovalve; 15-cooling vessel; 16-auxiliary circuit for thermal transfer.

2.3. Characterization

Polymerization was studied comparatively by determination of gravimetric conversion and reaction rate. Poly(acrylamide) samples were purified by re-precipitation in methanol and dried under vacuum at 40 ^{o} C. The polymer structure was characterized using Fourier Transform Infrared Spectroscopy (FTIR) experiment on a spectrophotometer DIGILAB Scimitar Series-USA, with 4 cm^{-1} resolution; it was kept constant the amount of polymer (5 mg) in the KBr tablet (500 mg).

Thermogravimetric analysis (TGA) was performed in air by means of a MOM – Budapest of Paulik, Paulik – Erdey type derivatograph, in the temperature range of 25 - 600 ^{o}C, at a constant heating rate of 12 ^{o} C x min^{-1} and reference material α-Al_2O_3, with simultaneous recording of thermogravimetrical TG, derived thermogravi-metrical DTG, differential thermal DTA, and temperature variation T. The activation energy of decomposition reaction E_a for the synthesized samples was calculated from TGA curves using Coats - Redfern and Reich – Levi method [8-11].

The DSC thermal analysis was recorded on a Mettler DSC-12E type differential scanning calorimeter (Switzerland) at a heating rate of 10°C/min in inert atmosphere of N_2, 25°- 400°C temperature range, under dynamic conditions. Pure indium was used as a standard for calorimetric calibration.

Intrinsic viscosity [η] was measured in aqueous dilute solutions using an Ubbelohde suspended level viscometer, at 25 ^{o} C.

3. Results and discussion

In the first experiment is followed the effect of heating technique DH and C on the polymerization development of acrylamide.

In the polymerization process, DH effects are mainly observed during the initiation step, when conversion and rate of reaction record significant increases. The study of the reaction assisted by HF electromagnetic field specifies a lessening of the activation energy, thinking up that through the application of a HF field the system entropy is modified.

Dielectric polarization, is primarily responsible for electromagnetic waves' heating of the substance. It is a relevant mechanism that involves the high frequency electromagnetic stimulated rotation and line up of molecules that have a dipole moment. The electric field component of the radiation causes the dipoles to respond. Alignment and randomization occurs approximately with a frequency of 27.12 MHz, generating heating as the rotational molecular motion is converted to translational motion via collisions with surrounding molecules.

Dielectric polarization depends primarily on the ability of the dipoles to reorientate in the applied electric field and is influenced by **dielectric constant** ε and **loss factor** tan δ [12]. The reaction medium that is the organic solvent, the more polar it is (the higher the dielectric constant it possesses) the more readily the irradiation is absorbed and the temperature increase is attained. In order to compare the abilities of different solvents used as reaction medium in solution polymerization to generate heat as a consequence of electromagnetic irradiation, their capabilities to absorb and to convert it into heat must be taken into account. This aspect is in relation with dielectric constant and dipolar moment, whose product - **electrostatic factor** EF [13] quantifies the efficiency with which the absorbed energy is converted into heat. As a consequence, the solvents used in this study will influence the polymerizations in the direction:

Water (EF= 148.9) > Glycerol (EF=108.8) > Ethylene glycol (EF=85.9)

The Figs. 2 a,b,c present the development of polymerization in the three solvents, with C and DH heating techniques. The reactions assisted by HF electromagnetic field have higher conversions and rate of reactions, while the initiation phase is diminished; this observation is valid for all the three solvents as polymerization media, comparative with the conventional heating. The result is more evidently for the variant with water as reaction medium. Thus, the conversion at 50 min is 81.68% for DH technique comparative to 48.20% for C technique. In ethylene glycol as reaction medium, the conversion increases from 33.09% (C) to 61.30% (DH) while in glycerol the increase is from 26.37% (C) to 74.22% (DH). Fig.2 a,b,c evidence also the growth of momentary rates of reaction for DH comparative to C technique. Such increases of conversions and reaction rates are pointed out in literature [14-16], for the synthesis assisted by electromagnetic field, but in the domain of microwaves. Table 2 contains the maximum rate of reaction registered for all the variants of synthesis.

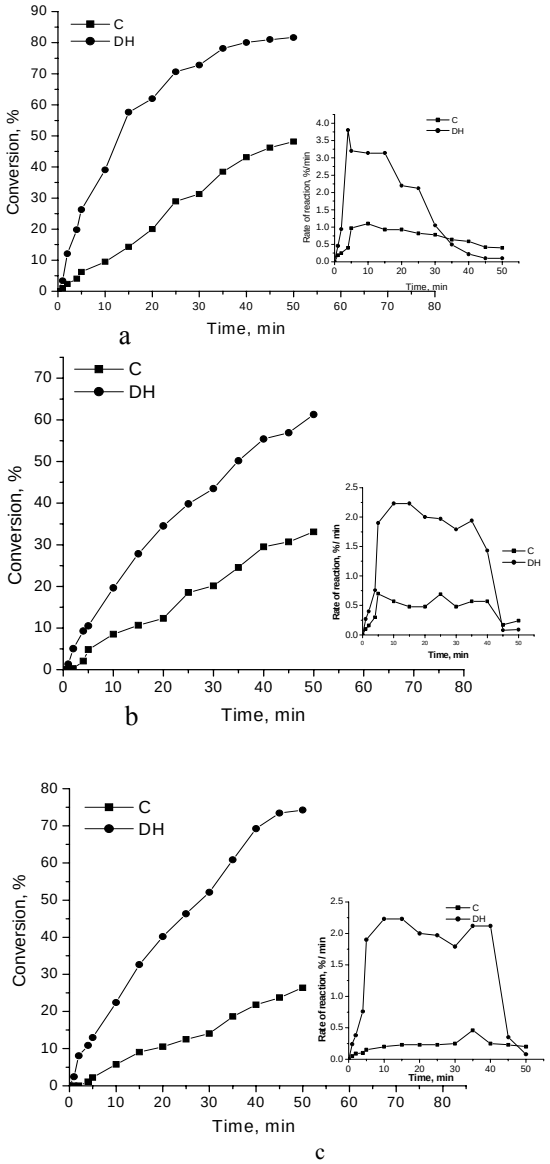

Fig. 2. Acrylamide polymerization by C and DH technique. Reaction medium: a-acetone; b-ethylene glycol; c-glycerol.

In a second experiment it is isolated the effect of HF electromagnetic field on the initiation step of acrylamide polymerization, by performing the reaction in aqueous medium with and without potassium peroxydisulphate. The data plotted in Fig. 3 underline the conversion as a function of irradiation energy; the reaction may be initiated by DH technique without initiator (2 in Fig. 3) but the conversion has lower values comparative to those realized in the synthesis with radical initiator (1 in Fig. 3), leading to the conclusion the initiator is a supplementary source of initiation.

Table 2. Maximum rate of reaction for DH and C heating techniques.

Reaction medium	DH		C	
	Time of reaction, min	Maximum rate of reaction, %/min	Time of reaction, min	Maximum rate of reaction, %/min
Water	4	3.80	10	1.1
EG	10	2.23	25	0.7
Gl	10	2.23	35	0.46

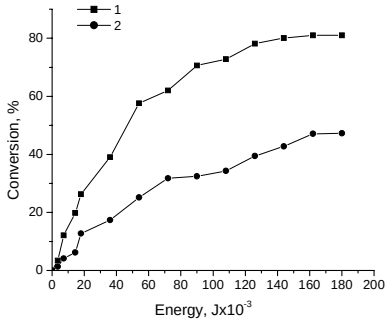

Fig. 3. Acrylamide polymerization by DH technique.1-with initiator; 2-without initiator.

Besides the modifications brought to the evolution of the polymerization process, the HF electromagnetic field influences the properties of the resulting polymers obtained. As shown in Fig.4, FTIR spectra of poly(acrylamide) synthesized with C and DH technique exhibited absorptions at 3050-3550 (symmetrical and asymmetrical valence vibrations of the N-H links in NH_2 groups), 1470-1700 (valence vibration of C=O link and deformation vibration of N-H link) and 1300-1400 cm^{-1} (C-N vibration), associated with the primary amide structure. It is underlined the poly(acrylamide) structure during DH technique did not change at all; only an increase of the characteristic bands'intensity in the spectrum of the sample synthesized by DH technique it is revealed.

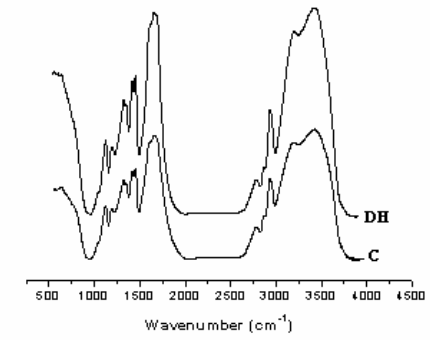

Fig. 4. FTIR spectra of polyacrylamide synthesized with conventional (C) and dielectric heating (DH) technique.

The intrinsic viscosity and thermal characteristics obtained by DSC and DTG analyses of poly(acrylamide) synthetized in water by applying DH and C techniques are summarized in Table 3. Intrinsic viscosity as a measure of molecular weight is increased with about 16.4 %. The electromagnetic field presence assisting poly(acrylamide) synthesis causes the increase of Tg, evidenced for polyacrylamide samples (from 168 to 175°C) and are according to the literature data [17].

Table 3. [η] and thermal characteristics of poly(acrylamide) synthesized by C and DH technique.

Technique	[η] dl/g	Tg [1] (°C)	Ti [2] (°C)	Tmax [3] (°C)	Tf [4] (°C)	Ea [5] (kJ/mol)
C	1.65	168	256	295	394	78.6
DH	1.92	175	268	315	417	98

[1] Tg – glass transition temperature
[2] Ti – initial oxidative decomposition temperature
[3] Tmax – temperature for maximum weight loss
[4] Tf – final temperature of thermal decomposition
[5] Ea – activation energy

The differences in thermal characteristics are not spectacular, but with some values' increases consisting on the average of 6.5 %. The appeared changes are attributed to the heat transfer with direct contact in the reaction mass realized by the electromagnetic field in dielectric heating technique. As a consequence, there are determined changes in mobility and "adaptation" of the solvent and monomer molecules, with effect on the growing macromolecular chain, too.

4. Conclusions

In the paper it is reported a promising, efficient and rapid method for the solution polymerization of acrylamide, with dielectric heating generated by the presence of a high frequency electromagnetic field of 27.12 MHz, comparative to conventional heating. There is monitored the reaction development in solvents with different dielectric characteristics. The experimental set - up is realized on an installation that allows the two heating techniques - dielectric and conventional - on the same unit.

In comparison with conventional heating, dielectric heating accelerates the reaction and give polymers with higher molecular weights and thermal stability.

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*Corresponding author: danaiordana@yahoo.com