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Abstract:

The present work describes a combination of microwave irradiation as a heating source and water as a solvent for carrying out a living/controlled polymerization of acrylamide. Reasonable results were obtained for a nitroxide-mediated radical polymerization (NMP) with a combination of a conventional hydrosoluble radical initiator and a β-phosphonylated nitroxide. The microwave enhancement of the polymerization was found to depend on the mode of irradiation, i.e., either a DYN mode or an SPS mode. The former mode corresponded to a dynamic control of the temperature by way of a high initial microwave power, and in this case, no specific microwave effect was observed. On the other hand, in the SPS mode, which is a pulsed power mode, the result showed a strong acceleration of the polymerization process (> 50 times) without the loss of the living/controlled polymerization characteristics which is relevant with a re-initiation of the polyacrylamide macroinitiator even after 100% of conversion.

Keywords: microwave**,** acrylamide, controlled/living polymerization, Nitroxide Mediated Polymerization.

1. Introduction

Controlled radical polymerization (CRP) is a well-known route for preparing (co)polymers with controlled functionalities and topologies, as well as targeted molar masses with low polydispersities. The CRP process requires selecting conditions that allow, or create, a dynamic equilibrium between a low concentration of active propagating chains and a large number of dormant chains, which are unable to propagate or self-terminate. There exist several CRP processes based on this fundamental understanding and the techniques that have received the most attention include Atom Transfer Radical Polymerization, (ATRP); Stable Free Radical Polymerization (SFRP), e.g., Nitroxide-Mediated Polymerization (NMP) and OrganoMetallic Radical Polymerization (OMRP); Degenerative Transfer (DT) processes, e.g., Reversible Addition Fragmentation Transfer (RAFT), and Macromolecular Design via the Interchange of Xanthates (MADIX).[1]

Microwave-assisted polymer chemistry is a rapidly growing field of research. In the last few years, various examples of reaction accelerations, selectivities, and higher yields have been reported.[2-9] Overviews on microwave-assisted polymerizations have recently been provided by Ritter [10,11] as well as Schubert and co-workers,[12-14] whereby special attention was given to microwave-assisted CRP. In *resumé*, the polymerization rates were found to be clearly faster under microwave (MW) irradiation than under classical thermal heating at identical polymerization temperatures and under controlled conditions. This was true for NMP of styrene in bulk[15], and methyl acrylate and *tert*-butyl acrylate in a relatively polar solvent (1,4-dioxane);[16] for RAFT polymerization of methyl methacrylate,[17] vinyl acetate,[17] and styrene,[17,18] and for ATRP of methyl methacrylate[19-21] and acrylonitrile in refluxing tetrachloromethane.[22] The effectiveness was seen to depend essentially on the method used for performing the MW-assisted polymerization. Even faster polymerization rates have mostly been obtained under MW irradiation. It is indeed difficult to compare the results due to the great variety of experimental conditions described within the studies. Results have been obtained with a domestic or monomode MW oven and various modes of irradiation. Demonceau[19] showed that a microwave effect was noted during ATRP of methyl methacrylate; an effect that strikingly depended on both the temperature and the method used, e.g., conventional microwave synthesis (CMS) or enhanced microwave synthesis (EMS), in the monomode MW oven. Their results differed from those reported by Schubert and co-workers [20] for the microwave-assisted ATRP of MMA using a copper-based system, thereby

demonstrating the absence of any 'microwave effect' in ATRP, in contrast to several literature reports[19,21], but without a consistent comparison of the irradiation method in terms of power and energy supplied to the reaction medium.

Microwave effects are obviously the subject of considerable current debate and controversy, and extensive research efforts are necessary to truly understand these and related phenomena. On the other hand, the combined use of microwave irradiation as a heating source and water as a solvent for synthetic organic transformations is a relatively new approach, as recently reported by Kappe et *al.*[23] Nevertheless, to the best of our knowledge, work involving microwave-assisted CRP in aqueous media has yet to be published. Recently, Erdmenger *et al.* have used water as solvent for the microwave-assisted free radical polymerization of styrene [24].

Thus, the issue of microwave effects on the controlled radical polymerization in water is the primary focus of this work. For that, the choice was made to carry our microwave-assisted NMP of acrylamide at high concentrations (40 wt-%) in a purely aqueous solution, using a combination of a conventional hydrosoluble radical initiator (Vazo56) and a β-phosphonylated nitroxide, SG1. Evidence of a living/controlled nature of the polymer is presented and the effects of the employed MW irradiation method are described.

Unlike other polyacrylamide derivatives that are soluble in common organic solvents, poly(acrylamide) PAM is only soluble in water, dimethylsulfoxide and glycerol. Moreover, the monomer is a powder, which inhibits the bulk polymerization from being considered at a reasonable temperature. Under such constraints, the controlled radical polymerization, CRP, of acrylamide in aqueous solution seems to be a realistic route, as both monomer and polymer are highly soluble in water up to 40 wt%, and respect the environmental benefits associated with microwave-assisted aqueous polymerizations.[25,26]

2. Experimental section

2.1 Materials

Acrylamide (AM) (purity >99%) was purchased from ABCR, and 2,2-azobis (2-methylpropionamidine) dihydrochloride, denoted VAZO56, was obtained from Dupont Chemicals. N-tert-butyl- N-[1-diethylphosphono-(2,2-dimethylpropyl) nitroxide] (DEPN), also called SG1, was kindly provided by Arkema and used as the counter radical. All

chemical products were used as received. Deionized water, with an electrical conductivity of 18.3 MΩ.cm at 25°C, was filtered through a 0.22 μm Millipore filter prior to use**.**

2.2 Polymerization

A bimolecular system, based on Vazo56 (initiator) and free SG1 (counter radical) was used to run polymerizations of AM at 40 wt%. The molar ratio $[SG1]_0/[Vazo56]_0$ was kept constant at 1.8 according to previous optimizations carried out for acrylamide[27] and organosoluble monomer.[28,29] Monomer solutions, containing a constant amount of initiator ($[AM]_0/2[Vazo56]_0$=500) were purged with nitrogen for 5 min directly in a 15-mL Pyrex culture tube with a screw-cap, or in a standard 10-mL Pyrex microwave process vial before being heated in an oil bath or through microwave irradiation. A total amount of 4.5 mL and 3 mL were heated conventionally in an oil bath and by way of microwave experiments, respectively. The polymerization was terminated by cooling in an ice bath (for the case with conventional heating in an oil bath) or with compressed air (for the microwave experiments) and the reactive medium was sampled for size exclusion chromatography coupled with light scattering detector (SEC-MALS). For the kinetic experiments, the same reaction mixture has been used to prepare several tubes and each tube was withdrawn at different time intervals.

2.3 ***Size exclusion chromatography coupled with multi-angle light scattering (SEC-MALS)***

The number-average molar mass (M_n), polydispersity (Ip), and polymer conversion (p) of the polyacrylamide (PAM) samples were determined by size exclusion chromatography (SEC) using a Waters Alliance 2690 (USA) chromatograph equipped with two Shodex OHpak columns (SB-804HQ, and SB-802.5HQ) and two online detectors: a differential refractometer and a DAWN® HELEOS™ II utilizing a 120-mW solid-state laser operating at 658 nm and fitted with a K5 cell. A 0.1-M solution of $NaNO_3$ was used as the eluent at a flow rate of 0.5 mL/min. Samples were prepared by diluting approximately 20 times the reaction mixture in 0.1M $NaNO_3$ and then filtering with a 0.45 μm filter (Millipore) after about 1 hour of stirring. Samples of 25 to 75 μL of these solutions were injected. The number-average molar mass and polydispersity were obtained from data collected and analyzed using the ASTRA SEC-software (version 5.3, Wyatt Technology Corp., USA). The calculation of molar mass was carried out according to the Zimm fit method. The differential molar mass distribution was carried out according to the common form: x(M)= dW(M)/dlog(M), where W(M) is the cumulative distribution (the weight fraction of sample having molar mass less than M). The refractive index increment, dn/dc, was determined to be respectively 0.184±0.001 and

0.144±0.001 mL/g for polyacrylamide and acrylamide according to the method described in the literature.[30,31]

Figure 1: SEC-MALS results for a typical experiment: CH run, 120°C, t = 20, 40 and 50 min (see Table 1). a) Chromatograms (top), and b) molar mass distribution (bottom). The three peaks on the left of the top figure correspond to the three peaks in the bottom figure.

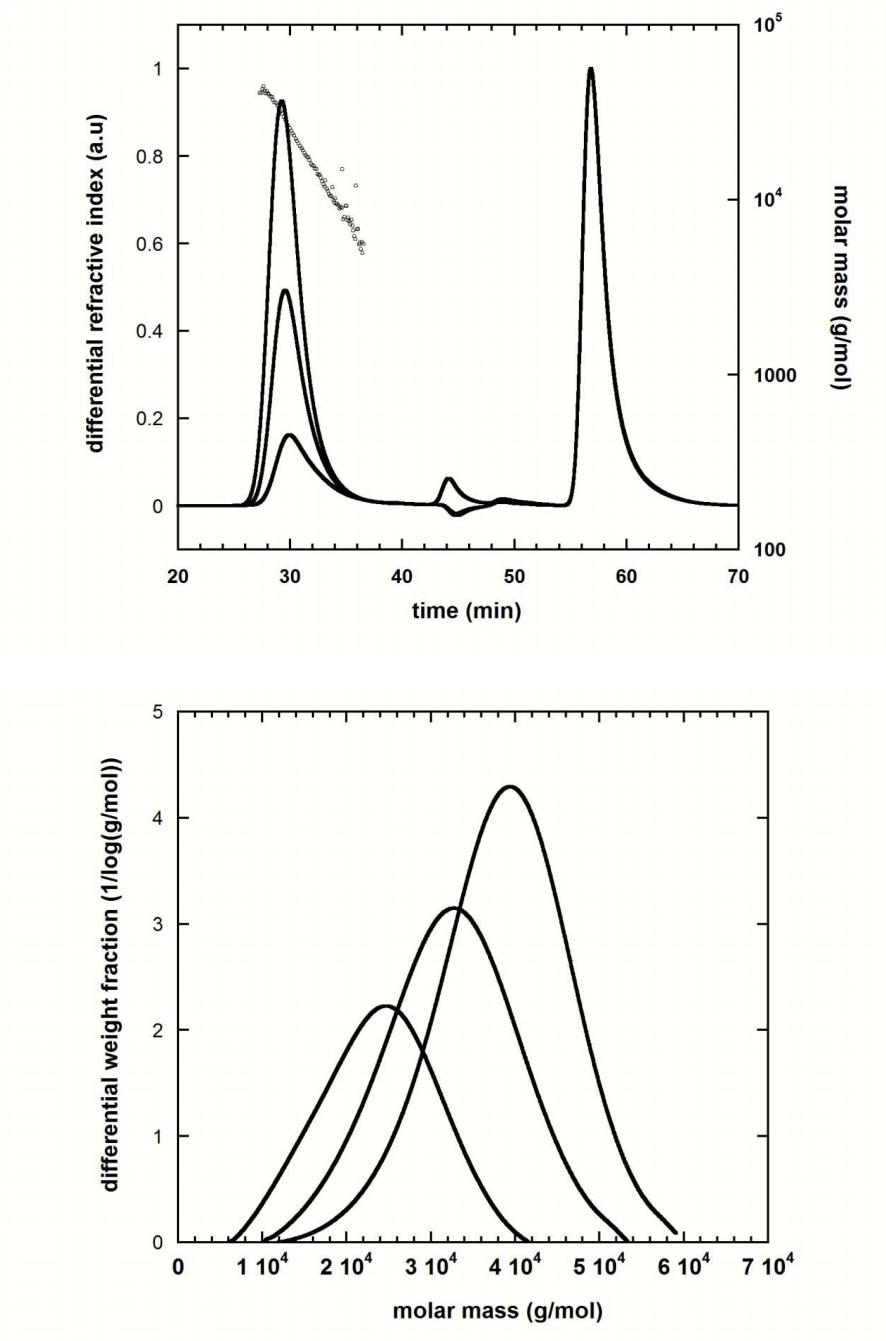


Figure 1 present a typical trace from SEC experiments on reactive media, displaying two characteristic peaks of the PAM polymer and acrylamide (AM) monomer. With knowledge of the refractive index increment of acrylamide and polyacrylamide in 0.1 mol.L^{-1} $NaNO_3$

solution, the polymer conversion, p, could be computed from the surface areas of the PAM and AM peaks, respectively:

$$p = S_{PAM}/(dn/dc)_{PAM} / (S_{PAM}/(dn/dc)_{PAM}+S_{AM}/(dn/dc)_{AM}) \quad (1)$$

Here, S_{PAM}, S_{AM} and $(dn/dc)_{PAM}$, $(dn/dc)_{AM}$ are respectively the surface area and the refractive index increment of PAM and AM.

The coupling of SEC with multi-detectors, such as a refractometer (RI) or a multi-angle light scattering detector, was performed in order to determine both the polymer conversion and the molar masses of PAM with decent accuracy. It is worth noting that systematic errors occurred due to the incorrect values of dn/dc and to the refractometer calibration factor, k. The effects of RI calibration on the polymer conversion and molar mass were found to be proportional to k^{-1}; the effects of dn/dc on p and Mw were respectively proportional to dn/dc and $(dn/dc)^{-1}$. For the p and Mw values, these systematic errors could be prevented by using the same refractometer detector for determining dn/dc and p. The error limits of 4% and 8% for p and Mw, respectively, were based on the averages and standard deviations from multiple experiments. The random errors inherent to each experiment were due to baseline fluctuations of each detector.

2.4 Viscometric measurements of polymer solutions

The steady shear rheological properties of the polymer solutions were measured with a Bohlin CVOR150 rheometer in controlled stress mode with a cone-plate geometry (radius = 20.0 mm, angle=0.096 rad, gap=0.150 mm). Stepped shear stress values were selected in order to allow shear rates ranging from 0.01 to 150 s^{-1}. The systems were allowed to reach steady state at each shear stress prior to registering the measured values. The temperature was controlled with a Peltier plate system and was set to 20.0±0.1°C.

2.5 Microwave Methods (DYN and SPS)

The NMP of acrylamide in aqueous solution was performed either in a Discover single-mode microwave synthesizer (from CEM Corp.) using the DYN and SPS modes, or in an oil bath with conventional heating, denoted CH. The DYN mode corresponds to a dynamic control of the temperature by use of a high initial microwave power, and the SPS mode is a pulsed power mode. In each case, the volume ratio between the reaction mixture and the reactor was maintained unchanged to provide a constant pressure during the polymerization process. Microwave-assisted polymerizations were carried out in standard Pyrex vessels (total capacity 10 mL) sealed with a Teflon septum cap. The temperature profiles of the polymerization

(power control) were monitored using a calibrated infrared temperature control mounted beneath the reaction vessel. The reaction parameters (temperature, power, cooling, stirring…) were set with a laptop and the SYNERGY software (version 1.35 from CEM Corp.). Each mode of irradiation corresponded to a specific set of parameters. For the pulse mode (SPS), these parameters included the power output (1W to 300W), the reaction time, the average temperature and the difference between this temperature and the lowest or highest bulk temperature (in our experiments ±2°C) and the maximum pressure allowed, i.e. the pressure at which the apparatus should stop the synthesis (17 bar in all experiments). The cooling system, based on a flow of compressed air at ambient temperature, and the stirring needed to be set at the beginning of the reaction (speed set to high). For the dynamic mode (DYN), the parameters were the bulk temperature, the maximum power output allowed (300W), the pre-reaction time of stirring (0 sec), the ramp time, i.e., the maximum time during which the apparatus was allowed to reach the desired bulk temperature (0 min), the reaction time, the stirring (speed set to high), the cooling system (Power Max off) and the maximum pressure allowed (17 bar in all experiments).

In the DYN mode, a dynamic control of the temperature was implemented by using a high initial microwave power, as shown in Figure 2a. The monitored temperature increased rapidly, i.e., in less than a few dozens of seconds, to the desired set point, T_P. However, upon reaching this temperature, the microwave power decreased or was shut off completely in order to maintain the target temperature without exceeding it. Compared to a non-polar solvent or monomer such as styrene, the T_p was reached much faster: more precisely, to reach T_p = 105°C, the required time was 35 s for acrylamide in a water solution and 350 s in styrene.

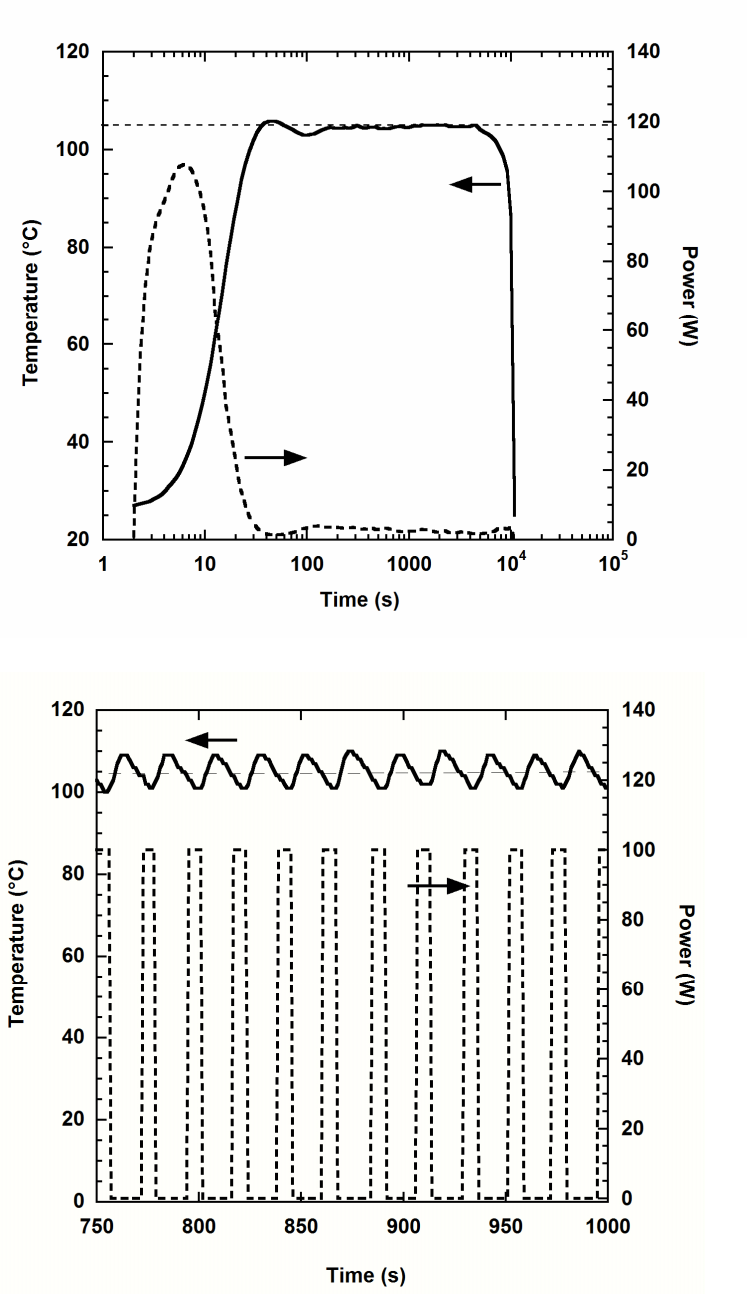
The SPS mode corresponded to a pulsed power mode in which the reaction temperature ±2°C was set, and attained by irradiation power. These experimental conditions were achieved by using a cooling feature consisting in compressed air. As shown in Figure 2b, in this mode, when the top limit of the targeted temperature was reached, the microwave power was shut off, the temperature decreased, and as soon as the lower instruction limit of the temperature was attained, the microwave power was reactivated. A pulsed MW power could thereby be obtained, providing an oscillation of the temperature around a set point. It is worth noticing that when the temperature instruction was T±2°C, the experimental conditions did not exceed T±4°C (Figure 2a), and this feature was mainly due to the inertia of the systems for one to three hours of irradiation, in the power range of 20-300W. On the other hand, the applied MW

power could be perfectly controlled. In the SPS mode, the supply of microwave energy to the reaction mixture could thus be obtained by the following equation:

$$E_{MW}=t_{MW}.\ P \quad (2)$$

where t_{MW} is the time during which the nominal MW power, P, is applied. This corresponds to the surface area under the power fit, as shown in Figure 2b (integration is used for the DYN mode).

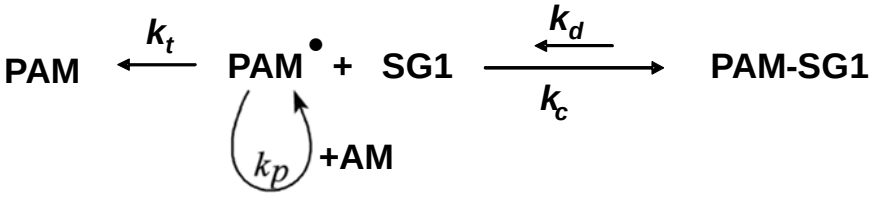
Figure 2: Profiles for temperature and power during microwave irradiation in DYN (top) and SPS (bottom) modes.



3. Results and discussions

3.1 Conventional heating (CH) versus dynamic mode (DYN)

Recently, Nicolay *et al.*[32] and Phan *et al.*[33] demonstrated that the polymerization in homogeneous aqueous solution was possible below the boiling point of water by using second-generation nitroxides, namely *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1). SG1 exhibits a higher activation/deactivation equilibrium constant than TEMPO as well as a good solubility in concentrated solutions of water-soluble monomers (> 10^{-2} mol/L in 40 wt-% of acrylamide, for example). Otherwise, very few water-soluble alkoxyamines have been described, and a majority of studies concerning NMPs in dispersed aqueous media have involved bicomponent or monocomponent initiating systems.[34-37] Recently, it was shown that reasonably controlled nitroxide-mediated polymerization of acrylamide could be achieved in a pure water solution at 120°C and high monomer concentration (40 wt%), using a bicomponent inititating system, i.e., a conventional hydrosoluble radical initiator (Vazo56) in combination with SG1.[27] The strategy adopted to prevent the loss of control of the polymerization and its lack of reproducibility involves adding an excess of scavenging nitroxide before triggering the polymerization. Usually in NMP, the amount of free nitroxide radicals present at the NMP equilibrium can be calculated from the equilibrium constant between active and dormant chains, $K=k_d/k_c$, the rate constant of self-termination, kt, and the rate constant of propagation, kp:[38]



Since these constants were unknown, the experimental conditions were determined according to previous work:[27] the molar ratio $r = [AM]_0/2[Vazo56] = 500$ for a constant acrylamide AM concentration of 40 wt% in water and a constant molar ratio $[SG1]_0/ [Vazo56]_0$ of 1.8. These conditions were far from optimized, but nevertheless, with such a system, a good compromise between kinetics and polymerization control was obtained, as can be seen from the discussion below.

Figure 3 displays the kinetic results and the living character of the polymerization for the CH and DYN modes, within a temperature range of 90 to 120°C (Table 1). The concentration of

active species remained constant regardless of the experimental conditions as evidenced from the straight semi-logarithmic plots (Figure 3a). Moreover, neither an induction period nor a steepening with the increasing conversion could be observed. Control over the growth of polymer chains was furthermore shown by the straight line of the molar mass versus polymerization yield (Figure 3b) along with unimodal aqueous SEC chromatograms. The polydispersities followed the expected trend[39] and decreased with increasing conversion, with a final Mw/Mn < 1.1 for all studied polymerizations. The downward curvature that was observed at low conversion in Figure 3b could not be attributed to the SEC separation since the MALS detector provides absolute molar masses. A lack of linearity at the early stage of the polymerization may be discussed. One possible reason could be a slow initiation resulting in the formation of fewer chains at low conversion. In the case of the azo-initiator, the production rate of primary radicals was dominated by the thermal decomposition and the initiator efficiency can be defined as the fraction of radicals produced in the homolysis reaction initiating polymer chains. The disappearance rate of the initiator can be expressed in terms of the initiator half time ($t_{1/2}$), defining the time it takes for the concentration of the initiator to reach half of its original value. The initiator half time is temperature dependant and, for VAZO-56, it was calculated to a value of 9 minutes at 90°C and 109 seconds at 105°C.[40] However, this was not obvious from the kinetic plots as no temperature effect could be observed in Figure 3b and no upward curvature indicating an increase in [PAM$^{\bullet}$] occurring in case of slow initiation is observed in Figure 3a.

Figure 3:

a) Kinetic plots of ln([AM]$_0$/[AM]) vs. reaction time for the NMP polymerization of acrylamide under conventional heating (CH) and dynamic microwave irradiation (DYN) at various temperatures: CH (full symbols), 120 °C (●), 115°C (■), 105°C (◆), 90°C (▼); DYN (open symbols), 105°C (◇), 97°C (△) and 90°C (▽).

b)The dependence of the number-average molar mass (M_n) and the polydispersity index (Ip = Mw/Mn), on the monomer conversion, p. Same symbols as in (a). The dashed lines are guides for the eyes.

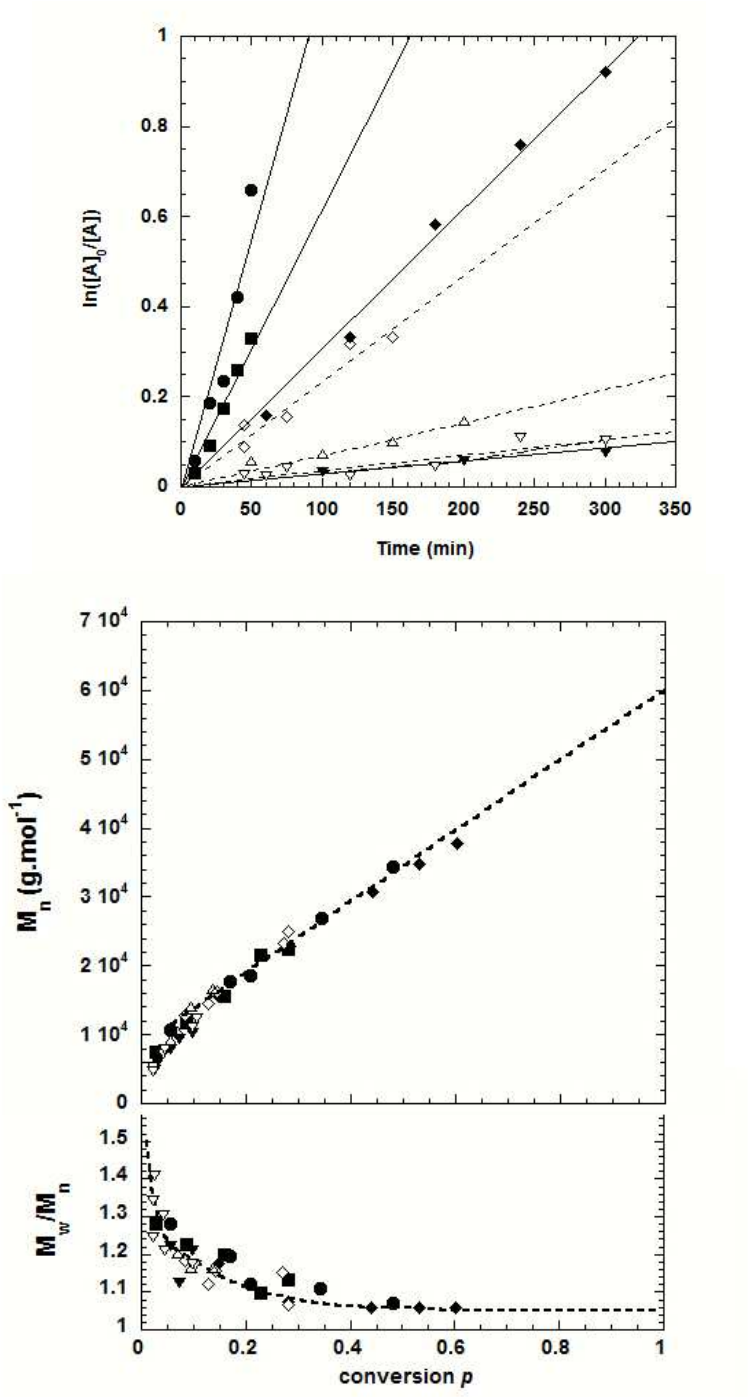


Table 1 : Temperature (T), polymer conversion (p), reaction time (t), number-average molar mass (M_n) and polydispersity index (Ip) of the NMP of acrylamide in aqueous solution using conventional heating (CH) and two microwave modes (DYN and SPS): r = [AM]/2[Vazo56] = 500 for a constant acrylamide (AM) concentration (40 wt%) and a constant molar ratio $[SG1]_0/ [Vazo56]_0 = 1.8$.

CH					DYN					SPS						
T (°C)	t (min)	p	Mn ($g.mol^{-1}$)	Ip	T (°C)	t (min)	p	Mn ($g.mol^{-1}$)	Ip	T (°C)	t (min)	P (W)	E_{MW} (kJ)	p	Mn ($g.mol^{-1}$)	Ip
120	10	0.056	10700	1.28	**105**	45	0.084	12900	1.18	**105**	60	10	35	0.16	16400	1.23
	20	0.170	17700	1.20		45	0.128	14600	1.12		60	50	89	0.90	59000	1.18
	30	0.210	18600	1.12		75	0.143	16300	1.16		60	100	116	0.97	59800	1.15
	40	0.344	27000	1.11		120	0.271	23200	1.15		60	150	133	0.99	60000	1.20
	50	0.482	34400	1.07		150	0.282	25000	1.07		60	200	142	0.99	60100	1.24
											60	250	156	0.99	61700	1.20
115	10	0.029	7450	1.28	**97**	50	0.056	9150	1.29		60	300	168	0.99	61500	1.15
	20	0.087	11800	1.23		100	0.069	10400	1.20							
	30	0.159	15600	1.20		150	0.096	14100	1.16	**90**	30	150	42	0.10	15800	1.40
	40	0.227	21600	1.10		200	0.136	16700	1.16		30	190	49	0.26	35400	1.27
	50	0.281	22500	1.13							60	50	60	0.05	8430	1.26
					90	45	0.027	5020	1.41		60	100	72	0.11	13900	1.20
105	60	0.147	15500	1.18		60	0.023	5380	1.24		60	150	81	0.18	19600	1.18
	120	0.282	22800	1.07		75	0.041	7160	1.31		60	160	84	0.33	24000	1.23
	180	0.441	30800	1.06		120	0.024	4660	1.34		60	170	86	0.34	23300	1.22
	240	0.532	34800	1.06		180	0.046	8000	1.21		60	180	87	0.23	22000	1.28
	300	0.602	37700	1.06		240	0.104	12400	1.17		60	190	118	0.94	60000	1.16
						300	0.098	11100	1.18		60	200	119	0.94	56700	1.29
90	100	0.032	5940	1.29							60	250	123	0.95	62700	1.18
	200	0.055	8000	1.22							120	150	196	0.95	59600	1.19
	300	0.098	10300	1.21							180	150	280	0.98	60600	1.19
	300	0.073	9350	1.12							240	150	377	0.99	63600	1.14
											300[a]	150	450	0.99	60400	1.15
										80	60	200	64	0.05	8330	1.34
											60	250	74	0.10	14600	1.37
											60	300	76	0.19	15500	1.37

a) used for chain extension polymerization

As expected, the kinetics depended on the temperature (Figure 3a) and the polymerization rate was significantly higher at 120 °C than at 90 °C. Indeed, the cleavage rate constant, k_d, depended on the dissociation energy of the alkoxyamine bond as well as the Arrhenius temperature, whereas the cross-combination constant, k_c, demonstrated non-Arrhenius temperature dependencies.[41] The time dependence could be approximated as first-order over a

significant range of the reaction time: $ln([AM]_0/[AM]) = k_{app}.t$. The obtained values for k_{app} (in s^{-1}) are reported in Figure 4 where they are also plotted versus 1/T according to the following Arrhenius relation,

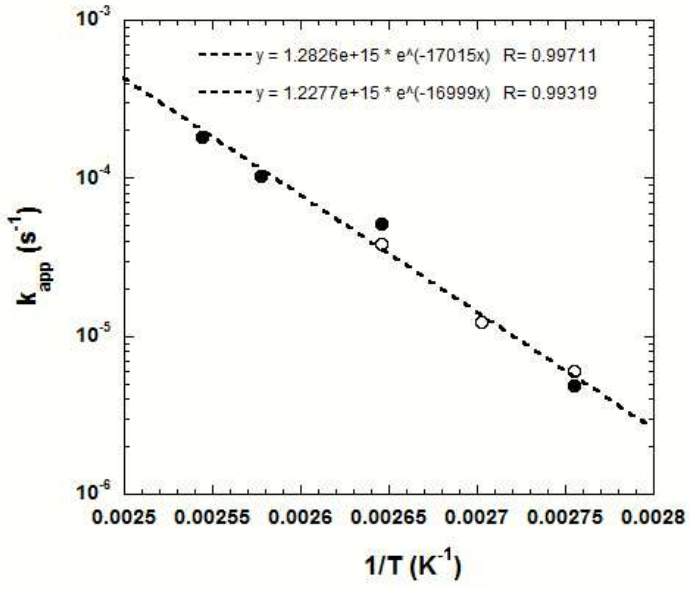
$$k_{app} = A \exp(-E_A/RT). \qquad (3)$$

Here, E_A is the apparent activation energy of the polymerization and R is the universal gas constant.

Figure 4 clearly shows that both the CH and DYN modes presented similar E_A values. Moreover, the value E_A= 140 KJ/mol, was of the same order of magnitude as that usually obtained in NMP.[38] This thus demonstrated the absence of specific MW effects in the case of the DYN mode.

While the plots at 90°C obtained by both the DYN and CH modes were in good agreement, a deviation was noticed at 105°C and was attributed to the experimental errors that were also present in Figure 3a. The absence of MW effects can be explained by the DYN parameters themselves, i.e., a high microwave power at the beginning of the polymerization increasing the bulk temperature to the set point as quickly as possible. Upon reaching the target temperature, the microwave power was decreased or completely shut off in order to maintain the desired bulk temperature, T_p, without exceeding it (Figure 2a). In the absence of microwave irradiation, classical thermal chemistry takes over, and the full advantage of microwave accelerated synthesis is lost.

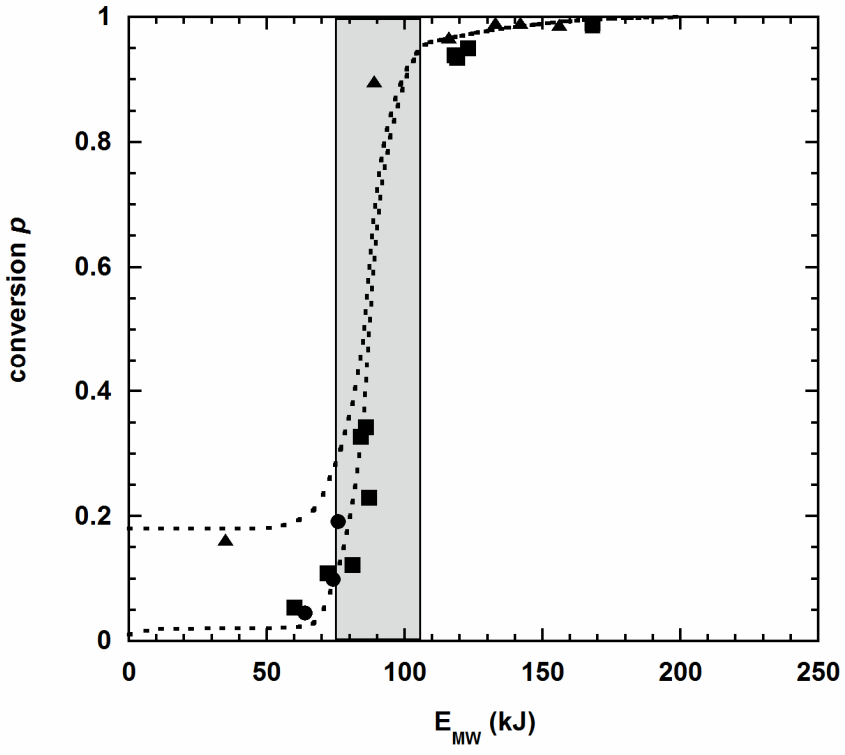
Figure 4: An Arrhenius plot of the NMP of acrylamide under conventional heating (CH, ●) and dynamic microwave irradiation (DYN, ○).



3.2 Pulsed mode (SPS)

To ensure that a high and constant level of microwave energy is applied during the polymerization, the previously described pulsed mode (SPS) was utilized. As opposed to the DYN mode, the reaction vessel is, in SPS mode, externally cooled with compressed air, while microwave irradiation is simultaneously administered. This way, more energy can be directly applied to the reaction mixture. With DYN, microwave irradiation is predominantly used to reach T_P faster. SPS mode polymerizations were performed during one hour at 80, 90 and 105 °C and the MW power ranged from 10 to 300 W (Table 1). Consequently, the MW energy varied from 10 to 170 kJ for a constant volume of reaction mixture (3 mL). Figure 5 shows the polymer conversion, p, obtained after one hour according to E_{MW}. At low E_{MW}, the conversion increased gradually up to a point of MW energy where the conversion displayed a jump. After this specific point, the conversion once again increased gradually up to complete conversion of the monomer. It seemed that this specific microwave effect was independent of the temperature and occurred at an E_{MW} of around 90 kJ.

Figure 5: The polymer conversion as a function of the microwave energy during one hour of the NMP of acrylamide under SPS microwave irradiation at various temperatures: 105°C (▲), 90°C (■) and 80°C (●).



This series of experiments (carried out at a constant reaction time) was completed by two series performed at constant power (150 and 190W) and temperature (90°C). In these cases, the reaction time was the only variable parameter, i.e., the microwave energy. At 190W and 150W, the polymer conversion increased sharply between 50 and 120 kJ (Table 1). This could correspond to a lowering of the concentration of nitroxide radicals in the medium. As shown in Figure 6, the variation of $\ln([AM]_0/[AM])$ vs time was not linear, thereby suggesting a loss of the "living character" of the polymerization. However, the control over the growth of polymer chains was evidenced by the linear evolution of molar masses with conversion as well as an acceptable polydispersitiy index below 1.3 and unimodal aqueous SEC chromatograms. Figure 7 shows this linear evolution of molar masses, and as can be evidenced, there was a perfect match to the results previously obtained in DYN and CH modes. One of the differences between the DYN and SPS modes was the use of air cooling during the latter. This is known to give rise to a significant underestimation of the temperature readout of the IR sensor since the air cools mainly the exterior of the reaction vessel. The effect that the temperature may have on the auto-acceleration polymerization is discussed in the following section.

Figure 6: Kinetic plots of $\ln([AM]_0/[AM])$ (full symbols) and polymer conversion, p (open symbols) vs. the reaction time for NMP of acrylamide under pulsed microwave irradiation (SPS) at 90°C and varying power: 150 W (ring) and 190W (square).

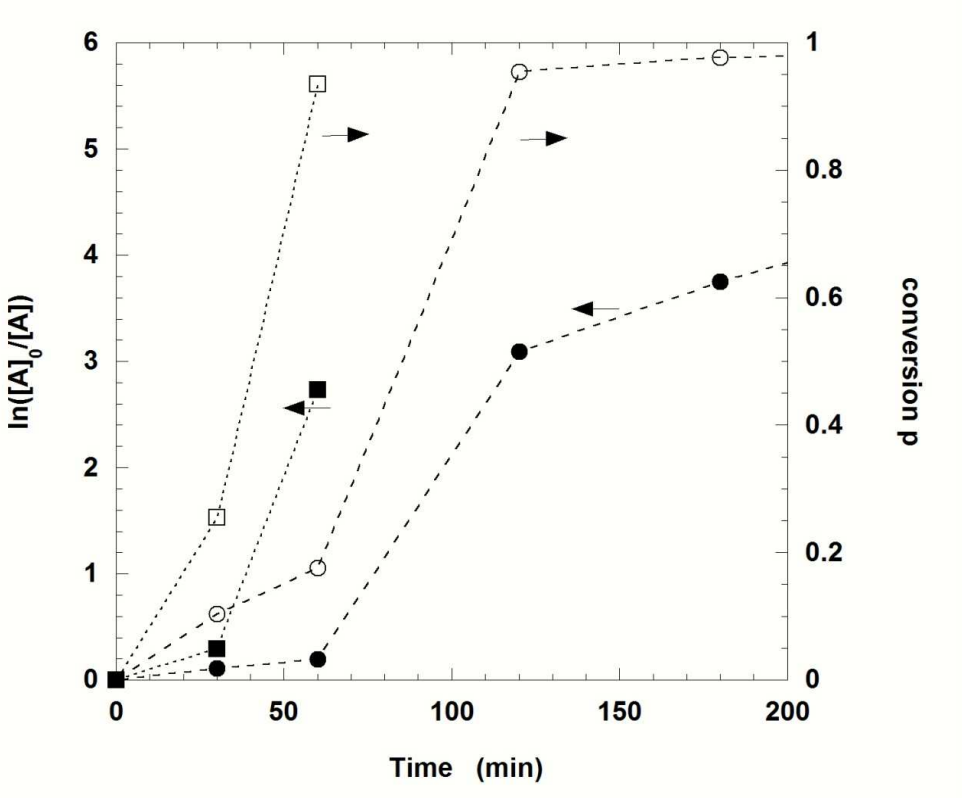
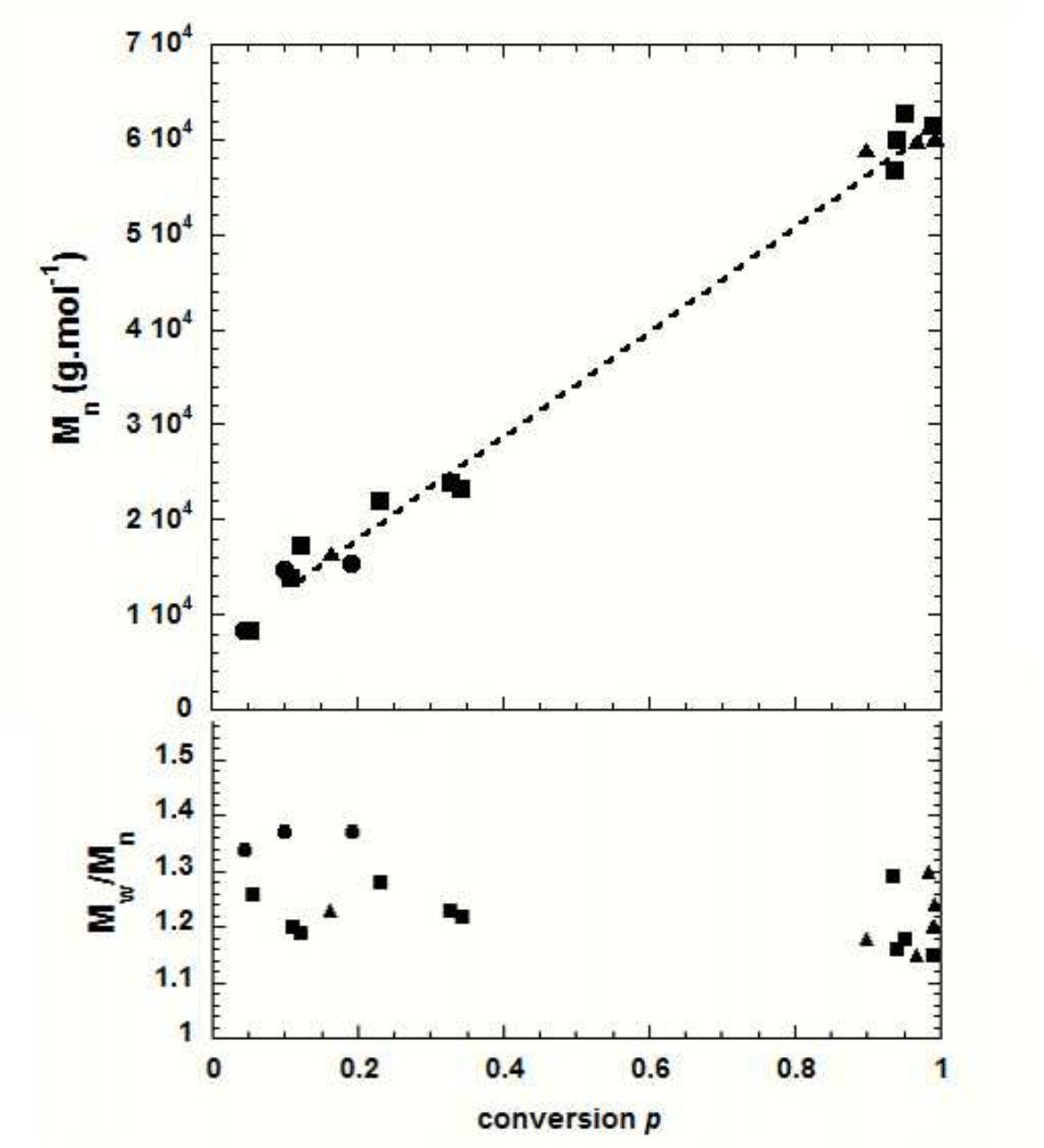


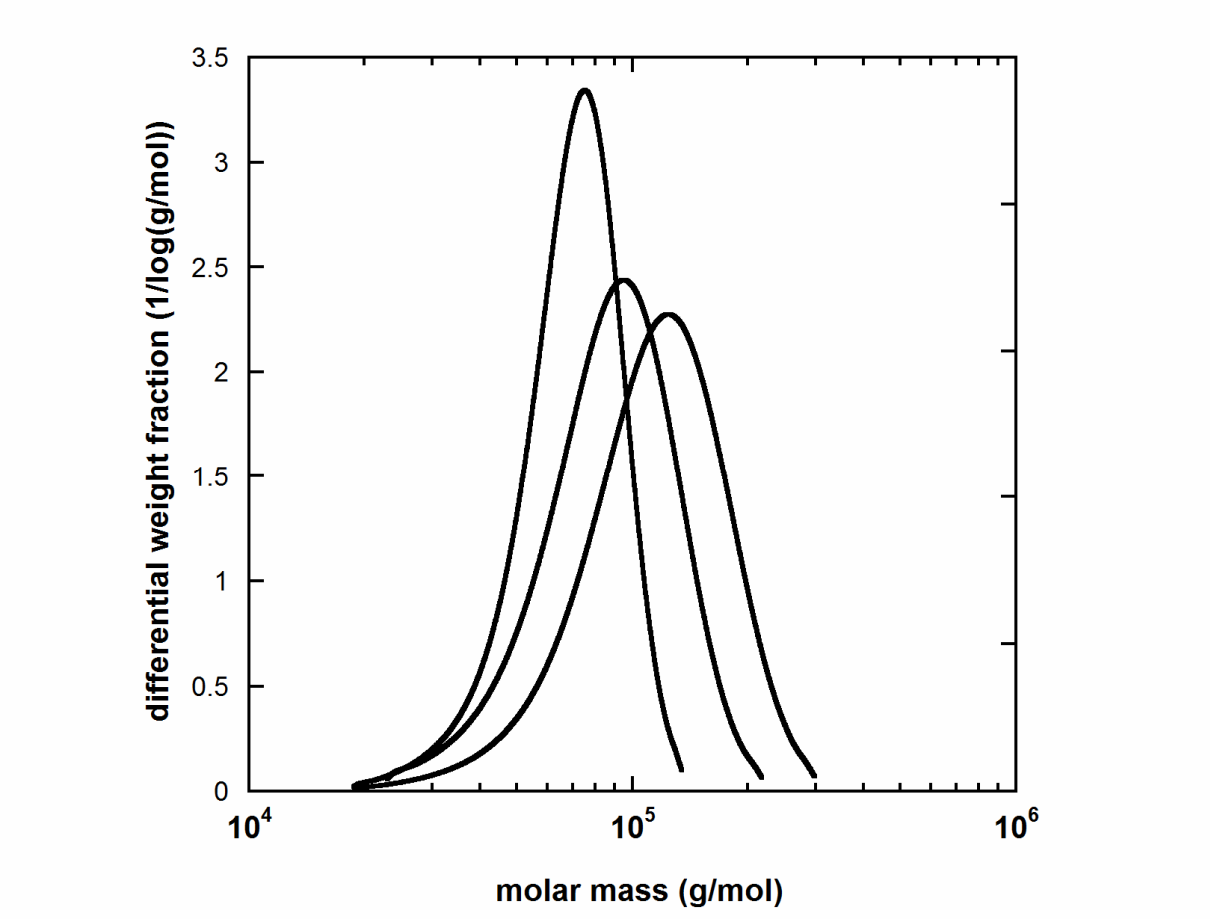
Figure 7: The number-average molar mass (M_n), and the polydispersity index (Ip=Mw/Mn), on the monomer conversion, p, for NMP of acrylamide under pulsed microwave irradiation (SPS) at 105°C (▲), 90°C (■) and 80°C (●) for the runs presented in figure 5 and 6 (the dashed lines provide the variation observed in Figure 3 for CH and DYN mode).



The living character of the PAM polymer chains produced with the vazo-SG1 system has been further confirmed by chain extension experiments with a second addition of the same AM monomer. The unpurified PAM formed at high conversion (p=99%) from aqueous NMP in SPS mode (90°C, 150W, 300 min, cf. Table 1) was used as a macroinitiator for further chain extension (Mn = 60400 g/mol and Ip=1.15). Two chain extension polymerizations, denoted E1 and E2, were carried out by a second addition of acrylamide to maintain the total

concentration of monomer plus macroinitiator at 40 wt%. For E1 and E2, respectively 0.5 g and 1.16 g of macroinitiator solution were completed up to 3g with a 40 wt% of acrylamide solution. All other parameters and procedures were the same as in the NMP procedure in SPS mode. E1 and E2 were irradiated 120 min at 90°C under 100W and 60 min at 90°C under 190W, respectively. The conversions measured by CES were found to be 6% and 42% for respectively E1 and E2, which corresponded to the targeted PAM molar masses of 77 700 and 100 400 g/mol. The M_n and Ip of the chain-extended polymer were increased up to 76 400 and 97 600 g mol^{-1}, with Ip = 1.17 and 1.25, respectively for E1 and E2. These results indicate that the PAM homopolymer, used as the macroinitiator, was effectively functionalized with nitroxide end groups. After the chain extension experiment, the molar mass distribution of the chain-extended product shifted to higher molar masses as compared to that of the initial PAM macroalkoxyamine (Figure 8). These experimental results exhibited a good control of PAM molar masses even at very high polymer conversion, *i.e.* even close to 100%, by Nitroxide Mediated polymerization under microwave irradiation in aqueous medium.

Figure 8: Molar mass distributions, differential (dashed line) and cumulative (continuous line), for chain extension polymerization: macroinitiator, E1 and E2 (from left to right).



3.3 Specific microwave effect

Despite the relatively large number of consistent publications in the area of microwave-assisted organic/polymer chemistry, the exact reasons why microwave irradiation is able to enhance chemical processes remain unknown.[2,4] Since the start of microwave synthesis, rate-accelerations and occasional variations in product distributions as compared to experiments by conventional heating have led to speculations regarding the existence of so-called "nonthermal" or "specific" microwave effects. According to investigations by Kappe,[2] Loupy[4] and coworkers, it can be understood that the differences between "nonthermal" and "specific" microwave effects depend on the scale of the observation, which is either micro- or macroscopic. The existence of so-called "specific microwave effects" is in principle undisputed since they cannot be reproduced by conventional heating. They should thus be the result of the uniqueness of the dielectric phenomenon in microwave heating, i) the superheating effect of solvents at the atmospheric pressure; ii) the selective heating such as the strong microwave absorption of the heterogeneous catalysts or reagents in a less polar medium of reaction; and iii) the elimination of the wall effects caused by the inverted temperature gradients.[2] In contrast, "nonthermal microwave effects" represent a controversial subject and have been suggested to result from a direct interaction - which is unrelated to a macroscopic temperature effect - of the electric field with specific molecules in a reaction medium [4]. In our work, the intention was not to enhance the microwave-heated reaction with a high temperature reaction that can rapidly be attained when irradiating polar materials/reaction mixtures under closed-vessel conditions in a microwave field. The microwave-assisted polymerization in an aqueous solvent was carried out at a temperature lower than 105°C and at low pressure. It is worth noticing that the experimental conditions used within this study were far from the near-critical or supercritical water condition[23] which involves T> 150°C, pressure > 4 bar; T> 374°C, p> 200 bar.

A microwave enhancement of chemical reactions takes place only during the application of microwave energy. This energy source provides a direct activation of the molecules in a chemical reaction, for which reason it would be undesirable to suppress its application as in the DYN mode. SPS ensures the application of a high and constant level of microwave energy. It was previously demonstrated that the experiments conducted with the DYN and CH modes were in good agreement and revealed no specific MW effects. The polymerization performed in SPS mode, on the other hand, exhibited a sharp increase in polymer conversion within 1 hour (Figure 5). As a comparison, the conversion, p, was lower than 0.5 for one hour

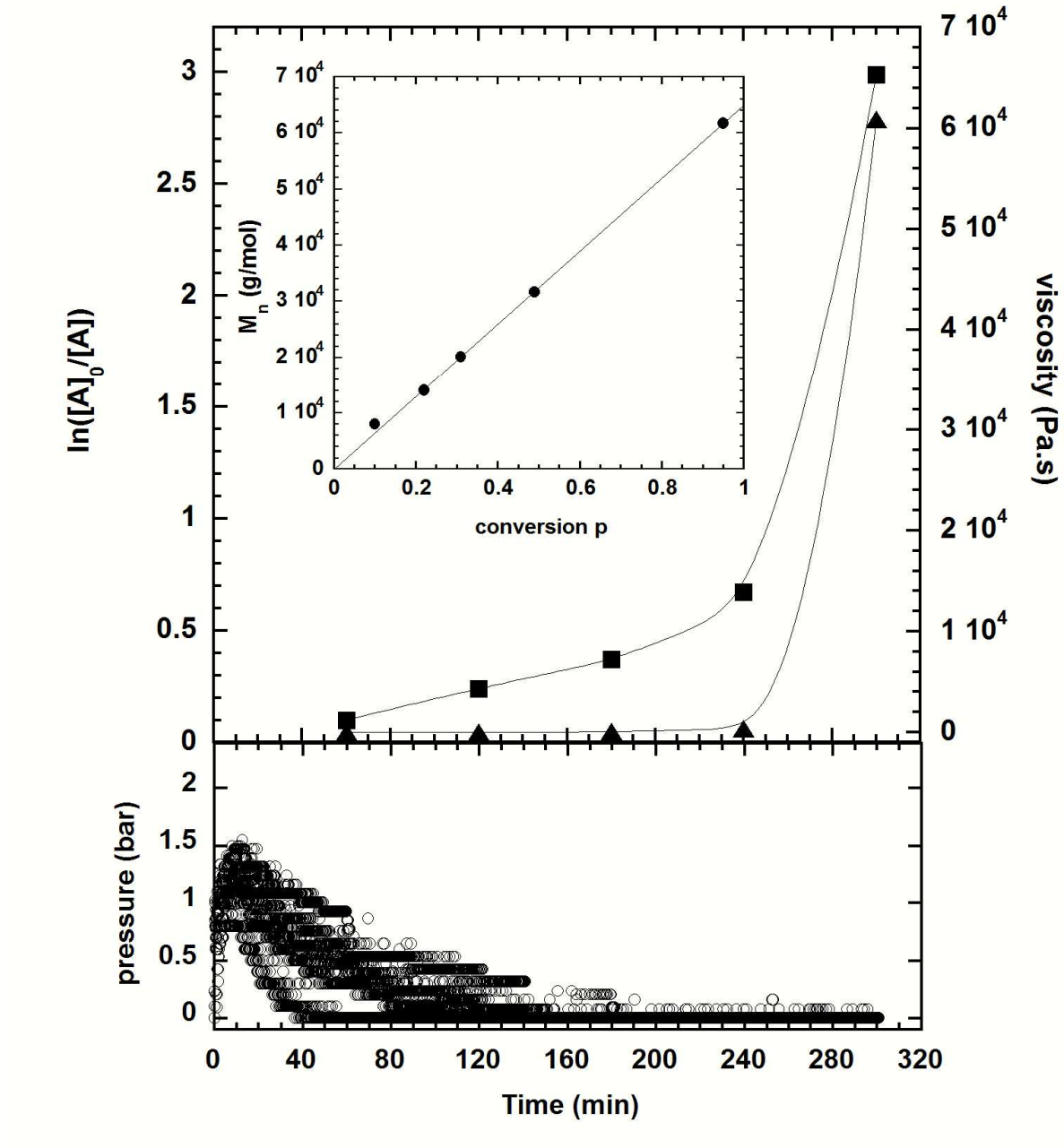
of reaction at 120°C in CH mode and below 0.3 at 105°C in the DYN and CH modes, i.e., at least 15°C above the temperature used in the SPS mode (extrapolated data of figure 3). The temperature control as measured by IR sensors (±4°C) was the same in both MW modes and could not explain the auto-acceleration polymerization. In fact, the use of IR sensors may be inappropriate for temperature measurements in microwave-heated reactions. The reason for this is that they can easily lead to a misinterpretation of results since the real reaction temperatures are unknown,[2] in particular for SPS modes where external cooling can underestimate the reaction temperature. To specify the origin of the auto-acceleration polymerization, a complementary polymerization series at 80°C was carried out only in SPS mode (P= 250W), during which the viscosity of each sample was measured and the pressure in the vessel was monitored.

In order for the results to be as reliable as possible, the same reaction vessels, reaction volumes and stirring (speed and magnets) were used in all experiments. Consequently, all parameters were identical apart from the time of irradiation, and therefore, a fair comparison based on the polymerization times and conversion could be carried out for the experiments performed solely in the SPS mode. Figure 9 presents a superposition of the kinetic plot results and the viscosity, and the inset displays the linear evolution of the molar masses according to the results previously discussed. As can be seen, the sharp rate enhancement of the acrylamide NMP appeared at 240 min ($p = 0.5$ and $E_{MW} >> 90$ kJ) and at the same time, the viscosity displayed a significant increase without raising the pressure inside the vessel. It was possible that the underestimation of the temperature reaction due to the IR sensors was even stronger after gelation of the polymerization mixture since the heat transport to the vessel wall worsened. This could explain the observation of a sudden increase in conversion. However, the auto-accelaration polymerization was not followed by a significant increase in pressure within the vessel, according to the precision of the pressure sensor as shown in Figure 9. It could thereby be assumed that the reaction temperature did not increase excessively after the gel point. As shown in Figures 6 and 9, the apparent constant rate of the auto-acceleration polymerization was estimated to be higher than 710^{-4} s^{-1}, corresponding to a theoretical temperature above 130°C according to the Arrhenius relation established previously.

An underestimation of the reaction temperature medium at the gel point could thus not be neglected. However this cannot be the sole explanation behind the auto-acceleration polymerization. Unfortunately, the CEM microwave reactor in the present study did not allow

the measurement of the real temperature inside the vessel during the SPS mode as a quantification of the reliability of the IR sensor.

Figure 9: Kinetic plots of ln([AM]$_0$/[AM]) vs. reaction time for NMP of acrylamide (■) and the corresponding viscosity of the reaction mixture (▲), under pulsed microwave irradiation at 80°C and 250W. Inset: the dependence of the number-average molar mass, Mn, on the monomer conversion, p (●). The lines are guides for the eyes. Below: superposition of measured pressures for each experiment.



It should be mentioned that a polymer solution at concentrations higher than c** enters a so-called concentrated regime in which each segment of the polymer chain lacks sufficient space [42]. The chains thus display a greatly reduced mobility as opposed to their counterparts in dilute (c < c*) or semi-dilute (c* < c <c**) solutions, and their viscosity increases very sharply with the concentration and molar mass of the polymer: $\eta \propto c^x$ with x= 15/4 in a good solvent, and $\eta \propto M^3$ (where c* is the overlap concentration). Typically, the volume fraction of the polymer at *c*** is between 0.2 and 0.3. For a polymer of a sufficiently high molar mass, there is a broad range of concentrations between *c** and *c***. In the present study, the monomer concentration was kept constant at 400 mg/mL and a polymer concentration higher than c**=200 mg/mL would correspond to a polymer conversion greater than p= 0.5. For all microwave experiments, it appeared that the auto-acceleration of the polymerization rate occurred at a conversion close to 0.5 (> 0.4 in figure 5) and with a microwave energy higher than 30 kJ per gram of reaction mixture.

Thus, for the present work, it can be suggested that the mobility of the long-chain radical species was significantly reduced as the viscosity increased, i.e., the radicals started demonstrating difficulties moving. On the other hand, under the sufficiently high energy of the electric field induced by the pulsed microwave mode, the molecules of water, monomers and counter radicals in the reaction system rotated and oscillated at a high speed before becoming polarized. At this gel point, the reactivity of the reaction system seems to be enhanced, either by increasing the propagation constant of the monomer (k_p) and/or by rate-enhancing reductions of the persistent radical concentration (e.g., hydroxylamine formation),[43] resulting in the considerable acceleration of the polymerization process without lack of living/controlled polymerization according to the prediction of the persistence radical effect theory,[44] i.e., the so called Fischer effect.[45]

The explanation that a microwave effect was induced by a mobility contrast between the polymer chain and the dipolar monomer/counter radical from a sufficient microwave energy is not obvious. Probably, the increase of the temperature and the mobility contrast arising from the gelification of the reaction media are concomitant. Future objectives include clarifying the respective parts of the rate-enhancing propagation of monomer, the rate-enhancing reductions of the persistent radical concentration and the temperature effect with the use of an internal sensor.

In addition, Kappe et *al.*[2] recently demonstrated that a multiple fiber-optic probe system was an accurate temperature measurement device in both microwave and conventionally heated reactors, and that an efficient stirring/agitation of microwave-heated reactions remains essential. In contrast to an oil bath experiment, even completely homogeneous solutions need to be stirred when single-mode microwave reactors are employed. If efficient stirring/agitation cannot be ensured, temperature gradients may develop as a consequence of inherent field inhomogeneities alongside a single-mode microwave cavity. In the case of homogeneous polymer synthesis in bulk or in solution, the medium can become extremely viscous, thus resembling a pseudo or "physical" gel. If the disruption of the stirring had given rise to inhomogeneities alongside the microwave vial with regard to the temperature, the distribution of the molar masses would have been prevented from reaching very high values. Indeed, the kinetic chain length in radical polymerization is a function of the polymerization rate, which, in turn, depends on the temperature. A too high variation in temperature alongside the microwave vial would have provided a broad distribution in molar masses[46] which was not observed. Thus, in our experimental device, the temperature along the length of the reactive medium can be supposed to be homogeneous but this feature cannot be extrapolated to bigger volumes.

4. Conclusions

The present work has demonstrated that the combined use of microwave irradiation as a heating source and water as a solvent provides a reasonable living/controlled polymerization of acrylamide by NMP. For the reaction, a combination of a conventional hydrosoluble radical initiator (Vazo56) and a β-phosphonylated nitroxide (SG1) was employed. The microwave enhancement of the polymerization depended on the mode of irradiation. The DYN mode corresponded to a dynamic control of the temperature by use of a high initial microwave power. In this case, no specific microwave effect was observed. For the SPS mode, which is a pulsed power mode, a strong acceleration of the polymerization process (> 50 times) without any loss of the living/controlled polymerization characteristics has been observed. In this case, a relevant efficiency of the re-initiation of the PAM macroinitiator has been demonstrated even after 100% of conversion of the first block. Moreover, a gelification of the reaction media has been observed with such mode.

The SPS mode seemed to represent a superior means of assuring microwave-assisted nitroxide mediated (co)-polymerization in water to achieve high conversion and low temperatures, *i.e.* below 90 °C, as measured with external IR sensors.

5. Acknowledgments

The “Conseil Géneral d’Aquitaine” is gratefully acknowledged for the PhD grant of J. Rigolini and many thanks are expressed to Arkema for providing the SG1 counter radical. We also thank Gérald Clisson for his technical assistance during the SEC experiments and CEM for the loan of the Discover unit.

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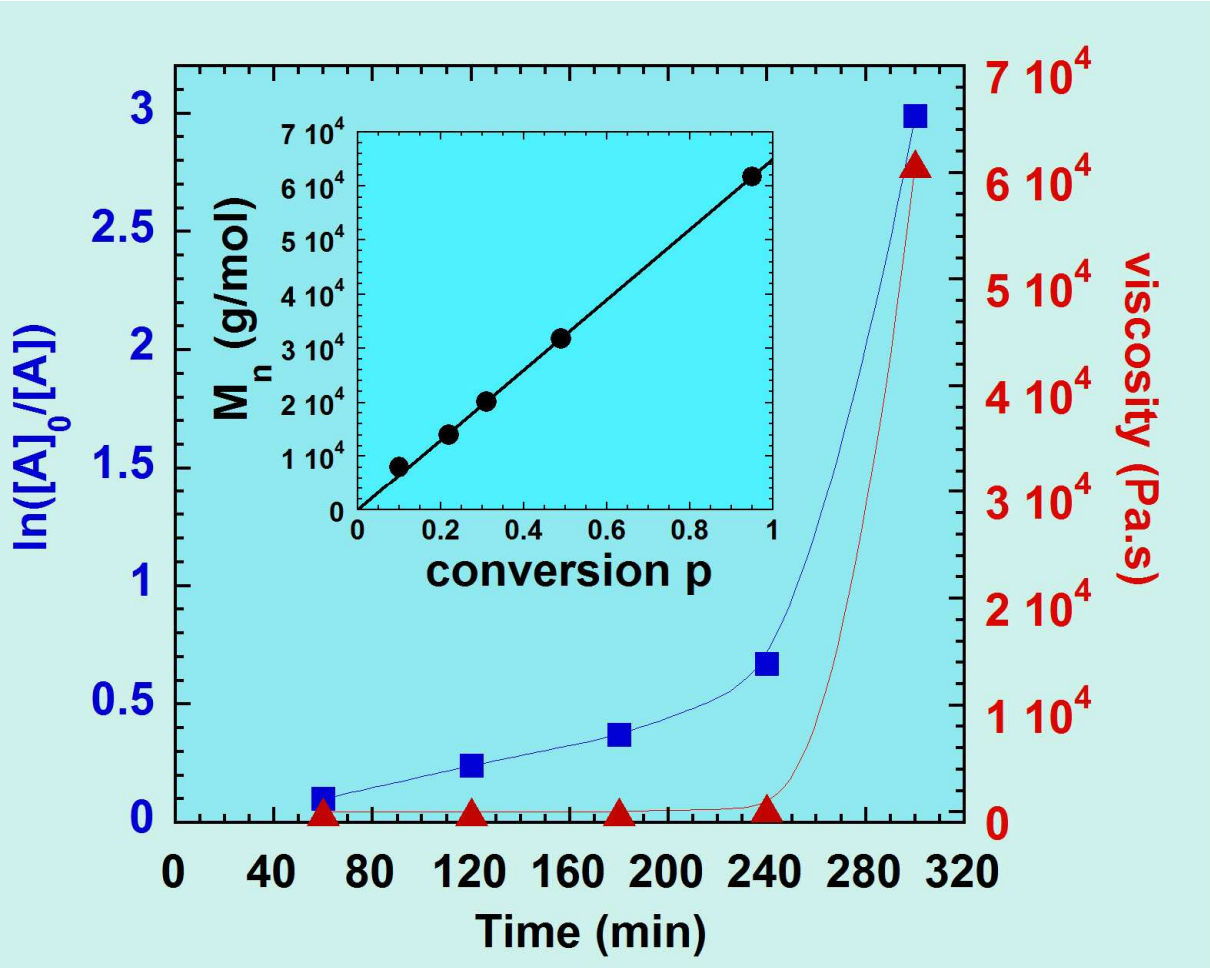
Graphical Abstract:

Microwave-Assisted Nitroxide-Mediated Radical Polymerization of Acrylamide in Aqueous Solution

Julien Rigolini, Bruno Grassl, Laurent Billon, Stephanie Reynaud and Olivier F.X. Donard



The SPS modes which is a pulsed power mode, represents a superior mean of assuring microwave-assisted nitroxide mediated (co)-polymerization in water at high conversion and low temperatures, i.e., below 90 °C, as measured with external IR sensors.

Captions to table and figures

Table 1 : Temperature (T), polymer conversion (p), reaction time (t), number-average molar mass (M_n) and polydispersity index (Ip) of the NMP of acrylamide in aqueous solution using conventional heating (CH) and two microwave modes (DYN and SPS): r = [AM]/2[Vazo56] = 500 for a constant acrylamide (AM) concentration (40 wt%) and a constant molar ratio $[SG1]_0/ [Vazo56]_0 = 1.8$.

Figure 1: SEC-MALS results for a typical experiment: CH run, 120°C, t = 20, 40 and 50 min (see Table 1). a) Chromatograms (top), and b) molar mass distribution (bottom). The three peaks on the left of the top figure correspond to the three peaks in the bottom figure.

Figure 2: Profiles for temperature and power during microwave irradiation in DYN (top) and SPS (bottom) modes.

Figure 3:

a) Kinetic plots of $\ln([AM]_0/[AM])$ vs. reaction time for the NMP polymerization of acrylamide under conventional heating (CH) and dynamic microwave irradiation (DYN) at various temperatures: CH (full symbols), 120 °C (●), 115°C (■), 105°C (◆), 90°C (▼); DYN (open symbols), 105°C (◇), 97°C (△) and 90°C (▽).

b)The dependence of the number-average molar mass (M_n) and the polydispersity index (Ip = Mw/Mn), on the monomer conversion, p. Same symbols as in (a). The dashed lines are guides for the eyes.

Figure 4: An Arrhenius plot of the NMP of acrylamide under conventional heating (CH, ●) and dynamic microwave irradiation (DYN, ○).

Figure 5: The polymer conversion as a function of the microwave energy during one hour of the NMP of acrylamide under SPS microwave irradiation at various temperatures: 105°C (▲), 90°C (■) and 80°C (●).

Figure 6: Kinetic plots of $\ln([AM]_0/[AM])$ (full symbols) and polymer conversion, p (open symbols) vs. the reaction time for NMP of acrylamide under pulsed microwave irradiation (SPS) at 90°C and varying power: 150 W (ring) and 190W (square).

Figure 7: The number-average molar mass (M_n), and the polydispersity index (Ip=Mw/Mn), on the monomer conversion, p, for NMP of acrylamide under pulsed microwave irradiation (SPS) at 105°C (▲), 90°C (■) and 80°C (●) for the runs presented in figure 5 and 6 (the dashed lines provide the variation observed in Figure 3 for CH and DYN mode).

Figure 8: Molar mass distributions, differential for chain extension polymerization: macroinitiator, E1 and E2 (from left to right).

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