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Radical Homo- and Copolymerization of Acrylamide and Ionic Monomers in Weak Magnetic Field

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Summary: The synergy between magnetic field (MF) and electrostatic interactions on the kinetics of radical homopolymerization of acrylamide (AM), acrylic acid (AA), its ionized form acrylate (A^-) and diallyldimethylammonium chloride (DADMAC), as well as AM/AA, AM/A^-, DADMAC/AA, and DADMAC/AM copolymerizations was investigated. The application of MF during the polymerizations significantly increased the monomer consumption rate (Rp) of all monomers in homo and copolymerizations and the molar masses of polyAA and polyNaA. The molar mass of polyAM and the copolymer composition of any monomer combination remained unchanged by MF. The electrostatic interactions between ionic monomers and growing radicals dominate for the monomers and conditions studied here.

Keywords: acrylamide; acrylic acid; magnetic field; radical polymerization; water-soluble polymers

Introduction

Magnetic fields (MF) are of potential technological and scientific interest because they may interact with matter in a homogeneous and instantaneous manner while exciting molecules selectively and controlling the course and the rate of radical reactions as well as the properties of the products.[1] In particular, the effects of MF on the kinetics and mechanism of the radical homo and copolymerization of water-soluble and ionic monomers could open new possibilities for synthesis and products.

MF effects have previously been observed for the radical homopolymerization of styrene,[2–9] methyl methacrylate,[10–15] and acrylamide.[16–18] In general, MF was found to increase the monomer consumption rate (Rp), and sometimes the molar masses of resulting polymers. A MF-induced increase of the efficiency of photoinitiators (Φ) and induced decrease of the rate of termination reactions have been proposed as mechanistic explanation. Such effects are, generally, treated in terms of the radical pair mechanism for intersystem crossing between spin states.[1,19] Primary radical pairs are usually created in a cage formed by solvent and monomer molecules. These radicals can be generated in singlet (S) or triplet (T_+, T_0, T_-) spin states. Radical pairs in S state have high probability to undergo recombination reactions and formation of cage products. Contrary, radical pairs in any of the T states cannot recombine and thus they have higher probability to escape from the cage and initiate polymerization. However, primary radical pairs may pass from one state to another through intersystem crossing mechanisms. The application of MF decreases substantially the probability for intersystem crossing to the S state and thus the probability of radical recombination by splitting out the Zeeman energy levels of the T states.[1,19] Then, if a significantly higher portion of primary radical pairs are generated in the T state,

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for example by the photochemical decomposition of some initiators, and quenched in the T_+ state by spin interactions with an externally applied MF, they will not recombine and they will have more probability to escape from the cage and become free radicals. As result, more radicals will be released to the polymerization medium increasing the Rp. Furthermore, under certain conditions, when two growing radicals encounter each other presenting a T state, they could not recombine, thus they would continue growing increasing the molar mass of final products.

Despite a number of publications reporting MF effects on the radical homopolymerization in organic solvents, studies in water and of copolymerizations are rare. Moreover, the influence of MF on the homo and copolymerization of ionic or ionized monomers was not subject of detailed investigations.

This contribution presents the MF effects of 0.1 Tesla on the radical homo and copolymerization of water-soluble, ionic and ionized monomers. The practically important monomers: acrylamide (AM), acrylic acid (AA), its ionized form acrylate (A^-) and diallyldimethylammonium chloride (DADMAC) were selected for case studies. The homopolymerization of AM under MF which will be used here as a reference system was subject of a detailed investigation published recently. [18] Some of the results will briefly be recalled for comparison.

Experimental Part

Materials

White crystals of ultra pure AM, four times recrystallized (Apply Chem, Switzerland), ultra pure AA (BASF, Germany), and a 65 wt% aqueous solution of DADMAC (Sigma-Aldrich, Germany) were selected as monomers. Special care was emphasized handling AM. AM is toxic in contact with skin and inhalation and it may cause genetic damage. An aqueous dispersion of phenyl-bis(2,4,6-trimethylbenzoyl)-phosphine oxide ($C_{26}H_{27}O_3P$) (Ciba Specialty Chemicals, Switzerland) served as photoinitiator. The water was of Millipore quality with 18.2 MΩ/cm of resistivity. Ethylene glycol 99% for synthesis (EG), HCl or NaOH, and HPLC grade acetonitrile and methanol (all Apply Chem, Switzerland) were used to adjust the viscosity, the pH of the polymerization medium, and for residual monomer analysis, respectively.

Polymer Synthesis

Polymerizations were performed in a 100 ml glass reactor equipped with an UV lamp, stirrer, condenser, gas inlet, and a heating/cooling jacket. The UV lamp had a primary output at 254 nm of wavelength and with an intensity $I_{UV} = 540$ erg/cm^2 at the surface of the lamp. The reactor was completely placed between the poles of an electromagnet. A thermostat adjusted the reaction temperature within ±1 K. Oxygen was removed from the initial monomer solution prior to the polymerization by purging N_2 during 30 min at room temperature (293 K) and 0 Tesla of MF intensity. After the degassing process the temperature was raised and the UV lamp was lighted to activate the photodecomposition of $C_{26}H_{27}O_3P$ and subsequently to initiate the polymerization. Simultaneously, the MF was adjusted to 0.1 Tesla. Polymerizations under the same conditions, but without MF, were performed for comparison. The polymerization procedure, conversion analysis, raw data treatment, calculation of kinetic parameters and the determination of intrinsic viscosity ($[\eta]$) of the obtained polymers have recently been described in detail.[18] The Rp was calculated as the negative derivative of the monomer concentration in time ($Rp = -d[M]/dt$). Conversion curves showed linearity ($r^2 > 0.99$) up to at least 15% conversion and 20 min of reaction time allowing a precise determination of the $-d[M]/dt$.

The AM, AA, A^- and DADMAC homopolymerizations for kinetic studies were performed with various initial monomer concentrations ranging from 0.025 to

0.15 mol/l, and using 10^{-6} mol/l of $C_{26}H_{27}O_3P$ as initiator with the exception of AM homopolymerizations which were initiated with 10^{-5} mol/l of the same initiator. Homopolymerizations for polymer characterization studies were carried out up to different conversions. A stock solution prepared with [monomer] = 0.5 mol/l and $[C_{26}H_{27}O_3P] = 10^{-6}$ mol/l was divided in several batches of 100 ml. Subsequently, they were polymerized up to different reaction times. All homopolymerizations were performed in 80 wt% aqueous solution of EG and T = 313 K and $C_{26}H_{27}O_3P$ resulted completely disolved in the reaction medium.

All copolymerizations were prepared with initial total monomer concentration of 0.4 mol/l. The molar fraction of one comonomer with respect to the other comonomer was ranged from 0.125 to 0.875. Consequently, the concentration of the comonomers varied from 0.05 to 0.35 mol/l. The initiator concentration, the polymerization temperature and the polymerization medium were 1.2 10^{-3} mol/l, 313 K and 50 wt% aqueous solution of EG, respectively. In all cases $C_{26}H_{27}O_3P$ resulted completely disolved in the reaction medium. The copolymer composition was determined analyzing the residual monomer concentrations.[20]

Homo and copolymerizations including AA or A^- were carried out at pH ≈ 2 or 12, to ensure, in the one hand, the complete neutralization of AA and, on the other hand, full ionization of A^-. Polymerizations of AA at 9 different pH from 2 to 12 were performed with and without MF using the same monomer concentration as in the other copolymerization series and $[C_{26}H_{27}O_3P] = 10^{-6}$ mol/l. The polymerization of neutralized AA at pH = 2 and fully ionized A^- at pH = 12 could be understood as homopolymerizations. Contrary, the polymerizations involving partial ionization of AA could be understood as copolymerization of AA and A^-. Thereof, the polymerization of AA at different pH will be discussed below as a copolymerization system.

Results and Discussion

Homopolymerization

Figure 1a–c presents the extent of the MF-induced increment of Rp as function of the initial monomer concentration of AM, AA, A^- and DADMAC, in homopolymerization reactions. All homopolymerizations, with and without MF, presented linear increments of Rp ($r^2 > 0.99$) with the augmentation of the corresponding initial monomer concentration. In addition, all homopolymerizations carried out under MF resulted with higher Rp than the polymerizations carried out without MF. Rp_{AM}^{MF} resulted 60% higher than Rp_{AM}

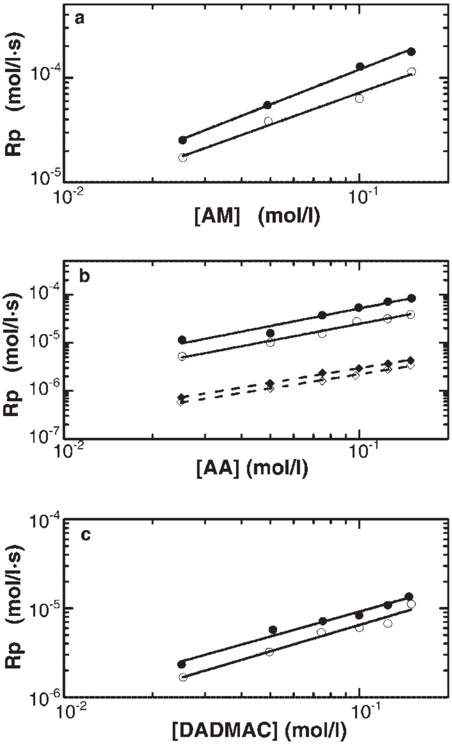

Figure 1.

Monomer consumption rate (Rp) as function of the initial monomer concentrations. a) AM (●,○). b) AA pH = 2 (●,○) and A^- pH = 12 (◆,◇). c) DADMAC (●,○). Filled symbols: MF = 0.1 Tesla, empty symbols: MF = 0 Tesla. $[C_{26}H_{27}O_3P] = 10^{-5}$ mol/l for AM polymerization and $[C_{26}H_{27}O_3P] = 10^{-6}$ mol/l for AA, A^- and DADMAC polymerizations. Common polymerization conditions: T = 313 K, solvent: 80 wt% EG in water.

(Figure 1a). The difference between both, Rp^{MF}_{AA} and Rp_{AA} as well as Rp^{MF}_{A-} and Rp_{A-} was about 33% (Figure 1b). Finally, Rp^{MF}_{DADMAC} resulted 30% higher than Rp_{DADMAC} (Figure 1c). It is important to mention that such MF-induced increments in Rp were constant over the range of initial monomer concentration for all monomers studied here.

In case of homopolymerization, $Rp = -d[M]/dt$, is the overall polymerization rate and it can be expressed in terms of the overall polymerization rate equation for photochemically initiated reactions: $Rp = k_p [M]^{\alpha} (\Phi e I_0 [I]/k_t)^{\beta}$. $[M]^{\alpha}$ and $[I]^{\beta}$ are the monomer and initiator concentrations in mol/l powered to their respective reaction order α and β. k_p and k_t are the propagation and termination rate coefficients (l/mol s), e is the molar absorptivity (l/mol cm) of the photoinitiator and I_0 is the light intensity in moles of light quanta per liter and second (mol/l s).

The slope of the linear regressions in Figures 1a–c yields directly the corresponding monomer exponent, α, of the polymerization rate equation. The α values are presented in Table 1.

The MF-induced increment of Rp is the result of a diminution of combination of T_+ spin quenched primary radical pairs and radical pairs formed during the encounter of growing polymer chains. This phenomenon may be interpreted as a MF-induced increment of Φ and a diminution of k_t.[18] The basic mechanism of propagation is suggested as not being affected by MF. MF effects associated with spin quenching in T_+ state require the interaction between two radicals, which is certainly not the case of a propagation step where only one radical at the polymer chain end participates in the reaction. However, a magnetically induced increment of k_p due to favorable molecular orientation of monomers and growing radicals, cannot be excluded a priori. Conversely, the identical polymerization paths for thermally initiated polymerizations of AM with and without 0.1 Tesla of MF proved that the MF orientation of monomers and growing radicals, and, consequently, its effects on k_p, are insignificant in the limits of the experimental conditions applied here.[18] Figure 1a–c and Table 1 confirm that the monomer exponents of AM, AA, A^- and DADMAC are not affected by MF. The slight differences between α^{MF} and α may be considered within the experimental error range. In general, α for AM was reported by other authors with values from 1.00[21,22] to 1.16[23].

Table 1.
Monomer exponents for homopolymerizations performed with and without MF.

Monomer	α^{MF}	α
AM	1.12	1.01
AA	1.20	1.17
A^-	1.01	0.98
DADMAC	0.93	0.98

Without MF, the α value for AA (1.17) resulted about 20% higher than the almost ideal value obtained for A^- (0.98). It suggests the formation of midchain radicals by intramolecular chain transfer,[24] changes in the AA concentration at the proximities of the radical center as a consequence of strong H-bonding between polymer segments, monomer and solvents[25] and dimerization of AA by H-bonding and dielectric changes in the reaction medium due to the presence of 80 wt% of EG in the polymerization medium.[26] If the monomer is fully ionized such as in case of A^- and DADMAC at low monomer concentration, these effects are prevented by electrostatic repulsion. Thus, only one monomer is added per each propagation step and α becomes ≈ 1. In conclusion, the application of weak MF can not deviate the dependency of Rp on the monomer concentration. Moreover, electrostatic interactions between monomers and growing radicals dominate over polymerization medium properties and MF determining the propagation mechanism.

The impact of MF on the final chain length becomes evident when analyzing $[\eta]$ of polymers synthesized with and without MF (Figure 2a–b). $[\eta]$ decreases with conversion in all cases. Interestingly, $[\eta]$ of polyAA and polyNaA^- synthesized

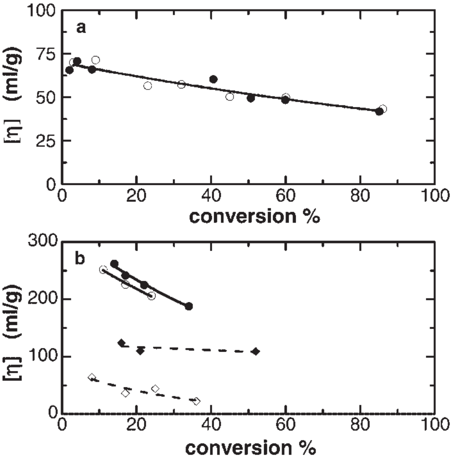

Figure 2.
Intrinsic viscosity ([η]) of homopolymers synthesized with (full symbols) and without (empty symbols) MF as function of conversion. a) polyAM (●,○). b) polyAA (●,○) pH = 2 and polyNaA (◆,◇) pH = 12. Common polymerization conditions: [M] = 0.5 mol/l, $[C_{26}H_{27}O_3P] = 10^{-6}$ mol/l, T = 313 K, MF = 0.1 Tesla, solvent: 80 wt% EG in water.

under MF resulted higher than [η] of the corresponding polymers obtained without MF. It suggests an increase of the molar mass of these polymers with MF. However, [η] of polyAM was not affected by MF. At first sight, this is somehow surprising due to the clearly proved increase of the initiator efficiency when MF was applied. Higher initiator efficiency should decrease the molar mass and thus, lower [η] could be expected for polymerizations performed under MF. However, the experimental observations reported here prove that [η] is keep constant or even increased by the influences of MF during the polymerization.

Compensation of the simultaneous increase of Φ and decrease of k_t was discussed as explanation.[18] On the one hand, situations where the MF-induced increase of Φ and decrease of k_t match and balance each other may result in invariability of the chain length with the application of MF. In this case, $[\eta]^{MF}$ will be equal to [η] as in the case of AM polymerization. On the other hand, situations where the MF-induced increase of Φ and decrease of k_t do not balance each other may result in modification of the molar mass with MF. Depending on the situation, if the increase of Φ, or the decrease of k_t, with MF dominates the kinetics, lower or higher molar masses can be expected with MF. Such an example is the polymerization of AA and A^- under MF, for which an increase of the [η] was found, in particular at high pH.

Copolymerization

The kinetic plots obtained for the AM/AA, AM/A^- copolymerizations are presented exemplary in Figure 3. The results for all copolymerizations are summarized in Table 2 and 3. In case of copolymerization, Rp is defined for each comonomer as the negative derivative of the corresponding comonomer with time. For the AM/AA copolymerization it is: $Rp_{AM} = -d[AM]/dt$ and $Rp_{AA} = -d[AA]/dt$. Note, the Rp of one of the comonomers is not the overall copolymerization rate.

In all cases, Rp significantly increased when the polymerizations were carried out in the presence of MF. The values for selected monomer concentrations are presented in Table 2.

AA polymerizes slightly faster than AM at pH = 2. For [AM] = [AA] = 0.20 mol/l it is $Rp_{AA} = 6.58\ 10^{-5}$ l/mol s, which is higher

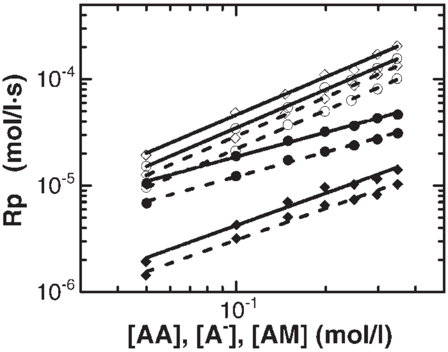

Figure 3.
Monomer consumption rate (Rp) for the individual monomers as a function of their concentrations. With MF (—), without MF (---); for pH = 2: AA (◇), AM (○); for pH = 12: A^- (◆), AM (●); $[C_{26}H_{27}O_3P] = 1.2\ 10^{-3}$ mol/L, T = 313 K, solvent: 50 wt% EG in water; MF = 0.1 Tesla.

Table 2.
Monomer consumption rates (Rp) of AM, AA, A^-, and DADMAC for their lowest, medium and highest concentrations [M] (mol/l) in the corresponding initial comonomer feeds.

	Rp 10^5 l/mol · s without MF			Rp 10^5 l/mol · s with MF		
Monomer	0.05	0.20	0.35	0.05	0.20	0.35
AM	0.97	5.01	10.13	1.52	8.35	15.73
AA	1.26	6.58	13.37	1.94	11.04	20.55
AM	0.69	2.10	3.12	1.06	3.23	4.69
A^-	0.14	0.66	1.03	0.19	0.97	1.41
AM	0.82	5.78	11.31	1.04	4.69	14.50
DADMAC	0.54	0.77	1.24	0.84	0.91	1.62
AA	1.36	7.44	9.00	1.04	6.47	11.00
DADMAC	0.46	0.93	1.00	0.56	1.44	1.62

than $Rp_{AM} = 5.01\ 10^{-5}$ l/mol s. It is also evident that, Rp_{AM} and Rp_{AA} increase with the monomer concentration in both cases, with and without MF. Though, comparing the appropriate values with and without MF, it is visible that both, Rp_{AM} and Rp_{AA} increased about 60% over all the range of monomer concentration when MF was applied. At pH = 12, AM is consumed much faster than A^-. Specifically, for $[AM] = [A^-] = 0.20$ mol/l, $Rp_{AM} = 2.10\ 10^{-5}$ l/mol s is about three times higher than $Rp_{A-} = 0.66\ 10^{-5}$ l/mol · s when the polymerizations were performed without MF. Interestingly, 0.1 Tesla of MF increased Rp to $Rp^{MF}_{AM} = 3.23\ 10^{-5}$ l/mol · s and $Rp^{MF}_{A-} = 0.97\ 10^{-5}$ l/mol · s, what is about 55% and 50%, respectively.

Rp_{AA} and Rp_{AM} are about 8 times higher than Rp_{DADMAC} when the comonomers concentration is 0.2 mol/l and the pH is 2 and 6, respectively. Therefore, the polymerization of DADMAC as copolymerization component seems neither to be affected by increasing the pH from 2 to 6, nor by exchanging AA by AM. This suggests that the copolymerization of DADMAC with neutral comonomers, such as AM and AA, is mainly governed by the electrostatic interactions between charged monomers and growing polymer chains. The contributions related to the structural differences between AM and AA remains only as secondary effect. Surprisingly, both, Rp_{AA} and Rp_{DADMAC}, presented increments between 20 and 50% when polymerized under MF. Though, the average increment of Rp resulted about 25% in both cases. Similarly, Rp_{AM} and Rp_{DADMAC} presented increments between 30 and 50% under MF, though the average increment resulted about 40% for both. Such experimental scatter is propagated to the copolymerization diagrams in Figure 4b.

The MF-induced increments of the Rp of comonomers in copolymerization systems can be explained by magnetic increase of Φ and decrease of the k_t^{i-i}, k_t^{i-j} and k_t^{j-j} termination rate coefficients. The superscripts i and j represent the components of a comonomer set. Exemplary, for the AM/AA case, the termination coefficient for reactions involving two growing radicals with AM or AA terminal units are k_t^{AM-AM} and k_t^{AA-AA}, respectively and when one radical has an AM terminal unit and the

Table 3.
Slopes of the logarithmic plots of Rp = f([M]).

Monomer	MF Tesla	AM/AA pH = 2	AA/DADMAC pH = 2	AM/DADMAC pH = 6	AM/A^- pH = 12
AM	0	1.20	–	1.38	0.77
AM	0.1	1.20	–	1.48	0.76
AA/A^-	0	1.21	1.14	–	0.98
AA/A^-	0.1	1.19	1.15	–	1.01
DADMAC	0	–	0.42	0.32	–
DADMAC	0.1	–	0.58	0.33	–

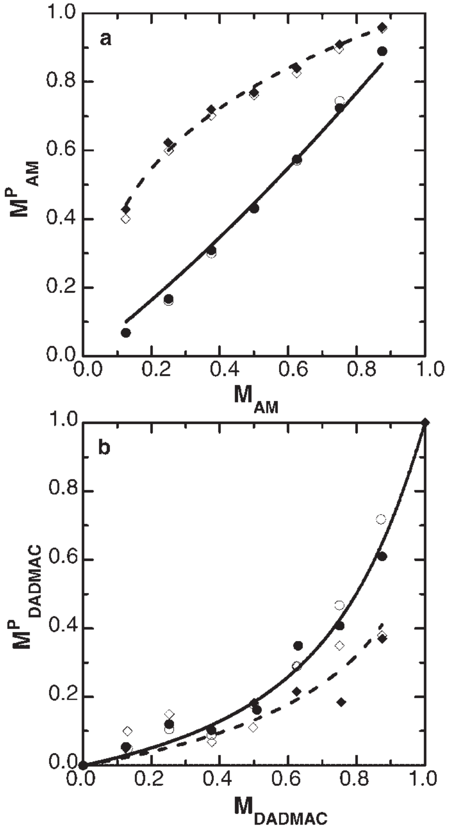

Figure 4.

Copolymerization diagrams. Copolymerizations with (filled symbols) and without MF (empty symbols). a) AM/AA at pH = 2 (●,○) and AM/A^- at pH = 12 (◆,◇). b) AM/DADMAC at pH = 6 (◆,◇) and AA/DADMAC at pH = 2 (●,○). [$C_{26}H_{27}O_3P$] = 1.2 10^{-3} mol/l; T = 313 K; solvent: 50 wt% of EG in water; MF = 0.1 Tesla.

other radical has an AA terminal unit the termination coefficient is k_t^{AA-AM}. Obviously, $k_t^{i-i} \neq k_t^{i-j} \neq k_t^{j-j}$. In addition, it is speculated that k_t^{i-i}, k_t^{i-j} and k_t^{j-j} are not affected in the same extent by an externally applied MF. The fact that the MF effect on [η] of homopolymers is different for different monomers, and these monomers were polymerized using the same photoinitiator, supports this speculation. However, the MF effect on termination reactions involving growing radicals with the same and different terminal units deserve investigation and it will be the subject of further studies.

Table 3 summarizes the concentration dependence of all monomer consumptions as slope of the appropriate curves. These slopes can be interpreted as the rate of increment of Rp of one comonomer with its concentration i.e. $dRp_i/d[M_i]$. Evidently, no influence of MF on the $dRp_i/d[M_i]$ can be concluded.

Based on these kinetics data the copolymerization diagrams were constructed, see Figure 4a–b. Briefly, the instantaneous molar fraction of monomer "i" in the copolymers (M_i^P) produced at the reaction time "t", can be expressed as a function of the actual rate of consumption of monomer "i" and monomer "j" from the solution: $M_i^P = d[M_i]/dt/(d[M_i]/dt + d[M_j]/dt)$. The residual monomer concentration in the withdrawn samples at different reaction times yields $d[M_i]/dt$ and $d[M_j]/dt$. Consequently, the actual copolymer composition can be determined at any time of the copolymerization. Full detailed deduction of the mathematical procedure is given in ref. 20.

Without MF, both comonomers in the AM/AA system present similar dRp/d[M]. However, the amount of AA units incorporated into the copolymer is higher than the amount of AA units in the comonomer feed due to Rp_{AA} is slightly higher than Rp_{AM} over the entire range of monomer concentration. When the pH vary from 2 to 12, the AM content in the resulting copolymer was significantly increased (Figure 4a). The electrostatic repulsion between the negatively ionized A^- monomer and equally charged growing radical impairs their approach and subsequent radical transfer for a propagation step. Finally, the incorporation of neutral AM monomer units into the copolymer results more favorable than the incorporation of ionized A^- units. A similar situation is found in case of AA/DADMAC and AM/DADMAC copolymerizations (Figure 4b). Here, Rp_{DADMAC} is much lower than Rp_{AA} and Rp_{AM} and the dRp_{DADMAC}/d[DADMAC] is 4.3 and 2.7 times lower than the slopes for AM and AA, respectively. In consequence, the copolymers result enriched with the neutral comonomer. However, the composition drift of AM/DADMAC copolymer is higher than for AA/DADMAC copolymer. This may be related to the differences in the ionic strength of the polymerization medium. pH = 2 in AA/DADMAC copolymerization was adjusted by addition of HCl with associated increase of the ionic strength of the polymerization medium. The excess of chloride ions may screen the positive charge of the quaternized ammonium allowing DADMAC monomers and growing radicals to approach, and to react easier than under the conditions of AM/DADMAC copolymerization at pH = 6.

Within the experimental error, no influence of the MF can be concluded. Thereof, the mechanism of addition of comonomer units to growing radicals is not affected by MF. This is confirmed after analyzing the copolymer-comonomer composition plots in Figure 4a–b. Here, the copolymers synthesized with and without MF resulted with similar, if not of identical composition. In conclusion, MF considerable increases the Rp of all comonomers. However, the electrostatic interactions between ionic monomers and growing radicals dominate the propagation and govern the copolymer composition in both polymerizations carried out with and without MF.

Figure 5 shows the plot corresponding to the polymerization of AA at different pH between 2 and 12.

This result confirms that the electrostatic effect dominates over the MF effect. Rp decreased from 280 to 24 mol/l s according to the ionization of monomers and growing radicals when the pH varied from 2 to 12. MF polymerizations were about 33% faster than those performed without MF at any pH. A competition between the long range electrostatic interaction and the short range MF interaction is proposed as explanation. Mechanistically, such competition may affect the polymerization path differently. On the one hand, the electrostatic repulsion between equally charged species affects the propagation and termination steps. On the other hand, the MF affects the initiation and termination steps. Thereof, termination steps are the only steps where both effects are present or coupled. However, it was proved that k_t can be modified differently by MF and electrostatic effects. If it is the case, the combination of MF with electrostatic effects could permit to adjust selectively every single step of polymerization.

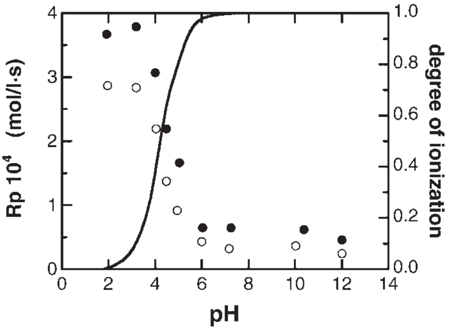

Figure 5.
AA polymerization rate (Rp) and degree of ionization of AA as monomer (—) as a function of pH and MF. [AA] = 0.4 mol/l, $[C_{26}H_{27}O_3P] = 10^{-6}$ mol/l and T = 313 K, MF = 0.1 Tesla (●), MF = 0 Tesla (○).

Conclusion

The Rp of AM, AA, A^- and DADMAC in homopolymerization and the Rp of each comonomer in AM/AA, AM/A^-, AM/DADMAC, AA/DADMAC and AA/A^- copolymerizations can be increased by the application of weak MF when photochemically initiated with $C_{26}H_{27}O_3P$ in aqueous solution. A dependency of the chain length of the obtained homo and copolymers on MF is suggested due to the invariability of the $[\eta]$ of polyAM with MF but the increment of $[\eta]$ of polyAA and polyNaA^- when synthesized under MF. The copolymer composition cannot be modified by the application of weak MF for the monomers and conditions studied here. A competition between a magnetically induced increase of the initiator efficiency and a magnetically induced decrease of the termination rate coefficient is proposed as mechanistic explanation of the modification of Rp and molar mass with MF. From the quantum physics point of view, these effects can be interpreted in terms of the radical pair mechanism for intersystem crossing between spin states. Of practical interest can be that the application of weak MF may control the Rp and the molar mass of homo and copolymers synthesized in aqueous solution without modifying recipe formulations, temperature profiles and other reaction conditions. The MF induced increment of Rp may directly be related to a reduction of residence times and productivity increase and the MF induced increment of the molar mass may be associated to the improvement of the quality of final products.

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