Magnetic field effects during styrene copolymerization with 2, 3-epoxypropyl methacrylate

L. E. NITA, A. P. CHIRIAC[*]

"Petru Poni" Institute of Macromolecular Chemistry, Grigore Ghica Voda Alley No. 41 A, RO - 700487 Iasi, Romania

Acomparative study regarding the magnetic fields effects during copolymerisation reaction of styrene with 2,3 – epoxypropyl methacrylate using a radical polymerisation in emulsion procedure is presented. The kinetic aspects are correlated with the reaction conditions: various compositions of the reaction mixtures, and the presence of the magnetic field. The obtained copolymers have been characterized by thermal (TG, DSC) methods. It has been established that the magnetic field presence increases the polymerisation rate and conversion, and the obtained copolymers have a higher molecular weight and thermal stability.

1. Introduction

Emulsions, which are opaque systems with droplet size ranging from 100 to 1000 nm, are stable systems and require mechanical work against colloidal instability. Emulsion polymerization processes offer convenient access to the synthesis of well defined micro-latex particles with easily controlled very high molecular weights, which govern the properties of the synthesized polymers. In addition the resulting polymer latexes being water based minimize environmental and safety hazards [1].

Latex particles bearing functional groups find numerous applications varying from additives for paint formulations to binding materials for biological molecules. Functional groups on the surface of latex particles commonly used are carboxyl, hydroxyl, amine, or quaternary ammonium groups [2]. The quaternary ammonium group provides the latex with a permanent cationic charge capable of binding latex particles with anionic materials like paper fillers [3] or nucleotides [4]. High surface charge densities of the latexes are required to generate a strong attractive force between two different particles. The charges on the latex particles are generally formed by using cationic surfactants or the copolymerization of hydrophilic, charged monomers with hydrophobic monomers. Several studies have appeared describing the emulsion copolymerization of hydrophobic and hydrophilic monomers [5].

Copolymerization of the monomers of different polarity in emulsions/micro-emulsions is a complex process, and the interpretation of the kinetic data is greatly affected by the partitioning of the monomers in different phases which in turn affects the actual mole ratio of the monomers in the microenvironment of the polymerization loci.

At the same time the interest for the chemical reactions investigation performed in a magnetic field has grown in recent years [6]. Some works on the magnetic field influence on the cross-linking of synthetic rubbers such as 1,4-polybutadiene, [7] poly(styrene-co- butadiene) [8], etc., has been published. The effect of a magnetic field on the emulsion polymerization of styrene initiated by dibenzyl ketone under UV irradiation was also reported by Turro et al. [9]. They showed that application of relatively weak magnetic fields (<0.05 T) substantially enhances the efficiency of the radicals escape from the micellar aggregates, so that the molecular weight of PS and the polymerization rate were increased.

In the present work we report a comparative study regarding the magnetic fields effects during the emulsion radical copolymerization of styrene with glycidyl methacrylate using a water-soluble initiator potassium persulfate in anionic o/w emulsions containing sodium lauryl sulphate as surfactant. The kinetic aspects are correlated with the reaction conditions: - various compositions of the reaction mixtures, - as well as classic and non-conventional procedure, respectively in magnetic field.

2. Experimental parts

2.1. Materials

The monomers styrene (c > 99 wt %, Fluka), 2, 3 – epoxypropyl methacrylate (c > 97 wt %, Fluka) were freshly distilled before use.

Lauryl sulfate ($C_{12}H_{25}O_4SNa$) from Sigma provenience (c > 95 wt %,)) without further purification was used as tension-active agent.

Potassium persulphate was recrystallized twice from double distilled water.

In all experiments the used water was double distilled and contained no foreign ions.

2.2. The synthesis process

The macromolecular compounds have been obtained through a continuous radical emulsion polymerization procedure according to the recipe presented in Table 1. The two variants of synthesis: classic and non-conventional in a continuous external magnetic field (of about 1500 G) lead to the obtainment of stable and uniform latexes.

Table 1. Polymeric matrices variant.

Monomer	Variant, % gravimetric			
	1	2	3	4
Styrene (S)	100	97	91	75
2,3 epoxypropyl methacrylat (GMA)	-	3	9	-
	-	-	-	-
	-	-	-	25
$K_2S_2O_8$[x)]	0.8	0.8	0.8	0.8
Surfactant agent [x)] Sodium lauryl sulphate	3	3	3	3

[x)] – relative to the monomers content

2.3. Characterization of the synthesized macromolecular compound

a) The kinetic study of the polymerization process was realized by gravimetric method with a precision electronic balance (A&D Co. Ltd. HR 200) and being compared the conversion values of the polymer samples synthesized with and without the MF presence.

b) DSC measurements were carried out by means of a Mettler 12E type differential scanning calorimeter, at a heating rate of 15°C/min under inert atmosphere of N_2, and a temperature range of about 25° - 400 °C.

c) TG and derivative thermo-gravimetry DTG curves were recorded on a MOM Budapest derivatograph under the following operational conditions: sample weight 50 mg, heating rate 12 °C /min, in air flow of 30 mL/min and with reference material α-Al_2O_3.

3. Results and discussion

The most important effects of the MF record during the initiation step, when the radical species emerged from specific processes, manifest there state as singlet or triplet state. The potassium persulfate, the used initiator, presents a first order decomposition reaction by breaking of the peroxidic bond which leads to radical pairs in the singlet state. The radicals' shifting from the singlet to the triplet state as a result of the MF presence, reduces the recombination efficiency of the radical pairs diminishing the "cage effect with the increase of the radicals lifetime as well of the initiation efficiency [10,11].

The kinetic study illustrated in Fig. 1, evidences the changes brought by the functional co-monomer upon the

reactions. Thus, owing to the GMA presence the copolymerization processes present an increased conversion for both synthesis variants: with or without the MF presence. At the same time, it can be observed the influence of the MF upon conversion, which is considerable: it increases especially in the first 15 minutes from the beginning of the reaction.
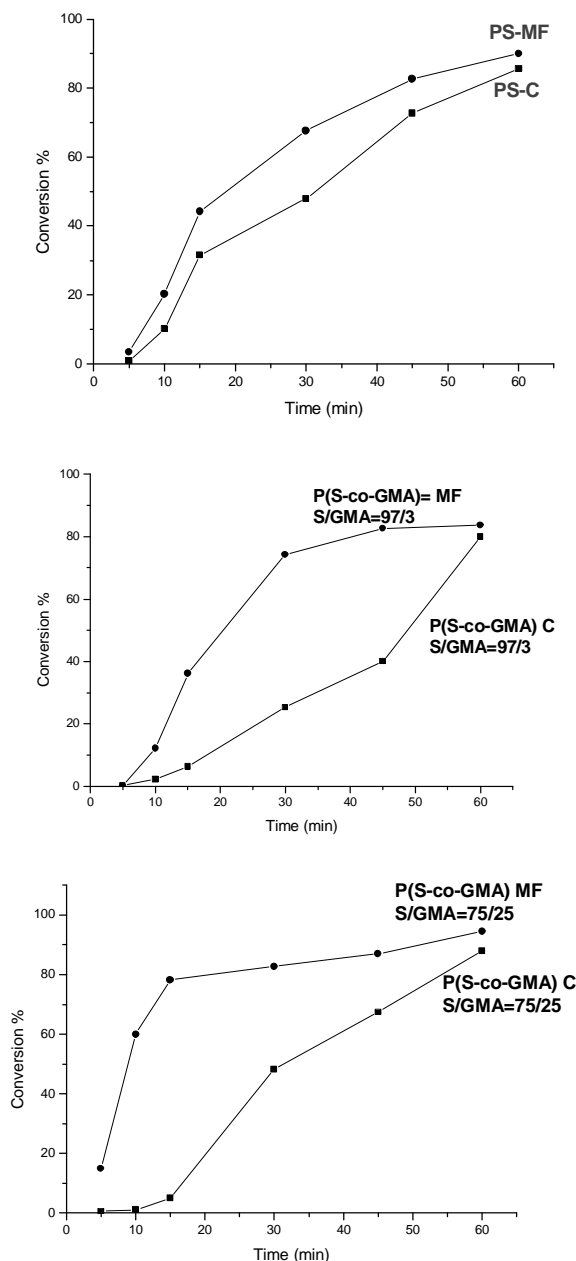

Fig. 1. Conversion curves corresponding to the polystyrene synthesis, respectively styrene Co-polymers with different ratio of GMA: classic (C) synthesis and in MF presence.

The MF presence determinates also considerable increases of the polymerization rate (Fig. 2).
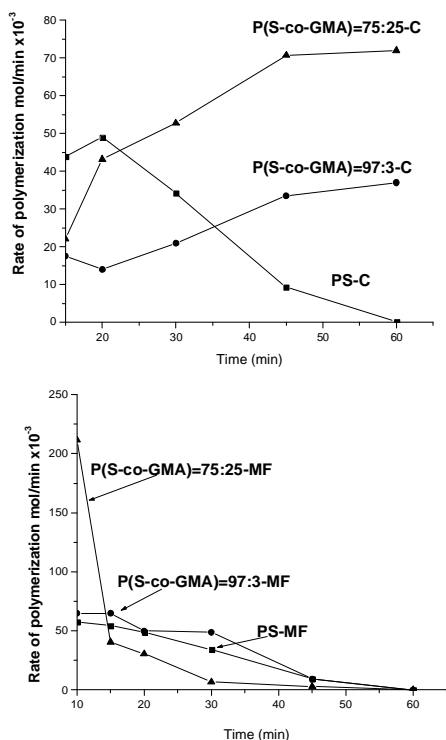
Fig. 2. The momentary polymerization rate correspondingly to the homo – polymer production and for the synthesized copolymers C and in MF.

The reduced induction period as well as the increase of conversion and polymerization rate is the consequence of transitions from the *singlet* to the *triplet* state through a Δg mechanism in the state of the obtained radical pairs [10-11].

The increase of the polymerization rate is attributed to the dual character of the magnetic field influence exerted on the one hand on the dynamic of molecular movement and on the other hand on the dynamic of radical spins [10-11].

The relationship between the polymerization rate and conversion value of the obtained homo- and respectively copolymers, prepared by classic C and in MF manner, (for the interval of time when the polymerization rate is linear) it is given in Fig. 3.

Table 2 presents the kinetic constants, respectively the reaction order value "n" and the constant "k" of the polymerization rate, of the radical processes of polymerization performed classic and in MF presence.

Table 2. The kinetic parameters.

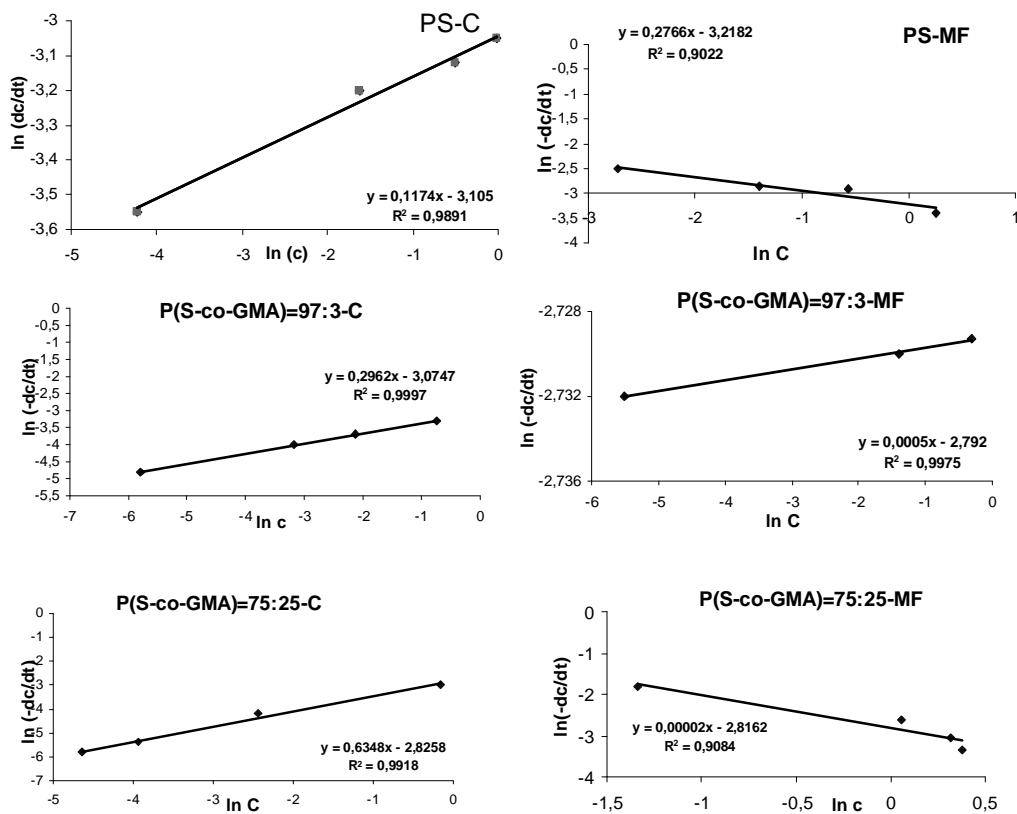| Samples	n		k	
	C	MF	C	MF
PS	0.1174	0.2766	3.105	3.2182
P(S-coGMA)=97:3	0.2962	0.0005	3.0747	2.792
P(S-co-GMA)=75:25	0.6348	0.0002	2.8258	2.8162

Fig. 3. The relationship between polymerization rate [ln (-dc/dt)] and logarithm of concentration ln c of the homopolymer, and the copolymers during the classic synthesis (C) and in MF presence.

These data underline again the MF influence: the MF presence attenuated - in the copolymers case- the difference is induced by the increase of amount of GMA both for n and k. Also, the reaction order *n* for the processes performed in the MF presence decreases with the increase of the GMA percent. This behaviour is in opposition to the case of the samples synthesised in a classical way. The polymerization rate constant, *k*, decrease in both cases (C and in MF) but the reduction is more evident for the process evolution in MF.

The obtained copolymers have been characterized by thermal (TG, DSC) methods. The MF presence during the polymerization reaction determines the ordering of the macromolecular chains, which generates an efficient disposing of the functional group to the polymeric particle surface.

The increasing of the GMA percent (3%, 9%) determines the increase of the thermal stability, especially for the polymers synthesised in the MF presence (Table 3). This fact can be explained by the possible cross-linking bridges, as well by a potential ordered structure of the polymers induced by the MF presence during the polymerization process.

The samples with the high amount of GMA (25%) present a lower thermal stability.

Table 3. The thermal characteristics for the synthesised samples.

Samples	T_g °C		T_i °C		T_{max} °C		T_f °C		T_{50} °C		ΔW%	
	C	CM	C	CM	C	CM	C	CM	C	CM	C	CM
PS	102	104	290	290	400	402	447	465	388	380	83	81
P(S-co-GMA)= 97:3	95	102	270	295	383	400	442	485	384	390	89.5	86.7
P(S-co-GMA)= 91:9	93	102	264	270	393	394	448	480	380	385	88	85.5
P(S-co-GMA)= 75:25	105	108	250	285	380	390	438	450	368	378	84	70

Δw - weight loss

[a] T_{10}, T_{50}- temperature corresponding to 10 % and 50 wt% weight loss

[b] T_m- temperature of the maximum rate of weight loss

[c] T_i – temperature corresponding to the beginning of the decomposition

4. Conclusions

It has been established that the presence of the magnetic field during the emulsion polymerization of styrene as well as the copolymerization of styrene with 2,3 epoxypropyl methacrylate increases the polymerisation rate and conversion, and the obtained copolymers are more stable from thermal viewpoint.

Reference

[1] N. K. Pokhriyal, P. G. Sanghvi, D. O. Shah, Langmuir **16**, 5864 (2000).
[2] D. J. Voom, W. Ming, A. M. Herk, Macromolecules **38**, 3653 (2005).
[3] J. E.Puig, S Corona, A.Maldanado, P. C Schulz, B. E. Rodríguez, E. W. Kaler, J. Colloid Interface Sci. **137,** 308 (1996).
[4] I. Capek, V. Juranicova, J. Polym. Sci., Part A: Polym. Chem. **34,** 575 (1996).
[5] Z. Zhang, Z. Zeng, Y. Chen, C. Wu, J. Gao, J. Appl. Polym. Sci. **66,** 2543 (1997).
[6] J. Huang, Q. Song, Macromolecules **26,** 1359 (1993).
[7] M. G. Martl, T. Pongratz, K. Hummel, Makromol. Chem., Rapid Commun. **4**, 649 (1983).
[8] M. G. Martl, R. Schaller, K. Hummel, Macromolecules **22**, 1753 (1989).
[9] N. J. Turro, M. F. Chow, C. J. Chung, C. T. Tung, J. Am. Chem. SOC. **105**, 1572 (1983).
[10] A. P. Chiriac, J of Applied Pol. Sci. **92**(2), 1031 (2004).
[11] A P. Chiriac, Journal of Polymer Science Part A: Polymer Chemistry **42**, 5678 (2004).

_____
* Corresponding author: achiriac@icmpp.ro