

Polymerization in a Magnetic Field, Part 17: Styrene Copolymerization with 2,3-Epoxypropyl Methacrylate

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ABSTRACT: The article presents a comparative study regarding the magnetic field influence intervened during styrene copolymerization with 2,3-epoxypropyl methacrylate using a radical emulsion polymerization procedure. The registered magnetokinetic effects were evidenced for different reaction compositions and temperatures. The field effect influenced the conversion, the polymerization rate,

and activation energy of polymerization process. An efficiency of magnetic field from the kinetic parameters has been established. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3029–3035, 2007

Key words: radical polymerization; magnetic field; magnetokinetic; vinyl monomers

INTRODUCTION

The interest in and availability for using a magnetic field (MF) to improve the kinetics and conversion of radical emulsion polymerization is known and constitutes already a tradition. The major theories of magnetic effects exploit the concept of singlet–triplet transitions in geminate and random radical pairs. They also reveal how internal and external magnetic forces that operate on the pairs can be employed to design or interpret magnetic field effects (MFEs) on chemical reactions. Thus, the modification of the electronic spin alignment to the triplet state as a result of the MF presence determines the decrease in the radicals recombination processes.^{1–3} In this way both the rate of polymerization as well as the molecular weight of the polymer can be controlled.^{4–9} Micellar aggregates ideally fulfill the basic requirement of the radical pair mechanism, namely, easy separability of the geminate radical pairs, followed by an extended period of diffusive reencounter. The phenomenon of “micellar supercage effect” was mentioned first by Turro and Chow.¹⁰

Emulsion polymerization is commonly employed to produce high molecular weight polymers at relatively rapid rates. Four fundamental ingredients are involved in this process: the dispersed droplets of monomer; an emulsifier such as a micelle-generating detergent; an initiator, and an aqueous dispersion medium. During synthesis, each component can be affected by the presence of a MF. However, for a polymerization process, the MFEs are mainly observed

during the radical initiation step owing to the radicals as intermediates with one unpaired electron spin which is not conserved. Thus, the MF influence becomes obvious when, in radical pairs from the system, the field will induce or prevent transitions between near fundamental electronic states. The changes in spin multiplicity of the radical pairs under the influence of the field determine the subsequent magnetokinetic effects.^{11,12}

MFEs were mentioned for the emulsion polymerization of styrene photoinitiated by dibenzyl ketone. Application of a moderate MF of 50–1000 G significantly accelerated the polymerization and resulted in an increase in the molecular weight of polystyrene formed in the emulsion polymerization, and explained through the hyperfine coupling mechanism of the radical pairs mechanism.^{4,6,7}

In our previous papers was investigated the kinetics of styrene polymerization in a MF of 0.25 T using different concentrations of initiator and various anionic surfactants.^{13–15}

The present article studies the possibilities to improve the reaction rate as well as the conversion of styrene polymerization and styrene copolymerization with 2,3-epoxypropyl methacrylate (GMA) by performing the reaction in the presence of a MF. Magnetic effects are of technological interest, as they offer a new way to perform radical processes. This is because through very weak perturbations of the MF, one can control chemical kinetics and thus the course and the rate of reactions that normally require much higher chemical energies.

In this context the emulsion radical copolymerization of styrene with GMA using a water-soluble initiator—potassium persulfate—and an anionic product—sodium lauryl sulfate—as surfactant, and in the

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presence of a MF of 0.15 T, is studied. The registered magnetokinetic effects are comparatively evaluated with the kinetic parameters achieved during polymerization without the field presence and they are also correlated with the reaction conditions: various reaction temperatures and, respectively, different ratios between the two monomers.

EXPERIMENTAL

Materials

The monomers styrene ($c > 99$ wt %, Fluka) and GMA ($c > 97$ 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 tensioactive agent. Dipotassium peroxydisulfate was recrystallized twice from twice distilled water. In all experiments, the used water was twice distilled and contained no foreign ions.

Polymerization process

The synthesis process was performed through emulsion polymerization procedure and was carried with and without the magnetic field (MF) presence, which

was described in detail before.^{13–15} The intensity of the used electromagnet was 1500 G. The reaction was carried out under the same conditions for both synthesis variants with and without the field, respectively: similar shape and geometry of vessel, and also the same reaction content and parameters as well as stirring. The intervened magnetokinetic effects during polystyrene synthesis and the obtainment of styrene copolymers with different ratios of GMA: 3% and 25%, respectively, were registered. The temperature influence on the polymerization process was also studied. In this context the syntheses were performed at four different temperatures: 60, 65, 70, and 80°C.

The conversion during the polymerization process was gravimetrically determined for both polymers variants synthesized with and without the MF presence. The determinations were made with a precision electronic balance (A and D Co. HR 200).

The polymeric matrices structure was evidenced by FTIR spectra (on a spectrophotometer, DIGILAB, Scimitar Series, USA; the resolution recording was 4 cm^{-1} ; 3 mg sample in 500 mg KCl tablet) and NMR spectra (in $CDCl_3$ recorded on a Bruker AMX 500 instrument) as can be observed from Table I.

TABLE I
Spectral Data of the PS and S-GMA Copolymers Synthesized Without and in MF Presence

Sample	FTIR (cm^{-1}) band assignment	Differences observed in MF presence	H-NMR chemical shift, δ (ppm)	GMA in copolymer % determined from NMR spectra		GMA in monomer wt % feed
				Classic	In MF	
PS	<ul style="list-style-type: none"> • CH_2 group (at 1450 cm^{-1} and 1460 cm^{-1}) • Benzene ring (700 cm^{-1}, 750 cm^{-1}) 	<ul style="list-style-type: none"> • Increased intensity in the MF presence • Higher intensity of the band in the MF presence comparatively with CW 	6.9, 7.4 (m-aromatic)	0	0	0
P(S-co-GMA) = 97:3	<ul style="list-style-type: none"> • CH_2 group (at 1450 cm^{-1} and 1460 cm^{-1}) • Benzene ring (700 cm^{-1}, 750 cm^{-1}) • 1720 cm^{-1} (C=O) str • $2800\text{--}3100$ (–CH str) 	<ul style="list-style-type: none"> • Increase in the MF presence • Higher intensity of the band in the MF presence comparatively with CW • Similar • Similar 	1.6 (CH_3), 3.6 (OCH_3) 3.6–3.7 {m overlapped, 2 CH_2 (epoxide)}, 6.9, 7.3 (m aromatic)	2.8	2.35	3
P(S-co-GMA) = 75:25	<ul style="list-style-type: none"> • CH_2 group (at 1450 cm^{-1} and 1460 cm^{-1}) • Benzene ring (700 cm^{-1}, 750 cm^{-1}) • 1720 cm^{-1} (C=O) stretching • $2800\text{--}3100$ (–CH stretching) 	<ul style="list-style-type: none"> • Increased intensity of the band in the MF presence • Higher intensity of the band in the MF presence comparatively with CW • Higher intensity of the band in the MF presence comparatively with CW • Higher intensity of the band in the MF presence comparatively with CW 	2.0 (CH_3), 3.6 (OCH_3), 3.6–3.7 {m overlapped, 2 CH_2 (epoxide)}	26.051	26.22	25

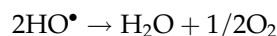
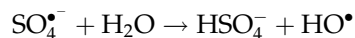
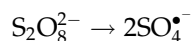
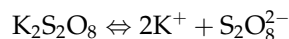
TABLE II
Polymers' Molecular Weights in Direct Dependence with the Reaction Conditions

Polymer composition	Syntheses performed	Polymers' molecular weight (E -04)		
		\overline{M}_n	\overline{M}_w	D
PSt	Classic	2.54	4.50	1.77
	In MF	3.70	5.70	1.54
P(S-co-GMA) = 97 : 3	Classic	3.80	6.40	1.68
	In MF	5.80	9.40	1.62

GPC measurements (THF, calibration versus polystyrene standard) are presented in Table II. They evidence the molecular weight of the polymers synthesized classically and in MF and also underline the MF influence.

RESULTS AND DISCUSSION

The capacities of dipotassium peroxydisulfate as initiator for performing radical processes of polymerization are well known. Its mechanism of thermal decomposition includes the following reactions:



Dipotassium peroxydisulfate has a first-order decomposition reaction with breaking of the peroxidic bond which leads to radical pairs in the singlet state.¹⁶⁻²⁰ At pH > 3 (pH of the polymerization reaction) the decomposition reaction of the persulphate anion leads at two active centers: $\text{SO}_4^{\bullet-}$ and HO^{\bullet} . The hydroxyls constitute the geminate radical (RP) pairs of the system.

Figures 1 and 2 illustrate the evolution of the conversion during polymerization reactions of styrene and styrene copolymerization with GMA with and without the MF presence and the reaction rates of these processes respectively.

As can be observed from the figures, growths of the reaction rate as well as for the conversion correspond to syntheses performed in MF, especially in the first 15 min from the beginning of the reaction. The registered magnetokinetic effects in syntheses initiated with dipotassium peroxydisulfate are explained according to the radical pairs mechanism and based on the singlet-triplet transitions in the GR pairs owing to the field presence. The resulted radical pairs have spin correlation according to the multiplicity of their direct precursors. The spin conservation rule in chemical reactions is followed, for energetic reasons, in subsequent processes of the radical pairs. Thus, singlet radical pairs will recombine only with singlet products, whereas triplet radicals will merely react with triplets, if enough energy is available. The changes in the radical pairs' multiplicity as a result of

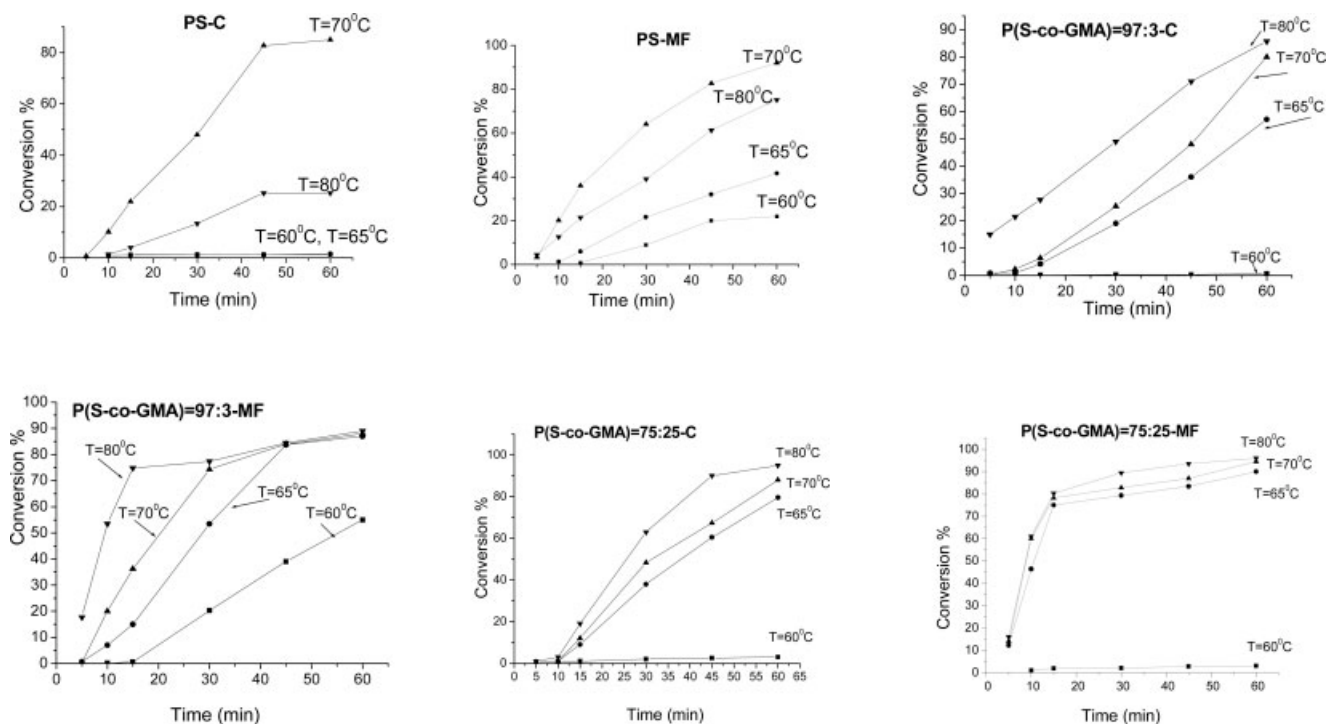


Figure 1 The temperature influence upon the polymerization processes performed with or without MF presence.

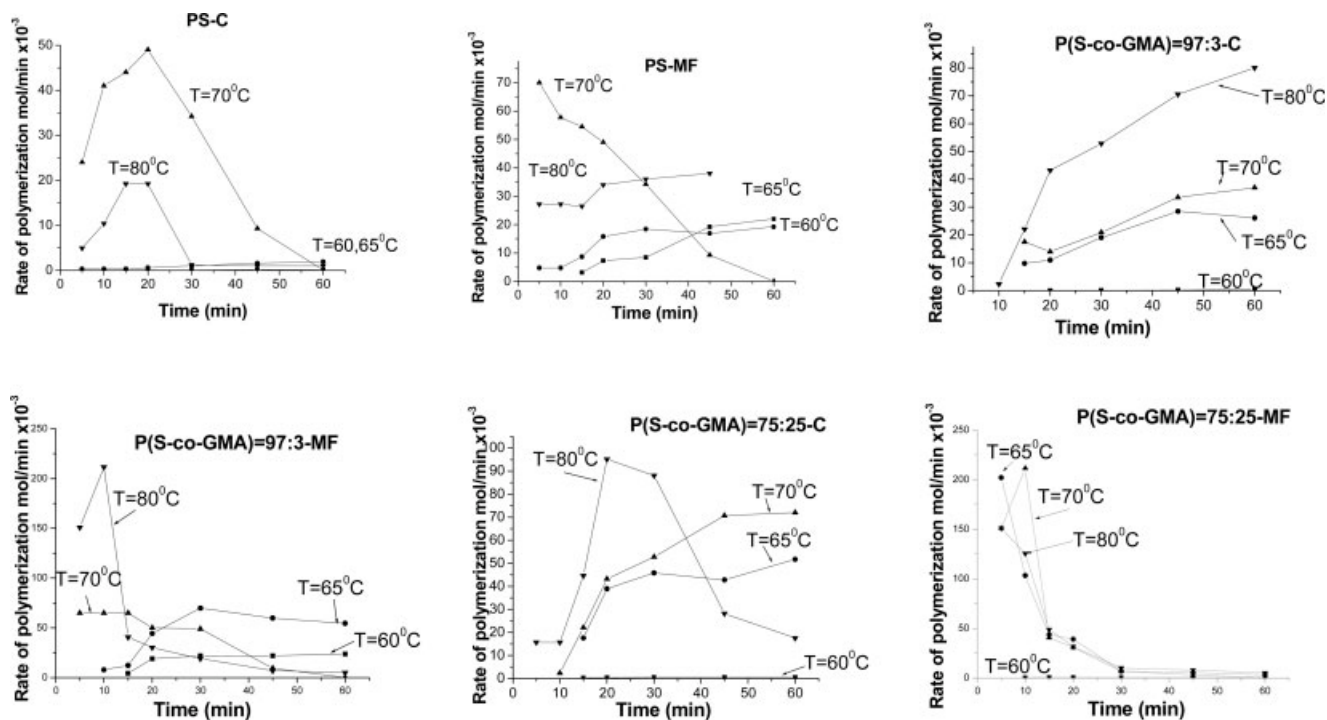


Figure 2 The temperature influence upon the polymerization rate corresponding to the synthesis process performed with or without the MF presence.

the MF presence are followed into the modification of the ratio between the cage to escape radicals, the reduction of the radical pairs recombination and diminishing the "cage effect". The singlet–triplet transitions are also concretized into longer lifetime for the radicals in the triplet state. Consequently, the initiation and the kinetics of the reactions are affected, considerably increasing the conversion and the polymerization rate. The MF influence is ascribed to the radical pair mechanism owing to *hyperfine interactions* ($\Delta g = 0$).

At the same time, the presence as well as growth of the functional comonomer content (GMA) determines supplementary increases in the conversion and polymerization rate, facts which are justified by the magnetic susceptibility and the polarity of the monomers.^{21–24}

The determination of the magnetic susceptibility of the monomers according to Pascal constants, with verification through Gouy or Quinque methods, leads to certain conclusions regarding the behavior of monomers in the MF, as discussed by Drago, and Kalinnikov and Rakitin.^{23,24} From estimations made by Pascal's method, the constants of the diamagnetic susceptibilities corresponding to monomers are $\chi_s = -73.67 \text{ cm}^3/\text{mol}$ and $\chi_{\text{GMA}} = 64.26 \text{ cm}^3/\text{mol}$. Experimental determinations (by means of the Quinque device, generally used in evaluating a liquid's magnetic susceptibilities) have confirmed the theoretical values of the characteristics.

The study evidences a more efficient influence of the MF in syntheses employing a more polar mono-

mer—GMA—as well as increased susceptibility in the presence of MF, facts which are sustained and in accordance with the values determined for the diamagnetic susceptibilities.

These aspects evidence dual character of the MFEs exerted on the dynamics of radicals spins and also on the dynamics of molecular movement.

Data concerning the dependence of the polymerization evolution on the reaction temperature presented in Figures 1 and 2 evidence an expected increase in the conversion and polymerization rate with the temperature growth. Exception is the homopolymer (polystyrene) obtainment; it seems that in this case the temperature of 70°C represents the optimum for the synthesis process. The reaction temperature influences the initiator decomposition rate with effects upon the conversion as well the polymerization rate. Also, the reaction temperature influences the radicals' mobility, determining an increase or decrease in the radicals' pairs recombination reactions.

The efficiency of the MF (E_{MF}) upon the synthesis process (Fig. 3) was determined according to the relation

$$E_{\text{MF}} = \frac{C_{\text{MF}} - C_{\text{C}}}{C_{\text{C}}}$$

where C_{MF} is the reaction conversion in the MF presence, and C_{C} is the reaction conversion performed without MF. It shows the favorable effect of the MF upon conversion. In the first 15–20 min of the reac-

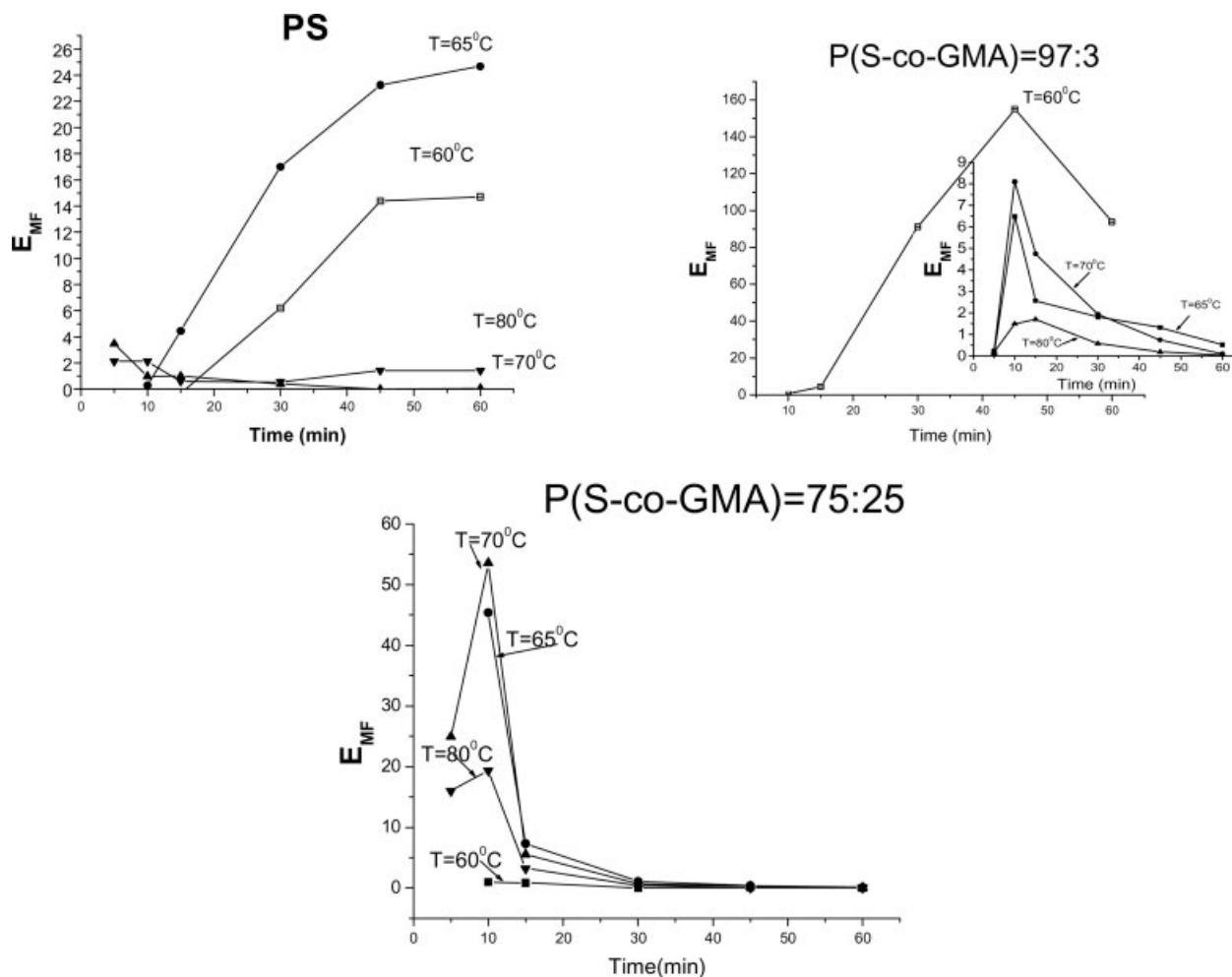


Figure 3 The efficiency of the MF during syntheses.

tion the increase of E_{MF} as a measure of reaction conversion is observed especially for the $P(S\text{-}co\text{-}GMA) = 97 : 3$ as well $P(S\text{-}co\text{-}GMA) = 75 : 25$ obtainment. At the same time, it is obvious that MF effects are more striking at low temperatures, conditions which do not disturb the order effected by the field upon the reaction components, and also the radicals' pairs recombination reactions are reduced.

From the Arrhenius plot of $\log K$ against $1/T$, the overall energy activation was calculated (Fig. 4). The activation energy diminution for the synthesis in the field is attributed to the entropy term modification through the MF application.⁷ MF effect can also be considered as being catalytic producing molecule distortions, growth of distance interactions, and modifications of the angles between bonds. In this way, alongside growth of the radicals lifetime generated by the field, they are configured structures more favorable for the synthesis performance.

The spectral analyses evidence the catalytic effect of the MF upon the structure of polymers syntheses in the field condition. Modifications occurring in

rotational spectra are explained by the orientation of the nuclear spins, molecular structure and interactions between them and are proved by an increase of the intensity of the vibration oscillations absorption, as well as by shifting of peaks.

The band intensity characteristic to $-\text{CH}_2$ group (from 1450 cm^{-1} and 1460 cm^{-1}) of poly(styrene) increases from 0.32 at 0.37 for the polymer synthesized in the MF presence (Fig. 5). The bands from 750 cm^{-1} and 700 cm^{-1} are also considerably increased with 19.44% respective 27.9%.

In the case of the copolymers with low percent of GMA the modifications of the intensity of the spectral band [Fig. 5(a,b)] as a result of the MF influence during syntheses are not so evident. The increase of the percent of the GMA—polar monomer and increased susceptibility at the MF presence—correspondingly enhances the intensity of the adsorption characteristic bands. Figure 5(c) illustrates with more clarity the differences in the adsorption bands between the FTIR spectra of the polymeric sample synthesized with and without the MF presence. The

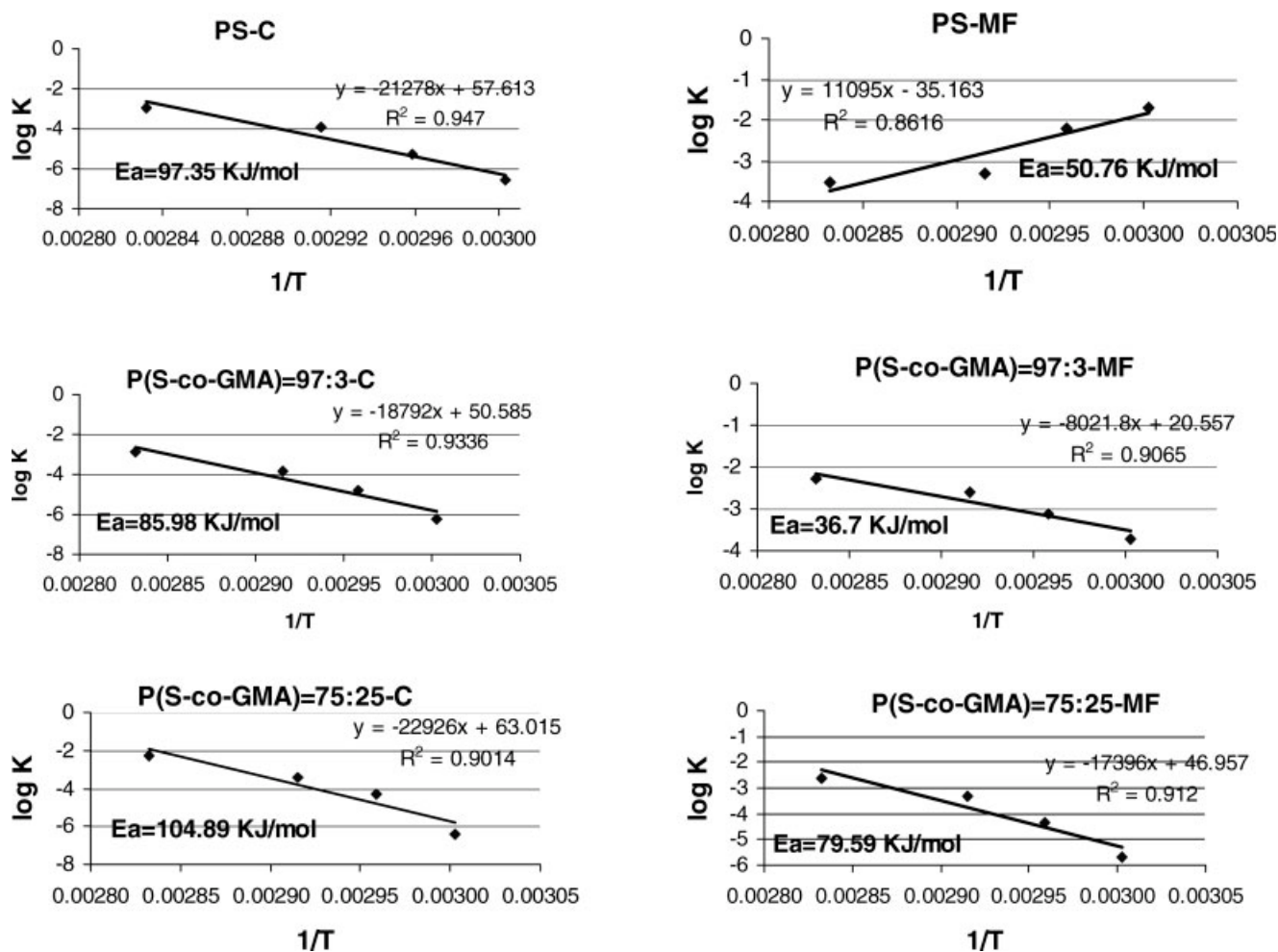


Figure 4 Activation energy determined for syntheses performed with and without the MF presence.

positive values confirm the MF effect upon the structure of the synthesized polymers.

The intensities of the vibration oscillation absorption corresponding to the polymers synthesized in the field are higher, owing to the modification of the strength constant introduced by the inductive and electromeric effects appearing supplementary in

the polymeric structures obtained in the field conditions.

CONCLUSIONS

The article confirms the possibilities to improve the reaction rate as well as the conversion of styrene poly-

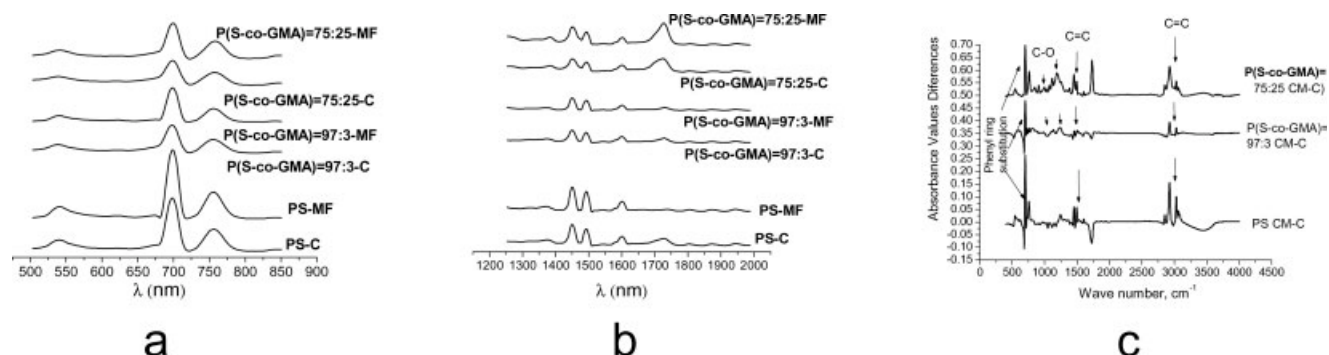


Figure 5 The FTIR spectra of the polystyrene and for the copolymers of the styrene with different ratios of GMA synthesized classically and in MF presence (a, b) and the difference between the adsorption band of the sample synthesized with and without the MF presence (c).

merization and styrene copolymerization with GMA by performing the radical emulsion polymerization in the presence of a MF. The registered magnetokinetic effects in syntheses initiated with dipotassium peroxydisulfate are explained accordingly to the radical pairs mechanism—hyperfine interactions ($\Delta g = 0$)—and based on the singlet–triplet transitions in the GR pairs owing to the field presence. It also shows a higher influence of the MF in syntheses employing a more polar monomer—GMA—as well as increased susceptibility on the MF presence, facts that confirm dual character of the MFEs exerted on the dynamics of radicals' spins and also on the dynamics of molecular movement. Through spectral analyses were evidenced the catalytic effects of the MF, with molecule distortions, growth of distance interactions, and modifications of the angles between bonds. Modifications occurring in rotational spectra of the polymers synthesized in the field were explained by the orientation of the nuclear spins, molecular structure and interactions between them and proved by an increase in the intensity of the vibration oscillations absorption, as well as by shifting of peaks.

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