

Polymerization in a Magnetic Field. 14. Possibilities to Improve Field Effect during methyl acrylate* Polymerization

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ABSTRACT: Magnetokinetic changes intervened in the radical polymerization of methyl acrylate in a continuous external magnetic field of 0.22 T was evidenced. The use of a matrix of polymerization, respectively, poly(ethylene glycol), was correlated with the obtained kinetic data. The occurring-magnetokinetic changes were justified by the radical pair mechanism, Δg , which corresponds to the benzoyl peroxide decomposition into a magnetic field. The intervened magnetokinetic modifications during the reactions

are correlated with the reaction conditions. The influence of the magnetic field is confirmed by the molecular weights of the obtained polymers, values interpreted from the viewpoint of the reaction conditions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1031–1036, 2004

Key words: magnetic field polymerization; methyl acrylate; poly(ethylene glycol)

INTRODUCTION

Magnetic effects can be of technological interest because they offer a new way to perform radical processes. This is because through very weak perturbations of the magnetic field (MF), one can control chemical kinetics, and thus the course and the rate of reactions that normally require much higher chemical energies.¹

Magnetokinetic effects observed in the polymerization processes carried out in a magnetic field are justified owed to the discovery and understanding of nuclear and electronic spin polarization during the reaction.^{2–6} Thus, magnetic field influences become 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. The mechanisms that explain the magnetic field influence in chemical radical processes include the radical pairs mechanism, triplet–triplet, and triplet–doublet pairs and triplet mechanism.^{7,8}

The singlet–triplet transitions in a radical pair in solution are affected by an external magnetic field.² The changes in the radical pairs' multiplicity are followed by modifications in the ratio of cage radicals to

escape radicals. Consequently, the initiation and the kinetics of the reactions are affected.

For the polymerization processes, the magnetic field effects are mainly observed during the initiation step, and their origins have been well treated in the reviews of Steiner.^{9,10} Thus, only by following conversion can one readily distinguish between magnetic field-dependent and -independent reactions.^{11–18}

The explanation of the magnetic field influence through the radical pairs mechanism is based on the existence of these species under to the effects of the field. Via different mechanisms, magnetic fields generate singlet–triplet transitions in the electronic state of radicals. For energetic reasons, the radical pairs in the triplet state display a decrease in the geminate reactions of recombination. The modification of the ratio of cage-to-escape radicals induces an increase in both initiation efficiency and reaction rate and yield owing to a diminishing of the "cage" effect.

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 modification of the electronic spin alignment to the triplet state (as a result of the magnetic field presence) determines the decreasing of the radicals' recombination processes. This phenomenon of "micellar supercage effect" was evidenced and mentioned by Turro.¹⁹

Studies concentrating on polymers with regular structure also mention the possibility of realizing such configurations in the presence of a continuous external magnetic field and a polymeric matrix of structuration. Thus, syndiotactic polystyrene was synthesized in

*See Polymerization in a Magnetic Field, 13. *Rev Roum Chim* 2000, 45(7–8), 689–695, for the prior article.

TABLE I
Intrinsic Viscosities (Where $[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_{rel})}}{c}$)
of PEG ($k = 32 \times 10^3$, $\alpha = 0.67$) Samples Used
as a Matrix of Polymerization

Sample	Average molecular weight	Intrinsic viscosities, $[\eta]$	η -relative	Concentration
PEG	≈1000	0.348	1.39	1%
		0.329	1.81	2%
		0.331	2.35	3%
PEG	≈2000	0.546	1.65	1%
		0.554	2.55	2%
		0.54	3.61	3%
PEG	≈4000	0.87	2.14	1%
		0.866	3.85	2%
		0.867	6.21	3%

a magnetic field and in the presence of polyvinyl-naphthalene.²⁰ The ordering of poly(methyl methacrylate) chains was registered, the structure depending on the magnetic field intensity.^{21,22}

Polarity and viscosity of solvents are also very important parameters in controlling the magnetokinetic effects that are explained through the radical pairs mechanism. The interdependence between magnetic effects and the characteristics of the solvent was discussed and underlined in some articles.^{23–25} In solvents with high viscosity, the radicals' lifetime growths are owed to slower diffusion of charge carriers species. The recombination reactions among radicals are limited, and it is possible that the spin evolution to the triplet state is a result of the magnetic field presence.

The purpose of this article is to show evidence of the possibilities of growing the magnetic field effect during the radical polymerization of the methyl acrylate in solution of organic solvent, and also the influence in the reaction system of a matrix of polymerization, respectively poly(ethylene glycol), and what the function of this added homopolymer is.

EXPERIMENTAL

Material

Methyl acrylate of Merck provenience was purified by vacuum distillation just before use.

The initiator utilized was benzoyl peroxide—0.3% with respect to the monomer—and has been purified by solving in cold CHCl_3 , precipitated in CH_3OH , and then dried on P_2O_5 .

The solvent used was acetone, in a ratio of monomer/solvent = 30/70 by weight, and was also distilled and dried over K_2CO_3 .

Three variants of poly(ethylene glycol) of Merck provenience having molecular weights of 1000, 2000,

and respectively, 4000, were as received. As the molecular weight of PEG increases, viscosity increases and unadulterated PEG behaves as a Newtonian fluid, with strain rates proportional to the applied stress.

Polymerization processes

The samples of poly(methyl acrylate) (PMA) were obtained by radical polymerization of methyl acrylate in a solution of organic solvent with and without the presence of a continuous electromagnetic field having the intensity of 2200 Gs and under the inert atmo-

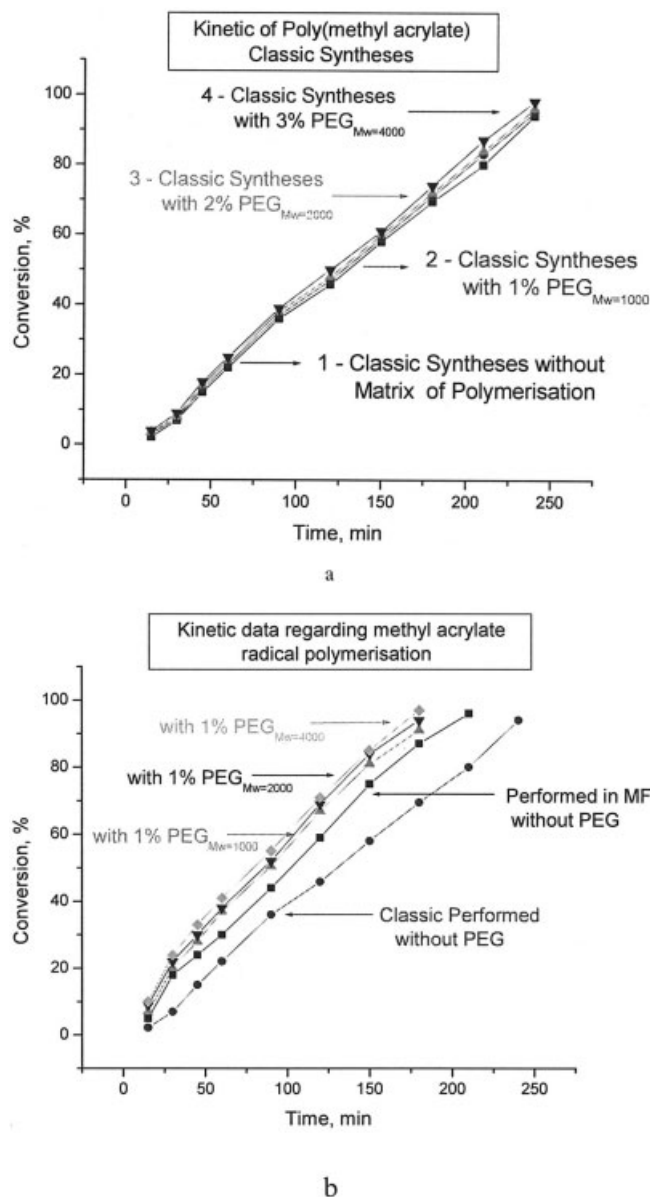


Figure 1 Kinetic evolution of the methyl acrylate polymerization process: (a) classic syntheses with and without PEG, and (b) reactions performed in magnetic field with the matrix of polymerization.

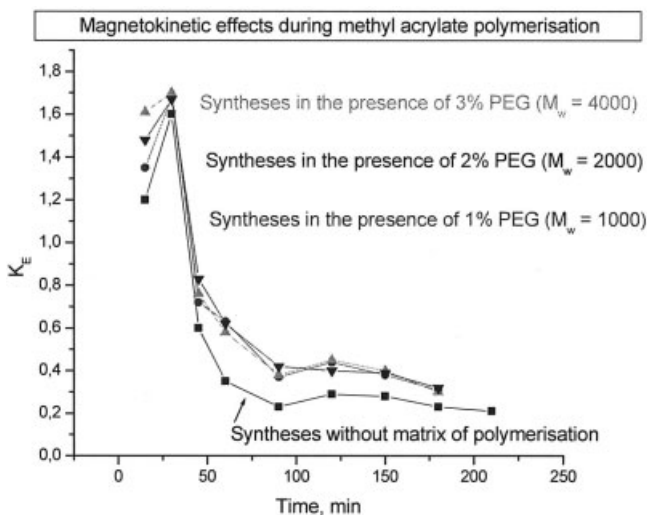


Figure 2 The magnetokinetic effects registered during methyl acrylate polymerization.

sphere of N₂. No stirring was applied during the polymerization processes.

The syntheses was conducted in the presence of the poly(ethylene glycol) (PEG) (having the mentioned molecular weights) as a matrix of polymerization in

different ratios, respectively, 1, 2, and 3% with respect to the monomer concentration.

Temperature was firmly maintained at 70°C, for both variants of processes in and out MF, through a thermostat, knowing that even a small growth of temperature is inadequate to evidence magnetic field influence.

After a 3-h reaction time the obtained polymers were precipitated in methanol and dried to a constant weight for the subsequent determinations.

Characterization

Intrinsic viscosities (dL × g⁻¹) were measured in acetone, using an Ubbelohde suspended, level viscosimeter, at 25°C ([η] = kM^α, k = 32 × 10³, α = 0.67).²⁶ Thus, the average molecular weight of used PEG as matrix of polymerization has been confirmed (Table I). At the same time, the obtained viscometric data have been employed as support for further investigation of the magnetokinetic evolution of the polymerization processes.

The kinetic data have been obtained through a gravimetrically study performed comparatively for both variants of the block copolymers synthesized through the procedures with and without the MF.

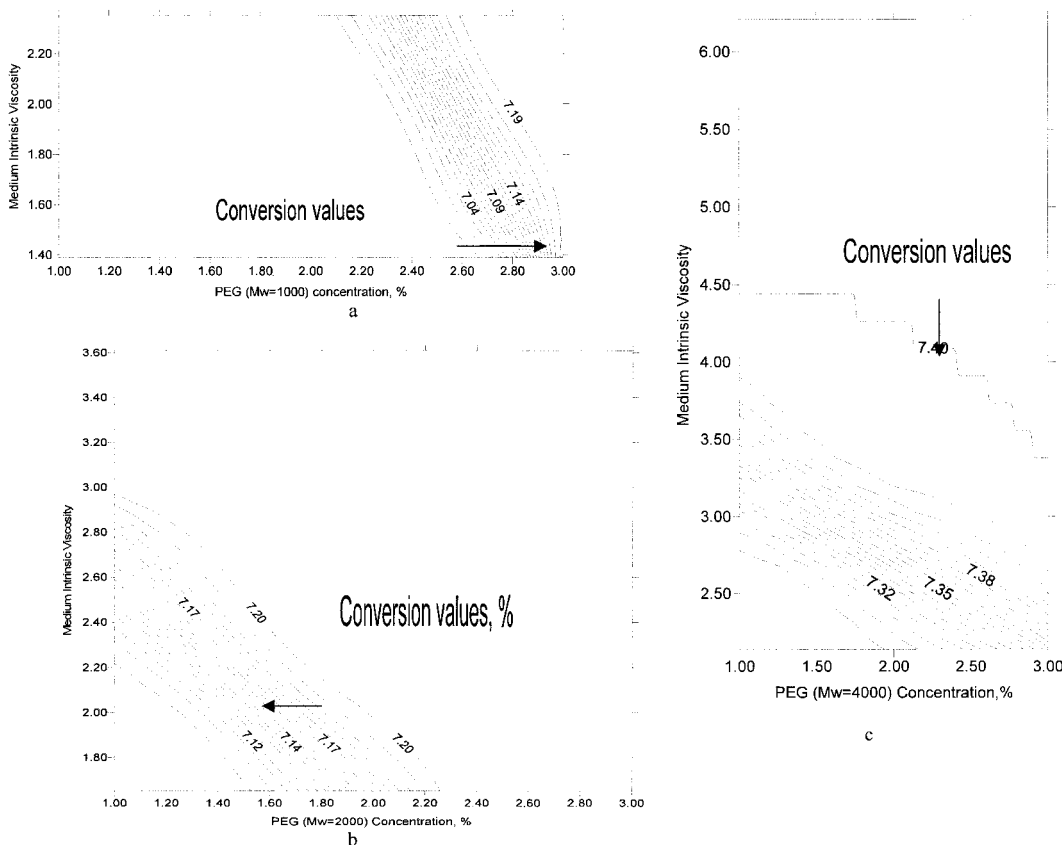


Figure 3 Interdependences between conversion values, PEG concentration, and medium intrinsic viscosity in the case of classic PAM syntheses.

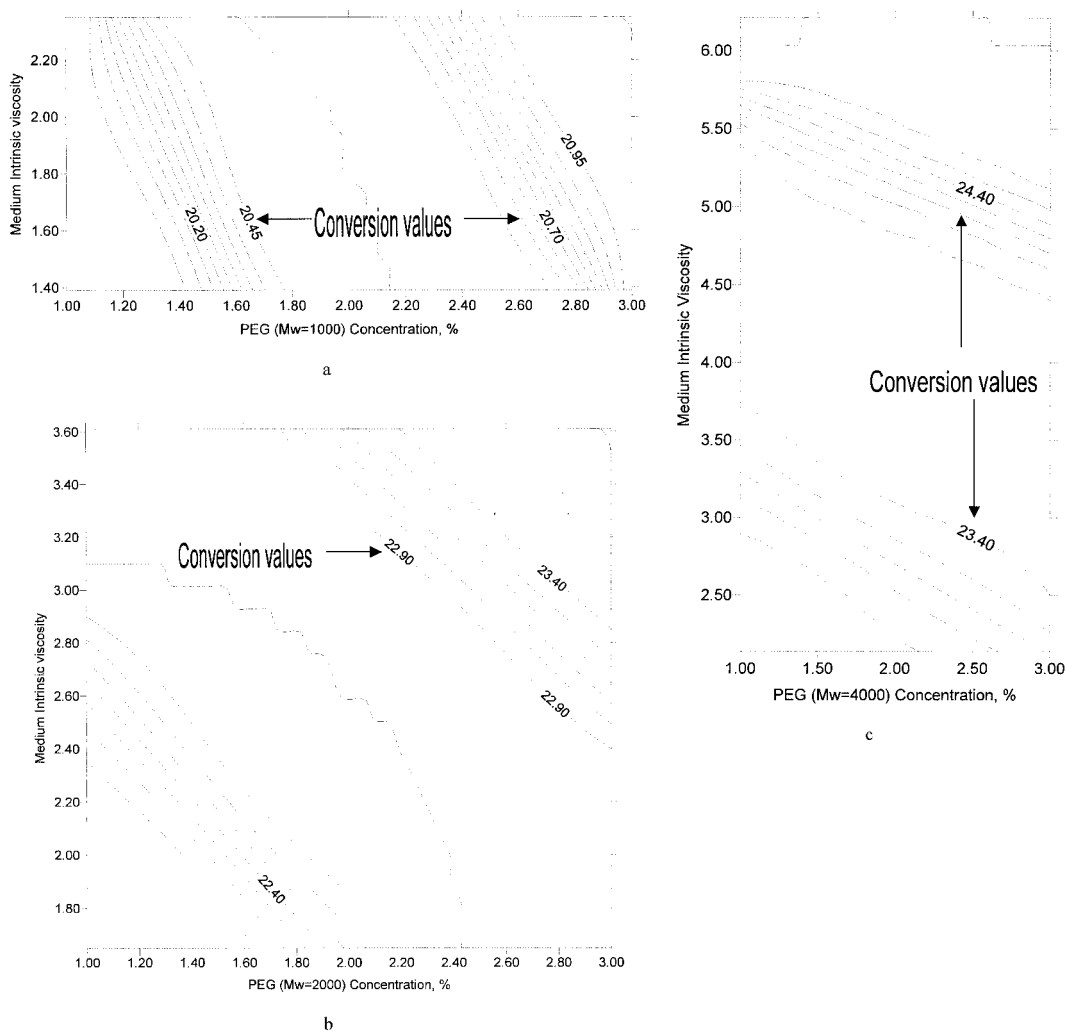


Figure 4 Interdependences between conversion values, PEG concentration, and medium intrinsic viscosity in the case of PAM syntheses performed in MF.

Macromolecular chains of PMA obtained with and without the MF presence were compared from the viewpoint of their molecular weights (GPC measurements in THF, calibration vs polystyrene standard) and characterized according to NMR spectra (recorded on a Bruker AMX 500 instrument, data performed in CDCl_3).

RESULTS AND DISCUSSION

Kinetic data

It has already been mentioned in what way the magnetic field can influence the kinetic of radical reactions of polymerization, respectively owing to the singlet-triplet transitions in the electronic state of radicals. The radical pairs mechanism—that includes mechanisms of RP singlet-triplet transitions according to Δg , hf and/or the relaxation mecha-

nism, which are based on the mentioned interactions—explains the dependence of chemical processes on the magnetic field.

A magnetic field effect in the decomposition reaction of BPO is attributed to an intersystem crossing in the singlet radical species according to the Δg mechanism.¹

Figure 1(a) and (b) illustrates the kinetic development of the methyl acrylate polymerization with and without the magnetic field presence and with no or by means of PEG. There are insignificant differences between evolutions and conversions registered for the classic syntheses performed in the presence of different concentrations of PEG (1, 2, and 3%) having the same molecular weights comparatively with the reactions performed without PEG. The same conclusion corresponds to the reactions achieved in the presence of the magnetic field. Only the modifications of the molecular weight of PEG, as well as its concentration,

bring some magnetokinetic effects, as can be seen from Figure 1.

Concerning the magnetic field effect, it is known that the benzoyl peroxide decomposition reaction in the field is concretized into a decrease of cage product formation according to the Δg mechanism. As normally expected, the most obvious magnetokinetic effects are registered at the beginning of the processes, during the reaction induction period after singlet-triplet transitions generated by the magnetic field in the electronic state of radicals. The existence of the radicals in the triplet state determines the reduction of the induction period of the reaction owing to a longer lifetime of radicals, and as a result, the initiation process is more efficient and the polymerization rate is higher. These recorded magnetokinetic effects K_E (with $K_E = (R_{P_{MF}} - R_{P_C})/R_{P_C}$, and $R_{P_{MF}}$ the rate of polymerization in MF, and R_{P_C} the classic rate of polymerization) are illustrated in Figure 2.

Next, figures present the interdependences between the conversion registered values (at 30 min time of reaction, when it was established that the highest magnetic field effect was established from the corresponding conversion values of the consequent processes) and subsequent concentrations of PEG having corresponding molecular weights.

Magnetic field effects according to the radical pairs mechanism depend essentially on the radicals' diffusive motion that must produce their efficient separation so that the magnetic field sensitive spin evolution may become manifest as a product yield. Pursuing Figures 3 and 4, it is evident that viscosity is a very important factor in controlling magnetokinetic effects. Thus, a proportional direct dependence of the magnetokinetic effects on the viscosity of reaction medium is observed. In reaction medium with higher viscosity (such as that with 3% PEG concentration or with PEG with a molecular weight of 4000) the radicals' lifetime growth, and consequently a slower diffusion of charge carriers species, the recombination reactions among radicals are limited, and the spin evolution to the triplet state as a result of the magnetic field presence is possible.

Figure 5 presents the magnetic field efficiency

$$E_{MF} = \frac{C_{MF} - C_C}{C_C}$$

determined according to C_{MF} , the conversion obtained during the PAM syntheses performed in magnetic field at 30 min reaction time, and C_C , the corresponding conversion for classic processes.

The proportional interdependence between the intervened magnetokinetic effects and intrinsic viscosity of the used medium is confirmed again.

It is well known that sometimes the MF influence cannot be put into evidence through the kinetic

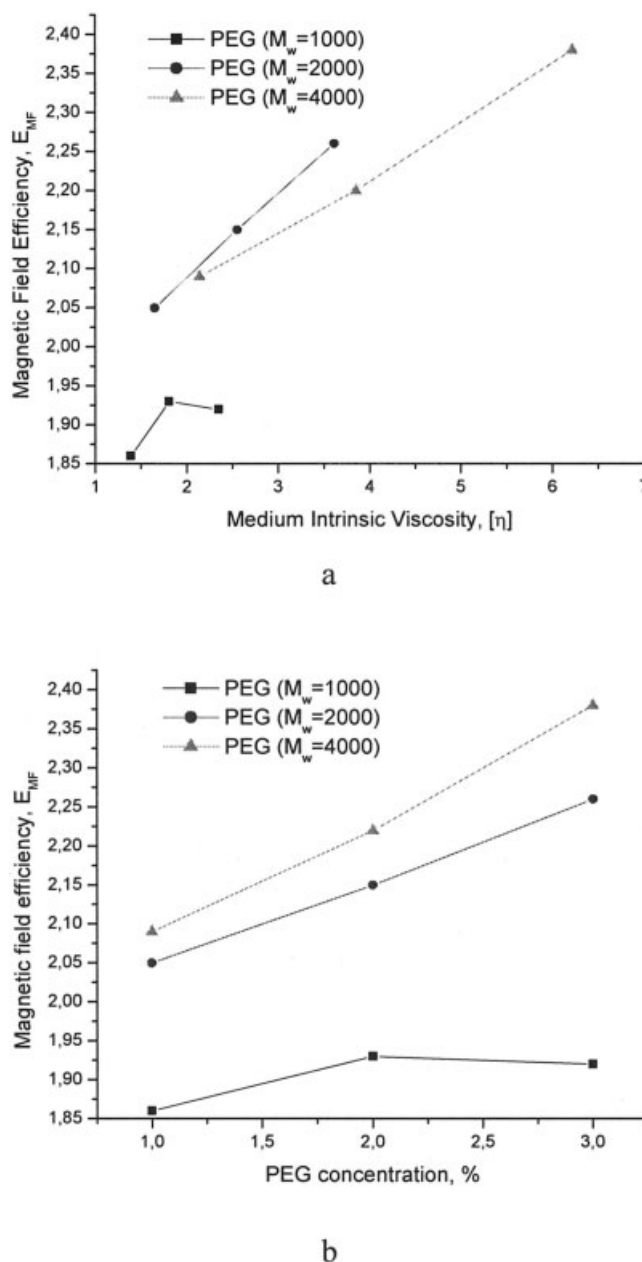


Figure 5 Interdependence between intervened magnetokinetic effects and medium intrinsic viscosity (a), respectively, PEG concentration (b).

changes. As a result, the kinetic data were completed by the determination of the molecular weights to evidence the MF effect as well the efficiency of the field. Thus, the magnetic field effect can be perceived as a dual character exerted on the one hand on the dynamics of molecular movement, and on the other hand on the dynamics of radical spins.

Table II presents the registered molecular weights of poly(methylacrylate) according to the reaction conditions. The benefit function of PEG for obtaining higher molecular weights is evident. The same effect has the presence of the magnetic field during the polymeriza-

TABLE II
Evolution of the Molecular Weights of Poly(methyl acrylate) According with the Reaction Conditions of Synthesis

Variant of polymer and/or syntheses		$\bar{M}_n \times 10^5$	$\bar{M}_w \times 10^5$	\bar{M}_w/\bar{M}_n
Classic		1.942	4.902	2.52
	PEG _(Mw) = 1000	4.360	7.050	1.62
	PEG _(Mw) = 2000	5.270	7.950	1.51
Classic and in the presence of 3% PEG	PEG _(Mw) = 4000	6.199	8.974	1.45
	In magnetic field	2.896	6.162	2.12
In magnetic field and in the presence of PEG	PEG _(Mw) = 1000	5.600	8.100	1.47
	PEG _(Mw) = 2000	6.050	8.700	1.44
	PEG _(Mw) = 4000	6.408	9.260	1.44

tion process, which is attributed to the action of the magnetic field on the macromolecular chains, termination by recombination being preferred to the detriment of disproportionation. In addition, the presence of the matrix of polymerization, PEG, as well of the magnetic field, determines a reduction of the macromolecular chains dispersity.

CONCLUSIONS

The article presents the benefit influence of the magnetic field presence during the syntheses of poly(methyl acrylate). As magnetokinetic field effects, a higher reaction rate and conversion is registered, and also a diminution of the induction period. At the same time, poly(ethylene glycol) exists, having different molecular weights, as the matrix of polymerization determines the improvement of the reaction evolution. It can also be concluded that in confirming magnetokinetic effects, the more important factor is growing of the reaction medium viscosity. Similarly, kinetic effects, as well for the improvement molecular weights of the polymers, are generated and determined by the magnetic field and poly(ethylene glycol) presence.

References

- Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko, A. L. Spin Polarization and Magnetic Effects in Radical Reactions; Elsevier Press: Amsterdam, 1984.
- Turro, N. J.; Kraeutler, B. *Acc Chem. Res* 1980, 13, 369.
- Lawler, R. G. *Acc Chem Res* 1972, 5, 25.
- Atkins, P. W.; Evans, G. T. *Adv Chem Phys* 1976, 35, 1.
- Freed, J. H.; Pedersen, J. B. *Adv Magn Reson* 1976, 8, 1.
- Pedersen, J. B. *Theories of Chemically Induced Magnetic Polarization*; Odense University Press: Odense, 1979
- Buchachenko, A. L. *Russ Chem Rev* 1976, 45, 761.
- Buchachenko, A. L. *Russ J Phys Chem* 1977, 51, 1445.
- Steiner, U. E.; Ulrich, T. *Chem Rev* 1989, 89, 51.
- Steiner, U. E.; Wolff, H. J. *Photochemistry and Photophysics*; CRC Press: Boca Raton, Boston, 1991.
- Simionescu, C. I.; Chiriac, A. P.; Neamtu, I.; Rusan, V. *Makromol Chem Rapid Commun* 1989, 10, 601.
- Simionescu, C. I.; Chiriac, A. P.; Neamtu, I. *Polym Bull* 1991, 27, 31.
- Simionescu, C. I.; Chiriac, A. P.; Chiriac, M. V. *Polymer* 1993, 18, 3917.
- Simionescu, C. I.; Chiriac, A. P. *Coll Polym Sci* 1992, 270, 753.
- Chiriac, A. P.; Neamtu, I.; Cazacu, G.; Simionescu, C. I. *Rozmarin, Gh. Angew Makromol Chem* 1997, 246, 1.
- Chiriac, A. P.; Simionescu, C. I. *J Polym Sci Part A Polym Chem* 1996, 34, 567.
- Chiriac, A. P.; Simionescu, C. I. *Prog Polym Sci* 2000, 25, 219.
- Neamtu, I.; and Chiriac, A. P. *Polym Testing* 2001, 20, 585.
- Turro, N. J.; Chow, M. F. *J Am Chem Soc* 1980, 102, 1190.
- Weller, A. *Phys Chem (Frankfurt/Main)* 1982, 130, 129.
- Junlian, H.; Zhu, P.; Ji, C.; Ruan, W. *Macromol Chem* 1992, 193, 243.
- Junlian, H.; Zhu, P.; Ji, C.; Ruan, W. *J Polym Sci* 1990, 8, 289.
- Junlian, H.; Song, Q. *Macromolecules* 1993, 26, 1359.
- Werner, H. J.; Staerk, H.; Weller, A. *J Chem Phys* 1978, 68, 2419.
- Staerk, H.; Busmann, H. G.; Kühnla, W.; Weller, A. *Chem Phys Lett* 1989, 155, 603.
- Beech, D. R.; Booth, C. *J Polym Sci A-2* 1969, 7, 575.