Polymerization in a Magnetic Field. XV Some Azo-Initiators Behavior in a High Magnetic Field*

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ABSTRACT: The effect of a high magnetic field of 7 T on styrene polymerization reactions was taken under study. The intervened magnetokinetic modifications are correlated to the system of radical initiation, respectively: benzoyl peroxide, 2, 2'-azobis(2-methylpropionitrile), 4, 4'-azobis(4-cyanopentanoic acid), and 1,1'-azobis (cyclohexan-1-carbonitrile). The reaction products are also characterized from the viewpoint of their molecular weights correlated with the reaction conditions, as well as their thermal stability. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1025–1031, 2005

Key words: polymerization kinetic; radical polymerization; magnetic field; styrene; thermogravimetric analysis

INTRODUCTION

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 (MF) effects on chemical reactions. Thus, magnetic field influence becomes obvious when the field will induce or prevent transitions between near fundamental electronic states in radical pairs of the system. The changes in spin multiplicity of the radical pairs under the influence of the field determine the subsequent magnetokinetic effects. There are already some known reactions of polymerization performed in MF with their occurred magnetokinetic effects explained on the basis of the radical pairs mechanism.[1]

Spin polarization and magnetic effects in free radical reactions are interconnected phenomena based on common physical mechanisms. These phenomena depend on the existence of a stage of interaction between the two radicals in a "cage," when they constitute a radical pair (RP). The magnetic effects induced by singlet–triplet transitions occur within the radical pair lifetime in the cage.[2,3] Consequently, the influence of external fields on S–T transitions will, under favorable conditions, result in an external field dependence of radical reaction rates.[4,5]

The types of interactions that are responsible for spin motion, such as Zeeman, hyperfine, and spin-rotational coupling interactions in radicals, as well as dipolar electron spin–spin and exchange interactions between radicals, all have been discussed in theoretical articles.[6,7] The radical pairs mechanism, which includes mechanisms of RP singlet–triplet transitions according to Δg, HF, and/or relaxation mechanisms that are based on the mentioned interactions, explains the dependence of chemical processes on the magnetic field presence.

In the present investigation we describe a comparative study among the behavior of four radical initiators, respectively, benzoyl peroxide, 2, 2'-azobis(2-methylpropionitrile), 4, 4'-azobis(4-cyanopentanoic acid), and 1,1'-azobis(cyclohexan-1-carbonitrile) during polymerization in solution of styrene in a continuous high magnetic field of 7 T.

EXPERIMENTAL

Radical polymerization of styrene (St) was conducted in solution, classically and in a continuous external magnetic field of 7 T (a cryomagnet for NMR spectroscopy; product of Oxford Spectrospin Cryomagnetic Systems from Max Planck Institute for Polymer Research, Mainz, Germany).

The study was performed with the following variants of initiators: benzoyl peroxide (BPO), 2, 2'-azobis (2-methylpropionitrile) (AIBN), 4, 4'-azobis(4-cyanopentanoic acid) (ABCV), and 1,1'-azobis(cyclohexan-1-carbonitrile) (ABCCH). Initiator concentration of $0.025M\%$, $0.05M\%$ and $0.08M\%$, respectively, was utilized (they were used without further purification).

The monomer as well solvent (tetrahydrofuran, THF) was distilled just before use, with the monomer/ solvent ratio being 1/5.

The reaction temperature was 65 °C. The reactions were performed in an argon atmosphere and without shaking.

The reactions in MF were realized in ampoules, with a capacity of 50 mL, with an appropriate geometry according to the field. A thermostat was used to heat the ampoules and to firmly maintain the temperature.

The obtained polymers were precipitated by methanol and then dried in a vacuum to constant weight.

Kinetic data

Kinetic data have been obtained through a gravimetrical study performed comparatively for both variant of polymers synthesized with and without MF.

NMR spectra

NMR spectra (in $CDCl_3$) were recorded on a Bruker AMX 500 instrument.

X-ray diffractometry

Wide-angle X-ray diffractographs for the powder polymer samples were recorded with a Philips PW 1840 X-ray diffractometer using Ni-filtered CuKα (λ = 1.5418 Å) radiation at 40 kV, 20 mA, and scanning speeds of 3 and 1.2° min^{-1}.

GPC measurements (THF, calibration versus polystyrene standard)

The molecular weight distribution of the polymers (obtained according to the mentioned procedures) has been determined to evidence and underline the MF influence.

TG and derivative thermogravimetry (DTG)

TG and DTG experiments were carried out on a MOM Budapest derivatograph under the following operational conditions: sample weight 50 mg, heating rate 12 °C/min in atmospheric air, and reference material α-Al_2O_3.

Reproducible data have been obtained for all experiments, considering the course of reactions, the determination of conversions, and the data concerning the characterization of polymers.
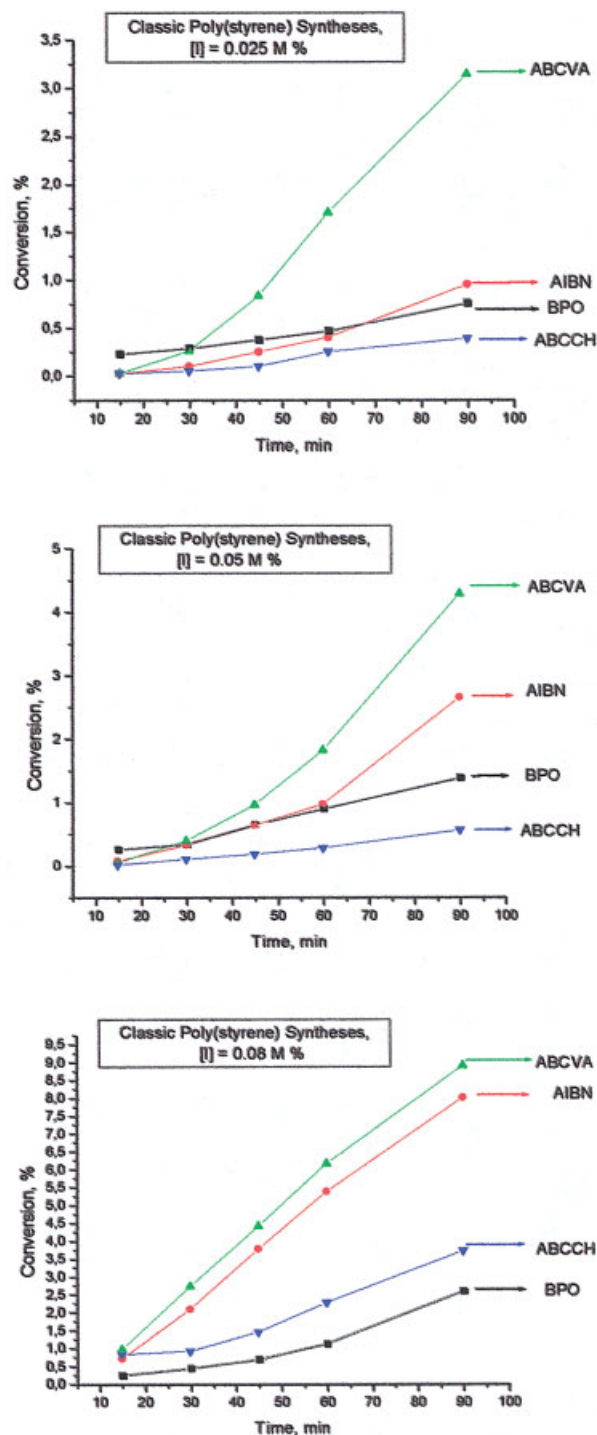

Figure 1 The evolution of the PSt classic obtainment.

RESULTS AND DISCUSSION

Kinetic data

The magnetic field effect upon the decomposition reaction of BPO is attributed to intersystem crossing in the singlet radical species according to the Δg mechanism. The thermal decomposition of AIBN produces a singlet radical pair with $\Delta g = 0$. As a result, the singlet
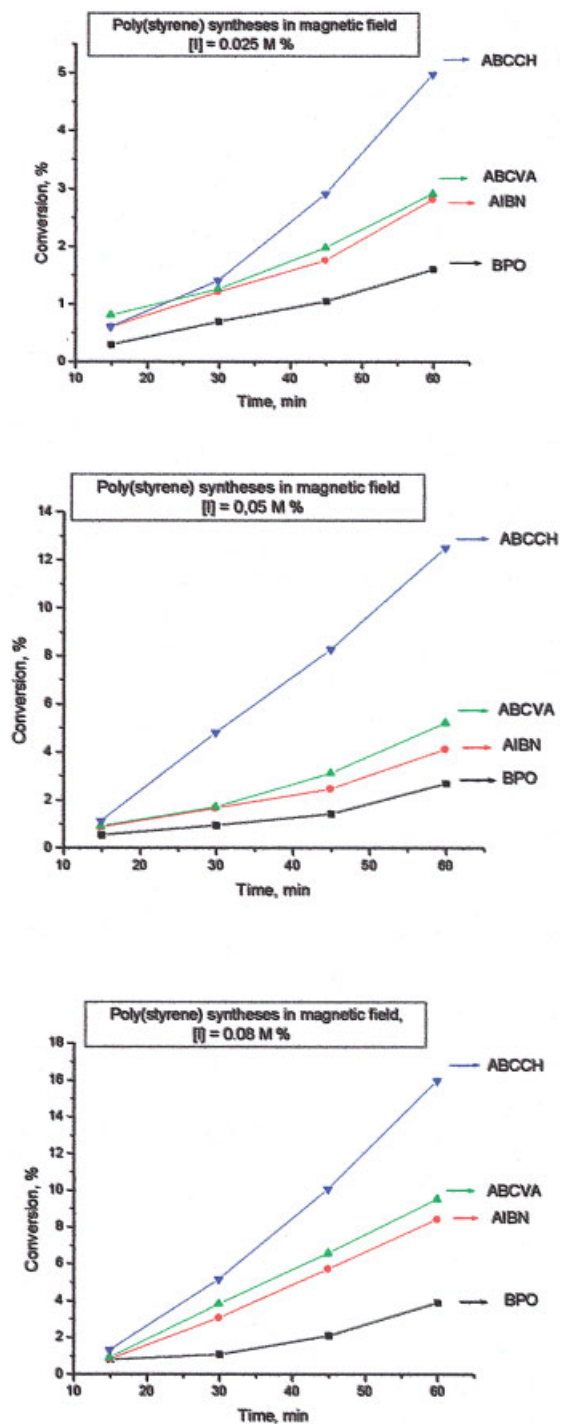
Figure 2 The evolution of the styrene polymerization in magnetic field.

St and MMA photopolymerization in the presence of AIBN[9–12].

Our analysis dealt with the behavior of AIBN, ABCV, and ABCCH as azo initiators during radical polymerization of St in a high MF in comparison with BPO.

to triplet conversion due to the Δg mechanism does not arise. Even so, there are some data in the literature that present studies for enhancing the AIBN efficiency in the initiating processes in MF, as, for example,

—the heterogeneous radical polymerization of acrylonitrile in the presence of AIBN[8];

—the use of poly(ethylene glycol) with sensitizer end group (as triplet sensitizer and surfactant) in the
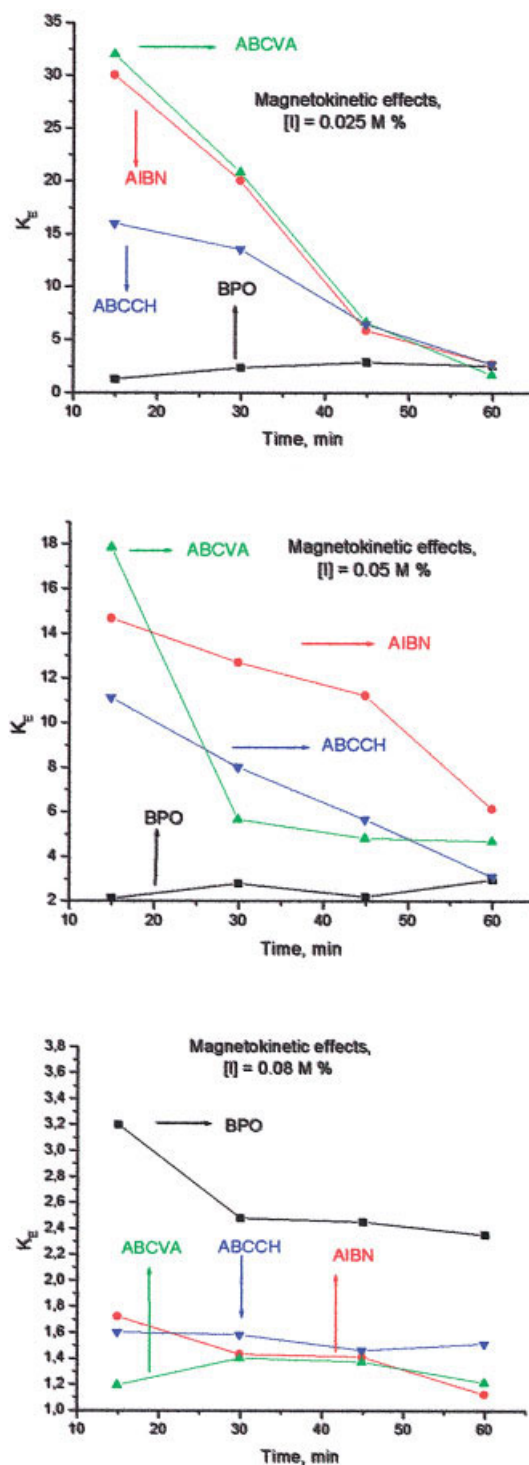
Figure 3 Magnetokinetic effects registered during the styrene polymerization process.

TABLE I
Polymer Molecular Weights in Direct Dependence with the Reaction Conditions

Variant of initiator	Syntheses performed	Polymers molecular weights ($\times e^{-4}$), initiator concentration, M %								
		0.025			0.05			0.08		
		$\bar{M}_n$	$\bar{M}_w$	D	$\bar{M}_n$	$\bar{M}_w$	D	$\bar{M}_n$	$\bar{M}_w$	D
BPO	Classic	3.112	5.670	1.82	3.007	4.7252	1.57	2.8605	3.8503	1.35
	In MF	4.4197	9.3874	2.12	4.385	8.2431	1.88	3.9882	7.5505	1.89
AIBN	Classic	2.9512	4.8979	1.66	2.0890	3.8174	1.83	1.8181	3.1627	1.74
	In MF	3.8418	6.4286	1.67	3.4968	5.475	1.57	2.6399	4.1391	1.57
ABCVA	Classic	2.0942	3.3753	1.62	1.5798	2.7606	1.75	0.9112	1.6897	1.85
	In MF	4.1530	6.8120	1.64	3.4597	5.3830	1.55	2.9811	4.6220	1.55
ABCCH	Classic	1.5951	3.5225	2.21	1.3518	3.2350	2.39	1.2312	2.9210	2.37
	In MF	5.6220	10.881	1.94	5.2623	10.682	2.03	4.3153	7.5596	1.75

The comparative kinetic behavior of styrene polymerization, with or without MF, having as initiators the mentioned four variants is illustrated in Figures 1 and 2.

The kinetic behavior of the classic polymerization processes agrees with the data regarding the decomposition rates (k_d) corresponding to the initiators used in the reactions, respectively $k_d^{BPO} = 2.0 \times 10^{-6}$, $k_d^{AIBN} = 3.2 \times 10^{-5}$, $k_d^{ABCVA} = 4.6 \times 10^{-5}$, $k_d^{ABCCH} = 6.5 \times 10^{-6}$.[13]

The MF influence is illustrated in Figure 2 and is present in all variants of effected syntheses. Thus, polymerization processes performed in the presence of MF are characterized by higher conversion and a decrease in the induction period.

Syntheses in MF initiated by ABCCH offer the most evident changes concerning the conversion values (Figs. 1 and 2). The results agree with those of Fox and Hammond.[14]

The recorded MKE, determined according to the relation $K_E = \dfrac{R_{pMF}}{R_{pc}}$, with R_{pMF} the rate (M/L × s) of polymerization in MF and R_{pc} the rate of classic polymerization, are illustrated in Figure 3.

Unexpectedly, the magnetokinetic effects (MKE) recorded in the case of BPO initiation are less evident than in other cases. A possible explanation can be the reaction temperature.

Magnetic field effects, concretized in higher reaction rates, are tidied up depending on the used initiators according to ABCVA > AIBN > ABCCH > BPO, offering the peak of evidences at the beginning of processes as a result of the reducing the cage effect. Also, growth of the initiator concentration doesn't coincide with a corresponding amplification of the MF influence on the contrary: most evidences are registered for the smallest initiator content. It seems to be normal for a higher content of initiator to have more effect upon synthesis processes than the perturbations achieved by the magnetic field.

In the case of azo initiators, MF acts by changing the state of radicals from the singlet to the triplet state through a HF mechanism, transitions which depend on the external MF strength. In high fields, when the external field exceeds the one induced by the magnetic nuclei, the HF mechanism manifests itself like the Δg mechanism. In such fields the spins of the unpaired electrons and magnetic nuclei precess independently, and the HF mechanism corresponds to the effect of an additional local MF that changes the unpaired electron precession frequency.[2] In high fields the T_+ and T_- levels do not interact with S and do not participate in S–T evolution. The HF mechanism results in equal average S and T_0 populations and the recombination probability in high magnetic fields is one-third that at low fields. MFE consists practically in reducing the cage effect and a corresponding growth of the initiator lifetime and efficiency.

The absence of continuous monotone dependences against time of the time courses of magnetokinetic effects is also remarkable. It must take into consideration that the magnetic field effect can be perceived as having 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. If at the beginning of the processes MFE are concretized primarily in reducing the cage effect, subsequently the influence of MF is also owing to the catalytic effect of the field.

Besides the modifications brought to the evolution of the polymerization process, the MF also influences the properties of the resulting polymers obtained through this unconventional method. The changes in the properties of the polymers synthesized in the MF are attributed to the field effect on the molecules that can be reshaped through growing distance interactions and modification of angles between bonds.

Sometimes the MF influence can't be evidenced through kinetic changes. As a result the kinetic data were completed by the determination of the molecular weights of the polymers and also their thermal stability to evidence the MF effect as well as its efficiency.
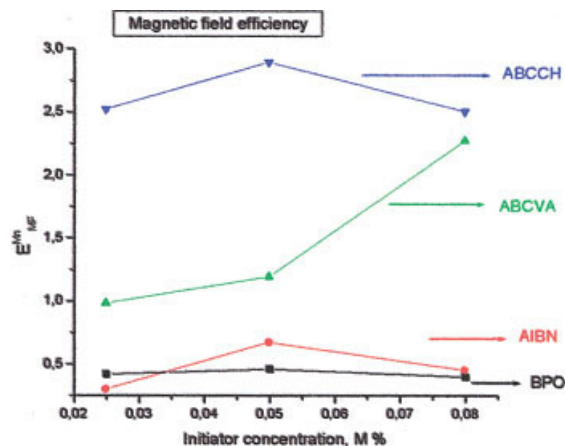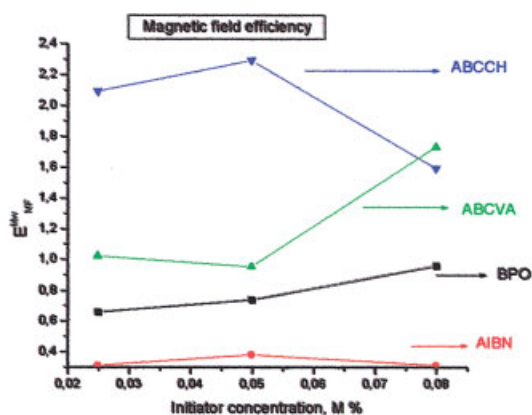
Figure 4 Magnetic field efficiency $E_{MF} = \dfrac{\bar{M}_{n_{MF}} - \bar{M}_{nc}}{\bar{M}_{nc}}$ determined in agreement with number-average molecular weights of PSt synthesized with and without MF.

The macromolecular compounds obtained in MF present higher molecular weights compared to their homologues synthesized in the absence of the field. This is attributed to the action of the MF on the macromolecular chains, termination by recombination being preferred to the detriment of disproportionation.
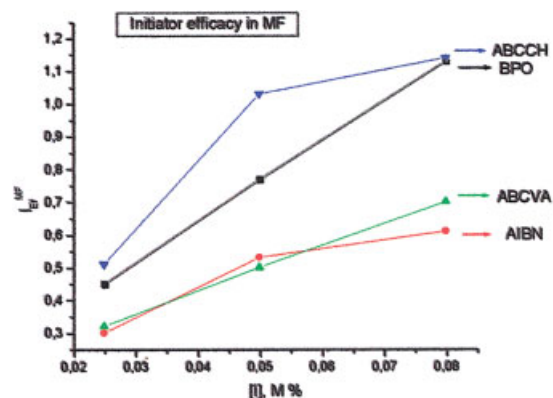
Table I presents comparative data obtained via GPC of polymers synthesized according to the four variants of initiators and the procedures with and without MF.

The molecular weights as well as the number-average molecular weights of PSt synthesized classically or in MF are in good agreement with kinetic data of the obtainment procedures.

The MF efficiency, estimated according to E_{MF} $= \dfrac{\bar{M}_{n,w_{MF}} - \bar{M}_{n,w_C}}{\bar{M}_{n,w_C}}$ presented in Figures 4 and 5 con-
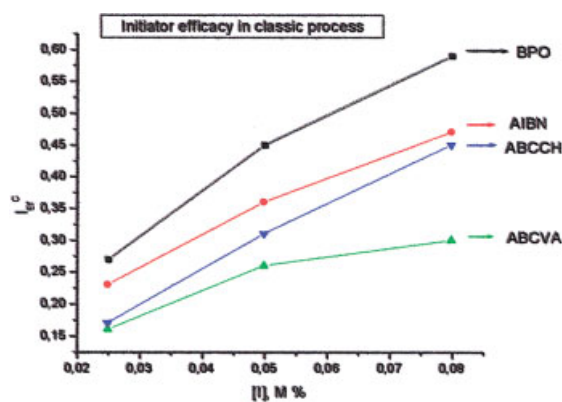

Figure 6 Initiator efficacy in MF $I_{Ef}^{MF} = \dfrac{\bar{M}_{w_{MF}}}{\bar{M}_{w_t}}$ determined in agreement with molecular weights of the PSt synthesized in the magnetic field and the theoretical one.

firms and emphasizes the registered MKE.

Considering the variable, $I_{Ef}^{C,MF} = \dfrac{\bar{M}_{w_{C,MF}}}{\bar{M}_{w_t}}$, as an initiator efficacy, (where $\bar{M}_{w_t}$ represents the theoretical molecular weight of PSt, which can be obtained according to the reaction conditions, and $\bar{M}_{w_{C,MF}}$ (respectively, the molecular weights obtained classically or in the MF procedure), Figures 6 and 7 illustrate its variation correlated to the method of synthesis.

NMR spectra of PSt synthesized classically or in the field [Fig. 8(a) and (b)] do not indicate structure modifications, such as, for example, tacticity. At the same time X-ray diffractographs (Fig. 9) present some changes intervened into the supramolecular structure of the homopolymer as a result of the MF presence during the synthesis process.

Thermal behavior of the polymers obtained with or without MF was assessed from their thermal degrada-

Figure 5 Magnetic field efficiency $E'_{MF} = \dfrac{\bar{M}_{w_{MF}} - \bar{M}_{w_C}}{\bar{M}_{w_C}}$ determined in agreement with molecular weights of PSt synthesized with and without MF.

Figure 7 Initiator efficacy in classic process $I_{Ef}^{C} = \dfrac{\bar{M}_{w_C}}{\bar{M}_{w_t}}$ determined in agreement with M_w of the PSt classically synthesized and the theoretical one.
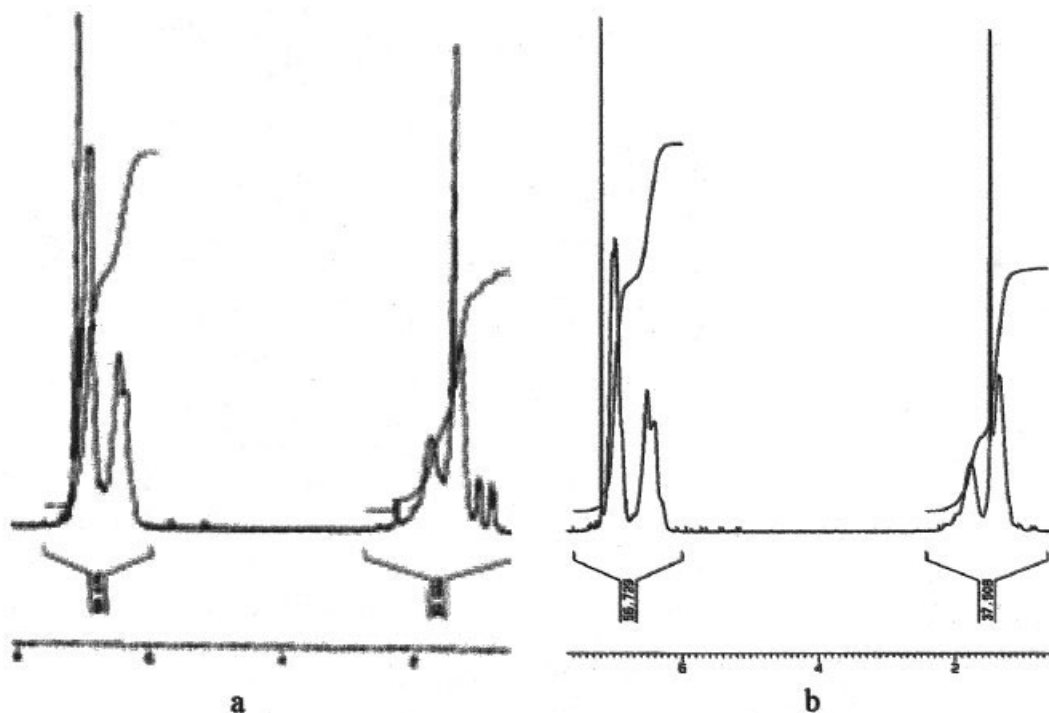
Figure 8   NMR spectra of PSt synthesized classically (a) and in the presence of MF (b).

tion pattern using TG techniques. The higher thermal stability of the polymers obtained in MF is demonstrated by the initial and maximum decomposition temperatures and the weight loss within the T_i–T_{max} interval (Table II). These higher values corresponding to the polymers obtained in MF were attributed to an ordered structure of the homopolymers as a result of the MF presence during synthesis.

To have a more complete image of the thermal behavior of the studied polymers, the modifications of E_a of the degradation process were investigated using both the Coats–Redfern[15] and the Levi–Reich methods[16,17]. The former method was used to evaluate the

E_a values (Table II) (with E_a obtained from the slope of the plot of ln c/T^2 versus $1/T$ (c being conversion)), while by the latter one, the changes of E_a with conversion during degradation were evaluated (Fig. 10) (using the inflection point, which is the point where the reaction rate is maximum and also based on the reaction order previous determined through the Coats–Redfern method). Visual inspection of the plots of the synthesized polymers (with or without MF) shows that the thermal degradation in the range 200–600 °C proceeds in one main step and at different rates, with a higher rate in the case of polymers classically synthesized.
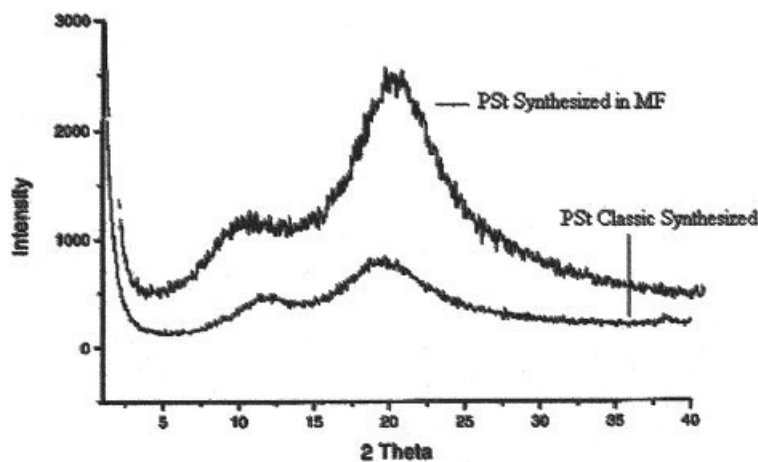

Figure 9   X-ray diffractographs of PSt synthesized with 0.05% AIBN initiator.

TABLE II
Thermal Characterization of the Studied Homopolymers

Characteristics	Polymers synthesized	BPO			AIBN			ABCVA			ABCCH		
		0.025	0.05	0.08	0.025	0.05	0.08	0.025	0.05	0.08	0.025	0.05	0.08
T_i	Classic	220	235	230	215	216	215	210	220	220	240	240	245
	In MF	250	255	250	275	268	260	260	255	250	275	260	260
T_{max}	Classic	365	370	370	365	370	365	365	370	365	375	370	365
	In MF	395	385	385	380	385	385	390	395	390	390	385	390
Weight loss within T_i–T_{max} interval, %	Classic In MF	47 32	47 33	46 35	45 32	44 34	48 36	47 33	48 35	44 36	43 32	42 33	44 32
Activation energy, kJ/mol	Classic	142	137	145	112	144	123	134	103	97	125	134	140
	In MF	162	165	170	155	160	155	160	155	150	143	160	160
Reaction order	Classic	1.2	1.4	1.5	1.5	1.7	2.1	1.0	1.2	0.9	1.4	1.6	1.6
	In MF	1.1	1.4	1.4	1.0	1.1	1.5	1.5	1.1	1.1	1.5	1.4	1.4

The initial and maximum decomposition temperatures as well as the weight loss within the T_i–T_{max} interval are sustained also by the changes of E_a with conversion during degradation, which present also higher values for the homopolymers obtained in the presence of MF.

CONCLUSIONS

The present article reports the influence of a high magnetic field of 7 T in the radical polymerization of styrene initiated by benzoyl peroxide, 2,2′-azobis(2-methylpropionitrile), 4,4′-azobis(4-cyanopentanoic acid), and 1,1′-azobis(cyclohexan-1-carbonitrile). The magnetic field effect is evidenced by the kinetic data obtained during the processes and also by the molecular weights of the reaction products synthesized in the field. According to the reaction conditions the magnetic field presence induces a higher efficiency of the azonitrile compounds as initiators compared to benzoyl peroxide.

The intervened magnetokinetic effects are attributed to changes in the state of radicals from the singlet to the triplet state through a HF mechanism, transitions which are due to a high strength of external magnetic field.
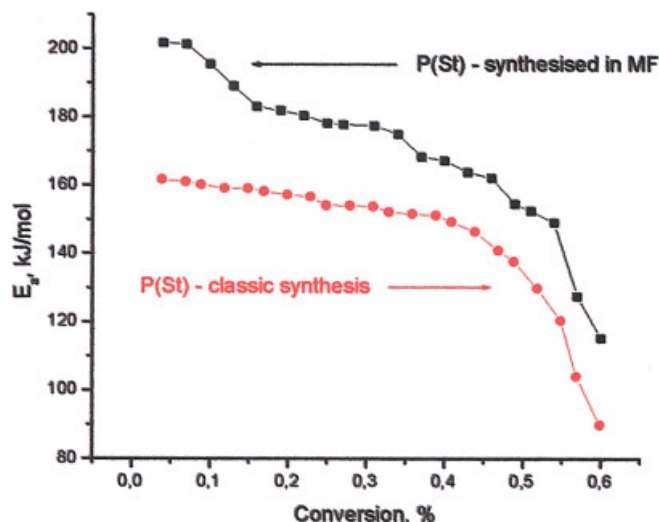
Figure 10 Dependence of E_a on conversion for PSt, using as initiator AIBN 0.025M%.

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