

Polymerization in Magnetic Field. XIX. Thermal Behavior of the Copolymers of Methyl Methacrylate with Glycidyl Methacrylate Synthesized in the Magnetic Field Presence

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Abstract: The paper evidences changes of thermal properties of poly(methyl methacrylate) as well as methyl methacrylate copolymers with glycidyl methacrylate (GMA) polymers synthesized classic and comparatively in a magnetic field. Samples of poly(methyl methacrylate) and methyl methacrylate copolymers with different amounts of GMA synthesized by radical emulsion polymerization with or without the presence of a continuous electro- magnetic field, they were thus compared. The thermal behavior was studied by Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA). The paper evidences the higher T_g as well as the higher thermal stability of the macromolecular chains structures synthesized in the presence of the electromagnetic field.

INTRODUCTION

The interest in the investigation of chemical reactions in magnetic field (MF) has grown in recent years [1-3]. The magnetic field effects (MFEs) were registered in the emulsion polymerization of styrene photoinitiated by dibenzyl ketone [4, 5]. Application of a moderate MF of 50–1000 G significantly accelerated the polymerization and resulted in an increase of the molecular weight of polystyrene obtained in the emulsion polymerization, due to the MFE attributed to a hyperfine mechanism [4, 5].

The copolymers containing glycidyl methacrylate (GMA) have received a special attention owing to their versatile applications such as for obtaining powder coating with better toughness, gloss and durability [6, 7]. The copolymerization of methyl methacrylate (MMA) with GMA has been studied previously and the reactivity ratios for this monomer pair have been also reported [8-10]. Their reactivity ratios are relatively close ($r_1(\text{GMA})=0.700\pm 0.001$ and $r_1(\text{MMA})=0.830\pm 0.002$ [10]), therefore we will consider similar behavior during reaction process in MF for both comonomers. Thermal behavior of PMMA and of MMA copolymers with GMA was also studied [10]. Piracha and Zulfiqar [11] studied the copolymers of MMA and GMA, with widely differing compositions, synthesized by bulk polymerization by using thermal volatilization analysis, thermogravimetry, differential thermal analysis and pyrolysis-mass spectrometry techniques. The apparent activation energies for the decomposition of the copolymers were calculated from the results of thermogravimetric experiments.

The condensable volatile degradation products have been identified after separation by sub ambient. Non-condensable products of degradation formed during thermogravimetric

analysis (TGA), were identified using a mass spectrometer attached to the TGA apparatus. They concluded that the presence of the second monomer (GMA) favors combination reactions rather than disproportionation as termination step. Thus, the copolymers degradation occurs only at high temperatures at which the polymers that have no terminal unsaturation degrade. This involves random scission followed by depropagation.

In our previous papers [12-14] it was presented a comparative study regarding the magnetic field effects upon copolymerization process between methyl methacrylate and glycidyl methacrylate using the procedure of radical emulsion polymerization. It has been established that the magnetic field affects both kinetic parameters of the synthesis as well as some of the characteristics of the macromolecular compounds [14].

In the present paper it is presented the effect of the MF upon thermal behavior of poly(methyl methacrylate) and methyl methacrylate copolymers with different amounts of GMA synthesized by radical emulsion polymerization with or without the presence of the field.

EXPERIMENTAL PART

Materials

The monomers methyl methacrylate (MMA) ($c > 99$ wt %, Merck), glycidyl methacrylate (GMA) ($c > 97$ wt %, Fluka) were freshly distilled before use.

Sodium lauryl sulfate ($\text{C}_{12}\text{H}_{25}\text{O}_4\text{SNa}$) – (SLS) from Sigma ($c > 95$ wt %,.) without further purification was used as tensioactive agent.

Potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$) – (KPS) was twice recrystallized from twice distilled water.

In all experiments the twice distilled water, which contained no foreign ions, was used.

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Polymerization Process

MMA copolymers with two different compositions of GMA (3 wt%, and 25 wt%) were prepared by emulsion polymerization of appropriate mixture of monomers at 70°C, with 0.8 wt % KPS and 3 wt % SLS respectively, in magnetic field (MF) and classical way (CW).

The polymerization reaction in the continuous electromagnetic field of 1500 G was made in the same conditions with classical variant: similar vessel shape and geometry, and the same reaction parameters and type of stirring. The emulsion polymerization process developed by classic way (CW) and in the presence of the magnetic field (MF) was described in detail in previous papers [12, 13].

The prepared polymeric samples were precipitated in methanol, purified by reprecipitation in methanol from acetone solution, dried under vacuum at room temperature for 48 hours and stored in desiccators.

The molecular structures was appreciated *via* the bands' identification of the FTIR spectra (on a DIGILAB, Scimitar Series, USA, spectrophotometer, the resolution recording was 4 cm⁻¹; sample concentration 3 mg in 500 mg KCl tablet). The composition of each copolymer was determined from NMR data.

DSC curves were recorded with a heat flow Mettler Toledo DSC-822 under inert atmosphere of nitrogen. The following procedure of heating/cooling was used:

- The first cooling: the samples were cooled from 25 to -70°C at a heating rate of 20°C/min; kept at -70°C for 1min.

- I RUN: one sample was heated from -70 to 150°C; with a heating rate of 20°C/min kept at 150°C for 1min;
- The second cooling: the samples were cooled at 50°C/min to -70°C and kept for 1 min.
- II RUN: the samples were finally heated to 150°C at 20°C/min.

The Tg values are determined at the inflection point on the thermo-analytical curves.

Thermo-gravimetric analysis was also performed in nitrogen atmosphere in a temperature range from 30°C to 700°C by means of TGA/DTA 851 Mettler. Two heating rates were used: 5 and 20C°/min. Two recordings were performed for each sample.

RESULTS AND DISCUSSION

Table 1 presents the characteristic bands from FT-IR spectra and composition of the copolymers synthesized by classical and in MF ways.

Spectroscopic characterization (Table 1) confirms the presence of both comonomers in copolymers structure in amounts close to those employed in reaction feed. As it is expected, the GMA corresponding bands – at 1600 cm⁻¹ and 2800–3100 cm⁻¹ – increase with the enhance of GMA content. Some indications about structural differences in the copolymers synthesized in MF presence in respect with those prepared by CW are also underlined. Thus, several bands show higher intensities (1600 cm⁻¹, 1690-1760 cm⁻¹, 1080 and 1300 cm⁻¹, 2800-3100 cm⁻¹). The intensities of the vibration oscillation absorption corresponding to the polymers

Table 1. Spectral Data of the PMMA and MMA-GMA Copolymers Synthesized without and in MF Presence

Sample	FTIR (cm ⁻¹) Band assignement	1	H-NMR Chemical shift (δ ppm)	2	
				CW	MF
PMMA	- 1380 cm ⁻¹ C-H absorption of the methyl group; -1690-1760 cm ⁻¹ the carbonyl (C=O) absorption; - 1080 and 1300 cm ⁻¹ the C-O absorption.	- similar - higher intensity of the band in the MF presence comparati-vely with CW;	2.0 (CH ₃), 3.6 (OCH ₃)	0	0
P(MMA-co-GMA)=97:3	- 1380 cm ⁻¹ C-H absorption of the methyl group; -1690-1760 cm ⁻¹ the carbonyl (C=O) absorption; - 1080 and 1300 cm ⁻¹ the C-O absorption. - 2800–3100 (–CH str),	-similar - similar -similar -similar	2.0 (CH ₃), 3.6 (OCH ₃) 3.6–3.7 {m overlapped, 2CH ₂ (epoxide)}	2,853	2,05
P(MMA-co-GMA)=75:25	-1600 cm ⁻¹ –C=O stretching - 1080 and 1300 cm ⁻¹ the C-O absorption. 1380 cm ⁻¹ C-H absorption of the methyl group; -1690-1760 cm ⁻¹ the carbonyl (C=O) absorption; - 2800–3100 (–CH str)	- higher intensity of the band in the MF presence comparati-vely with CW. - higher intensity of the band in the MF presence comparati-vely with CW; - higher intensity of the band in the MF presence comparati-vely with CW; -similar	2.0 (CH ₃), 3.6 (OCH ₃) 3.6–3.7 {m overlapped, 2 CH ₂ (epoxide)}	26,05	26,92

1 - Differences observed in spectra of compounds obtained in MF presence.
2 - GMA in copolymer % determined from NMR spectra.

synthesised in the field are attributed to the modification of the strength constant introduced by the inductive and electro-meric effects appearing supplementary in the polymeric structures prepared in the field conditions.

The DSC thermo-analytical curves of samples prepared by classic way and in magnetic field respectively are given in Figs. (1 and 2). A transition (glass transition) is observed in all curves in the first and second run. The temperature corresponding to the inflection point of the transition depends on the synthesis conditions and copolymer compositions (Table 2).

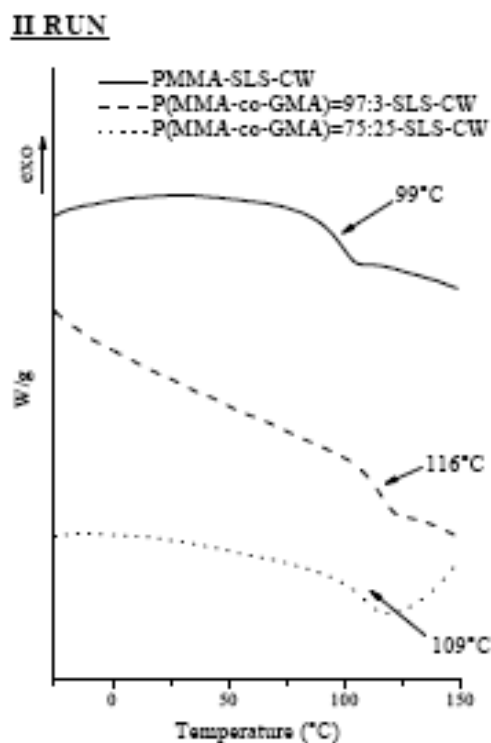


Fig. (1). The DSC curves of the samples synthesized by classical way.

In the first run (not shown) a small endothermic peak was evidenced at about 70-75°C for all 3 polymeric samples. This peak does not appear in the second run. Fig. (1) corresponds to second run. Here transition corresponding to T_g is

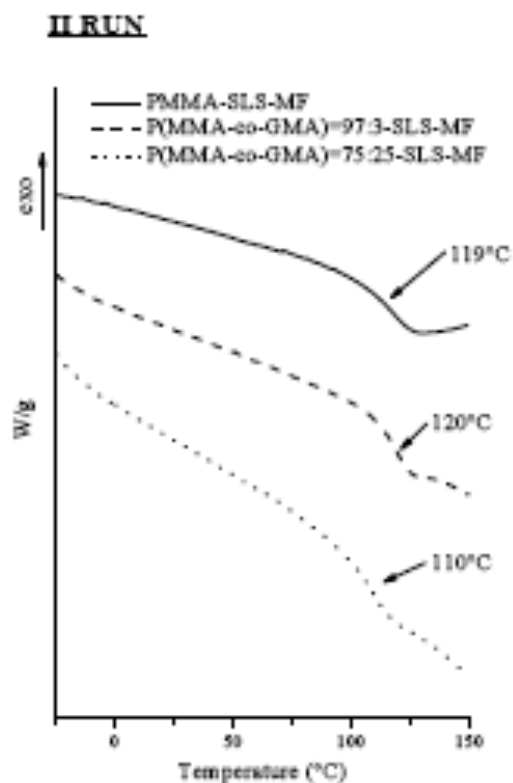


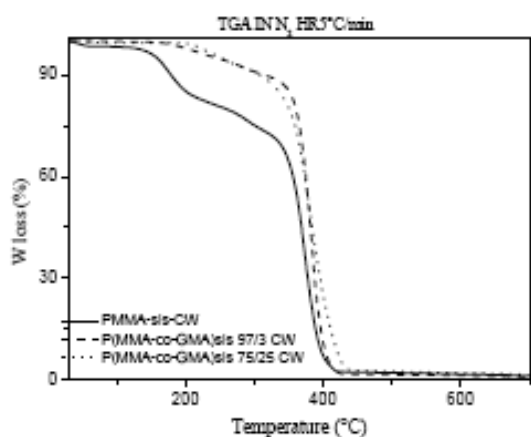
Fig. (2). The DSC curves of the samples synthesized by MF way.

more evident. For PMMA-SLS-CW, T_g was found at 99°C; adding 3 wt% of GMA causes the increase up to 116°C and the value decreases to 109°C when GMA is 25% (Table 2). If we compare the values of I run and II run, it is evident that the values are similar with the exception of PMMA-SLS-CW. This sample has the obtained values placed in the interval 95-108°C which was also given in literature [15]. The samples synthesized in MF exhibit well evident transition temperatures at 119, 120 and 110°C for PMMA, P(MMA-co-GMA)=97:3, and P(MMA-co-GMA)=75:25, respectively. Again the sample with highest GMA content shows a T_g at 110°C, lowered than for PMMA-SLS (Table 2).

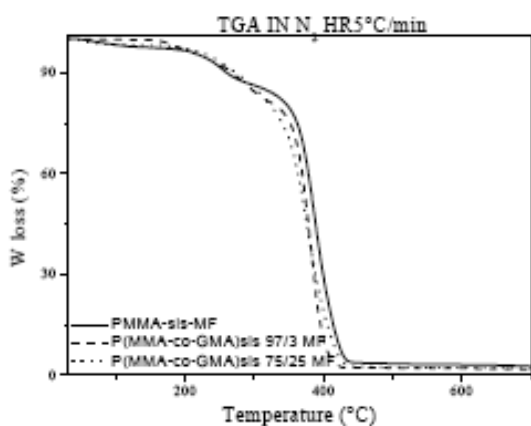
If we compare the CW sample with those prepared in MF (Fig. 1 and 2) it can be observed that the MF induces an increase of the T_g values, especially in case of PMMA (99°C

Table 2a. T_g , the Onset Temperature (T_i) and the Temperature of the Maxima of the Peak (T_{max}) for Samples Synthesized in CW and in MF Presence

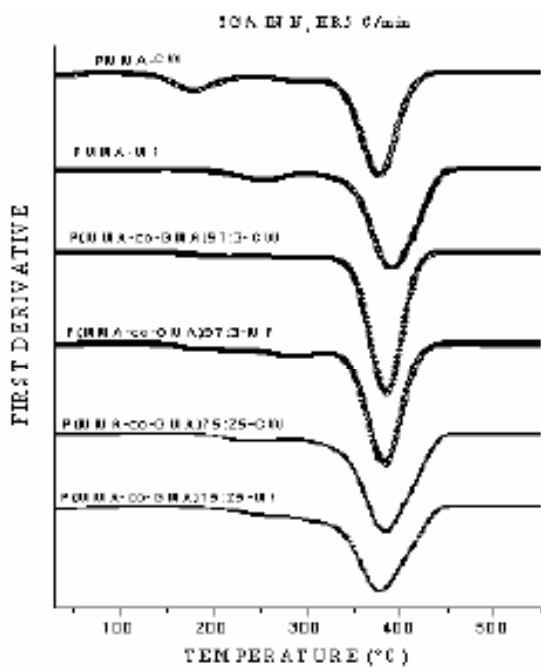
Samples	T_g II RUN (°C)	First peak		Second (main) peak	
		T_i HR 20°C/min	T_{MAX} HR 20°C/min	T_i HR 20°C/min	T_{MAX} HR 20°C/min
PMMA- CW	99	140	200	325	394
PMMA- MF	119	248	280	342	414
P(MMA-co-GMA)=97:3- CW	116	-	-	328	402
P(MMA-co-GMA)=97:3- MF	120	255	310	345	402
P(MMA-co-GMA)=75:25- CW	110	-	-	345	403
P(MMA-co-GMA)=75:25- MF	109	270	315	350	411



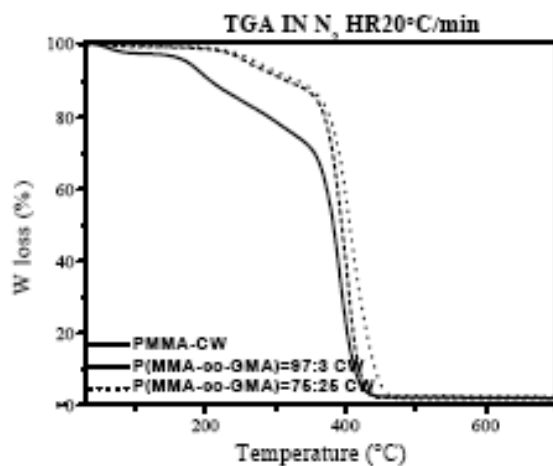
(a)



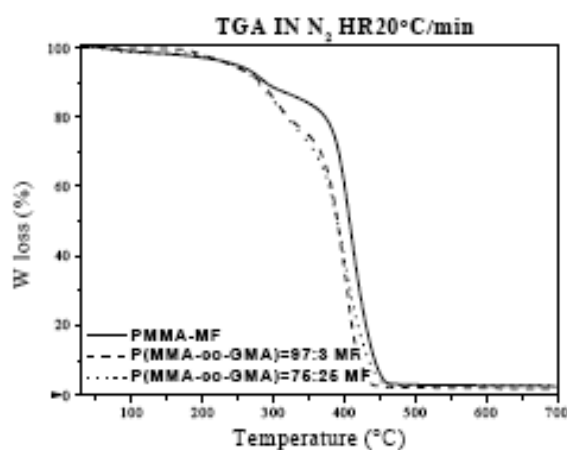
(b)



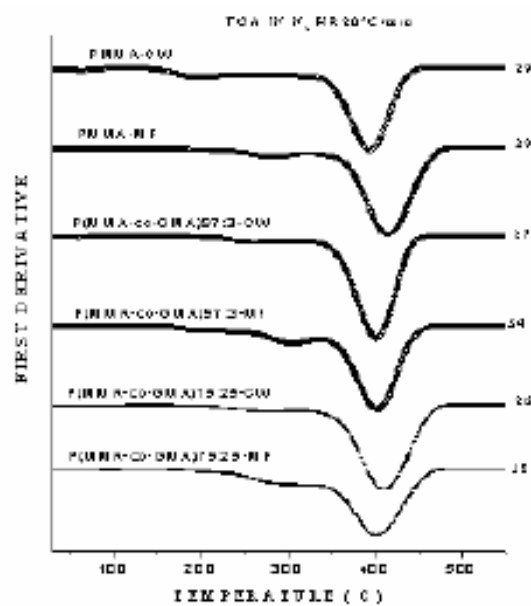
(c)



(a)



(b)



(c)

Fig. (3). TGA curves for PMMA and GMA/MMA copolymers polymerized by CW (a), in MF presence (b) and DTG curves of all samples studied (c) (dynamic atmosphere of nitrogen 5 °C/min).

Fig. (4). TGA curves for PMMA and GMA/MMA copolymers polymerized by CW (a), in MF presence (b) and DTG curves of all samples studied (c) (dynamic atmosphere of nitrogen 20 °C/min).

Table 2b. The Characteristic Temperature of Decomposition of the Samples CW Synthesized and in MF Presence

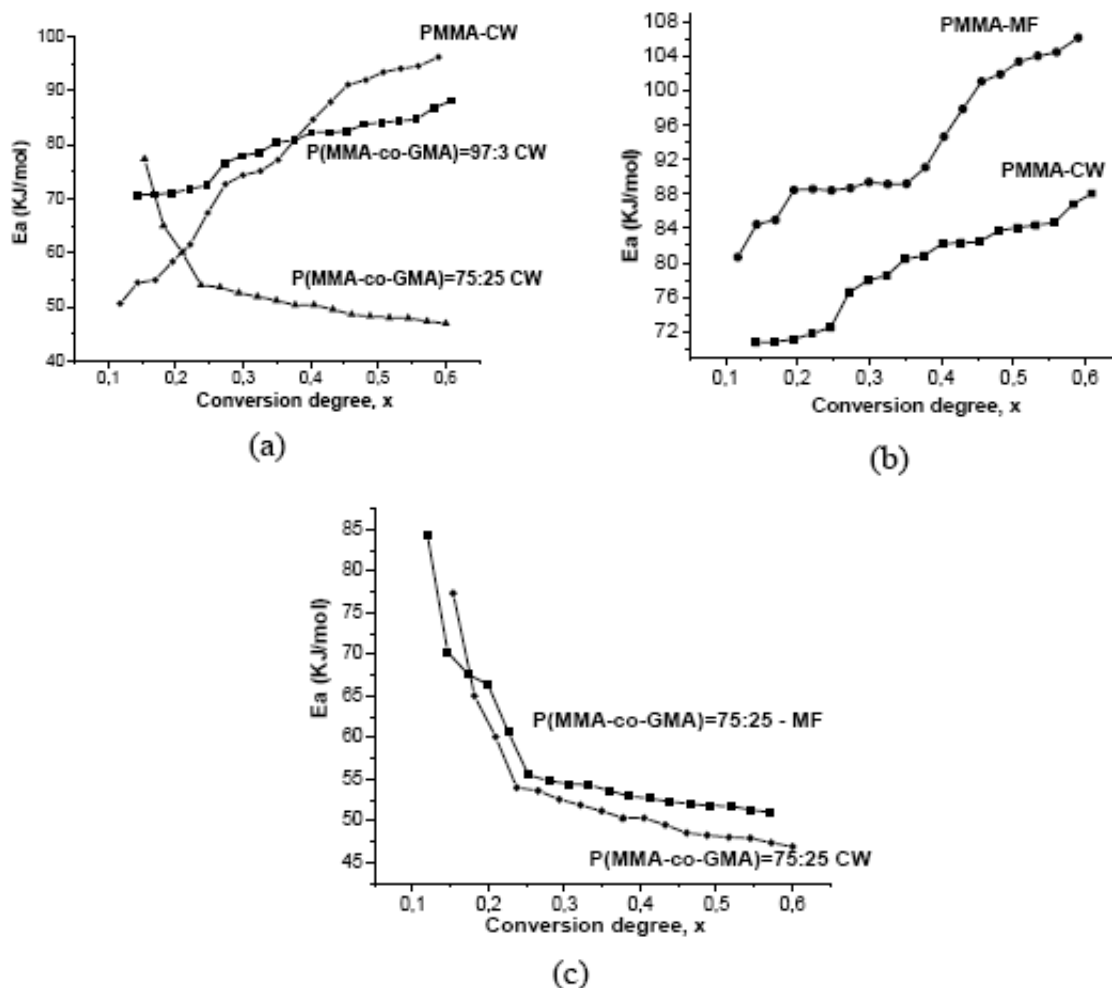
Samples	$T_{50} \text{ } ^\circ\text{C}$		$\Delta W\%$		n		$E_a \text{ (kJ/mol)}$	
	CW	MF	CW	MF	CW	MF	CW	MF
PMMA	245	308	96.5	82.8	0.9	0.3	64.1	78
P (MMA-coGMA) 97: 3	250	250	93	73.5	0.7	0.2	54.5	76
P (MMA-co-GMA) 75: 25	210	180	92	66	0.5	0.1	34.3	42

Δw - weight loss at final of the process.

T_{50} - temperature corresponding to 50 wt% weight loss.

n- reaction order.

E_a - global activation energy

**Fig. (5).** Activation energy of the samples.

CW in respect with 119°C -MF Table 2). The increase of T_g values are explained by morphological changes of the samples synthesized in MF presence being attributed to the catalytic effect of the field on the molecules that can be reshaped through growing of distance interactions and modification of angles between bonds. Studies are in progress to confirm this hypothesis. Table 2 reports also the onset temperature (T_i) and temperature of the maxima of the peak corresponding to the first derivative (T_{max}) from the TGA/DTG curves. The maximum fits to the main inflection point of the curves. There is a difference between thermal behavior of the

samples prepared in MF presence comparable with those CW prepared – Figs. (3 and 4) and data from Table 2 –. For all samples from the former category an additional thermogravimetric step appears at temperature ranging from 248°C to 270 °C with maximum temperature of weight loss of 280-315°C. The weight loss varies between 11.6% wt for PMMA -MF to 13.8 wt% and 19.8 wt% for copolymers with 3% and 25% GMA content respectively. Generally thermal characteristics corresponding to the samples polymerized in MF are superior of those polymerized by CW. PMMA has the best

thermal stability when it is synthesized in the presence of magnetic field.

This behavior is also confirmed by the variation of the activation energy with conversion degree which was determined using the Reich-Levi method and Coats equation based on the weight loss during the thermo-oxidative process [16, 17, 18]. The evolution of the activation energy values correlated with the GMA content is presented in Fig. (5) and Table 2b. At a given MMA/GMA ratio, growth of the GMA content determines the decrease of the activation energy. At the same time the MF presence determines an increase of the global activation energy E_a (Fig. 5b, c).

The influence of the MF on the thermal behavior is explained on the pre-ordering-structure of the copolymers as a result of the magnetic field presence during syntheses [19, 20].

CONCLUSIONS

PMMA as well as MMA copolymers with a monomer bearing functional groups – 2,3 epoxy propyl methacrylate – have been obtained by classical and in magnetic field polymerization process. It has been established that the presence of the magnetic field during emulsion polymerization of methyl methacrylate and methyl methacrylate copolymerization with GMA leads to the homo- and copolymers exhibiting higher glass transition temperatures and complex thermal stabilities. The increase of T_g values are explained by morphological changes of polymers synthesized in MF presences, being attributed to the catalytic effect of the field on the molecules that can be re-shaped through growing of distance interactions and modification of angles between bonds as well as to the modification of the strength constant introduced by the inductive and electromeric effects appearing supplementary in the polymeric structures prepared in the field conditions.

Structural and morphological studies are in progress to confirm this hypothesis.

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