

KINETIC ASPECTS REGARDING METHYL METHACRYLATE POLYMERIZATION IN A HIGH MAGNETIC FIELD

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Abstract: It is evidenced the effect of a high magnetic field of 7 T in some reactions of methyl methacrylate polymerisation. The intervened magneto-kinetic modifications are correlated with the system of radical initiation, respectively: benzoyl peroxide, 2, 2' azo-bis (2-methyl-propionitrile), 4, 4' - azo-bis (4-cyano-pentanoic acid), and 1, 1' azo-bis (cyclohexan -1- carbonitrile). The reaction products are also characterized from the viewpoint of their molecular weights and thermal stability simultaneous with the reaction conditions.

Key words: *magnetic field, methyl methacrylate radical polymerization*

INTRODUCTION

Spin polarisation 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. The magnetic effects induced by singlet – triplet transitions occur within the radical pair lifetime in the “cage” [1-4]. The dependence of chemical reactions on the magnetic field presence can be included in the following cases or combinations of them:

- dependence through $\Delta g\beta B$ effect ($\Delta g = g^\alpha - g^\beta \neq 0$) (with g – gyration rate, β - Bohr – Procopiu magneton, and B – magnetic field intensity) ;
- dependence owing to the hyperfine interactions ($\Delta g = 0$) ;
- dependence owing to a combination of the Δg effect and hyperfine interactions.

Certain property enhancements may be obtained in polymeric materials if they are processed in a magnetic field. Just as electric fields are used in the processing of materials on an industrial scale, so will magnetic fields be used once they have been more explored for these applications. Thus, the utilization of continuous external magnetic fields during a reaction can lead to an improvement in some properties of synthesized macromolecular compounds. These include very low conductivities, transparencies, and low elasticity module, chemically tunable properties and good processability. These added to the basic

importance of magnetic molecular materials justify interest in their potential usefulness, and consequently they have received tremendous attention in recent years [5-8]. In one of our previous paper we reported the effect of a high magnetic field (MF) of 7 T during methyl methacrylate polymerisation initiated by the following azo-compounds: (1) 2, 2'- azo-bis (2-methylpropionitrile), (2) 4, 4' - azo-bis (4-cyano-pentanoic acid), and (3) 1, 1' azo-bis (cyclohexan -1- carbonitrile). The MF influence was concretized in obtainment of higher conversions and a reducing of the induction period of the reaction. In the present investigation, in order to confirm the magnetic field effect (MEF) upon the decomposition reaction of mentioned azo-initiators as well upon the obtained macromolecular compound, a comparative study concerning some characteristics of the synthesised polymers with and without the MF presence, it is performed.

EXPERIMENTAL SECTION

Radical polymerisation of methyl methacrylate (MMA) was conducted in solution classic and in a magnetic field of 7 T (a cryomagnet for NMR spectroscopy – product of Oxford Spectrospin Cryomagnetic Systems).

The study was performed with the following variants of initiators: benzoyl peroxide (BPO), 2, 2' azo-bis (2-methylpropionitrile) (AIBN), 4, 4' – azo-bis (4-cyano-pentanoic acid) (ABCV), and 1, 1' azo-bis (cyclohexan -1- carbonitrile) (ABCCH).

The reaction conditions were:

the monomer and solvent were distilled just before use;

a initiator concentration of 0.025 M%, 0.05 M% and respectively 0.08 M% has been utilized;

the ratio monomer / solvent (tetrahydrofuran - THF) was 1/5;

the reaction temperature was 65° C;

the initiators were used without further purification

the reactions have been performed in an inert atmosphere of Argon and without shaking.

For the reactions in magnetic field were realised ampoules, with a capacity of 50-ml, with an appropriate geometry according to the field. A thermostat has been used to heat the ampoules.

The same reaction conditions have been used for the polymerisation performed in or out the magnetic field of 7 T (a cryo-magnet of 7 T for NMR spectroscopy – a product of Oxford Spectrospin Cryomagnetic Systems).

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

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 magnetic field influence.

TG and derivative thermogravimetry (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 -Al₂O₃.

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 N₂, and 25°- 400°C temperature range.

Reproducible data have been obtained for all experiments, considering the course of reactions, the determination of conversions and average molecular weights of the synthesised polymers.

RESULTS AND DISCUSSION

Magnetic field influence becomes obvious when, in radical pairs from the system, the field will induce or prevent transitions between near fundamental electronic states. 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. Thus changes in spin multiplicity of the radical pairs under the influence of the field determine the subsequent magneto-kinetic effects (MKE). As was already mentioned the strength of the continuous external magnetic field lead to magnetic-field-dependent chemical yields and kinetics for the processes. The application of a strong external magnetic field to a radical pair determines the "splitting" of T_+ and T_- from T_0 , however T_0 and S remain degenerate.

Taking into account the mechanism of thermal decomposition of the initiators and also the intensity of the continuous external magnetic field in which the reactions have been developed, MKE registered in methyl methacrylate polymerization reactions were included in a typical case of hf -mechanism in high magnetic field. In these conditions of high field only the intersystem crossing from S to T_0 was possible and thus $1/3$ of the geminate triplet population undergone cage recombination and $2/3$ (T_+) can escape. The radicals escaped from the cage enhance and consequently the quantum yield for the polymerization in the cage increases. The increase of both initiation efficiency and reaction rate and yield was brought by the modification of the ratio of "cage" to "escape" radicals, which coincide with the diminution of the "cage" effect phenomenon. As normally expected the most obvious magneto-kinetic effects were registered at the beginning of processes, during the reaction induction period after singlet - triplet transitions generated by the magnetic field in the electronic state of radicals.

The magnetic field effect can be also 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. Thus, the obtained kinetic data were completed by the determination of the molecular weights to evidence the MF effect as well the efficiency of the field knowing that the macromolecular compounds obtained in magnetic field present higher molecular weights as related to their homologues synthesised in the absence of the field (Table 1). This fact is attributed to the action of the magnetic field on the macromolecular chains, termination by recombination being preferred to the detriment of disproportionation.

Table 1
Molecular weights values of the synthesized polymers

Initiator variant, %		$M_w \times 10^{-5}$ – Synthesis variant		$M_n \times 10^{-5}$ – Synthesis variant		P – Synthesis variant	
		Classic	In MF	Classic	In MF	Classic	In MF
POB	0.025	10.5	24.19	5.49	11.89	1.91	2.03
	0.05	9.67	22.47	3.95	9.49	2.45	2.37
	0.08	4.79	15.55	3.30	7.89	1.45	1.97
AIBN	0.025	9.52	15.79	6.22	7.51	1.53	2.10
	0.05	8.98	14.34	5.70	7.04	1.58	2.04
	0.08	7.89	12.39	5.23	6.53	1.51	1.89
ABCV A	0.025	9.05	15.15	5.00	8.38	1.81	1.81
	0.05	8.50	11.53	4.66	6.65	1.82	1.73
	0.08	7.12	9.94	3.99	5.88	1.78	1.69
ABCC H	0.025	2.18	15.95	1.30	8.35	1.68	1.91
	0.05	2.07	14.72	1.20	7.46	1.7	1.97
	0.08	1.92	11.58	1.07	5.38	1.79	2.15

The comparatively data obtained via GPC corresponding to the polymers synthesized according to the fourth's variants of initiators and the procedures in and out the magnetic field confirm and emphasize the registered kinetic data and MKE.

Thermal behaviour of the polymers, obtained with or without the MF presence, was also assessed from their thermal degradation pattern using TG techniques in order to evidence MF effect upon the reaction products synthesised in the field presence. It is evidenced the higher thermal stability of the polymers obtained in MF demonstrated by the initial and maximum decomposition temperatures and the weight loss within $T_i - T_{max}$ interval (Table 2). These higher values corresponding to the polymers obtained in MF were attributed to zones with ordered arrangement into the polymeric structures as a result of the magnetic field presence during the synthesis.

The modifications of E_a of the degradation process were investigated using both Coats – Redfern [9] and Levi – Reich methods [10-11] for having a complete image of the thermal behaviour of the studied polymers. The former method was used to evaluate the E_a values (Table 2), while by the latter one, the changes of E_a with conversion during degradation was evaluated (Figure 1). Visual inspection of the plots of the synthesised polymers (with or without the MF presence) shows that the thermal degradation in the range 150 °C – 600 °C proceeds in one main step and at different rates, with higher rate in case of polymers classic synthesised.

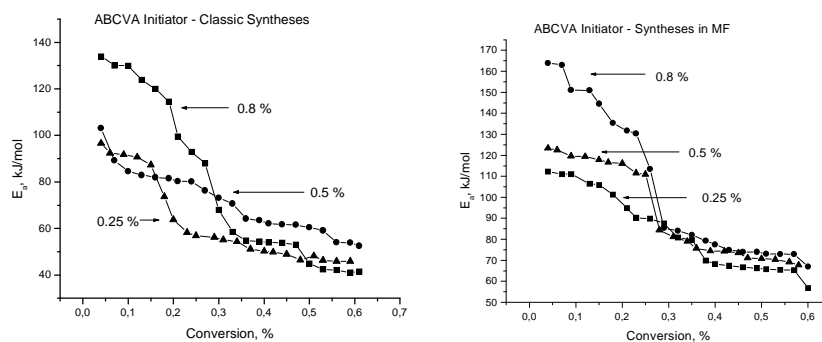
Table 2
Thermal characterization of the studied polymers

Characteristics	Polymers syntheses	Initiator variant											
		POB, %			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	165	160	160	150	162	157	138	140	132	140	140	145
	In magnetic field	180	185	180	175	180	180	175	180	175	175	180	175
T_{max}	Classic	325	327	330	315	340	325	345	330	332	315	330	355
	In magnetic field	360	365	365	355	355	350	360	365	360	350	355	360
N^*	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 magnetic field	1.1	1.7	1.4	1.0	1.1	1.9	1.5	1.1	1.1	1.5	1.4	1.4
ΔW^*	Classic	47	47	46	45	44	48	47	48	44	43	42	44
	In magnetic field	32	33	35	32	34	36	33	35	36	32	33	32
E_a^{***}	Classic	142	137	145	112	144	123	134	103	97	125	134	140
	In magnetic field	162	165	170	155	160	155	160	155	150	143	160	160

N^* - Reaction order

ΔW^{**} - Weight loss within $T_i - T_{max}$ interval

E_a^{***} - Activation energy, kJ/mol



a

b

Fig. 1. - Dependence of E_a on conversion for PMMA synthesis: classic (a) and in MF (b) with different percentage of ABCVA initiator

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

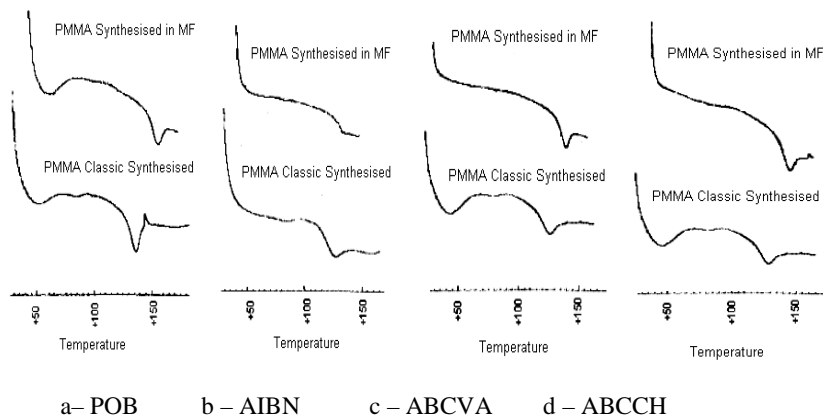


Fig. 2. - DSC shapes of PMMA synthesized with 0.05% initiator variants with and without the MF presence

The higher thermal stability of the PMMA synthesized in MF is confirmed also by DSC measurements. T_g values for the classic synthesized polymers (100 °C – 120 °C) correspond to values from literature. However, higher glass transition temperatures are registered for all variants of (homo) polymers synthesized in MF, even these modifications are only into a range of 3 to 5°.

CONCLUSIONS

The present paper confirms the influence of a high magnetic field of 7 T in the radical polymerisation of methyl methacrylate initiated by benzoyl peroxide, 2,2' azo-bis (2-methyl-propionitrile), 4,4' - azo-bis (4-cyano-pentanoic acid), and 1,1' azo-bis (cyclohexan-1-carbonitrile) being evidenced through the modifications brought upon some characteristics of the polymers by the MF during syntheses.

Thus, magnetic field effect is evidence by the molecular weights of the reaction products synthesised in the field as well as by a higher thermal stability of polymers synthesised in the field.

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