Polymerization in a magnetic field: 1. Influence of esteric chain length on the synthesis of various poly(methacrylate)s

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This paper describes the influence of an external continuous magnetic field on the radical bulk polymerization of methyl, ethyl and butyl methacrylates. The variation in the effect of the field on the ester's alkylic substituent length is described. The processes were compared with the classical bulk method. Some properties of the synthesized poly(methyl methacrylate), poly(ethyl methacrylate) and poly(butyl methacrylate) are also presented.

(Keywords: magnetic field; polymerization; methacrylates)

INTRODUCTION

Most vinylic, acrylic and dienic monomers may be subjected to radical polymerization. Acrylic and methacrylic esters are well known as polymerization monomers, their high reactivity permitting lower amounts of initiators in the synthesis as well as a shorter reaction time compared with other vinylic monomers (although at a higher polymerization temperature). Also, it is well known that the polymerization heat of acrylates and methacrylates increases when the carboxylic hydrogen is progressively substituted by methyl, ethyl, butyl, etc. groups. This is due to the steric hindrances preventing growth in proportion to the head–head or tail–tail additions, compared to the head–tail or tail–head ones with an increase in length of the alkylic substituent chain. The existence of steric hindrances is also seen in the case of acrylates compared with methacrylates by the higher values of the former's polymerization rates.

In the last few years the influence of an external continuous magnetic field on the development of the polymerization reaction of some vinylic, acrylic or methacrylic monomers has been reported[1–9]. This reduces the reaction's induction period, increasing both polymerization rate and conversion. The modifications were attributed to the transitions in the radical pairs from the singlet to the triplet state induced by the field's presence.

The literature also gives indications of the modification of some physico-chemical characteristics of the magnetized solutions[10–14]. Thus, there have been modifications of surface tension, electrical conductivity, density and optical properties caused by restructuring occurring in solution, by changes in the interaction between atoms and molecules and their aggregation, and by force interactions and dipole–dipole orientation interactions as a result of magnetization. The field's effect was also observed experimentally in the properties of the products as a result of reactions developed in a magnetic field[15–20].

This paper discusses the influence of an external continuous magnetic field on the radical polymerization in bulk of some methacrylates with various esteric chain lengths as well as the dependence of the field's effect on the alkylic substituent length. Thus polymerization reactions of methyl, ethyl and butyl methacrylate having occurred in the classical manner were performed in parallel in a continuous magnetic field of 0.11 T, the synthesis variants being compared in relation to the temporary polymerization rate, activation energy and conversion. The products of the reaction were also compared from the viewpoint of their properties.

EXPERIMENTAL

Methyl, ethyl and butyl methacrylate were subjected to radical polymerization in bulk under the synthesis conditions shown in *Table 1*. The methacrylic esters were twice distilled on a vacuum line and then stored at −20°C prior to use. As initiator, benzoyl peroxide was used (dissolved in cold chloroform, precipitated in methanol and dried in phosphorus pentoxide), 0.3% with respect to the monomer. The obtained samples of poly(methyl methacrylate), poly(ethyl methacrylate) and poly(butyl methacrylate) were separated and purified by dissolving in acetone and precipitating with methanol and the homopolymers were then dried under vacuum at 40°C.

For determination of the molecular weights the synthesized homopolymers were fractionated by using acetone–methanol as a solvent–non-solvent mixture. The molecular weights were determined using the Mark–Houwink relation, applied to the first fractions of the homopolymers as follows:

For poly(methyl methacrylate)

$$[\eta] = 7.24 \times 10^{-3} \bar{M}_w^{0.76} \qquad (1)$$

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Table 1 Conditions for the synthesis of poly(methyl methacrylate), poly(ethyl methacrylate) and poly(butyl methacrylate)

		Reaction conditions[a]		
Monomer	Synthesis variants	Temperature (°C)	Time (min)	Magnetic induction (T)
Methyl methacrylate (MMA)	A	70	30	–
	B	70	30	0.11
Ethyl methacrylate (EMA)	C	70	30	–
	D	70	30	0.11
Butyl methacrylate (BuMA)	E	70	30	–
	F	70	30	0.11

[a] Radical polymerization with 0.3% benzoyl peroxide as initiator

Table 2 Data for the occurrence of reactions

Synthesis variants	Polymerization rate at different times[a]						Conversion at 30 min (%)
	V_5	V_{10}	V_{15}	V_{20}	V_{25}	V_{30}	
A	0.05	0.50	1.40	1.80	1.90	2.10	38
B	0.70	0.80	2.10	3.10	3.60	4.50	80
C	–	0.39	1.05	1.40	1.60	2.40	30
D	0.30	0.75	1.60	2.00	2.70	6.70	57
E	–	0.32	0.60	1.15	1.48	3.27	24
F	0.12	0.73	0.94	1.35	2.14	9.51	41

[a] V_i in mol l^{-1} s^{-1}

For poly(ethyl methacrylate)

$$[\eta]=2.83\times10^{-3}\bar{M}_w^{0.79} \qquad (2)$$

For poly(butyl methacrylate)

$$[\eta]=0.974\times10^{-4}\bar{M}_w^{0.68} \qquad (3)$$

Intrinsic viscosities (dl g^{-1}) were measured using an Ubbelohde suspended-level viscometer. The investigated temperature range extended from 20 to 50°C.

The synthesized homopolymers were characterized by their thermal stability (Paulik–Paulik–Erdely type derivatograph, heating rate of the polymeric films, 12°C min^{-1} in air, differential thermal analysis drop calibration with $NaNO_3$). All experiments were reproducible and analysed the course of the reaction as well as the properties of the homopolymers obtained.

RESULTS AND DISCUSSION

The influence of the external magnetic field on the bulk radical polymerization processes which led to obtaining poly(methyl methacrylate), poly(ethyl methacrylate) and poly(butyl methacrylate) was assessed by comparing the conditions of synthesis presented in *Table 1. Figure 1* plots conversion *versus* time for the two variants of methacrylic polyester synthesis, i.e. in and out of a continuous external magnetic field with a 0.11 T intensity. Thus the influence of the magnetic field in the polymerization of methyl methacrylate is seen by an increase in conversion from 38% (in variant A – the classical one) to 80% (see *Table 2*) along with a reduction in the reaction's induction period (*Figure 1a*) and activation energy (*Table 3*).

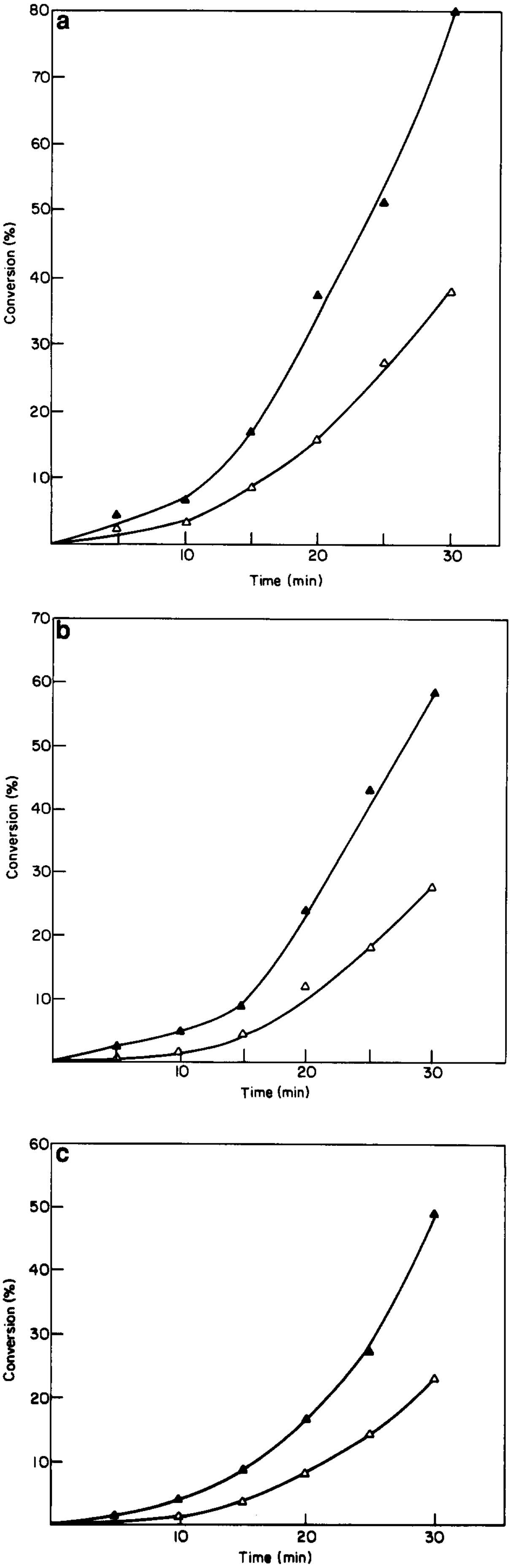

Figure 1 The development of bulk polymerization (▲) with and (△) without application of the magnetic field. a, Methyl methacrylate; b, ethyl methacrylate; c, butyl methacrylate

Table 3 Characterization of the synthesized homopolymers

Homopolymer synthesized through variant	Activation energy (kcal mol^{-1})	$\bar{M}_w \times 10^{-3}$	Initial decomposition temperature, θ_i (°C)	Temperature of maximum decomposition, θ_{max} (°C)	Weight loss within $\theta_i - \theta_{max}$ interval (%)
A	23	320	165	320	38.30
B	18	430	180	330	26.00
C	25	720	160	270	36.00
D	19	930	180	290	26.00
E	26	1100	145	240	34.50
F	20	2500	180	265	24.00

In obtaining poly(ethyl methacrylate) the increase in conversion through application of the external magnetic field is 1.9-fold (*Table 2*), which occurs concomitantly with reductions in the induction period (*Figure 1b*) and the activation energy (*Table 3*). It must also be noted that, as the reaction progresses, the temporary polymerization rate is significantly increased (*Table 2*).

The contribution of the magnetic field to the synthesis of poly(butyl methacrylate) is also seen in an increase in conversion of 1.71-fold (*Table 2*) and in a decrease in the induction period (*Figure 1c*) and the activation energy (*Table 3*). Significant increases in the temporary polymerization rate are recorded at longer reaction times (*Table 2*).

Such behaviour may lead to the following conclusions:

1. Reduction in the reaction's induction period and an increase in conversion are a consequence of transitions from the singlet to the triplet state in the radical pairs. An increase in the initiation efficiency through a reduction in the 'cage' effect increases the life of the initiator radicals in the triplet state as a result of the presence of the magnetic field.
2. An increase in the temporary polymerization rate, together with a decrease in the activation energies, are caused by the orientation of the reaction compounds, i.e. polar monomers, within the magnetic field. The polymerization rate increases with reaction time, especially in the case of esters with longer alkylic chains, as a consequence of the difficulties in ordering caused by steric hindrances.

From estimations made by Pascal's method[24] the constants of the diamagnetic susceptibilities corresponding to monomers are: $\chi_{MMA} = -28.25$, $\chi_{EMA} = -40.11$, $\chi_{BuMA} = -63.83$. Experimental determinations (by means of the Quinque device, generally used in evaluating a liquid's magnetic susceptibilities[25]) have confirmed the theoretical values of the characteristics. Consequently, in accordance with the values determined for the diamagnetic susceptibilities, the magnetic field's effect should be more evident and efficient in syntheses employing butyl methacrylate compared with the other two monomers.

The 70°C temperature at which the reaction is developed generates disorder in the particles of the components of the polymerization system through thermal agitation. In parallel with singlet–triplet transitions, the magnetic field also tends to order the system's polar compounds. Normally, for greater lengths of the alkylic substituents of methacrylic acid, ordering will be more difficult due to steric hindrances. This requires a longer period, which is reflected in higher values of the temporary polymerization rates, corresponding to longer reaction times. It also explains the reduction in the anticipated effect of the magnetic field upon the polymerization reaction of butyl methacrylate (a monomer with the lowest diamagnetic susceptibility) compared with ethyl and methyl methacrylate.

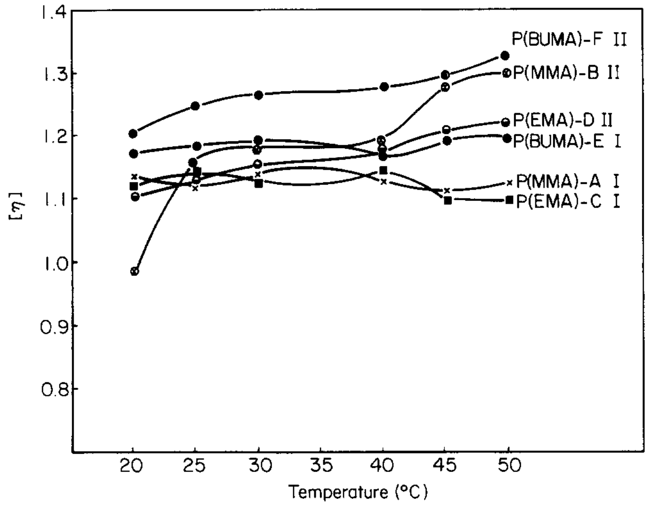

Figure 2 Variation of intrinsic viscosity with temperature for the benzene solutions of the synthesized homopolymer variants in (II) and out of (I) the magnetic field

The conclusions reached by the characterization of the synthesized homopolymers agree well with the literature[4,26,27]. Thus the polymers obtained in a magnetic field are thermally more stable; they show increased values for the initial and maximum decomposition temperatures and lower values for weight losses on the $T_i - T_{max}$ decomposition interval compared to their homologues obtained in the absence of a magnetic field (*Table 3*).

Determinations of the average molecular weights of the poly(butyl methacrylate), poly(ethyl methacrylate) and poly(methyl methacrylate) indicate increased values for these characteristics in polyesters obtained in a magnetic field. The explanation lies in the breaking reactions considered as occurring mainly by the combination process due to the 'orientation-ordering' of the macromolecular chains in a magnetic field (*Table 3*).

The behaviour of intrinsic viscosities with temperature of the solutions of polymers synthesized in the magnetic field does not coincide with variations in viscosities corresponding to solutions of similar homopolymers, obtained by the classical procedure, in the absence of the magnetic field. Consequently, a continuous increase in viscosity with temperature was recorded (*Figure 2*), which does not agree with the conformational modifications mentioned in the literature. This may be generated by a certain 'reorganization' induced by the field of the structure of the polymers obtained in the new conditions, the new orientations opposing the modifications that might intervene through polymer–solvent interactions with temperature, or by the disorder created by the new structure.

CONCLUSIONS

In polymerization reactions of methyl, ethyl and butyl methacrylate the magnetic field induces reductions in the induction period as well as increases in polymerization rate and conversion. This is attributed to an increased efficiency of initiation as a result of transitions in the radical pairs from the singlet to the triplet state, which is accompanied by a reduction in the 'cage' effect and possibilities of recombination as well as an increase in the life of the initiator's radicals. In parallel with the modifications produced upon the initiator radicals, the field induces orderings of the polar compounds in the polymerization system. This order is more difficult to achieve when the length of the alkylic substituent of the methacrylic esters is increased due to steric hindrances. This is emphasized by a reduction in the magnetic field effects on the polymerization reaction and through the values of the temporary polymerization rates.

The magnetic field also influences the properties of the homopolymers obtained. Thus, the polyesters synthesized in a magnetic field are characterized by improved thermal stability and higher molecular weights. Further investigation is in progress to understand the details of the field effect.

REFERENCES

1 Wong, S. K. *J. Chem. Phys.* 1973, **58**, 985
2 Kalinnikov, V. T. *J. Chem. Phys.* 1959, **1**, 1
3 Zhou Chaohua and Zhantai Huiwen *Lanzhou Daxue Xuebao, Ziran Kexueban* 1988, **24** (1), 53
4 Turro, J. N. *J. Am. Chem. Soc.* 1980, **102**, 7391
5 Turro, J. N. *J. Am. Chem. Soc.* 1983, **105**, 1572
6 Imoto, M. *Makromol. Chem., Rapid Commun.* 1981, **2**, 703
7 Turro, J. N. *Acc. Chem. Res.* 1980, **13**, 369
8 Imoto, M. *J. Macromol. Chem. Sci.* 1987, **A24**, 111
9 Huang Junlian *China Sci. Bull.* 1989, **38**, (18), 1539; *Chem. Abstr.* 1990, **113**, 6902
10 Simionescu, C. I. and Chiriac, A. *Makromol. Chem., Rapid Commun.* 1989, **10**, 601
11 Vernadkii, V. I. *J. Union Mineral.* (*Zap. Vses. Mineral. Ova.* in Russian) 1960, **89**, 102; *Chem. Abstr.* 1960, **54**, 11869
12 Allen, A. O. 'The Radiation Chemistry of Water and Aqueous Solutions', Gosatomizdat, Moscow, 1963 (in Russian)
13 Gurikov, I. V. 'Aspects Regarding the Kinetic and Physico-Chemical Stabilization of Water Structure of Electrolytes and Non-Electrolytes', Znanie, Ukr. SSR, 'Himiceskaia Promyslenosti', Kiev, 1980 (in Russian)
14 Roosevelt, F. *Rec. Quim. Ind.* 1971, **40**, 474; *Chem. Abstr.* 1972, **76**, 92069
15 Ladik, J. J. *Theochem.* 1989, **57** (3–4), 289
16 Tsvetkova, E. A. *Doklad. Akad. Nauk., BSSR* 1989, **33** (12), 1093
17 Geranin, N. A. *Fiz. Tverd. Tela* 1990, **32** (4), 1172
18 Sokolik, I. A. *Visokomol. Soedn.* 1987, **3**, 203
19 Pankov, S. P. *Visokomol. Soedn.* 1982, **A24** (8), 1701
20 Casagriande, C. *Am. Chem. Soc. Polym. Prepr.* 1983, **24** (2), 273
21 Drago, R. S. 'Physical Methods in Chemistry', Izdatelistvo 'Mir', Moscow, 1981, p. 131
22 Kalinnikov, V. T. 'Introduction to Magnetochemistry', Izdatelistvo 'Nauka', Moscow, 1980, p. 46 (in Russian)
23 Baxendale, J. H. *J. Polym. Sci.* 1946, **1**, 237
24 Chinai, S. H. *J. Polym. Sci.* 1956, **19**, 463
25 Krause, S. *Polymer* 1961, **3**, 565
26 Simionescu, C. I. and Chiriac, A. *Colloid Polym. Sci.* 1992, **270**, 753
27 Simionescu, C. I., Chiriac, A. and Neamtu, I. *Polym. Bull.* 1991, **27**, 31