POLYMERISATION OF METHYL METHACRYLATE AND CARBONISATION OF POLY(METHYL METHACRYLATE) IN THE PRESENCE OF $Mg(ClO_4)_2$

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Carbonisation of poly(methyl methacrylate), which was prepared by polymerisation of methyl methacrylate initiated with 2,2'-azobis(isobutyronitrile) in the presence of 0—380 mmol/l of $Mg(ClO_4)_2$, has been studied. It was found that $Mg(ClO_4)_2$ accelerates both methyl methacrylate polymerisation and polymer decomposition at 300—700°C. The decomposition is accompanied with an increased carbonisation. Carbonised samples are paramagnetic; the paramagnetic particle concentration increases with increasing perchlorate concentration and temperature, respectively.

Pyrolysis or thermooxidative degradation of poly(methyl methacrylate) up to 500°C leads exclusively to monomer evolution[9]. Depolymerization can be reduced by the addition of various inorganic additives; $Mg(ClO_4)_2$ has a special position among them[2]. This compound not only forms complexes with monomer as do also the other Lewis' acids but it is capable of initiating polymer oxidation at higher temperatures.

In this study we compare the effect of $Mg(ClO_4)_2$ on methyl methacrylate polymerisation initiated with 2,2'-azobis(isobutyronitrile) or with dibenzoyl peroxide at 60°C with the effect of $Mg(ClO_4)_2$ on poly(methyl methacrylate) at temperatures higher than 300°C, *i.e.* under conditions when pronounced carbonisation takes place. Carbonisation of poly(methyl methacrylate) occurring during its thermooxidative decomposition was evaluated by weighing the residue after oxidative pyrolysis and by measuring its paramagnetism by means of ESR method. Gaseous products of carbonisation were determined by pyrolytic chromatography. As a consequence, the mutual relation between depropagation and carbonisation of poly(methyl methacrylate) in the presence of $Mg(ClO_4)_2$ was studied and the reaction mechanism was discussed.

EXPERIMENTAL

Methyl methacrylate was freed from the inhibitor and distilled under nitrogen at low pressure. Dibenzoyl peroxide and 2,2'-azobis(isobutyronitrile) were purified by recrystallisation from chloroform solutions. Anhydrous magnesium perchlorate (Xenon, Lodz), anal. grade, was used without further purification.

Polymerisations were performed at 60°C under nitrogen blank in sealed ampoules. Polymer was isolated by precipitation with methanol and dried to constant weight. For chemiluminiscence measurements the polymer was prepared by polymerisation in bulk. The polymerisation was carried out for 5 hours at 60°C. Under these conditions not more than 5% by wt. of the originally present initiator was decomposed.

Chemiluminiscence measurements were performed on a PU SNK 7M spectrometer made at the Institute of Chemical Physics, Academy of Sciences USSR, Moscow. The apparatus was equipped with a photomultiplier FEU-38 whose photocathode Sb, Na, K, Cs has a sensitivity maximum at 460 nm. Measurements were carried out at 115°C in air. Chemiluminiscence intensity was expressed in arbitrary units ($1{\cdot}4 \cdot 10^{-13}$ A at the resistance of $1 \cdot 10^{11}\,\Omega$).

Carbonisation of $Mg(ClO_4)_2$ containing polymer blocks in air was performed in quartz test tubes placed in a temperature controlled laboratory furnace. The time of carbonisation was 20 minutes. The ESR measurements were done immediately after cooling the pyrolysed sample down to the room temperature. ESR spectra were taken on a X-band spectrometer E-4 Varian at microwave power 10 mW and modulation amplitude 0·2 mT. Concentration of paramagnetic particles, whose spectrum is represented by a singlet, was expressed in arbitrary units as $c = h.(\Delta H)^2/ms$, where h is the line height in cm, ΔH is its width in mT, m is the weight of carbonised residue and s is the adjusted spectrometer sensitivity.

The products of pyrolyses of poly(methyl methacrylate) samples containing $Mg(ClO_4)_2$ were investigated in the temperature range of 300—700°C on a pyrolyser[3] which was coupled with a gas chromatograph. The weighed amount of the sample was placed into a dosing equipment situated above the pyrolytic furnace and with the aid of a magnet the sample was introduced into the furnace. Gaseous products were carried with a carrier gas (air) into a chromatographic column 2 m

TABLE I

Polymerisation Rate of Methyl Methacrylate at 60°C in the Presence of $Mg(ClO_4)_2$ or $ZnCl_2$ Initiators: I_a 2,2'-azobis(isobutyronitrile), I_b dibenzoyl peroxide.

Additive (A)	$[A]_0$ mmol/l	$R_p \cdot 10^4$ mol/l . s	k' l/mol	Additive (A)	$[A]_0$ mmol/l	$R_p \cdot 10^4$ mol/l . s	k' l/mol
	$[I_a]_0 = 7{\cdot}3$ mmol/l				$[I_b]_0 = 12{\cdot}3$ mmol/l		
$Mg(ClO_4)_2$	0	1·66		$Mg(ClO_4)_2$	0	1·70	
	76	2·50	5·60		76	1·90	3·40
	190	3·25			190	2·26	
	380	4·45			380	3·52	
	$[I_a]_0 = 5{\cdot}0$ mmol/l[a]				$[I_b]_0 = 39{\cdot}3$ mmol/l		
$ZnCl_2$	0	2·15		$Mg(ClO_4)_2$	0	2·80	
	54	2·38	3·72		76	3·70	6·25
	188	3·30			190	5·50	
	241	3·98			380	8·15	

[a] Data taken from ref.[5].

in length, filled with polyester of sebacic acid and kept at 120°C. The chromatograph was equipped with a conductivity detector. The rate of oxidative pyrolysis was expressed in arbitrary units and determined from the height change of the methyl methacrylate chromatographic peak.

RESULTS AND DISCUSSION

The conversion curves of methyl methacrylate polymerisation initiated at 60°C with 2,2'-azobis-(isobutyronitrile) (7·3 mmol/l) in the presence of $Mg(ClO_4)_2$ (concentrations: 0, 76, 190, 380 mmol/l) are linear up to the conversion of about 10%. The same course was observed also for dibenzoyl peroxide initiated polymerisations. The polymerisation rate, R_p, in the given concentration range linearly increases with increasing $Mg(ClO_4)_2$ concentration. At the concentration of 380 mmol/l the rate is approximately triplicate when compared with perchlorate free system (Table I).

As for the others Lewis' acids, the acceleration of methyl methacrylate polymerisation in the presence of $Mg(ClO_4)_2$ is due to the complex formation of $Mg(ClO_4)_2$ with monomer (M) or with a growing radical which exhibits a higher rate constant of propagation. On the other hand the termination rate constat of growing complexed radicals decreases[4]. The constant k' determined from the empirical equation postulated by Imoto[5]

$$R_p = k \,.\, [I]_0^{1/2} \,.\, [M] \,.\, (1 + k'[A]_0)\,, \qquad (1)$$

(I initiator, A additive) is in the range of 3 to 7 l/mol (Table II).

TABLE II

Carbonisation of Poly(Methyl Methacrylate); Polymerisation Initiated by Dibenzoyl Peroxide (12·3 mmol/l) in the Presence of $Mg(ClO_4)_2$ as an Additive (A)

Symbols: m amount of carbonised residue, c concentration of paramagnetic particles in the residue.

T °C	$[A]_0$ mmol/l	m %	c a.u.	T °C	$[A]_0$ mmol/l	m %	c a.u.
350	76	4·0	0·048	450	76	1·4	0·099
	190	7·3	0·062		190	2·2	0·135
	380	13·6	0·096		380	4·4	0·185
400	76	1·6	0·080	500	76	1·0	0·105
	190	3·6	0·101		190	1·8	0·188
	380	6·7	0·156		380	3·4	0·256

In order to establish whether $Mg(ClO_4)_2$ influences the rate of dibenzoyl peroxide decomposition we have measured at 115°C the time dependence of chemiluminiscence of poly(methyl methacrylate) blocks containing dibenzoyl peroxide and magnesium perchlorate (Fig. 1). Assuming that $I \sim -d[I]/dt$, where I is the chemiluminiscence intensity[6], we have obtained the following data:

$Mg(ClO_4)_2$, mmol/l	0	76	190	380
I_{max}, a.u.	5190	6480	8670	13200
k, 10^{-4} s^{-1}	4.6	5.4	5·3	5·3

Both from the figure and the given data we can see that the chemiluminiscence intensity at its time maximum I_{max} increases with increasing initial $Mg(ClO_4)_2$ concentration, while the rate constants of first order reaction determined from the descending curve parts stay, for the initial initiator concentration of 39·3 mmol/l, practically constant. Therefore, the rate of initiator decomposition is not influenced in the concentration ratio studied by the presence of $Mg(ClO_4)_2$.

This is in agreement with the calculated value of the critical concentration ratio according to which an increased initiator decomposition rate in the presence of $ZnCl_2$ (ref.[4,5]) at 50°C occurs at the value of the $[ZnCl_2]/[I]_0$ ratio higher than 85. A gradual increase of maximum value of chemiluminiscence intensity with increasing

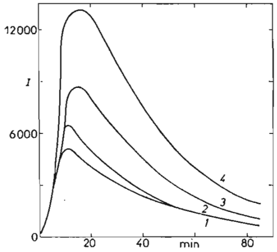


FIG. 1

Time Dependence of Chemiluminiscence (115°C) of Poly(Methyl Methacrylate) Blocks Prepared by Initiation of Dibenzoyl Peroxide (60°C) with $Mg(ClO_4)_2$

$[Mg(ClO_4)_2]_0$, mmol/l: *1* 0, *2* 76, *3* 190, *4* 380.

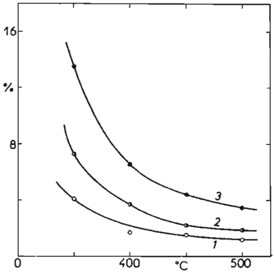


FIG. 2

Dependence of Residual Weight Amounts (w%) of Poly(Methyl Methacrylate) ($[I]_0$ = = 12·3 mmol/l at Temperature

$[Mg(ClO_4)_2]_0$, mmol/l: *1* 76, *2* 190, *3* 380.

$Mg(ClO_4)_2$ concentration can be explained by the formation of a nonidentified chemiluminiscence activator in a slow nonradical decomposition reaction of dibenzoyl peroxide due to the presence of $Mg(ClO_4)_2$.

The pronounced carbonisation of polymer takes place when poly(methyl methacrylate) blocks with magnesium perchlorate are heated in air at 300°C. Products of carbonisation are strongly paramagnetic.

The weight amount of carbonised residue obtained at given temperature after 20 minutes increases with increasing initial amount of magnesium perchlorate (Table II). On the other hand the weight of residue at a given magnesium perchlorate concentration decreases with increasing temperature of thermooxidative degradation (Fig. 2). The concentration of paramagnetic particles in a carbonised sample increases both with the temperature and the $Mg(ClO_4)_2$ concentration (Table II), respectively. At the same time the amount of monomer formed by radical depolymerisation of the polymer also decreases (Table III). The ratio of monomer formed from the polymer whose polymerisation was initiated by dibenzoyl peroxide at the concentration of 12·3 mmol/l in the presence of 380 mmol/l of $Mg(ClO_4)_2$ and from the polymer without perchlorate is in the 300—700°C range constant and equal to about 0·5. It is necessary to note that in the air a more extensive degradation of the polymer followed by a monomer oxidation takes place. In nitrogen, the amount of monomer in volatile products of pyrolysis at 725°C is about 80·6% (ref.[7]), while in air its amount drops to 25% (Table III). It seems, that also the quality of the excessive initiator strongly influences the oxidative polymer degradation in the early reaction stages. In the presence of 2,2'-azobis(isobutyronitrile), whose radicals are not very reactive in transfer reactions, and in the presence of 380 mmol/l of perchlorate, the amount of monomer formed at 500°C reaches 75% (in the presence of dibenzoyl peroxide only 50% is assumed).

TABLE III

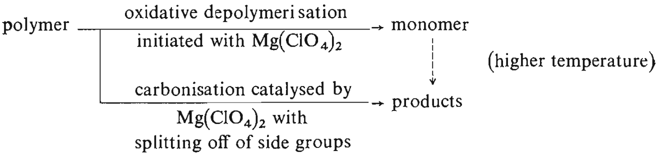
Effect of $Mg(ClO_4)_2$ on Thermooxidation Destruction of Poly(Methyl Methacrylate)

Polymerisation initiators: I_a 2,2'-azobis(isobutyronitrile), I_b dibenzoyl peroxide. Symbols: *S* peak area, *v* rate of decomposition.

T °C	$[Mg(ClO_4)_2]_0$ mmol/l	*S* cm^2	*v* a.u./g
	$[I_b]_0 = 12{\cdot}3$ mmol/l		
300	0	5·09	1·37
		5·96	1·09
300	380	2·59	5·78
		3·17	5·44
400	0	5·99	2·30
400	380	3·17	12·80
600	0	2·60	14·78
		2·51	

T °C	$[Mg(ClO_4)_2]_0$ mmol/l	*S* cm^2
600	380	1·48
		1·36
700	0	1·32
700	380	0·77
	$[I_a]_0 = 7{\cdot}3$ mmol/l	
500	0	4·40
	76	4·19
	190	3·79
	380	3·50

The comparison of chromatograms of gaseous products of thermooxidative destruction of poly(methyl methacrylate) in and without the presence of perchlorate (380 mmol/l) leads to the conclusion that perchlorate accelerates polymer decomposition; at 300 and 400°C the factor of acceleration ranges from 5 to 6 (Table III). Also other products than monomer are observed, *e.g.* hydrogen or methane (negative peak *1* in the chromatogram), or the products represented by peaks *2*, *3* and *4*. The product represented by peak *2*, whose retention time corresponds to CO_2, is formed not only due to the effect of perchlorate on the polymer but it also appears if monomer alone is dosed into the pyrolyser at temperatures above 600°C (Fig. 3). It was found that the product 2 is not formed at 400°C by direct interaction of $Mg(ClO_4)_2$ with methyl methacrylate since it was not observed provided that the solution of $Mg(ClO_4)_2$ in methyl methacrylate was dosed into the pyrolyser under analogous condition used for the $Mg(ClO_4)_2$–poly(methyl methacrylate) system. Therefore, the thermooxidative poly(methyl methacrylate) destruction in the presence of $Mg(ClO_4)_2$ should mostly proceed according to the following reaction scheme:



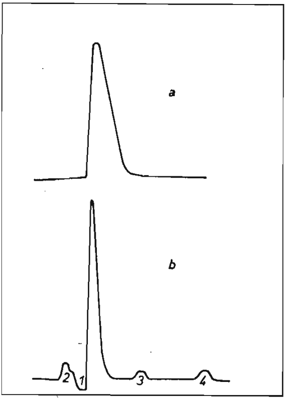


Fig. 3

Chromatography of Products of Thermooxidative Destruction of Poly(Methyl Methacrylate) in the Air (400°C) without $Mg(ClO_4)_2$ (*a*) and with 380 mmol/l of $Mg(ClO_4)_2$ (*b*)

Initiator: Dibenzyol peroxide (12·3 mmol/l).

The monomer formation will be faster but the overall amount formed lower (Table III) because a part of the polymer, due to the interaction with $Mg(ClO_4)_2$, evolves volatile products from the side groups leaving thus the carbonised residue.

An interesting conclusion is found if the product of the carbonised residue weight and the concentration of paramagnetic particles for $Mg(ClO_4)_2$ containing samples is plotted against temperature (Fig. 4). This product, at temperatures above 400°C, stays approximately constant and depends only on the initial amount of perchlorate in the system. It seems, therefore, that the integral amount of paramagnetic centers is in the sample formed directly in the initial stage of the thermooxidation and that the increase of paramagnetic particles in the course of the process is caused only by the sample weight decrease. It is worth noticing that the stationary level of the integral paramagnetism evidently correlates with the initial perchlorate concentration (Fig. 4).

As the paramagnetism of carbonised residues is usually associated with the formation of network from condensed aromatic cycles[8] and as the depolymerisation reaction will be under the given conditions finished (according to the records of pyrolytic chromatography the duration of the whole process is about 3–4 minutes), it is possible to ascribe the sample weight decrease, when the integral paramagnetism is independent of temperature, to the changes which take place in the fundaments of condensed networks of the carbonised residue. The most probable process is the aromatisation accompanied by hydrogen or methane evolution.

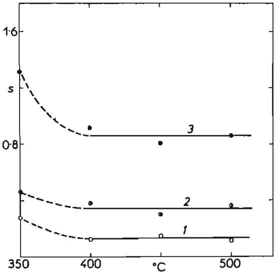


FIG. 4

Dependence of Product (*s*) of the Carbonized Residue of Poly(Methyl Methacrylate) and Concentration of Paramagnetic Particles at Temperature

$[Mg(ClO_4)_2]_0$, mmol/l: *1* 76, *2* 190, *3* 380.

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