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High conversion synthesis of poly(methyl methacrylate)

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SUMMARY

The possibilities to obtain high conversion in the bulk polymerization of methyl methacrylate a) with an additional initiation through ultrasonation or b) by development of the reaction in a magnetic field, are followed. The realized processes were compared to the classical bulk method. Some properties of the synthesized homopolymers are also presented.

INTRODUCTION

Bulk polymerization in a homogeneous system is largely applied - at industrial scale - when the process is conducted at high conversion degrees. An anormal dependence of the process rate and polymerization degree on the conversion degree appears in such circumstances.

The dependence of the rate and polymerization degree on the concentration of monomer and initiator has been thoroughly described for several vinyl monomers (1 - 8).

The literature in the field states the possibility of performing the polymerization reaction through ultrasonation employed as a mechano-chemical initiation method (9).

Also, application of a magnetic field - of several hundred gausses - during a polymerization reaction results in the increase of the rate, the conversion and the polymerization degree (10 - 14).

The present note discusses the realization of high conversions in the bulk synthesis of poly(methyl methacrylate), with additional initiation through ultrasonation or through the development of the reaction in a magnetic field, and compares these processes with the classical polymerization procedure . The homopolymers obtained according to the above mentioned methods are characterized.

EXPERIMENTAL

Methyl methacrylate (MMA) has been bulk polymerized, according to the synthesis conditions presented in Table 1. The B synthesis variant was performed by ultrasonation of the system subjected to the reaction, while in case C, the polymerization process was conducted in a magnetic field of 0.1 T intensity.

The polymerization reactions have been studied com-

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Table 1. Polymerization of methyl methacrylate

Reaction conditions[x)]	Synthesis variants A	B	C
Reaction temperature, °C	70	70	70
Reaction time, min	30	30	30
Ultrasonation frequency, Hz/min	-	20	-
Ultrasonation time, min	-	3	-
Magnetic induction, T	-	-	0.11

x) - radical polymerization with 0.3 % benzoyl peroxide, as initiator.

paratively, by determination of gravimetric conversion, polymerization rate and activation energy.

PMMA samples have been purified by reprecipitation from acetone solution, in methanol as precipitant, finally dried under vacuum at 40°C. Polymer fractionation was performed by use of acetone/methanol solvent/non-solvent mixture.

The molecular weights were determined using the Mark-Houwink relation applied to the first fraction of the polymers.

$$[\eta] = 7.24\cdot10^{-3}\,\overline{M}_w^{0.76} \quad \text{(benzene (B), 25°C)(15).}$$

Intrinsic viscosities ($dl\cdot g^{-1}$) were measured in B, methyl ethyl ketone (MEK) and dioxane (D), using an Ubbelohde suspended-level viscometer. The measurements were performed at 20-50°C.

The synthesized polymers were characterized from the viewpoint of their thermal stability (Paulik-Paulik-Erdely-type derivatograph, the heating rate of the polymer films being 12°C/min in air, differential thermal analysis calibration with $NaNO_3$).

All experiments were reproducible, considering the course of reaction as well as considering the analysed properties of the obtained homopolymers.

RESULTS and DISCUSSION

The development of the polymerization processes of MMA - plotted graphically in Figure 1 - evidences that, as compared to the classical synthesis, the induction period of the reaction was diminished, as a consequence of additional initiation through ultrasonation.

Lowering of the induction period is even more obvious when the process occurs in a magnetic field. The phenomenon may be explained by shifting of the radicals from the singlet to the triplet state, which results in the decrease of the cage effect, accompanied by the reduction of their recombination possibilities and also, by the orientation of the monomer in the field.

Concomitantly with the reduction of the reaction induction period, conversion increases, from 38.12 % for 30 min, in the case of classical bulk synthesis, to 65.40 % for

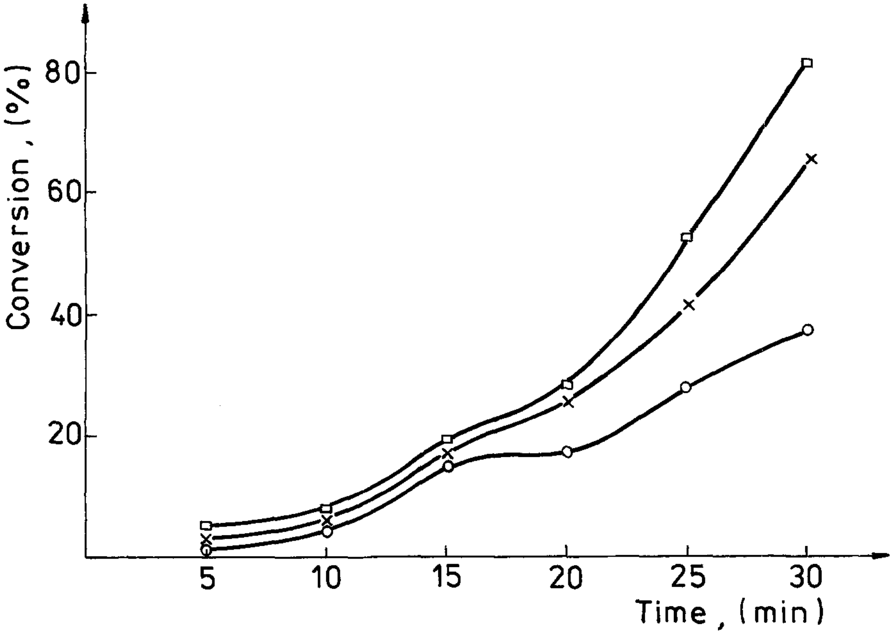

Figure 1. The development of the MMA bulk polymerization : classical (○), with additional initiation through ultrasonation (×) and for the reaction in the magnetic field (□).

the variant B, and to 80.30 %, respectively, in the process occurring in a magnetic field.

The decrease of the induction period and the increase of monomer conversion to polymer are in agreement with the values of the momentary polymerization rates and those of the activation energies (Tables 2 and 3).

Table 2. Polymerization rate of MMA (V) at moment (i) for the different synthesis variants

Variant	Polymerization rate (V) at moment (i)x)					
	V_5	V_{10}	V_{15}	V_{20}	V_{25}	V_{30}
A	0.05	0.50	1.40	1.60	1.90	2.10
B	0.60	0.65	1.90	2.10	2.70	3.60
C	0.70	0.80	2.10	3.10	3.60	4.50

x) - V_i in $mol \cdot l^{-1} \cdot s^{-1}$

Thus, the polymerization rate at 30 minutes is doubled in the magnetic field synthesis, while the variant employing an ultrasoned reaction system records an increase of about 60 %, as compared with the classical polymerization reaction.

The behaviour, under conditions of thermal degrada-

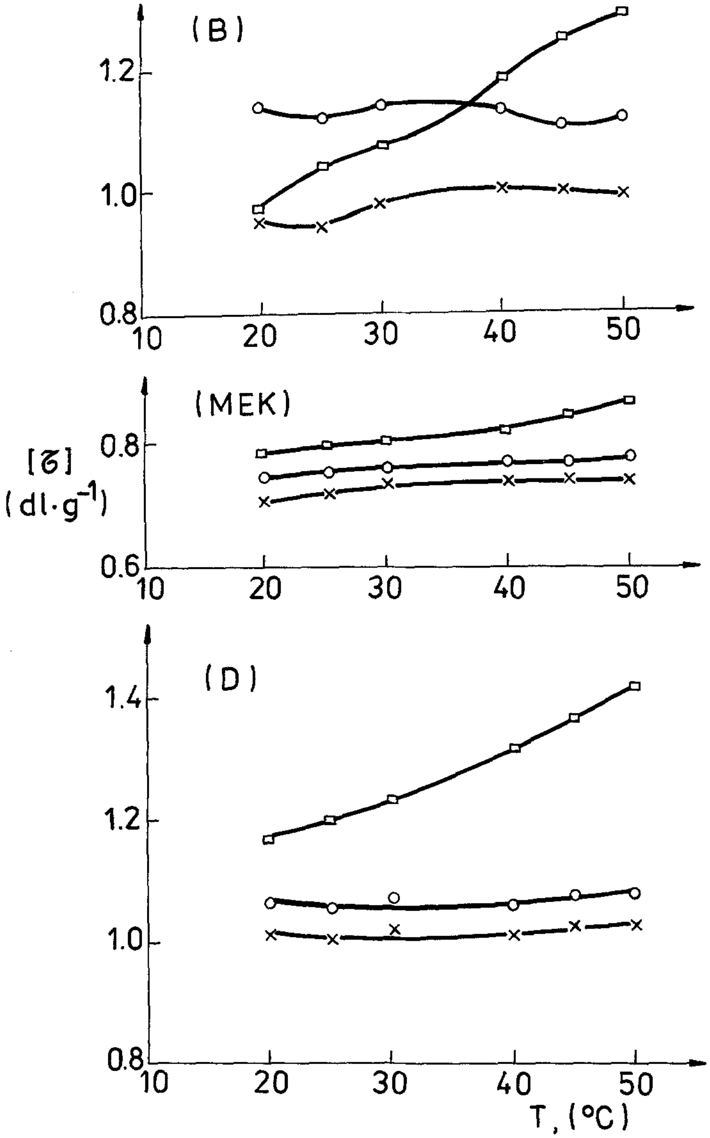

Figure 2. Variation of intrinsic viscosity with temperature for PMMA fractions in B, MEK and D :

□ – $\bar{M}_w = 430 \cdot 10^3$; ○ – $\bar{M}_w = 320 \cdot 10^3$; × – $\bar{M}_w = 270 \cdot 10^3$

tion, of the polymers synthesized according to the variants discussed is presented in Table 3. No significant differences of the initial or maximum decomposition temperatures were recorded; they range within the same domain of values.

Table 3. Some characteristics of the synthesized polymers

PMMA variant	Initial decomposition temperature, θ_i/°C	Temperature of maximum decomposition θ_{max}/°C	Weight loss within θ_i - θ_{max} interval in %	Activation energy in kcal/mol
A	165	322	30.30	22.72
B	160	322	28.04	18.85
C	180	327	26.08	17.68

Molecular weight determinations of the PMMA agree with the conditions of the syntheses. The polymer synthetized in bulk, according to the classical method, has a molecular weight calculated according to the Mark-Houwink relation of 320000. Additional initiation through ultrasonation induces a reduction of the molecular weight up to 270000. Occurrence of the magnetic field polymerization involves an increase of the PMMA molecular weight up to 430000.

The intrinsic viscosity of a polymer solution represents a measure of the intramolecular forces, steric hindrances, secondary van der Waals forces, as well as other types of interactions. The graphical representation of the intrinsic viscosity of PMMA fractions in B, MEK, D with temperature is given in Figure 2. The observation to be made is that the polymers synthesized according to variants A and B have the same behaviour, namely conformational modifications around 30°C and 45°C. The PMMA obtained in the magnetic field does not show the same aspect of the intrinsic viscosity variation with temperature, a continuous increase being recorded. Such a behaviour may be attributed to the modifications appearing in the relatively ordered structure (induced by the presence of the magnetic field during the synthesis) of the polymer, as a result of the temperature increase. Viscosity increases are more evident when the solutions are obtained in non-polar or low polarity solvents, where no polymer-solvent interactions occurred.

The conclusion is that high conversions may be attained in the process of bulk synthesis of PMMA, performing the reaction in a magnetic field or by an additional initiation through ultrasonation.

The homopolymer obtained in magnetic field presents a higher stability as compared with the PMMA obtained through classical bulk procedures or through additional initiation by ultrasonation, it has a higher molecular weight and a relatively ordered structure.

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