Polymerization of methyl methacrylate with mechano-chemically synthesized macroinitiators

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The polymerization of methyl methacrylate initiated by acrylonitrile- based homopolymers and copolymers synthesized mechanochemically by vibratory milling has been studied. The factors influencing the conversion and poly(methyl mehtacrylate) molecular weight are discussed. Both characteristics depend on polymerization parameters (reaction time, temperature and initiator concentration) as well as on macroinitiator synthesis conditions (duration of the vibratory milling process, comonomer ratio). The polymerization product consists of poly(methyl methacrylate) and small amounts of poly(acrylonitrile-g-methyl methacrylate)copolymer.

(Keywords: methyl methacrylate; macroinitiators; metallo-polymers; free radical mechanism; poly(acrylonitrile); copolymers)

INTRODUCTION

Recent studies have reported the polymerization of methyl methacrylate in the presence of polychelates, which contain non-bonding atoms (with electron pairs, e.g. nitrogen and oxygen) and complexing centres (e.g. Fe, Cu, etc.) in their chains. The presence of water (as a participant with the monomer, the macromolecular ligand and the metal) in the formation of the transition complex was found to be responsible for the polymerization by a radical mechanism.

The polymerization of methyl methacrylate (MMA) was carried out by using complexes of Cu (II) ions and either α-amylase, lysosine[1,2], polyamides[3-5], poly(*N*-vinyl imidazole[6]), invertase[7], a Fe(III)–invertase system[8], or poly(vinyl benzyl trimethyl) ammonium salts[9] as initiators.

Complexes of the above type are formed by the macromolecular compound and the aqueous solution of the metallic ions in the presence of the monomer. Recently, the mechano chemical polymerization of some vinylic monomers (in the presence of some metallopolymers) was achieved[10]. The reaction can proceed in water (with lower conversions) or dimethylformamide (DMF), (with higher conversions).

The aim of the paper presented here is to study the polymerization of MMA in the presence of acrylonitrile-based homo- and copolymers synthesized as macroinitiators mechanico-chemically. The factors affecting the conversion and the molecular weight of the obtained polymers (PMMA) are discussed.

EXPERIMENTAL

The homo- and copolymers used as macroinitiators were synthesized by vibratory milling either acrylonitrile or mixtures containing acrylonitrile, α-methyl styrene and/or vinyl acetate under inert atmosphere, at 18° ±2°C, with different milling times (24–192 h), using vessels and milling balls made from V_2A steel (total mass 6 kg, 9 mm diameter, and the filling ratio (η) was 0.5%). The syntheses were carried out on a Labowi LS-40 RDG mill, at a frequency of 25 Hz and vibration amplitude of 4 mm[11,17].

The DMF soluble fraction was separated from the milling reaction product and subsequently used as macroinitiator. The soluble polymer had a molecular weight between 3000–7000 (determined osmometrically) and a Fe content between 0.3–2.7% as estimated by Mössbauer spectroscopy and emission spectroscopy[12-14,16].

Methyl methacrylate was purified by washing with NaOH aqueous solution (15%) followed by drying on Na_2SO_4 with vacuum distillation.

The macroinitiator was placed in glass ampoules of 150 mm length and 20 mm diameter, dissolved in DMF (2–5 ml) and then 5 ml monomer was added. A set of experiments was performed with 0.1 g of macroinitiator, 5 ml H_2O and 5 ml monomer. The ampoules were connected to a vacuum line, cooled in liquid nitrogen and the traces of air removed at 10^{-3} Torr. After the third air removal the frozen ampoules were closed under vacuum. The polymerization reactions were carried out at temperatures varying between 20°–80°C, for 10–60 h, without stirring. After reaction their content was precipitated in excess methanol. The polymer was separated by filtration, then washed and dried.

The conversion was calculated by the relation:

$$c\% = \frac{a-b}{m} \times 100$$

where: a = amount of reaction product; b = amount of

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macroinitiator; m = amount of monomer; $c\%$ = conversion.

The toluene soluble and insoluble fractions obtained from the synthesis were characterized by i.r. spectral measurements (KBr pellets, Perkin Elmer spectrophotometer).

The toluene insoluble fraction was titrated turbidimetrically in a DMF solution (0.01%) by using methanol as a precipitating agent. A FEK 56 M (USSR) spectrophotometer, green filter, was used.

The molecular weight was determined viscosimetrically, by the single point method, in toluene, at 20°C ($K = 0.71 \times 10^{-4}$, $\alpha = 0.73$)[15].

The results obtained have shown the capacity of mechano-chemically synthesized acrylonitrile-based homo- and copolymers to initiate the polymerization of methyl methacrylate in polar liquid media (H_2O, DMF).

The polymer obtained in the presence of DMF represents a mixture of two fractions, one soluble in toluene, and the other soluble in DMF. According to i.r. analysis, the toluene soluble fraction represents a homopolymer (PMMA). The spectrum of the DMF soluble fraction presents an absorption band at 2240 cm^{-1} (–CN group). Based on these results, two hypotheses have been considered, namely, (a) the existence of a physical mixture of PMMA and macroinitiator, and (b) the existence of a graft copolymer. To elucidate the chemical nature of the product, turbidimetric titration was performed. The experimental data show the presence of a single component, i.e. a graft copolymer of the macroinitiator. The PMMA macroradicals are stabilized through chain transfer reactions, with the macroinitiator forming active centres on the macromolecular chain. The active centres determine the appearance of grafted structures.

The polymerization of MMA induced by the mechano-chemically synthesized macroinitiators is influenced by several factors depending both on the synthesis of macroinitiator and of MMA polymerization conditions.

Influence of macroinitiator amount

To study the influence of macroinitiator amount, the syntheses were performed in DMF, using two acrylonitrile-based homopolymers obtained with different milling times. The experimental data are plotted in *Figure 1*. An increase of conversion with the amount of the macroinitiator, is observed in both cases.

Influence of DMF amount

Previous experiments[10] have shown that the highest conversions were attained using DMF as the reaction medium. When the reaction was carried out in water (2 ml), at 50°C for 20 h, the yield was about 4%; but when the reaction was carried out in the presence of DMF (2 ml) the conversion reached 7% (the macroinitiator used was poly(acrylonitrile) obtained by vibratory milling of acrylonitrile for 72 h). The explanation is that DMF (the solvent of the macroinitiator) remains in the precipitated particles which appear when the monomer is introduced. Under these conditions, a good contact is established between the components of the reaction.

The volume of water used has practically no influence on the conversion levels (with 5 ml and 10 ml H_2O the conversions were 4.1 and 3.9, respectively), but the volume of DMF used proves to be an important factor. Varying the DMF volume between 2 and 5 ml gave the results shown in *Figure 2*. The decrease of PMMA conversion with the increase of DMF amount, is due to the decrease of the concentration of the macroinitiator in the system. Also, the increase of DMF amount determines the shift of the process towards being homogenous (PMMA being soluble in this solvent). The viscosity of the system is decreased, the mobility of the macroradicals in solution increases, and termination reactions are favoured. Under these conditions, both the molecular weight of the polymer and conversion decrease.

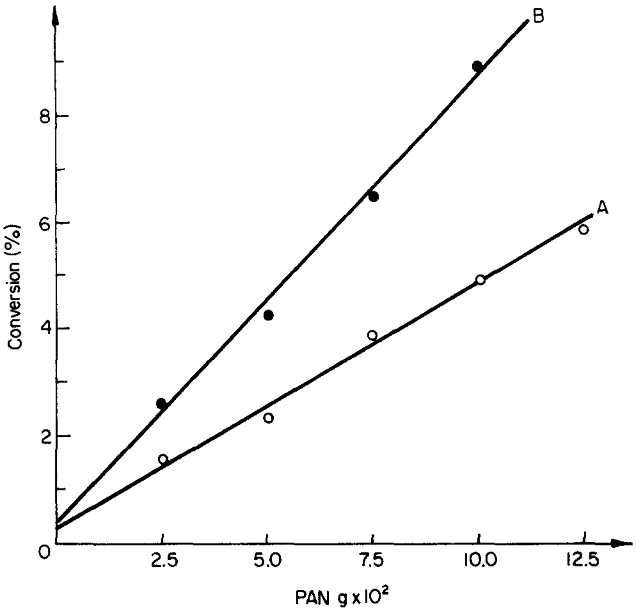


Figure 1 Influence of macroinitiator on the conversion into PMMA with 5 ml MMA and 2 ml DMF. PAN obtained: curve A: after milling for 72 h; curve B: after milling for 108 h

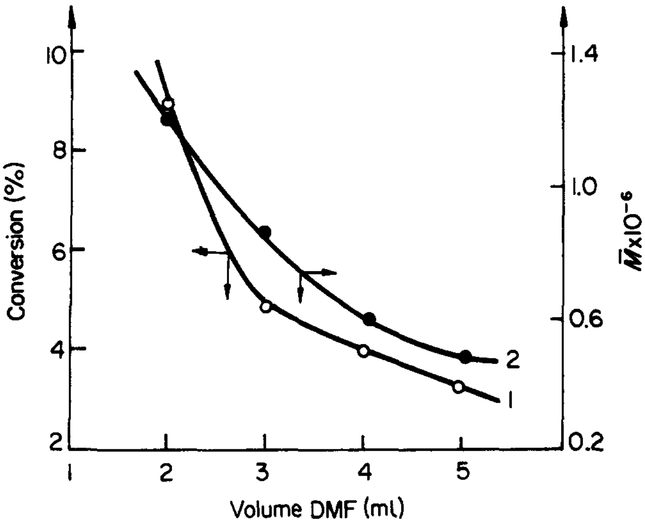


Figure 2 Influence of DMF on MMA polymerization (macroinitiator: 0.1 g PAN), synthesized after 108 h, 5 ml MMA, 20 h, 50°C. (1) conversion, (2) molecular weight

Influence of reaction time

Two sets of experiments have been carried out to study the influence of polymerization duration. The results are given in *Figure 3*. The first set of experiments was performed in DMF (2 ml) and the second in the presence of water (5 ml). It can be seen from *Figure 3* that the DMF system is more efficient.

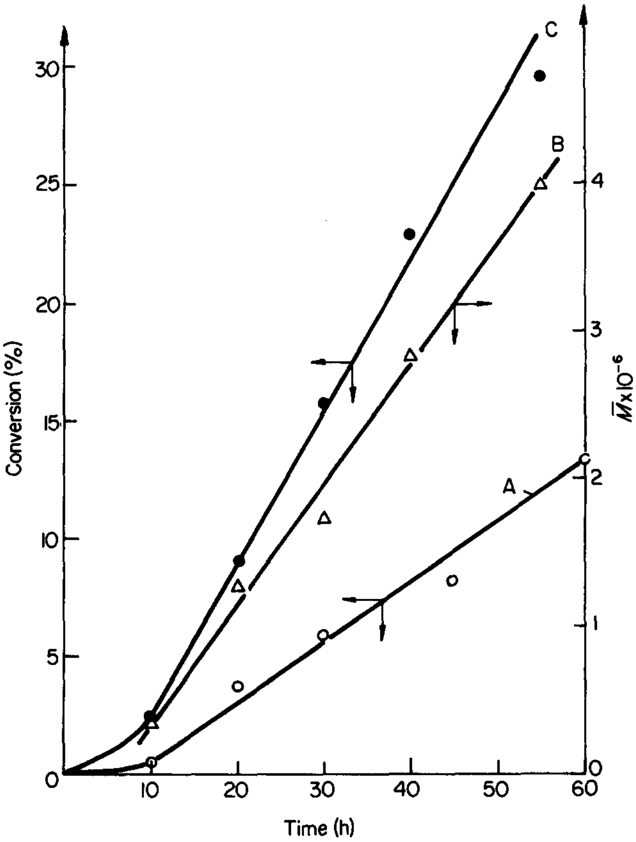


Figure 3 Influence of time on MMA polymerization (0.1 g PAN synthesized in 108 h, 5 ml MMA, 50°C). Curve A: variation of conversion with 5 ml H_2O; curve B: variation of molecular weight with 2 ml DMF; curve C: variation of conversion with 2 ml DMF

When the increase of conversion over the same time period is considered it is possible to conclude that the concentration of active species remains approximately constant throughout the process.

Influence of temperature

These experiments were performed in H_2O and DMF, at 20°–80°C, for 20 h (see *Figure 4*). In all cases, the increase of temperature produced an increase in the levels of conversion. The experiments carried out in DMF gave higher conversions. It has to be remembered that small conversions (1.5%) are also obtained at room temperature, suggesting the existence of a low activation energy for the process.

For the moment no explanation can be given for the increase of the molecular weight with temperature.

Influence of the synthesis duration of the macroinitiator

Previous studies[10] have shown that MMA polymerization is only possible in the presence of a mechano-chemically synthesized metallo-polymer. In their absence the conversions obtained are about 0.2%. However, when the synthesis was carried out in the presence of poly(acrylonitrile) (chemically synthesized) and $FeCl_3$, a conversion of about 2% was reached at 50°C after 20 h. This proves the formation of a complex between Fe^{3+}, nitrogen atoms of the substituents in the PAN chain, DMF, and monomer molecules, which results in appearance of free radicals initiating the polymerization. Hence, the presence of Fe or some other transition metal (of variable valence) is quite necessary. The initiating efficiency is also expected to increase as the amount of the complexed metal is increased. The polymers synthesized mechano-chemically show a particular structure (in comparison with their homologues) obtained by classical methods due to the presence of metallic atoms bound either covalently or by coordination. The amount of metal in the polymer is correlated to its nature as well as the conditions of the mechano-chemical synthesis. Thus, the chemically bound Fe in PAN reaches 3% after 192 h of milling (as determined by spectral measurements)[14]. Hence, the conversion levels of MMA to polymer with macroinitiators synthesized at different durations would be different.

Four sets of polymerizations were performed using PAN and its copolymers with vinyl acetate (VA) and α-methyl styrene (MS) as initiators. The results obtained by the polymerization with 0.1 g macroinitiator, 2 ml DMF, 20 h at 50°C are shown in *Figures 5* and *6*. It is evident that products of increased initiating capacity are obtained by increasing the duration of synthesis of the macroinitiator (*Figure 5*, curve 1). Evidently, this effect is due to the increase in the metal content of PAN structure (curve 2).

The same conclusions arise from *Figure 6* regarding the use of some acrylonitrile-based copolymers obtained at different milling durations. It must be pointed out that the highest initiating efficiency for the radicalic polymerization is shown by the AN:MS copolymer (curve C) while the ternary copolymer has a lower activity (curve A).

Influence of AN content in the macroinitiator

The previously mentioned data clearly show that the efficiency of MMA polymerization increases with increasing the metal content in the polymeric initiator. The content of the metal is a function of both the milling

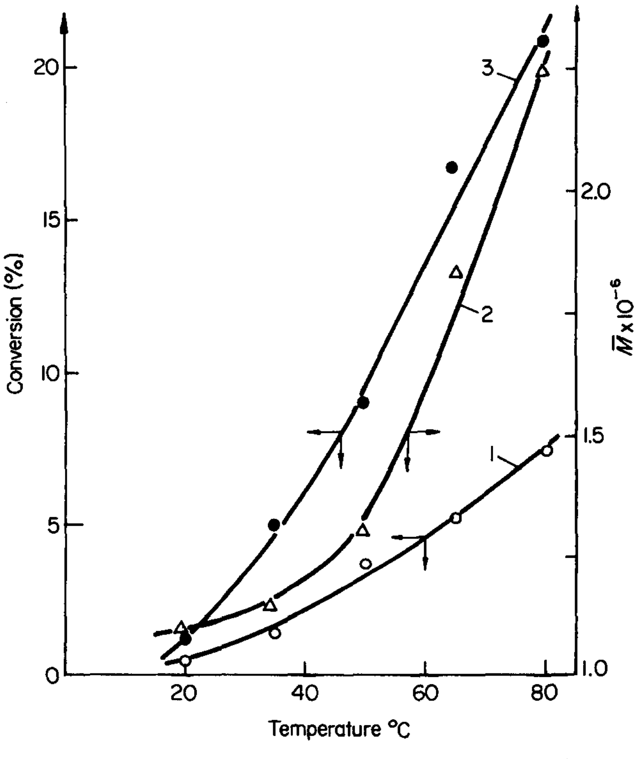


Figure 4 Influence of temperature on MMA polymerization (0.1 g PAN synthesized after 108 h, 5 ml MMA, 20 h). Curve 1: variation of conversion with 5 ml H_2O; curve 2: variation of molecular weight with 2 ml DMF; curve 3: variation of conversion with 2 ml DMF

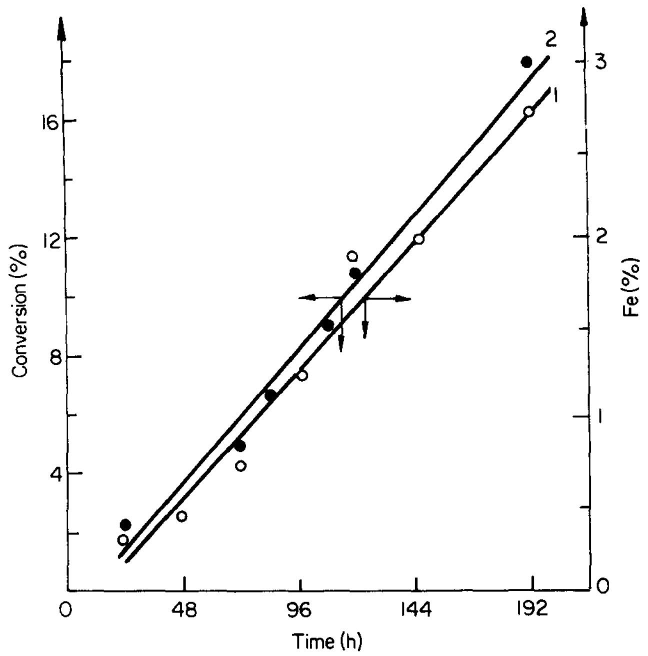


Figure 5 Influence of duration of macroinitiator synthesis on MMA polymerization (0.1 g PAN, 2 ml DMF, 20 h, 50°C). Curve A: variation of conversion; curve B: variation of amount of Fe chemically bound

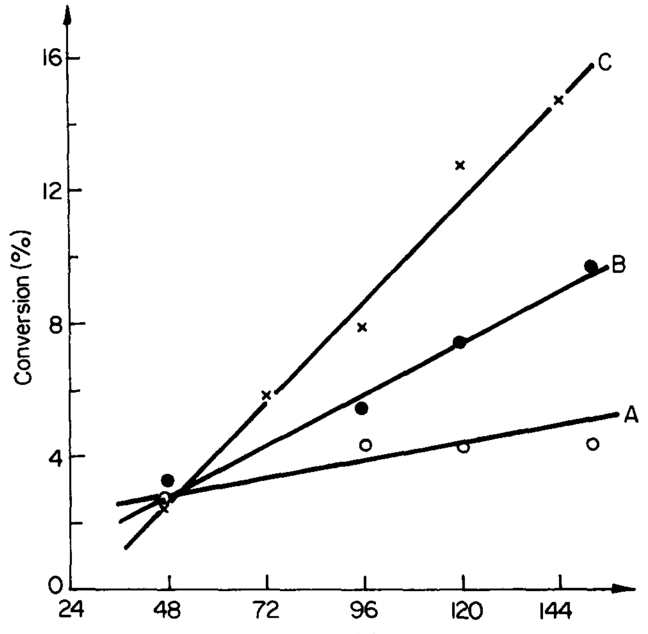
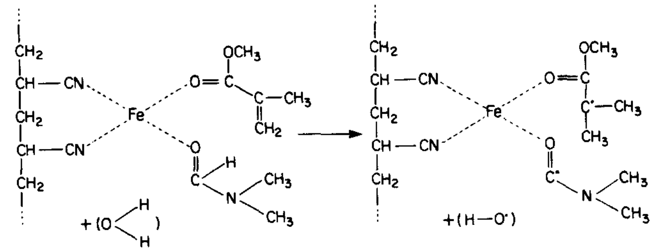


Figure 6 Influence of synthesis duration on the conversion of some acrylonitrile based copolymers into PMMA (0.1 g macroinitiator, 20 h, 50°C, 2 ml DMF). Curve A: AN:VA:MS copolymer (18:1:1); curve B: AN:VA copolymer (9:1); curve C: AN:MS copolymer (9:1)

duration (*Figure 5*, curve 1) and the chemical nature of the polymer. Thus, the amount of the chemically bound metal must increase with increasing nitrogen content of the macroinitiator. Acrylonitrile proved to be more reactive than MS and VA in the mechano-chemical polymerization[12,17]. Consequently, its concentration in the copolymer chains increased with increasing monomer concentrations in the initial mixture. In *Figure 7* (curves A and B) the nitrogen content of the AN:VA:MS and AN:VA copolymers is seen to increase with increasing the AN concentration in the initial monomer mixture. Consequently, the conversion to PMMA also increases with AN content under similar polymerization conditions. This effect appears for all the copolymers used as macroinitiators (*Figure 7*, curves C, D and E).

Hence, the increases in the polymerization efficiency with increasing AN content in the initial mixture, are a consequence of increases in the number of Fe atoms complexed with the nitrogen atoms from the macroinitiator.

Based on the presented data one can affirm that MMA may be polymerized in the presence of mechanochemically synthesized macroinitiators, through a free radical mechanism, supported by the reaction inhibition by either hydroquinone or atmospheric oxygen. The initiation is performed due to the formation of a transition complex which causes labilization of the vinylic bond of the monomer:



The radical formed from the monomer continues the chain growth, and promotes chain transfer reactions to the macroinitiator. These reactions are responsible for the appearance of grafted structures.

The macroradicals formed in either water of DMF can also participate in the initiation of polymerization or in the termination reaction.

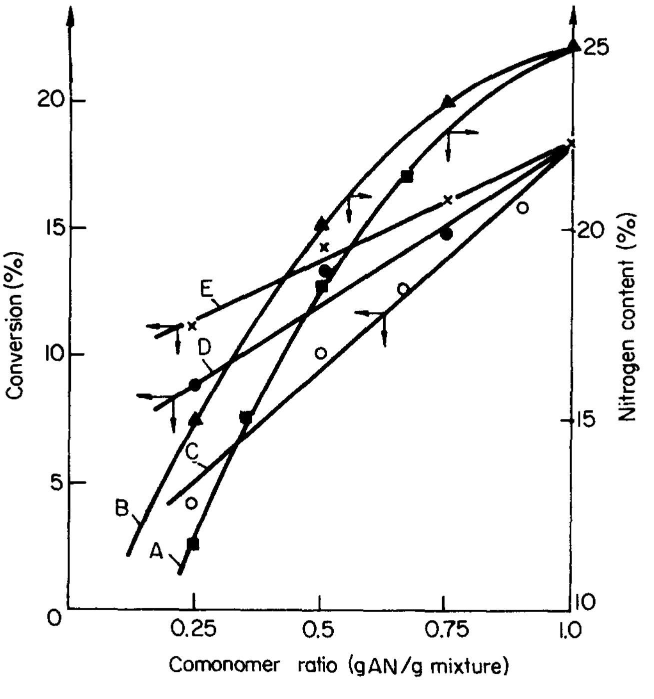


Figure 7 Influence of comonomer ratio (in the initial mixture) on the nitrogen content of macroinitiator. Curve A: AN:VA:MS copolymer; curve B: AN:VA copolymer and on the conversion into PMMA (0.1 g macroinitiator, 2 ml DMF, 5 ml MMA, 40 h, 50°C). Curve C: AN:VA:MS copolymer; curve D: AN:VA copolymer; curve E: AN:MS copolymer

CONCLUSIONS

(1) The complex system formed from the mechano-chemically synthesized metallo–polymers in either water or DMF can initiate the polymerization of methyl methacrylate.

(2) The polymerization of methyl methacrylate with mechano-chemically synthesized macroinitiators is influenced by the reaction time, temperature, macroinitiator levels, the synthesis conditions of the macroinitiator and its chemical nature, and the water or DMF content.

(3) The polymerization of methyl methacrylate with mechano-chemically synthesized macroinitiators proceeds via a free radical mechanism.

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