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Polymerization of Methyl Methacrylate Initiated with Invertase and Copper(II) Ion in Water

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SUMMARY

The paper is concerned with the polymerization of methyl methacrylate initiated with invertase and copper(II) ion in water. The effect of invertase amount, $CuCl_2 \cdot 2H_2O$ amount and temperature on conversion and molecular weight of the formed polymer are presented. The overall activation energy was estimated to be 63.91 kJ/mole.

INTRODUCTION

Last years, a number of papers reported the polymerization of methyl methacrylate (MMA) in water, in presence of nylon 6 (IMOTO et al., 1971), nylon 3 (NISHIMURA et al., 1976; OUCHI et al., 1976) or α-amylase (IMOTO et al., 1977) and copper(II) ion. The proposed polymerization mechanism, of radical nature, involved the formation of chelate bonds between the copper(II) ion, MMA monomer, water molecule and the electron-donating oxygen atoms in the polyamide (polypeptide) chain.
In this context, in a previous paper, the room temperature polymerization of MMA, in water, in presence of an enzyme, invertase, and $FeCl_3$, was reported (SIMIONESCU et al., 1982); the mentioned study is part of our research on unconventional polymerization reactions.
The present paper is concerned with the polymerization of MMA in water, initiated by a system of invertase and $CuCl_2 \cdot 2H_2O$ and presents the effect of different factors on the progress of the process.

EXPERIMENTAL

Invertase (β-D-fructofuranoside:fructohydrolase; E.C. 3.2.1.26) was a commercial product prepared by Serva. MMA was purified by usual method. Pure commercial cupric chloride was used without further purification.
MMA and the reagents were placed in long reaction ampoules connected to a high vacuum line, frozen in li-

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quid nitrogen, evacuated twice at 10^{-2} Torr and sealed. The ampoules were shaken in a thermostat (mild shaking, 6 shakings/ 7 sec. every 15 min.). The reactions were performed at four different temperatures, namely 60, 65, 70 and 75°C. After reaction the contents of the tubes were poured in large amounts of methanol to precipitate the polymer. After filtration the products were kept in hot water for several hours, to remove the enzyme, dried and weighed. No grafting of invertase with MMA was observed.
The number-average degree of polymerization was determined by using the equation of WELCH (1962):

$$\log \bar{P}_n = 3.346 + 1.32 \log [\eta] \qquad (\text{benzene, } 30^{\circ}\text{C})$$

RESULTS AND DISCUSSION

The results concerning the effect of the amount of invertase present in the system on the polymerization process, at 60°C and 7 hours polymerization duration, for a constant $CuCl_2 \cdot 2H_2O$ concentration, are presented in Figure 1a. The evolution of conversion and molecular weight versus the amount of cupric chloride in the system, for a constant amount of invertase, is given in Figure 1b.

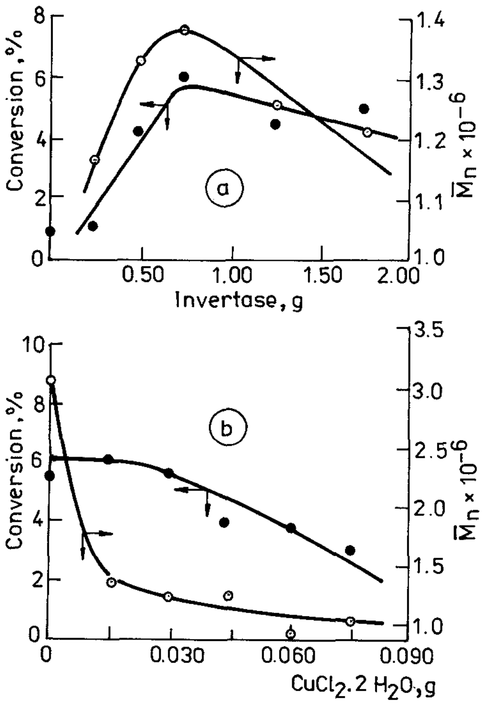

Figure 1.
a. Evolution of conversion and molecular weight versus amount of invertase (MMA, 5 ml; H_2O, 15 ml; $CuCl_2 \cdot 2H_2O$, 0.015 g; 60°C, 7 hours).
b. Evolution of conversion and molecular weight versus amount of $CuCl_2 \cdot 2H_2O$ (MMA, 5 ml; H_2O, 15 ml; invertase, 0.75 g; 60°C, 7 hours)

With the increase of invertase content up to a certain value, both molecular weight of the formed polymer and conversion strongly increase, while for higher invertase amounts, a decrease of both parameters is noted. The solubility of MMA in the water layer is very limited; pure thermal polymerization of the monomer, carried out in the absence of the enzyme, proceeds, but in a much smaller extent.

As concerns the effect of cupric chloride, the increase of Cu(II) ion concentration determines, after a certain concentration range in which polymer yield remains almost constant, a decrease of the conversion, while its presence strongly diminishes the molecular weight of the polymer.

Time - conversion curves obtained at four different temperatures are presented in Figure 2. Up to a certain polymerization period, which depends on the temperature of the process and decreases with the increase of the temperature, the conversion is rising strongly (up to values depending on the working temperature), while for long polymerization periods it remains almost constant (60 and 65°C) or even diminishes (70 and 75°C). Considering these experimental data, one has to remember, first, that with the increase of the temperature, the enzyme is denaturated (MARCONI et al., 1974)(invertase has its optimum activity at 55°C). Considering the possible formation of chelate bonds between the copper(II) ion, the monomer, water molecule and the electron-donating atoms of the enzyme chain, the denaturation process should imply the decrease of conversion with polymerization period with increasing the reaction temperature.

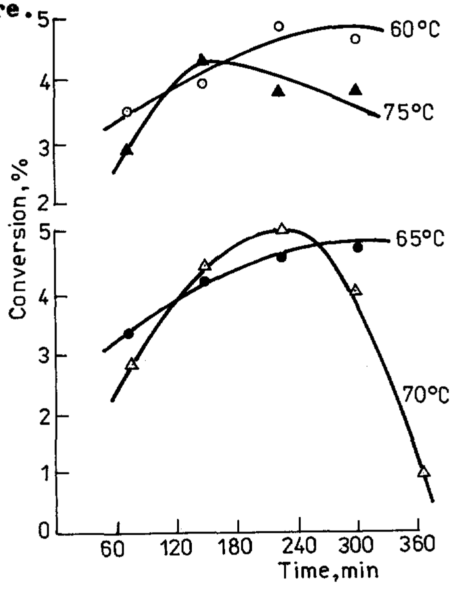

Figure 2.
Time - conversion curves for different reaction temperatures (MMA, 5 ml; H_2O, 15 ml; invertase, 1 g; $CuCl_2\cdot 2H_2O$, 0.015 g)

Figure 3 presents the evolution of the molecular weight of the polymer in time, for four different temperatures. With increasing the polymerization period, the molecular weight increases up to a period of about 4 hours, excepting the case when the working temperature was 75°C.

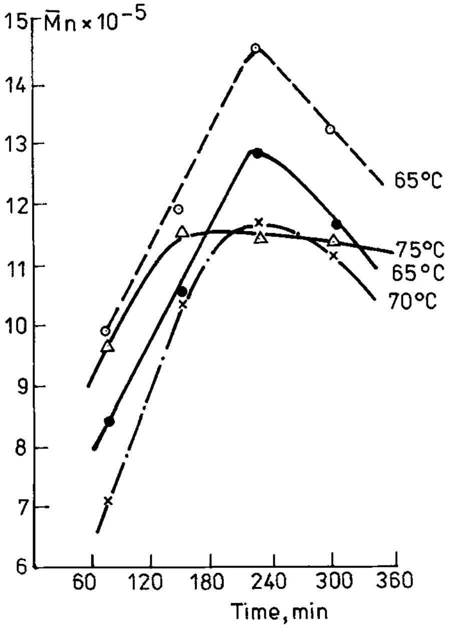

Figure 3.
Time - molecular weight curves for different reaction temperatures (MMA, 5 ml; H_2O, 15 ml; invertase, 1 g; $CuCl_2\cdot 2H_2O$, 0.015 g)

Both Figure 2 and 3 give the experimental results obtained for optimum reaction conditions (invertase, 1 g and $CuCl_2\cdot 2H_2O$, 0.015 g).
The experimental time - conversion data were used to calculate the overall rate constants of the polymerization process. The obtained values were $k_{60^\circ C}=0.2226\cdot 10^{-3}$ $k_{65^\circ C}=0.3145\cdot 10^{-3}$, $k_{70^\circ C}=0.4193\cdot 10^{-3}$, $k_{75^\circ C}=0.5505\cdot 10^{-3}$ (in $mole\cdot l^{-1}\cdot min^{-1}$).
In the interpretation of the experimental data presented, one has to consider not only the denaturation of the enzyme at elevated temperatures, but also the concomitent existence of some other different phenomena. So, the decrease of conversion with the increase of the amount of cupric chloride in the reaction milieu (Figure 1b) could be due to the inhibition by Cu(II) ion, according to the reaction

$$R^\bullet + CuCl_2 \longrightarrow RCl + CuCl$$

At the same time, one has to consider the possible exis-

tence of depolymerization reactions, appearing especially at elevated temperatures and long polymerization periods. The presence of Cu(II) ions in the system could eventually catalyse these reactions.
To check up the action of depolymerization reactions, 0.1196 g poly(methyl methacrylate) having the molecular weight $\bar{M}_n = 3.041 \cdot 10^6$, 3.066 ml MMA, 1 g invertase, 0.015 g cupric chloride and 15 ml water were introduced in an ampoule, evacuated twice at 10^{-2} Torr, sealed and then heated at 75°C for 5 hours. The reaction yielded 0.1209 g polymer, the $\bar{M}_n$ being $2.200 \cdot 10^6$. In the same conditions, but in the absence of the introduced polymer and starting from 5 ml MMA, the conversion was about 3.91%. In the presence of the polymer, excluding the action of depolymerization reactions, the reaction should yield 0.2344 g polymer (the newly formed polymer added to the polymer previously introduced). Considering these data, one has to accept the intervention of depolymerization reactions.
The Arrhenius plot (Figure 4) allows the estimation of the overall activation energy as being 63.91 kJ/mole.

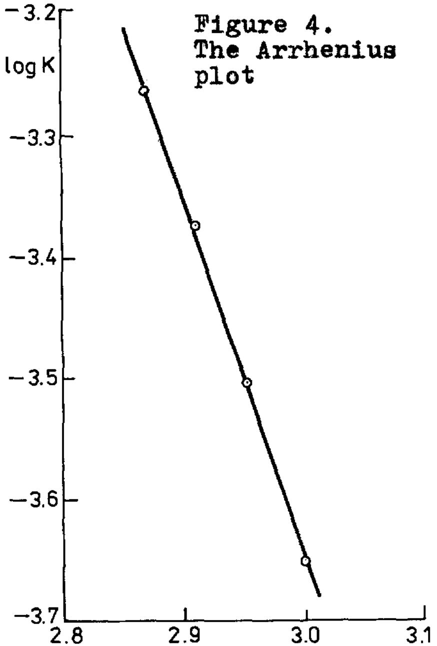

Figure 4.
The Arrhenius plot

CONCLUSIONS

The aqueous invertase solution can initiate the polymerization of methyl methacrylate in the presence of appropriate amounts of cupric chloride. The overall activation energy of the process was estimated to be 63.91 kJ/mole.

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