

SOLUTION POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF THE QUATERNARY AMMONIUM CHLORIDE

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Abstract

In the solution polymerization of an inhibitor containing methyl methacrylate in toluene initiated by dibenzoyl peroxide, the addition of a quaternary ammonium chloride reduces the lag time and decreases the polymerization rate. The complex mixture formed from the inhibitor in this reaction system seems responsible for these effects.

INTRODUCTION

The use of quaternary ammonium compounds in the preparation of polymers from vinyl monomers is not as common as in other fields of polymer science. Baxendale et al. [1] noted the enhancement of the polymerization rate on addition of $\text{RNMe}_3 \text{Br}$ in the aqueous solution polymerization. Lebedev et al. [2] recognised quaternary ammonium compounds as active agents in emulsion polymerization. Rasmussen and Smith [3,4]

utilised the ability of quaternary ammonium compounds to phase transfer the persulfate anion to initiate the polymerization. Freedman [5] reviewed the progress in this area. Ghosh and Maity [6-8] studied the influence of some quaternary ammonium bromides and chlorides in the solution polymerization of methyl methacrylate. They found that the initiation was inhibited by hydroquinone indicating a radical mechanism, as well as that some basic aprotic solvents enhance the polymerization rate whereas some protic ones diminish it. They also proposed two mechanisms of action of quaternary ammonium compounds. Jagodic and Perdih [9] demonstrated that different anions in quaternary ammonium compounds have different influences on the reaction constant and the lag time of bulk polymerization of methyl methacrylate. In the same system, Perdih [10] tested a larger number of counteranions and found that in several cases the interchange of anions between quaternary ammonium compounds and dibenzoyl peroxide prevailed by far as the first step of reaction. In view of these results the influence of a quaternary ammonium chloride in the solution polymerization of methyl methacrylate seemed to be worth reexamining.

EXPERIMENTAL

Chemicals

Methyl methacrylate (**MMA**) stabilized with 10 mg/kg Topanol A (2-*tert.*-butyl-4,6-dimethylphenol) (**Inh**) was obtained from Akripol, Trebnje. Dibenzoyl peroxide (**DBPO**) and alkyl benzyl dimethylammonium chloride (**QCl**) were obtained from Merck, Darmstadt, whereas toluene and methanol from Kemika, Zagreb.

Polymerization

Polymerizations were performed in a 1 L glass reactor equipped with a mixing system and thermostated to $79.5 \pm 0.5^\circ\text{C}$. The monomer solution contained MMA and toluene, 100 g each. After attaining constant temperature, QCl was dissolved in the mixture. After its dissolution, 0.7 g of DBPO was added. In predetermined intervals, 2 mL of

solution was removed, mixed with 100 mL of methanol and after staying overnight at room temperature the precipitate was filtered off, washed with methanol, dried and weighed. Each experiment was performed at least three times.

Analyses

The lag time was estimated by extrapolation of the linear part in the conversion plot to zero conversion, and the polymerization rate from its slope.

Mean molecular weights (M_w) were determined by size exclusion chromatography on a Waters/Varian chromatograph equipped with μ -Styragel 10^3 , 10^4 columns, with tetrahydrofuran as solvent and relative to polystyrene standards.

Thin layer chromatography was performed on silica sheets (Merck No. 5554) with benzene as the mobile phase and UV detection.

RESULTS AND DISCUSSION

In previous work [9,10] the bulk polymerization of MMA was followed by dilatometry. In order not to take into account the low MW compounds observed earlier [10], the methanol insoluble polymer was determined by gravimetry.

From the conversion vs. time curves were deduced the data presented in Table 1. These data demonstrate that the inhibition period (lag time) as well as the rate of polymerization decrease with increasing the amount of QCl in the reaction mixture. The polymerization rate constant and M_w of the formed polymer tend to level off at a molar ratio of inhibitor : QCl of over **1 : 5**. The lag time decreases with increasing addition of QCl and levels off at a molar ratio of inhibitor : QCl of about **1 : 10**. This is somewhat similar to the situation in bulk MMA [10] where the lag time levelled off at an approx. eightfold excess of QCl. According to [10], QCl reacts with DBPO to form chlorine and/or peroxybenzoyl chloride, whereas MMA, anisole, or phenol get chlorinated if

present. The QCl exponent observed in the present work is -0.16. For bromide salt, it was positive at low QBr concentrations and negative at higher ones [6].

Table 1. Lag time (t_l), polymerization rate constant (k), and mean molecular weight (M_w) of the formed polymethylmethacrylate at various QCl concentrations.

[MMA] = 4.52 mol L⁻¹, [DBPO] = 0.013 mol L⁻¹, [Inh] = 2.5*10⁻⁵ mol L⁻¹

QCl*10 ⁴ (mol L ⁻¹)	Inh : QCl	t_l (min)	$k*10^4$ (L ^{1/2} mol ^{-1/2} s ⁻¹)	M_w (kg mol ⁻¹)
0	1 : 0.00	58	5.32	50
0.25	1 : 0.98	53	4.76	
1.24	1 : 4.88	46	3.57	110
2.48	1 : 9.76	35	3.25	
4.52	1 : 17.8	34	3.02	120

In the present work DBPO is in a 26 to 500 fold molar excess over QCl. The decrease in the concentration of DBPO caused by its reaction with QCl is thus less than 4% of its initial value. This small decrease in DBPO concentration can not account for almost halving the lag time and the polymerization rate. Thus the decrease and levelling off of the lag time and the polymerization rate can not be ascribed to the decrease of initial DBPO content but to another effect. The chlorination of the inhibitor seems at first sight the most probable candidate since phenol has been chlorinated during previous tests [10]. The decrease of the inhibition period together with the rate of polymerization indicate that on reaction of the inhibitor with DBPO and QCl, its inhibiting activity decreases to a final value and at the same time it is converted into a retarder. In bulk MMA, on increasing addition of QCl, at the usual inhibitor concentration, a decreasing inhibition was observed and no retardation [10]; increasing retardation was observed if the inhibitor concentration was increased up to ten times above the usual. Both the decreasing inhibition and increasing retardation have been observed in the toluene - MMA solution at the usual concentration of the inhibitor.

To test the hypothesis that the chlorinated inhibitor is responsible for the observed effects, the inhibitor, DBPO, and QCl in a molar ratio of 1: 2 : 5 were reacted in toluene at room temperature as well as at 80°C. After removing the polar matters including benzoic acid and the Q-benzoate, thin layer chromatography of the products revealed a mixture of at least 12 UV-absorbing compounds. This is in sharp contrast to the composition of the inhibitor containing one major and one trace compound as well as to the results of reaction of phenol [10] where only 2-chlorophenol and a dichlorophenol were detected. On the other hand, the number of formed compounds is nearly twice that presented by Chirinos-Padrón and Allen [11] for oxidation products of simple phenolic antioxidants with peroxides. The formed mixture had the same influence on the polymerization of noninhibited MMA in solution as if the solution contained the inhibitor and QCl. Simple chlorinated phenols tested for comparison expressed a much weaker inhibiting and retarding action than the mentioned reaction mixture. From the existing evidence can be concluded that the reaction of a phenolic inhibitor with DBPO is faster in the presence of QCl giving rise to a more complex product mixture responsible for the reduction of lag time and retardation of polymerization.

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POVZETEK

Pri raztopinski polimerizaciji inhibitor vsebujočega metilmetakrilata v toluenu, sproženi z dibenzoil peroksidom, dodatek kvarternega amonijevega klorida skrajša začetni čas in zmanjša hitrost polimerizacije. Za ta pojav je vzrok zmes spojin, ki nastanejo iz inhibitorja v tem reakcijskem sistemu.