Polymerization of Methyl Methacrylate in Water and Water–Ethylene Glycol Mixtures

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SYNOPSIS

The polymerization of methyl methacrylate (MMA) was carried out in water and in water–ethylene glycol (EG) mixtures using sodium bisulfite as initiator. The rate of polymerization was found to be dependent on the initiator, the monomer, and ethylene glycol concentrations to the powers 0.68, 1.08, and 1.5, respectively. Addition of ethylene glycol increased both the rate of polymerization and the viscosity average molecular weights of the obtained polymers, while the rate of polymerization was found to decrease with temperature. The apparent activation energies were found to be 13.79 and 10.45 kJ/mol in water and in water–ethylene glycol mixture (50/50) (v/v), respectively.

INTRODUCTION

The polymerization of MMA in water,[1-3] in water–alcohols,[4] and in water–organic solvent mixtures[5] was studied. The addition of alcohols and organic solvents lowered the viscosity average molecular weights owing to transfer reactions caused by such organic liquids. Ouchi et al.[6] found that the behavior of the initiating system of polyethylene glycol (PEG), copper II ion, and water for the polymerization of MMA was similar to that of the system of starch, copper II ion, and water.[7,8] It was previously reported that PEG promoted the aqueous polymerization of MMA initiated with an aqueous solution of sodium polystyrene sulfonate.[9]

In this work we studied the effect of ethylene glycol on the polymerization of MMA using sodium bisulfite as initiator.

EXPERIMENTAL

Materials

MMA monomer was a product of Merck Schuchardt (Germany) purity 99%, stabilized with 100 ppm hy-droquinone, density 0.942–0.944 g/cm^3 at 20/24°C. It was washed with a few drops of sodium hydroxide (5%), followed by a small amount of distilled water. The MMA monomer was separated with a separating funnel, dried over anhydrous sodium sulfate, and finally fractionated using a fractionating column of about 15 theoretical plates. The fraction that boiled at 100.0 to 100.5°C was used. Sodium bisulfite was a product of El-Naser Pharmaceutical Chemical Co., ARE, Laboratory Chemical Division. Ethylene glycol was a product of VEB laborchemie Apolde, Germany. Hydroquinone and methanol were products of Prolabo, France; chloroform was AR grade.

Polymerization of Methyl Methacrylate

The sodium bisulfite (initiator) was put in a 250-mL well-stoppered conical flask; the water, ethylene glycol, and finally the monomer were added. The conical flasks were then put in an automatically controlled water bath at the required temperature. The reaction was stopped by making the solution alkaline using a few drops of 2% sodium hydroxide solution. The precipitated polymer was filtered, washed with distilled water and methanol, and dried in an electric oven at 105°C to constant weight. The conversion of monomer to polymer was determined gravimetrically.

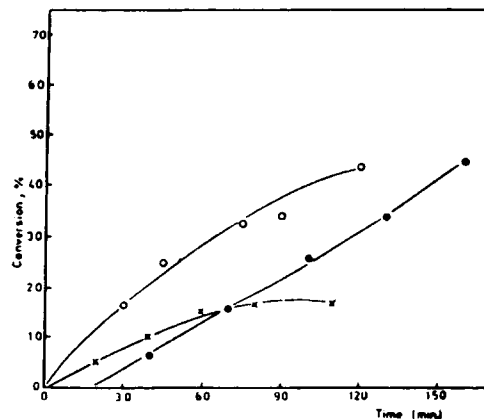* To whom correspondence should be addressed.
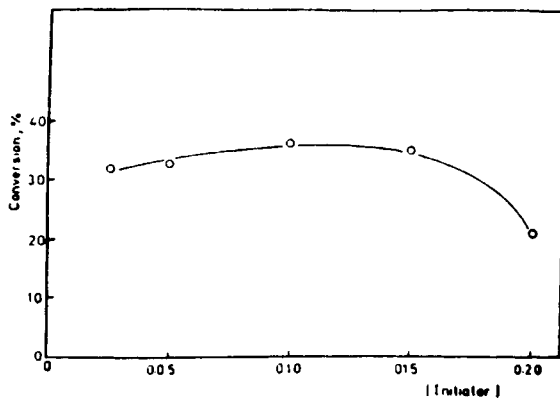
Figure 1 Conversion percent vs. initiator concentration in EG–water mixture (50/50% v/v).

Figure 2 Conversion–time plots for different initiator concentrations: (O) 0.10, (X) 0.05, and (●) 0.025 mol/ L.

Polymer Precipitation and Purification

The polymer was dissolved in pure benzene (thiophene free) to obtain approximately a 2% polymer solution. The polymer was then precipitated by the addition of the polymer solution to methanol and stirred for a period of time. The precipitated polymer was filtered and dried at 105°C.

Determination of Intrinsic Viscosity

The intrinsic viscosity [η] for each polymer was determined from the relation η_{sp}/C versus C for dif-

ferent polymer concentrations (from 0.1 to 0.8 g/ dL) using Ostwald viscometer to calculate η_{rel}, where its values were found to be in the range of 2.19 to 2.59. The intercept of the obtained straight line with η_{sp}/C axis equals to the [η] and the slope of this relation is $\bar{K}[\eta]^2$, where $\bar{K}$ represents the Huggins coefficient in the following Huggins equation:

$$\eta_{sp}/C = [\eta] + \bar{K}[\eta]^2 C$$

Table I   Variation of Initial Rate of Polymerization of MMA with Ethylene Glycol Initiator, Monomer Concentrations, and Temperature

| Reaction Medium (%) (v/v)		Initiator Conc. (mol/L)	Temp. (°C)	Monomer Conc. (mol/L)	Initial rate × 10⁶ (mol/L s)
EG	H₂O				
—	100	0.10	40	0.28	6.39
20	80	0.10	40	0.28	16.67
40	60	0.10	40	0.28	25.93
50	50	0.10	40	0.28	77.78
50	50	0.025	40	0.28	0.98
50	50	0.05	40	0.28	1.32
50	50	0.10	40	0.28	2.51
50	50	0.10	40	0.14	46.60
50	50	0.10	40	0.28	21.20
50	50	0.10	40	0.56	10.40
—	100	0.10	40	0.28	6.66
—	100	0.10	50	0.28	15.55
—	100	0.10	60	0.28	28.00
50	50	0.10	40	0.28	38.89
50	50	0.10	50	0.28	27.45
50	50	0.10	60	0.28	13.33
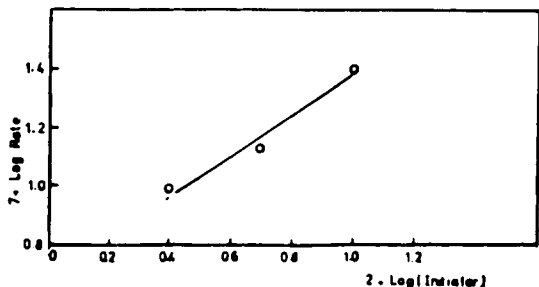
Figure 3 Log rate vs. log (initiator).

The value of Huggins coefficient ($\bar{K}$) for the different polymer concentrations was found to be close to 0.38.

The viscosity average molecular weights ($\bar{M}_v$) for the respective polymer were calculated from the corresponding [η] values by using the following equation:

$$[\eta] = 48 \times 10^{-6}\ \bar{M}_v^{0.80}$$

The viscosity measurements were made in chloroform at 25°C.[10]

RESULTS AND DISCUSSION

Effect of Initiator Concentration

Polymerizations of MMA (2.8 g) in water–ethylene glycol mixtures (50/50 v/v) using sodium bisulfite (0.1 mol/L) as initiator were carried out at 40°C for a period of 2 h. The data are presented in Figure 1. The conversion of monomer to polymer was found
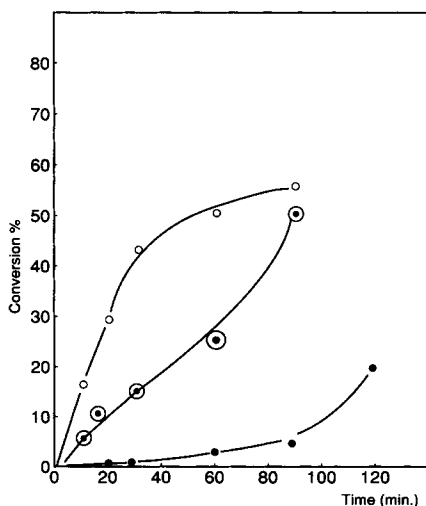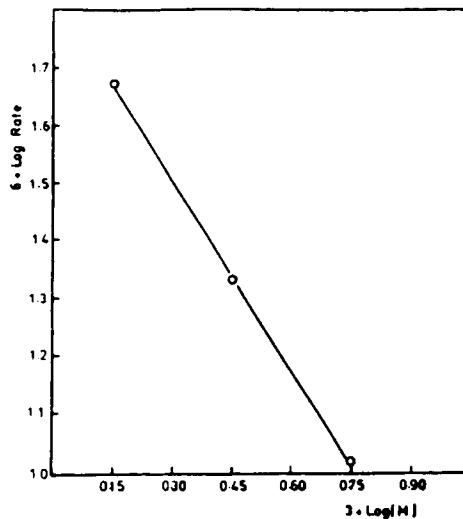

Figure 5 Log rate vs. log (MMA).

to increase with increasing initiator concentration up to 0.10 mol/L and then decrease. The conversion time curves for the polymerization reactions at different initiator concentrations are represented in Figure 2, and the initial rate values are shown in Table I. From Table I and Figure 2 it is obvious that both maximum conversion and the initial rate of polymerization increased with increasing initiator concentrations. The double logarithmic plot of initial rate of polymerization in mole/L s versus initiator concentration in mol/L is presented in Figure 3. The rate of polymerization was found to be dependent on the initiator concentration to the 0.68 power.
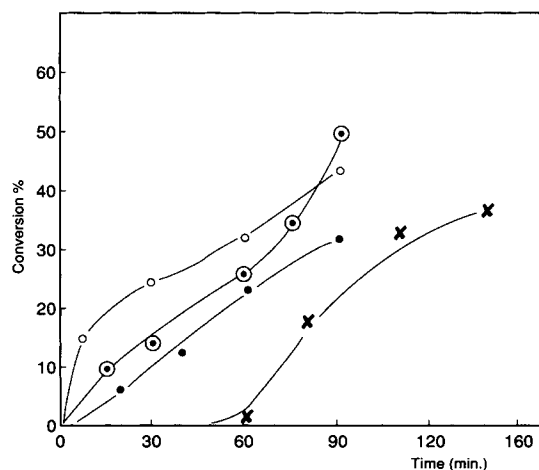

Figure 4 Conversion–time plots for different monomer concentrations: (O) 0.14, (⊙) 0.28, and (●) 0.56 mol/L.

Figure 6 Conversion–time plots for different EG ratios (v/v): (x) 0%, (●) 20%, (⊙) 40%, and (O) 50%.

Figure 7   Log rate vs. log (EG) ratio.

Figure 9   Conversion–time curves for the polymerization of MMA in water–EG mixture (50/50) (v/v): (⊙) 40°C, (●) 50°C, and (○) 60°C.
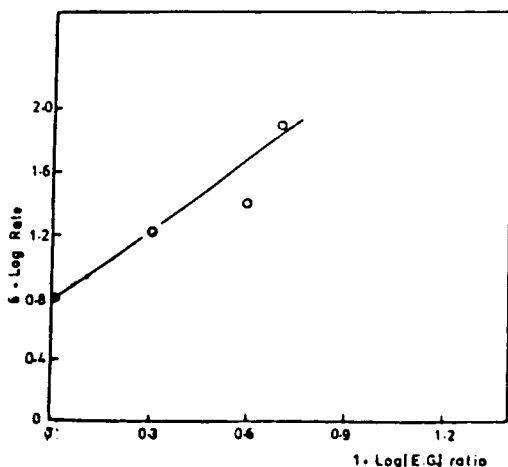
Effect of Monomer Concentration

Figure 4 shows the effect of different MMA monomer concentration from 0.14 to 0.56 mol/L on the initial rate of polymerization and maximum conversion at 40°C. The polymerization reactions were carried out at fixed initiator concentration ([NaHSO$_3$] = 0.10 mol/L) and in water–ethylene glycol mixtures (50/50) (v/v). The initial rates data are present in Table I. Figure 5 shows double logarithmic plot of initial rate of polymerization against initial monomer concentration. It is found that the rate of polymerization is proportional to the MMA concentration to the 1.08 power.

Effect of Ethylene Glycol

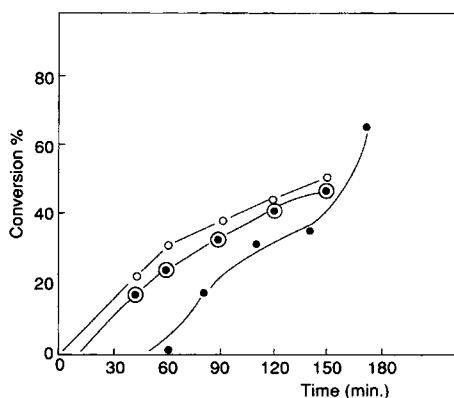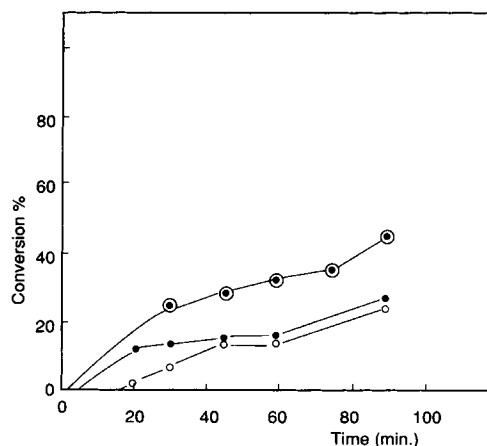Polymerization of MMA (0.28 mol/L) was carried out in different water–ethylene glycol mixtures (100

mL) (v/v) using sodium bisulfite (0.10 mol/L) as initiator at 40°C. The conversion was plotted versus time for the polymerization reactions (Fig. 6). Figure 6 and Table I show higher polymerization rates and lower induction period on increasing ethylene glycol in the polymerization medium. A plot of log rate versus log ethylene glycol ratio is shown in Figure 7. The dependence of polymerization rate on ethylene glycol is to the power 1.5.

Effect of Temperature

The effect of temperature on the rate of polymerization of MMA in water and in water–ethylene glycol mixture (50/50) (v/v) at a temperature range of 40–60°C was studied. The conversion–time plots
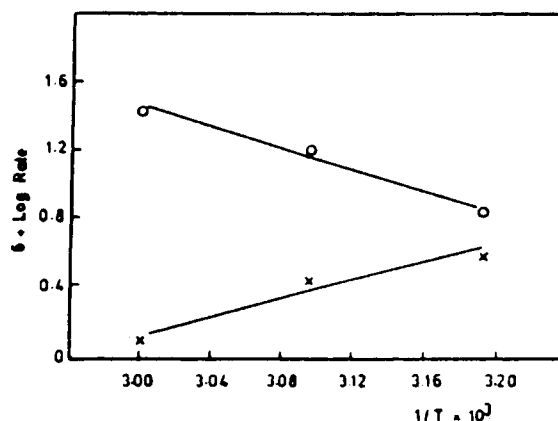

Figure 8   Conversion–time plots for the polymerization of MMA in water: (○) 60°C, (⊙) 50°C, and (●) 40°C.

Figure 10   Log rate vs. 1/T: (○) in water medium and (X) in EG–water mixture (50/50) (v/v).

Table II   Effect of Water and Water–Ethylene Glycol Mixtures on $\overline{M}_v$ Values of PMMA

Reaction Medium (%) (v/v)		Conversion (%)	$[\eta]$ (g/dL)	$\overline{M}_v \times 10^{-5}$ (g/mol)
Water	Ethylene glycol			
100	—	29.7	2.23	5.7
80	20	50.2	2.77	7.0
60	40	52.0	2.80	7.0
50	50	55.1	2.81	7.0
40	60	35.4	2.75	6.9

are represented in Figures 8 and 9. The initial rates of polymerization are present in Table I. From Table I and Figure 9 it is obvious that the initial rates of polymerization decrease with increasing temperature. This may be due to the hosting effect caused by EG for sodium ions of the initiator by decreasing the generation of free radicals. Figure 10 is an Arrhenius plot that shows that the relationship between log initial rate of polymerization and $1/T$ in a temperature range of 40–60°C forms straight lines in water and in water–ethylene glycol mixture. From the slope of the straight line, the overall activation energy (E_a) was calculated as 13.79 kJ/mol in water. The result obtained for polymerization in the water–ethylene glycol mixture was 10.45 kJ/mol.

Viscosity Average Molecular Weights (M_v Values)

The $\overline{M}_v$ values of polymethyl methacrylate (PMMA) prepared in water and in water–ethylene glycol mixture were determined. From Table II it is clear that the $\overline{M}_v$ values for PMMA obtained in different water–ethylene glycol mixtures were higher than those obtained in water; this may be due to the increasing solubility of monomer in the presence of ethylene glycol. Also, it was found that the $\overline{M}_v$ values for the PMMA prepared in water–EG mixtures increase with temperature owing to the hosting character of

EG, i.e., $\overline{M}_v$ values were found to be 1.4×10^6, 1.5×10^6, and 1.7×10^6 at 40, 50, and 60°C, respectively.

CONCLUSIONS

It can be concluded that the rate of polymerization was found to be dependent on the initiator, the monomer, and ethylene glycol concentrations to the powers of 0.68, 1.08, and 1.5, respectively. The presence of ethylene glycol in the polymerization medium increased both the rate of polymerization and the viscosity average molecular weights. The rate of polymerization decreased with temperature in water–ethylene glycol mixtures. The apparent activation energy in water and water–ethylene glycol mixture decreased from 13.79 to 10.49 kJ/mol, respectively.

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