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SOME KINETICS PARAMETERS FOR THE CATIONIC POLYMERIZATION OF α- METHYL STYRENE AND STYRENE CATALYZED BY SULFURIC ACID AND PHOSPHOROUS PENTOXIDE

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INTRODUCTION

The effect of polymerization time, temperature, monomer concentration on the rate of polymerization and molecular weight of the polymers prepared from α-methyl styrene using sulphuric acid catalyst had been previously investigated (Şanlı, Pulat, 1981). It was observed that the molecular weight of the polymers increased as the temperature decreased. On the other hand, the rate of polymerization increased to a certain temperature then decreased. Change in the polymerization time did not affect the molecular weight of the polymers obtained. It was also reported that as the monomer and catalyst concentration increased the rate of polymerization also increased. α-methyl styrene was polymerized using different amounts of water as cocatalyst. As the water concentration was increased the rate of polymerization and the molecular weight of the polymers were decreased (Şanlı, Pulat, 1982).

In the polymerization of styrene catalyzed by phosphorous pentoxide, the rate of polymerization was found to be proportional to the second power of the monomer concentration.

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As the concentration of water increased the rate of polymerization also increased to a certain value of concentration and then it decreased. The maximum rate was reached when the ratio of water concentration to phosphorous pentoxide concentration was 0.69. Although the water affected the rate of polymerization, the molecular weight of the polymers produced were not affected. The overall rate constants was given for three different temperatures, and the total activation energy of the reaction was also found (Coşkun, Pulat, 1, 1983, Coşkun, Pulat, 13, 1983) but the kinetics treatment for the number average degree of polymerization was not carried out.

On the other hand, in the polymerization of α-methyl styrene catalyzed by sulphuric acid kinetics parameters such as overall rate constant, the ratio of the individual rate constants, activation energies were not reported in the previous studies. As a part of broader study on the polymerization of α-methyl styrene and styrene we have reported some kinetics parameters and compared them with the other systems.

EXPERIMENTAL

Materials

Styrene and α-methyl styrene were purified as in reference (Kanoh et al. 1962, Randal et al, 1962). The method suggested by S. Okamura (Okamura et al, 1961) was used to purify methylene chloride. Chloroform, sulphuric acid, phosphorous pentoxide, and methanol were reagent grade materials and used without further purification. Toluene was purified as in reference (Coşkun, Pulat, 1983).

Synthesis of Polymers

Polymers were synthesized as described in the previous studies (Şanlı Pulat, 1981 ,Coşkun and Pulat, 1983) in a round bottom three necked flask fitted with stirrer thermometer and micro pipette, placed in a thermostate. Dry ice-acetone was employed as an external cooling medium when required. In the α-methyl styrene polymerization methylene chloride, in the case of styrene choroform were used as solvents. Polymers were precipitated by discharging the clear polymer solution into methanol.

Rates of polymerization were found by the gravimetric estimation of the precipitated polymers.

RESULTS and DISCUSSION

Effect of temperature on the rate and number average degree of polymeriztion.

A series of reactions were carried out at different temperatures ranging —25 °C to —78 °C at a constant concentration of 0,924 M α-methyl styrene and 1.05 x 10^{-2}M sulphuric acid concentration. The reactions were stopped after polymerization time of one hour by pouring into methanol and getting it precipitated. Plots of rate of polymerization and degree of polymerization vs temperature were shown in fig (1,2).

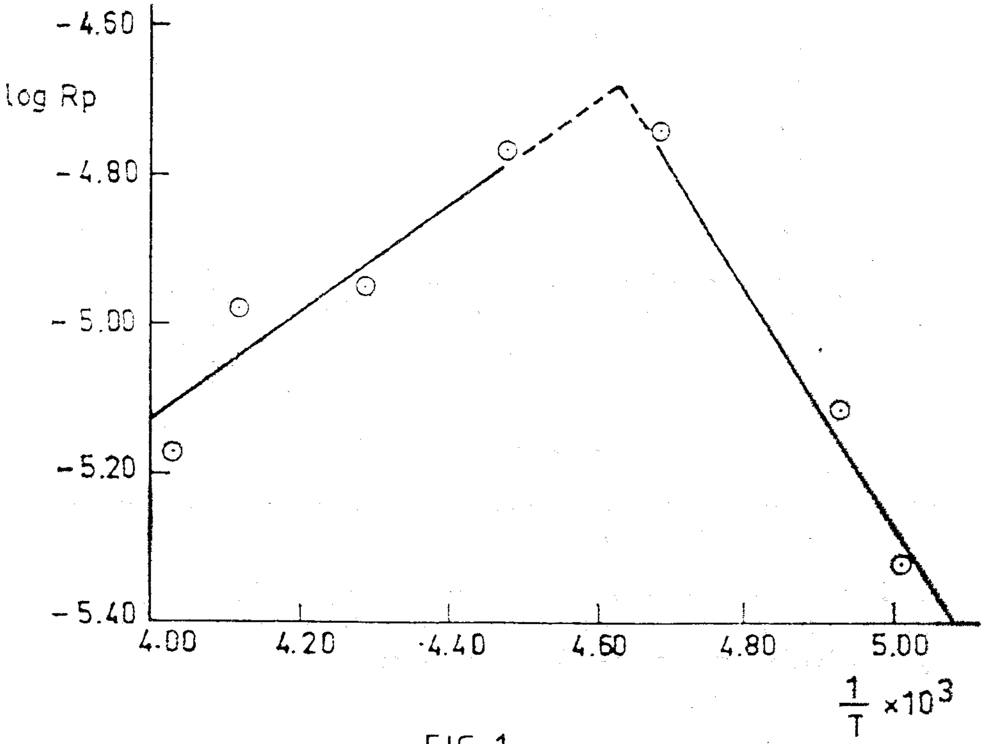

FIG.1

Figure 1: Effect of temperature on the rate of polymerization of α-methyl styrene.

Activation energy of the overall reaction was found from the slope of the lines in fig 1 as 30,6 kJ mol^{-1} in the —60 °C to —70 °C and —13,6

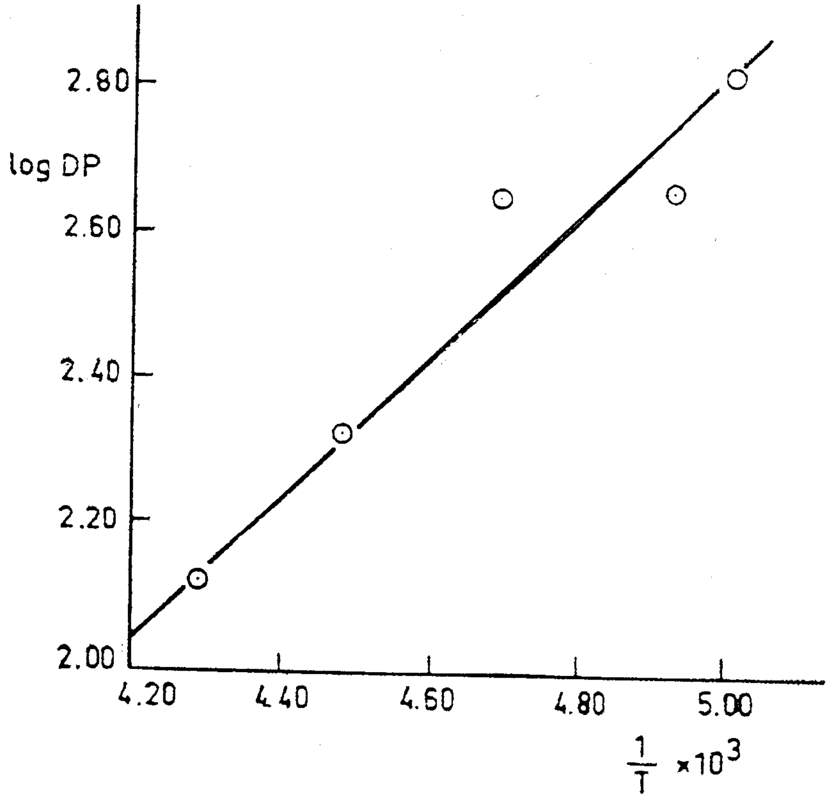

FIG. 2

Figure 2: Dependence of number average degree of polymerization on temperature for the polymerization of α-methyl styrene.

kJ in the —25 °C to —50 °C temperature range. Substituting 35.4 kJ mol^{-1} for E_p and 56.4 kJ mol^{-1} for E_i which were found in styrene polymerization into the well known equation

$$Ea = E_p - E_i - E_k \qquad (1)$$

as an approximation the value of E_i was found 51.6 kJ mol^{-1}. From the slope of the line in fig (2)E_{Dp} was found as —17.3 kJ mol^{-1}.

Our equation to express the rate of monomer disapearance is;

$$-\frac{d\,[M]}{dt} = \frac{k_i\,K_p}{Kt}\,[M]^2\,[H_2SO_4] \qquad (2)$$

provided that the factors depending upon temperature here are the invidual rate constants k_t usually decreases more rapidly than either k_i or k_p as the temperature is decreased the quantity $k_i k_p / k_t$ and the rate of polymerization increases. This situation will be valid until a very low temperature such as —57 °C. The minus sign of the overall ativation energy we found is not a suprising result above —60°C Further decrease in temperature decreases the rate of polymerization (Fig 2) from which we will get the overall activation energy with a positive sign.

On the other hand E_{Dp} is always negative and E_{Dp}, E_a, so the number average degree of polymerization increases as the temperature is decreased.

Similar arguments with essentially the same reservations will be applied to $\overline{DP}$ using the following equation

$$\overline{DP} = \frac{k_p\ [M]}{k_m\ [M] + k_t} \tag{3}$$

If the temperature is decreased transfer to monomer and termination reaction are slowed down to a much greater extent than the propagation reaction. Therefore higher-molecular-weight-polymers will be formed.

Polymerization of sytrene was carried out at a constant concentrations of 1.64 M styrene and 9.4×10^{-2} M phosphorus pentoxide concentration in the temperature range of —20 °C to +20 °C for 1h of polymerization time. Plot of the degree of polymerization vs temperature was shown in fig (3). The value of the overall activation energy was given as 46.1 kJ mol^{-1} previously (Coşkun, Pulat, 1983). The value of E_{Dp} for styrene polmerization is found as —32.8 kj mol^{-1}.

Effect of α-methyl styrene concentration on the rate of polymerization.

A series of reactions were performed at different monomer concentrations raging 0.51–1,03 M and catalyst concentrations of 1.25 x 10^{-2}M H_2SO_4 and polymerization time of 1 h. Plots of rate of polymerization vs monomer concentration are shown in fig (4). Experimental rate constant (Kex) was found from fig. 4 as 5.0 x 10^{-3} L^2 mol^{-2} sec^{-1}.

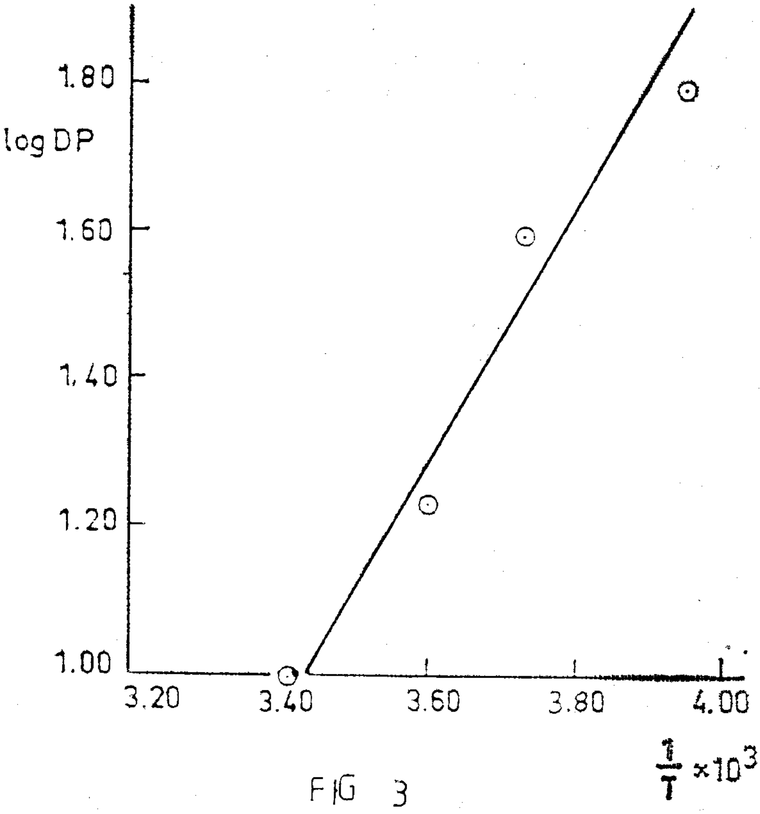

Figure 3: Dependence of number average degree of polymerization on temperature for the polymerization of styrene.

Effect of co-catalyst on the α-methyl styrene polymerization.

α-methyl styrene has been polymerized at constant concentrations of 0,924 M monomer, 7.6×10^{-3}M sulfuric acid concentration changing the water concentration 1.2×10^{-3}M — 5.8×10^{-3} M. Plots of $1/\overline{DP}$ vs water concentration was shown in fig (5). Mathematical expression of the line in figure (5) was in agreement with the following equation.

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + \frac{k_{tr}}{k_p} \frac{[H_2O]}{[M]} \tag{4}$$

From the slope of the line, transfer constant of chain breaking reaction (k_{tr}/k_p) was found as 0.20. Since there is no data available in the li-

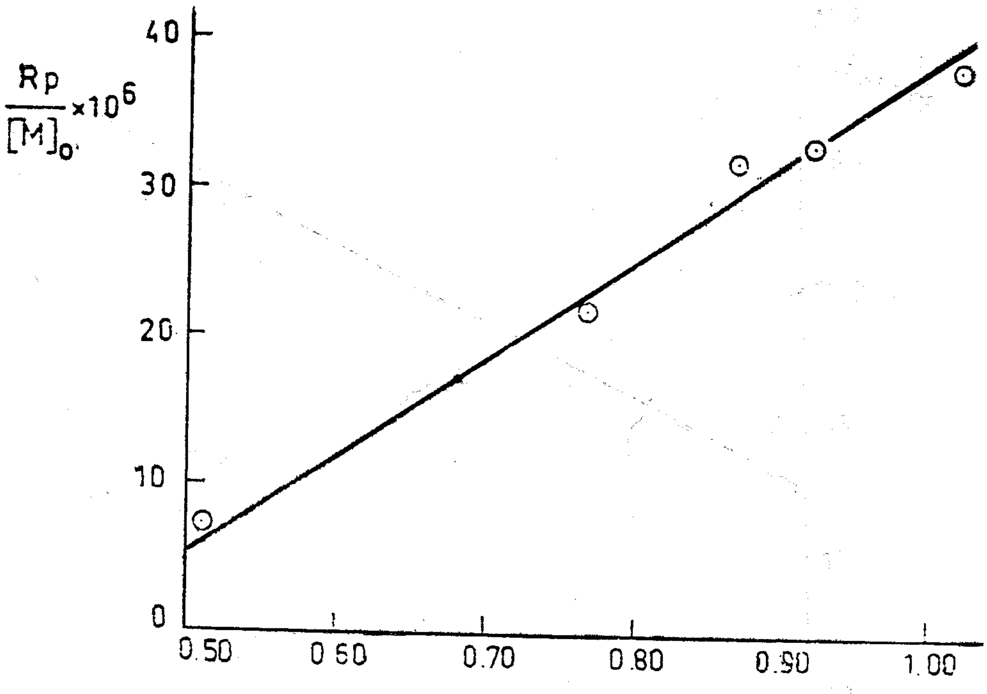

FIG. 4

Figure 4: Effect of monomer concentration on the rate of polymerization of α-methyl styrene.

terature for α-methyl styrene it is not possible to compare our results with other findings. However the same constant for ethyl alcohol in the sulfuric acid catalyzed polymerization of styrene was given as 1.6 in reference (Jenkinson, Pepper, 1961).

CONCLUSION

It is difficult to compare the kinetics parameters of different systems with one another because the initial and internal kinetics are often different in the systems. However, activation energies and rate constants are tabulated in table (I) and (II) comparatively.

The ease with which the monomers undergo cationic polymerization increases approximately in the order of butadiene < styrene < isop-

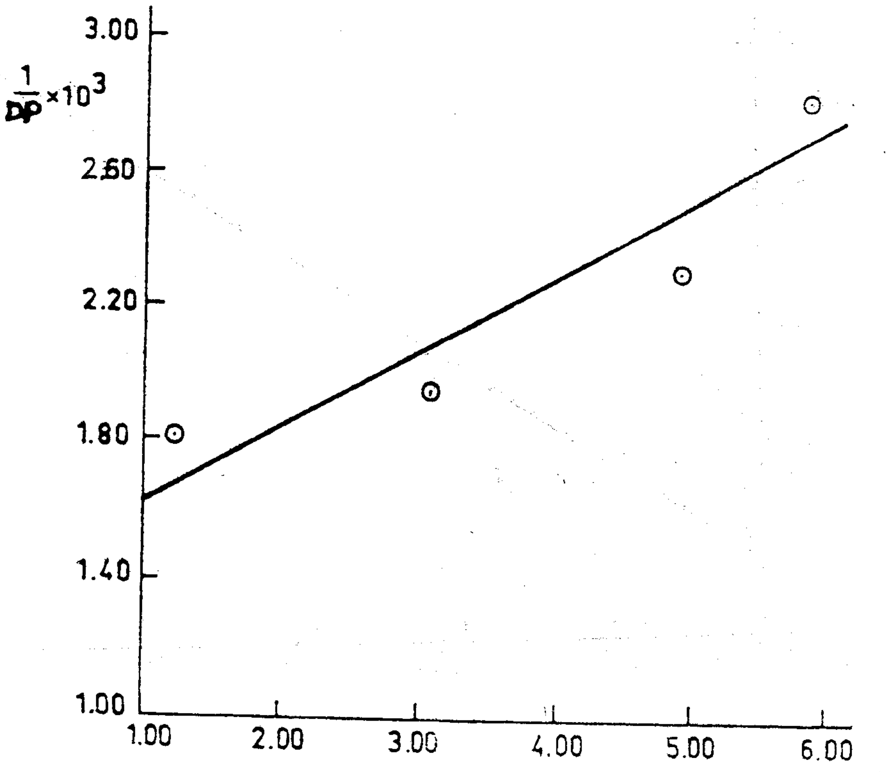

FIG. 5

Figure 5: Dependence of number average degree of polymerization on cocatalyst concentraration for the polymerization of α-methyl styrene.

Table I. Activation energies for the cationic polymerization of styrene and α-methyl styrene (Activation energies in $kJmol^{-1}$ units)

Monomer	Catalyst	Solvent	E_a	E_{Dp}	E_p	E_t	E_i
Styrene	P_2O_5	$CHCl_3$	46.1	–32.8	—	68.2	
Styrene (Hayes, Paper, 1961)	H_2SO_4	$(CH_2Cl)_2$	—	—	—	35.4	56.4
α-methy (styrene)	H_2SO_4	CH_2Cl_2	30.6 –13.6	–17		52.7	51.6

rene < α-methyl styrene < cyclopropane < propylene < isobutene < ethyl vinyl ether.

Table II. Rate constants for the cationic polymerization of styrene and α-methyl styrene.

Monomer	Catalyst	Solvent	t(°C)	K_{ex} 10^3 ($L^2mol^{-2}Sec^{-1}$)	transfer	K_{tr}/k_p
Styrene (Coşkun, Pulat, 1983)	P_2O_5	$CHCl_3$	—20	0.9	—	—
Styrene (Jenkinson, Pepper 1961)	H_2SO_4	$(CH_2Cl)_2$	+25	—	C_2H_5OH	1.6
α-methyl Styrene	H_2SO_4	CH_2Cl_2	—60	5.0	H_2O	0.20

Comparing the value of the overall activation energy of α-methyl styrene with that of styrene we come to the conclusion that α-methyl styrene undergo cationic polymerization faster than styrene does because of the lower activation energy. This results is in accordance with the above sequence.

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