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KINETICS STUDIES and SOLVENT EFFECT ON THE SULPHURIC ACID INITIATED POLYMERIZATION OF STYRENE

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ABSTRACT

Polymerization of styrene initiated by sulphuric acid in methylene chloride was investigated. The rate of polymerization was proportional to the first power of sulphuric acid concentration, to the first power of monomer concentration at 16°C and to the second power of monomer concentration at 0°C. A lineer relation between the temperature and limit viscosity numbers of the polymets was derived. The overall activation energy was reported as almost zero kcal in the 16°C to -12.5°C temperature range. The overall rate constant and the rate constants of initiation, propagation and termination reactions were found as $1.4\text{x}10\ ^{2}\text{L}^{2}\text{mol}^{-2}\text{s}^{-}$-, 7, $4\text{x}10\ ^{5}$ $\text{Lmol}^{-}\text{-s}^{-}$-, $8{,}1\text{x}10^{-3}\ \text{Lmol}^{-1}\text{s}^{-1}$, $4.3\text{x}10^{-3}\text{Lmol}^{-1}\text{s}^{-1}$ respectively.

The rate of polymerization increased as the dielectric constant of the solvent inscreased and a lineer relation is derived between the dielectric constant of the solvent and the reate of polymerization.

INTRODUCTION

It has been long agreed that the polymerization of styrene and α-methyl styrene induced by sulphuric acid in general proceeds through a cationic mechanism (Heiligman 1951, Şanlı, Pulat 1981, Şanlı, Pulat 1982, Şanlı et al. 1985). Several reports on the cationic polymerization of styrene have been reported (Tsuda 1960, Hayes et al. 1961, Jenkinson et al. 1961, Burton et al. 1961, Albert et al. 1961, Kazaryan et al. 1980, Peniche et al. 1973).

Hayes et al. have studied the kinetics of polymerization initiated by sulphuric adic in 1-2 dichloroethane. They reported that polymer yields depend on the initial acid concentration but not on that of monomer. The molecular weights were relatively low.

Peniche et al. proposed that the polymer yield has enhanced by addition of small amounts of trihaloacetic acid which also acted as catalyst for polymerization of syrene in 1-2 dichloroethane at room remperature.

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Kazaryan et al. has derived a mathematical equation for calculation of molecular weight distribution and polydispersity. The calculated molecular weight distribution agreed with the experimental results.

Tsuda has polymerized styrene in methylene chloride using sulphuric acid and hydrochloric acid as initiator. He reported that catalyst gave polymers of high molecular weight at low temperatures. However kinetics study was not reported for this system. In this work we have intended to determine overall rate constant, activation energy, individual rate constants for the polymerization of styrene in methylene chloride.

The nature of the growing species in cationic polymerization depends on greatly the position and type of the counteranion associated with the propagating carbonium ion (Kumar, Gupta 1978). The position of the counteranion can be altered by varying the dielectric constant of the solvent. The number of solvent–seperated ion pairs, contact ion pairs and free ions change with the polarity of the polymerization medium. The present work describes also a relation between the dielectric constant of the solvent and the rate of polymerization.

EXPERIMENTAL

Materials

Styrene (Petkim Co.) was purified as described by (Hayes et al. 1961). After the removal of the inhibitor by shaking with 10 % NaOH solution followed by repeated washing with the conductivity water, the monomer was vacuum distilled and dried over anhydrous calcium chloride. Methylene Chloride (Merck Co.), methanol (Merck Co.), benzen (Merck Co.), Acetone (Delta Co.) were used as supplied. Sulphuric acid (Fluka Co.) was used by checking the concentration before each run either titrating with NaOH or gravimetric sulphate determination. Nitrogen gas was purified by succesive passing through NaOH solution and P_2O_5 succesively.

Synthesis of Polystyrenes (PS)

Polystyrene was synthesized in a round bottom flask fitted with a mechanical stirrer, thermometer and a nitrogen gas inlet. Flask was placed in a thermostat. Following 15 minutes passage of nitrogen stream through solvent, monomer mixture, predetermined amount of sulphuric acid was added at the desired temperature The reaction was continued further for a fixed period of time. Dry ice–acetone was employed as an external cooling medium when required. Polymers were precipitated by discharging the clear polymer solution into methanol; filtered, washed with methanol and dried at 40°C in a vacuum oven overnight.

Characterization

Limit viscosities of the polymers were determined at 30°C in benzene using Ubbelohde viscometer, having an efflux time of 114 s. Viscosity molecular weight of polymers calculated from Mark–Houwing equation taking $K = 0.97x10^{-7}$ dlg^{-1}, $\alpha=0.74$.

IR spectra of polymers dispersed in KBr discs were obtained by using a Perkin Elmer spectrometer.

Rates of polymerizotions were found by the gravimetric determination of the precipitated polymers,

RESULTS and DISCUSSION

Effect of Temperature

Dependence of the rate of reaction, percent conversion and molecular weight of polymers on the temperature are shown in Table I. Table I reflects that although the rate of polymerization and percent conversion are not affected, the molecular weight of polymers increases with the decreasing temperature. The activation energy of overall reaction is found as almost zero (-0.3) k cal). However the overall activation energy in the perchloric acid initiated polymerization of styrene in the 0°C–25°C temperature reange and in the dichloroacetic acid initi ated polymerization of tysrene in the 0°C–40°C temperature range in ethylene dichloride were reported previosly as 8.0 k cal mol–^{1} and 6– k cal mol^{-1} respectively (.Pepper, Reilly 11962. Brown. Mathieson 19 1957).

Table I. Effect of temperature on the rate of polymerization and viscosity molecular weight (Mv) of polymers

($[M]_0$ = 1.723molL^{-1}, $[H_2SO_4]_0$ = 1.275x10^{-1} mol L^{-1} polym. time = 1h)

Temperature (°C)	% Conversion	$\left(\frac{-d[M]}{dt}\right)$x 10^5 (mol L^{-1}s^{-1})	Limit Viscosity Number $[\eta]$ (dLg^{-1})	$\bar{M}_v$x10^{-3}
16	94.7	45.4	0.059	6
0	99.3	47.7	0.085	9
-12.5	99.3	47.7	0.140	14

A relation between limit viscosity number and temperature isderived as in equation 1 whicd

$$\log\ [\eta[\ = 8.32\mathrm{x}10^{2}\ \frac{1}{T} - 4.11 \qquad (1)$$

may be useful in selecting polymerizotiou temperature to synthesize known molecular weight polymers A similar lineer dependence of limit viscosity number on temperature have been reported in the polymerization of α–methyl styrene initiated by sulphuric acid in methylene chloride (Şanlı, Pulat, 1981)

Effect of Initiator Concentration

Results of experiments carried out at different sulphuric acid concentrations were presented in Table II. As it is seen from the table increase in initiator concentration increases the percentage conversion and the rate of polymerization but decreases the molecular weight of the polymers as expected in this temperature range.

Table II. Influence of initiator concentration on the rate of polymerization and molecular weight of polymers
($[M]_0$ = 1.727 mol L^{-1}, Temp: 0°C polym. time: 30 min)

$[H_2SO_4]_0 \mathrm{x} 10^2$ (mol L^{-}-)	% Conversion	$\left(\frac{-d[M]}{dt}\right) \mathrm{x}\ 10^5$ (mol $L^{-}s^{-1}$)	$\bar{M}_v\ \mathrm{x}10^{-3}$
7.31	21.8	20.9	20
5.62	32.5	31.2	11
18.17	93.8	90.1	9

The slope of the line in the logaritmic plot of the rate of polymerization versus sulphuric acid concentration was found as 1.21 which shows the first order dependence on sulphuric acid concentration (Figure 1). First order kinetics with respect to initiator concentration was also reported in the polymerization of α–methyl styrene in methylene chloride and styrene in ethylene dichloride,. (Şanlı, Pulat 1982, Burton, Pepper 1961, Hayes, Pepper 1961).

Effect of Monomer Concentration

A series of experiments were performed at different monomer concentrations ranging 0.43–1.72 M at 16°C and at 0°C. Results are shown in Table III. The rate of polymerization plotted versus monomer concentration (Figure 2, 3) indicate that the reaction is first order

Figure 1. Dependence of the rate of polymerization on sulphuric acid concentration ($[M]_0 =$ 1.73 mol L^{-1}, Temp: 0°C, Polym. Time: 1h.)

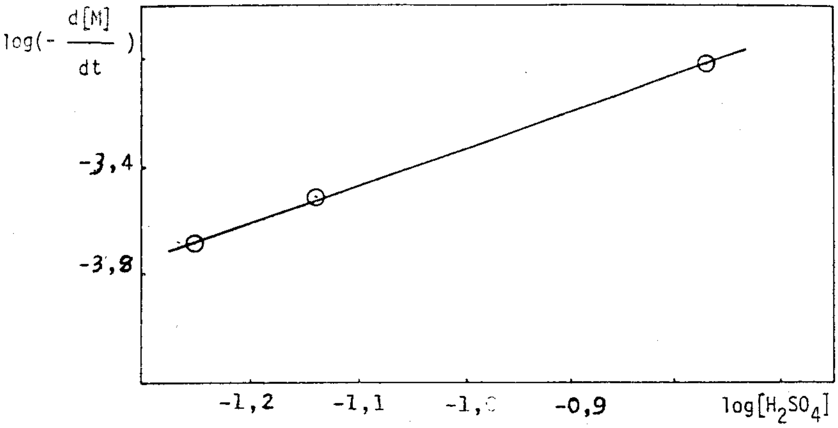


Table III. Effect of monomer concentration on the rate of polymerization and molecular weight of polymers (Polym. time = 1h)

Temperature (°C)	$[H_2SO_4]_0$ (mol L^{-1})	$[M]_0$ (mol L^{-1})	% Conversion	$\frac{-d[M]}{dt}$ x10^5 (mol $L^{-1}s^{-1}$	$\bar{M}v \times 10^{-3}$	($\bar{D}\bar{P}$)
16	0.109	0.86	88.2	21.2	6.7	55
		1.29	94.1	33.9	6.0	58
		1.72	96.5	46.4	7.3	60
0	0.128	0.43	29.1	3.5	–	
		0.86	62.3	14.3	7.3	70
		1.29	82.5	29.7	8.0	77
		1.72	99.3	47.7	9.0	87

in respect to monomer concentration (slope = 1.1) at 16°C and second order (slope = 1.9) at 0°C. The results confirm the rate equations 2,3. Equation 2 and 3 imply the bimolecular (transfer to monomer) and unimolecular termination respectively.

Figure 2. Log $\left(-\frac{d[M]}{dt}\right)$ vs log [M] at 16°C

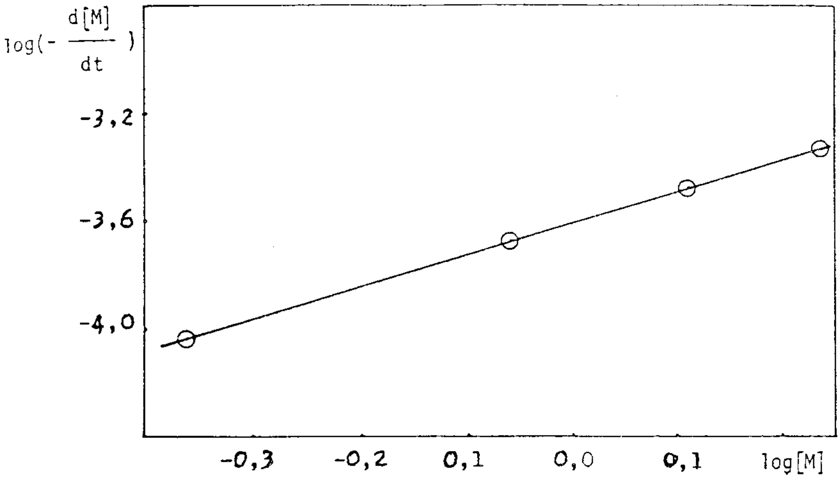
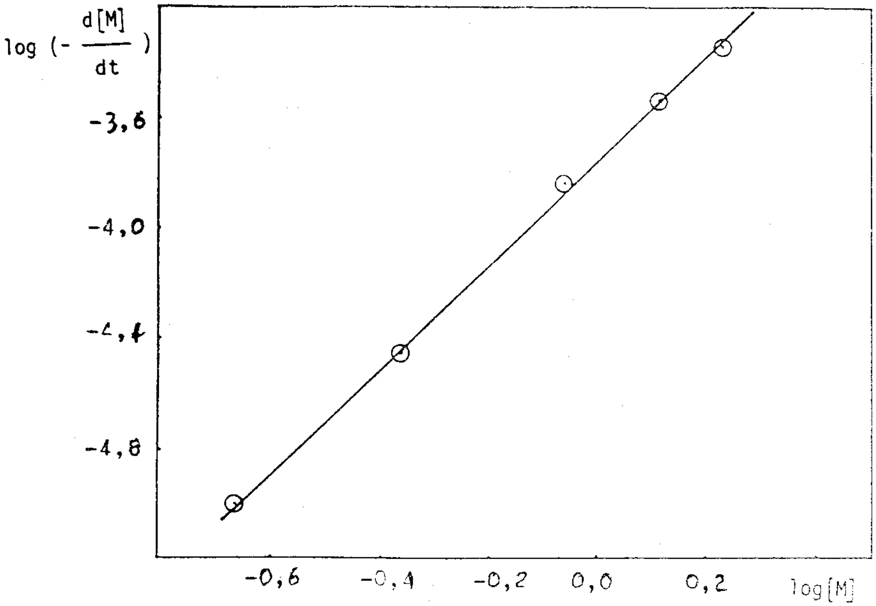


Figure 3. Log $\left(-\frac{d[M]}{dt}\right)$ vs log [M] at 0°C

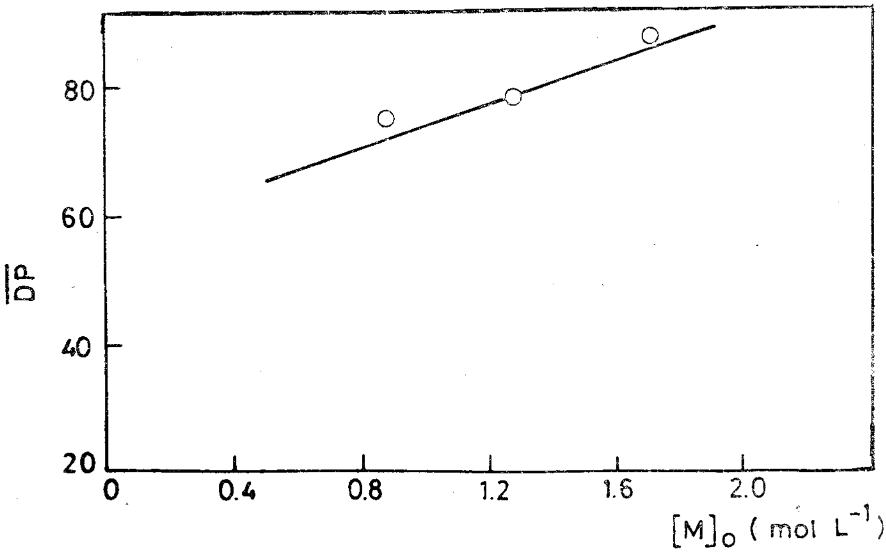


$$-\frac{d[M]}{dt} = k\ [H_2SO_4]\ [M] \qquad (16°C) \qquad (2)$$

$$-\frac{d[M]}{dt} = k\ [H_2SO_4]\ [M]^2 \qquad (0°C) \qquad (3)$$

From the slope of the lines in the plot of $-\frac{d[M]}{dt}$ versus [M] at 16°C and $-\frac{d[M]}{dt}$ versus $[M]^2$ at 0°C and using the constant value of sulphuric acid concentration, the overall rate constants of the polymerization are found as 2.7×10^{-3} $Lmol^{-1}s^{-1}$ at 16°C and 1.4×10^{-3} $L^2\ mol^{-2}\ s^{-1}$ at 0°C. From the plot of $\overline{DP}$ versus [M] (Figure 4) the ratio of the rate constants of chain propagation to termination k_p/k_t is calculated as 58 at 0°C.

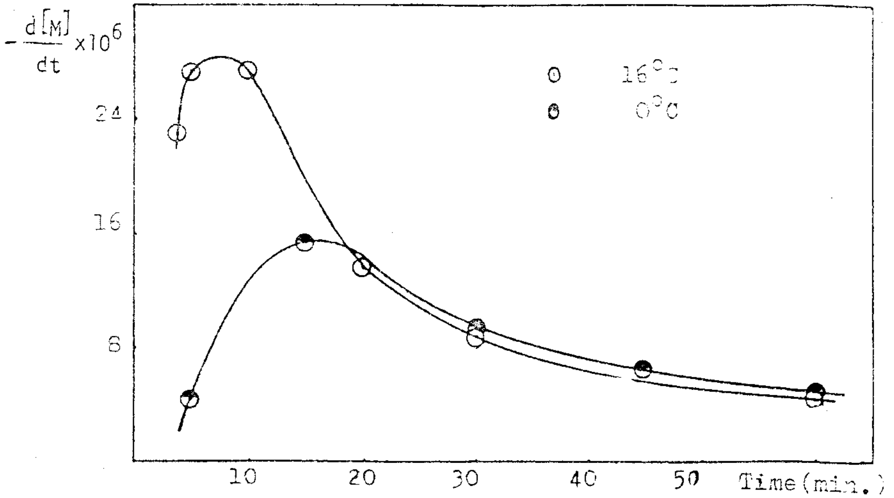
Figure 4. The dependence of the average degree of polymerization on monomer concentration at 0°C.



Effect of Polymeriazation Time:

The time – conversion curve for sulphuric acid initiated polymerization of syrene in methylene chloride is similar to that in 1.2 dichloroethane. (Hayes, Pepper 1961). Kinetic curve (Figure 5) show that the reaction preceded by an induction period the length of which increases with decreasing temperature. Maximum rate of polymerization is reached in 5 minutes at 16°C and 15 minutes at 0°C. (Figure 5). Using the logaritmic conversion function versus polymerization time shown in Figure 6, the rate constant of termination reaction was calculated as 4.3×10^{-3} s^{-1}. From the overall rate constant derived in the previous sections the value of $k_i x k_p$ was calculated as $6.0 x 10^{-6}$ L^2 $mol^{-2} s^{-1}$ at 0°C and inserting the value of k_t in k_p/k_t ratio, the value of k_p and k_i are found as $8.1 x 10^{-3}$ $Lmol^{-1} s^{-1}$ and $7.4 x 10^{-5}$ $Lmol^{-1} s^{-1}$ respectively.

Figure 5. The dependence of the rate of polymerization on polymerization time at 0°C; and 16°C



Effect of Polymerization time on molecular weight is not high, however as the temperature lowered effect on molecular weight increases (Table IV).

Effect of Solvent

Styrene was polymerized in solvents of varying dielectric constants at 16°C. As can be seen from Table V. Increase in the dielectric constant (D) of the solvent increases the percentage conversion and the rate of polymerization. A lineer relation which fits the equation 4 is derived between the dielectric constant of the solvent and the rate of polymerization.

Figure 6. Ln $\frac{[M]_0}{[M]}$ versus t (time) at 0°C

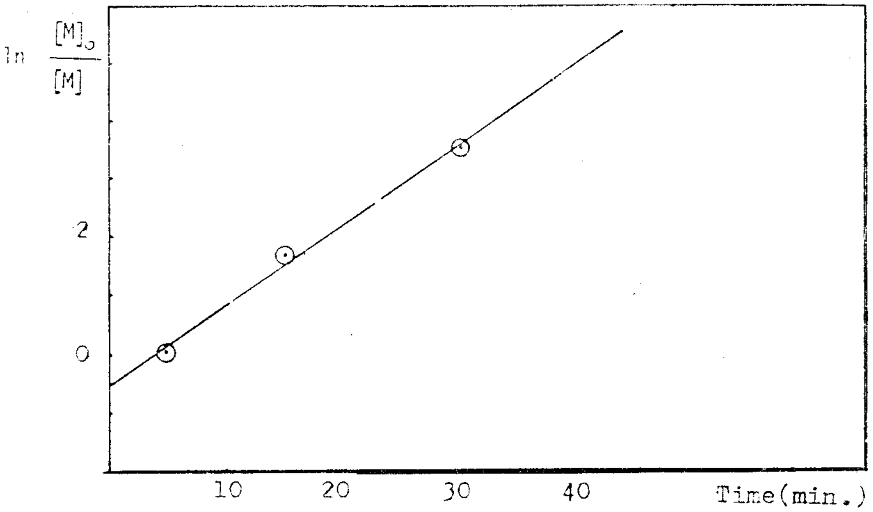


Table IV. Effect of polymerization time on the molecular weight of polymers.

Temperature (°C)	$[H_2SO_4]_0$ (mol L^{-1})	Polymerization Time (Minutes)	$\bar{M}_v x10^{-3}$
16	0.109	5	5.0
		10	6.0
		20	6.5
		30	7.0
0	0.127	5	4.0
		15	7.0
		45	8.5
		60	9.5

$$\log\left(-\frac{d[M]}{dt}\right) = 7.3x10^{-2} D -4.1 \qquad (4)$$

The dielectric constant of the solvent also affects the molecular weight of the polymers synthesized profoundly (Table V). Similar results were observed in the polymerization of styrene initiated by acethyl perchlorate and perchloric acid. (Reilly, Pepper 1962, Masuda, Higashimura 1971)

Table V. Effect of solvent on the rate of polymerization and molecular weight of polymers ($[M]_0 = 1.433$ mol L^{-1}, $[H_2SO_4]_0 = 0.152$, mol L^{-}, polym. time = 1h)

Solvent	Dielectric Constant (SD)	% Conversion	$\frac{-d[M]}{dt}$ x10^5 (mol $L^{-1}s^{-1}$)	$\bar{M}_v$
n-Hexane	1.89	23.4	9.3	1000
Toluene	2.44	32.4	12.9	1500
Methylene Chloride	9.08	95.4	37.9	5000
1-2 dichloro ethane	10.00	97.6	39.9	6000

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