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TURQUIE

Effect of Temperature and Solvent on the Cationic Polymerization of Styrene Initiated by Phosphorus Pentoxide (II).

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SUMMARY

Effect of temperature on the cationic polymerization of styrene was investigated by performing the polymerization reaction at different temperatures. The total activation energy of the reaction was measured to be 45.14 kj mol^{-1} between -20°C and + 20°C. The limiting viscosity numbers of all the polymers prepared at different temperatures were measured. Below room temperature a relationship between the limiting viscosity numbers and the temperature was obtained as follow,

$$\log [\eta] = 9.80 \times 10^{-2} \frac{1}{T} - 2.70$$

The polymers were prepared in four different solvents and the rate of polymerization in each solvent was measured. Between the rates of polymerization and the dielectric constants of the solvents, the following equations were obtained.

$$\log \left(- \frac{d\,[M]}{dt} \right) = -4.42 + 0.123\ D$$

$$\log \left(- \frac{d\,[M]}{dt} \right) = -5.11 + 4.208\ \frac{D-1}{2\ D+1}$$

Polymerization reactions were carried out in air and nitrogen atmosphere.

The rates of polymerization and the average molecular weights of the polymers were found the same in these experiments.

INTRODUCTION

The cationic polymerizations are the polyaddition reactions in which the growing species are electrophilic. The rate of polymerization depends on the solvent, temperature, the counterion and the type of monomer.

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(5). The position of the counteranion can be altered by varying the dielectric constant of the solvent. The numbers of solvent-seperated ion pairs, contact ion pairs and free ions change with the polarity of the polymerization media. When the dielectric constant of solvent increases, solvent-seperated and contact ion pairs dissociate to free ions. The rate of propagation is increased by the increase in the free ion concentration.

The effect of temperature on the rate is given by Arrhenius equation, $k = Ae^{-E_a/RT}$. Where k is the overall rate constant and E_a is the total activation energy of the cationic polymerization.

EXPERIMENTAL

A) Purification of Materials

Methylene chloride and chloroform: The method suggested for ethylene chloride by S. Okamura et al(1). was used.

n–Hexane: n–Hexane was purified according to the method suggested by N. Kanoh et. al.(2).

Toluene: Toluene was purified as follow:

It was shaken with concentrated H_2SO_4, washed with the aqueous solution of Na_2CO_3 and again washed with water. It was dried over $CaCl_2$ and distilled in the presence of Na(3).

B) The Effect of Some Factors On The Cationic Polymerization of Styrene Initiated by P_2O_5

B.1) Effect of temperature

The polymerization reactions were carried out by keeping the concentration of styrene and phosphorus pentoxide constant at —20°C, —5°C, +5°C, +20°C, +30°C and +40°C in the presence of chloroform. The rates of polymerization were measured by means of the gravimetric method. The results are summarized in Table I. The plots of the rate of polymerization versus temperature and log $\left(-\frac{d[M]}{dt}\right)$ versus $\frac{1}{T}$ are shown

Table I

The variation of the rate of polymerization with temperature. $[M]_0 = 1.640$ mol l^{-1}, $[P_2O_5]_0 = 0.094$ mol l^{-1}, time: 30 min., solvent: chloroform

t°C	$-\frac{d[M]}{dt} \times 10^5$ (mol $l^{-1}sec^{-1}$)	$\frac{1}{T} \times 10^3$	$\log\left(-\frac{d[M]}{dt}\right)$
+ 40	22.1	—	—
+ 30	24.7	—	—
+ 20	27.3	3.41	— 3.56
+ 5	14.6	3.60	— 3.84
— 5	6.6	3.73	— 4.18
— 20	1.6	3.95	— 4.80

in Fig. 1 and Fig. 2. From the slop of the straight line in Fig. 2 the total activation energy of the reaction was found to be 45. 14 kj mol $^{-1}$.

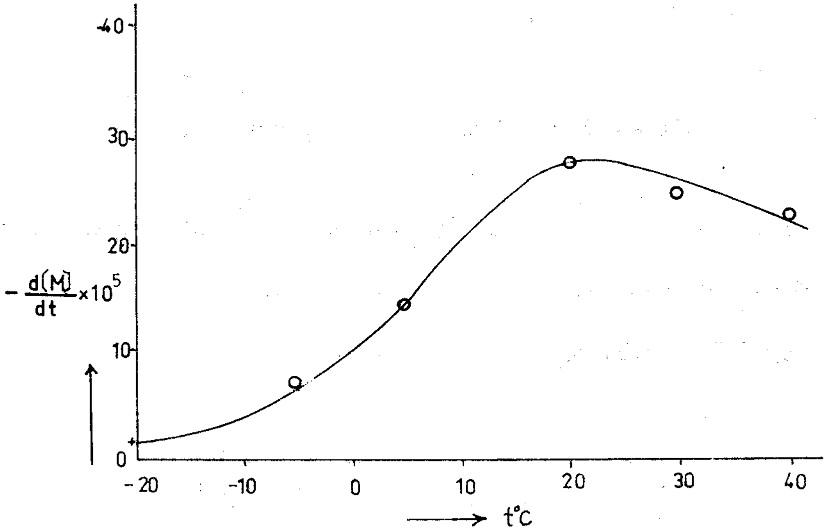

Fig.1. : The plot of the rate of polymerization versus temperature

The limiting viscosity numbers of the polymers produced at different temperatures were determined. The results are shown in Table II.

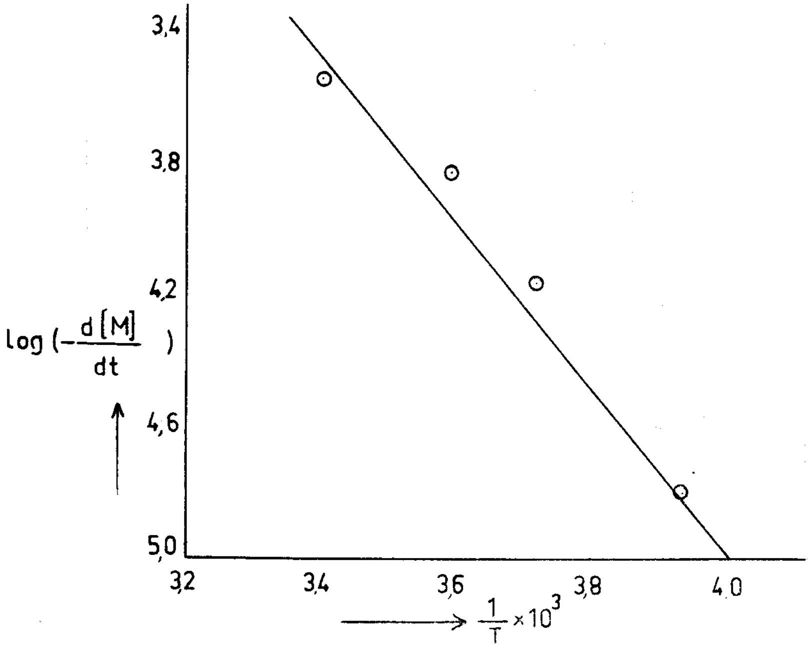

Fig. 2.: The plot of log $\left(-\frac{d\,[M]}{dt}\right)$ versus $\frac{1}{T}$

It is cleared that the plot of log $[\eta]$ against $\frac{1}{T}$ is a straight line (Fig. 3). The equation of this straight line can be given as follow,

$$\log\,[\eta] = 9.80 \times 10^{-2}\,\frac{1}{T} - 2.70$$

Table II

t°C	$[\eta]$ (ml g^{-1})	$\frac{1}{T} \times 10^3$	log $[\eta]$
+ 40	4.2	3.20	0.623
+ 30	3.9	3.30	0.591
+ 20	4.1	3.41	0.613
+ 5	5.6	3.60	0.748
— 5	9.7	3.73	0.987
— 20	13.2	3.95	1.121

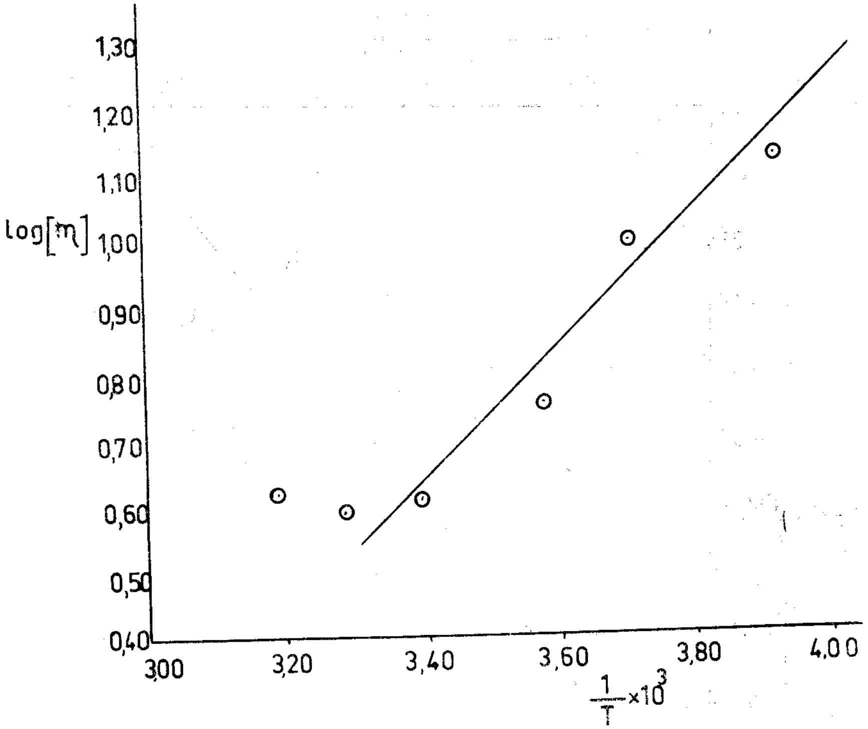

Fig. 3.: The plots of log [η] versus $\frac{1}{T}$

B.2) Effect of Solvent:

The rates of polymerization were determined in the various solvents having different dielectric constants (D). The results are given in Table III. From these values, the plot of log (–d [M] / dt) versus D (in Fig. 4 a) and the plot of log (–d [M] /dt) versus (D–1) /(2D+1) (in Fig. 4b) vere plotted. From these figures the following linear equations were obtained.

$$\log\left(-\frac{d\,[M]}{dt}\right) = 4.42 + 0.123\ D$$

$$\log\left(-\frac{d\,[M]}{dt}\right) = -5.11 + 4.208\ \frac{D-1}{2\,D+1}$$

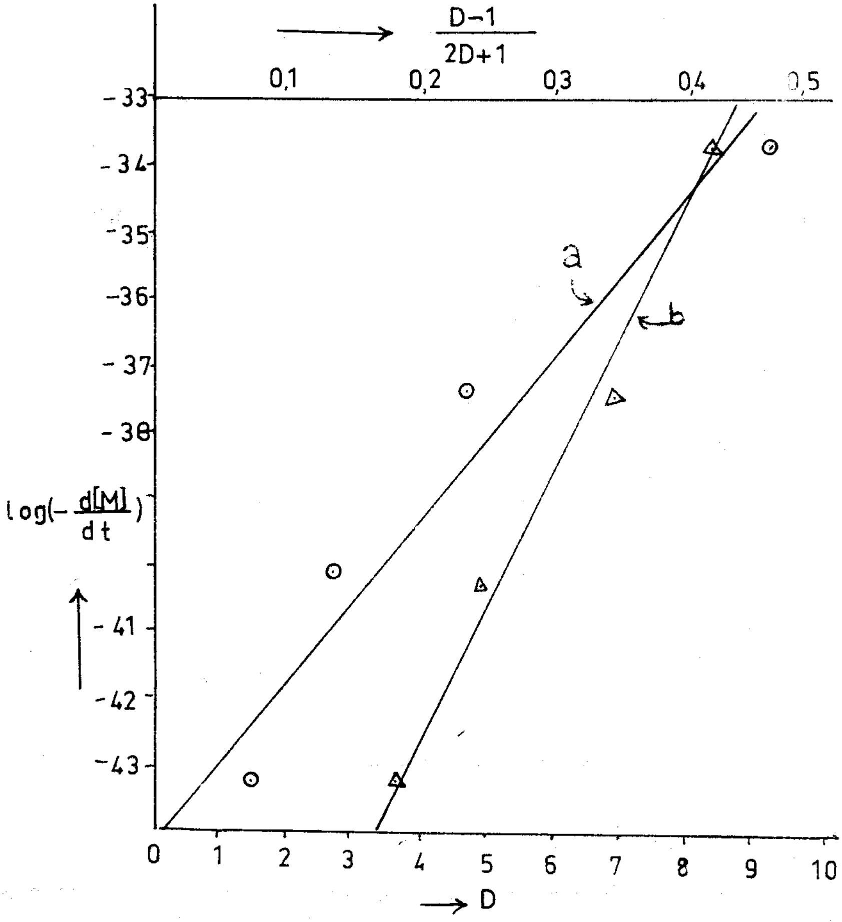

Fig. 4.: The plots of log $\left(-\frac{d\,[M]}{dt}\right)$ versus D and $\frac{D-1}{2D+1}$

Any relationship between the vicosity average molecular weights of the polymers and the dielectric constants of the solvents couldn't be established.

B.3) Effect of the reaction media:

Effect of the reaction media on the cationic polymerization of styrene was investigated by carrying out the experiments at 0°C in the air

Table III

Effect of solvent on the cationic polymerization of styrene initiated by P_2O_5.
time: 30 min., temperature: + 20°C, $[M]_0 = 1.460$ mol l^{-1}, $[P_2O_5] = 0.070$ mol l^{-1}

Solvent	Dielectric constant (D) of the solvent at 20°C(4)	$-\frac{d[M]}{dt} \times 10^5$ (mol $l^{-1}sec^{-1}$)	$\log\left(-\frac{d[M]}{dt}\right)$	$\frac{D-1}{2D+1}$
n-Hexane	1.89	4.7	— 4.328	0.186
Toluene	2.44	9.3	— 4.032	0.245
Chloroform	4.81	17.9	— 3.747	0.359
Methylene chloride	9.08	46.2	— 3.335	0.422

and nitrogen atmosphere. Nitrogen gas was dried by passing over $CaCl_2$ $-P_2O_5$ respectively and then saturated with chloroform before use. The results are summarized in Table IV.

Table IV

Effect of the reaction media on the cationic polymerization of styrene
$[M]_0 = 1.460$ mol l^{-1}, $[P_2O_5]_0 = 0.061$ mol l^{-1}, time: 60 min.,
solvent: chloroform, temperature: 0°C

the reaction media	$-\frac{d[M]}{dt} \times 10^5$ (mol $l^{-1}sec^{-1}$)	$[\eta]$ (ml g^{-1})
air	4.1	6.1
nitrogen	4.5	6.3

According to the values given in Table IV, the rates of polymerization and the limiting viscosity numbers vere not affected from the reaction media.

RESULTS and DISCUSSION

It is well known that in the free radical polymerization reactions, rate of polymerization increases with the reaction temperature.

In the cationic polymerization of styrene this has been observed with some exception that as the temperature increases the rate of polymerization increases to about room temperature then starts to decrease.

The total activation energy of the reaction was calculated to be 45.14 kj mol^{-1} between —20°C and + 20°C .The similar results was found by C.P.Brown[(6)]. On the other hand, as the reaction temperature decreases the molecular weights of the polymers increase, so low temperature is required to prepare high melecular weight polymers.

In this study we have also given a linear relationship between the reaction temperature and the limiting viscosity number of polystyrene. In the cationic polymerization the number of the growing spacies effects rate of polymerization as well as molecular weights of polymers. Number of the growing spacies called solvent-separated ion pairs, contact ion pairs and free ions change with the polarity of the reaction media.

In this study we have also observed that the rate of the polymerization of styrene increases with the dielectric constant of the solvent, but no change has been observed in the molecular weights of the polymers since the dissociation of the initiator increases with increasing the polarity of the reaction media, more growing center will be produced in the polar solvent ,therefore the molecular weights of the polymers will decrease with the polarity of solvent. These results are similar to that given in references (6, 7, 8, 9).

ÖZET

Stirenin fosfor pentoksitle farklı sıcaklıklarda katyonik polimerizasyonu yapılarak polimerizasyon hızına sıcaklığın etkisi araştırıldı. —20°C ile +20°C sıcaklıklar arasında toplam aktivasyon enerjisi Ea = 45.14 kj mol^{-1} olarak bulundu. Elde edilen polimerlerin limit viskozite sayıları tayin edilerek oda sıcaklığının altındaki sıcaklıklarda polimerlerin limit viskozite sayılarının sıcaklıkla

$$\log [\eta] = 9.80 \times 10^2 \frac{1}{T} - 2.70$$

eşitliğine göre değişitiği sonucuna varıldı.

Dielektrik sabitleri farklı dört değişik çözücüde polimerizasyonlar yapılarak reaksiyon hızına çözücünün etkisi araştırıldı. Polimerizasyon hızı ile kullanılan çözücünün dialektrik sabiti arasında aşağıdaki bağıntılar bulunmuştur.

$$\log \left(- \frac{d\,[M]}{dt} \right) = - 4.42 + 0.123\ D$$

$$\log \left(- \frac{d\,[M]}{dt} \right) = - 5.11 + 4.208\ \frac{D - 1}{2D + 1}$$

Polimerizasyon reaksiyonu bir kez kuru azot atmosferinde bir kezde havada cereyan ettirilmiştir. Polimerizasyon hızında ve elde edilen polimerlerin molekül ağırlıklarında bir değişme gözlenmemiştir. Buradan oksijenin katyonik polimerizasyonu etkilemediği sonucuna varılmıştır.

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