COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série : B Chimie

TOME : 29 ANNEE : 1983

Kinetics Studies on the Cationic Polymerization of Styrene Catalyzed by Phosphorus Pentoxide (I).

by

M. COŞKUN and E. PULAT

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Universite d'Ankara

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les diciplines scientifique représentées à la Faculté des Sciences de l'Université d'Ankara.

La Revue, jusqu'à 1975 à l'exception des tomes I, II, III etait composé de trois séries

Série A : Mathématiques, Physique et Astronomie,
Série B : Chimie,
Série C : Sciences Naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A_1 : Mathématiques,
Série A_2 : Physique,
Série A_3 : Astronomie,
Série B : Chimie,
Série C_1 : Géologie,
Série C_2 : Botanique,
Série C_3 : Zoologie.

A partir de 1983 les séries de C_2 Botanique et C_3 Zoologie ont été réunies sous la seule série Biologie C et les numéros de Tome commencerons par le numéro 1.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté des Sciences de l'Universiteé d'Ankara. Elle accepte cependant, dans la mesure de la place disponible les communications des auteurs étrangers. Les langues Allemande, Anglaise et Française seront acceptées indifféremment. Tout article doit être accompagnés d'un resume.

Les articles soumis pour publications doivent être remis en trois exemplaires dactylographiés et ne pas dépasser 25 pages des Communications, led dessins et figures portes sur les feuilles séparées devant pouvoir être reproduits sans modifications.

Les auteurs reçoivent 25 extraits sans couverture.

l'Adresse : Dergi Yayın Sekreteri,
Ankara Üniversitesi,
Fen Fakültesi,
Beşevler – Ankara
TURQUIE

Kinetics Studies on the Cationic Polymerization of Styrene Catalyzed by Phosphorus Pentoxide (I).

M. COŞKUN and E. PULAT*

Chemistry Department, Faculty of Science-Art, University of Fırat-Elazığ-Turkey

*Chemistry Department, Faculty of Science, University of Ankara–Ankara–TURKEY

(Received 24 June 1983 and accepted 17 October 1983)

SUMMARY

Polystyrenes were prepared by keeping temperature and the amount of phosphorus pentoxide constant, but changing the monomer concentration.

Rate of polymerization was found to be proportional to the second power of the monomer concentration. The number average degrees of polymerization were determined by the viscosity measurements. From the slope of the graph plotted $1/\overline{DP}$ versus $1/[M]_0$, the ratio of $(k_{tr-s}[S]_0 + k_t)/k_p$ was found to be 0.11*.

Dependence of the rate of polymerization of styrene on the concentration of phoshorus pentoxide was observed as the first order reaction in the experiments conducted at three different temperatures. At these temperatures the overall rate constants were determined as follows:

at + 20 °C; 10.0×10^{-4} l^2 mol^{-2} sec^{-1}

at + 5 °C; 7.6×10^{-4} l^2 mol^{-2} sec^{-1}

at — 20 °C; 0.9×10^{-4} l^2 mol^{-2} sec^{-1}

and the total activation energy (E_a) was found to be 46.1 kj mol^{-1}.

Polymerization reaction were performed by adding of varying amounts of water into the reaction vessel. The rate of the polymerization increased as the amount of water increased; passing throughgh a maximum, and then started to fall as the amount of water increased. At the maximum rate the ratio of $[H_2O]/[P_2O_5]$ was computed to be 0.69. Although the water effected the rate of polymerization as indicated above, the molecular weights of the polymers produced were not effected by the amount of water.

---

* If the normal transfer reactions take place as well the normal termination reactins, the following equation exists between the number average degree of polymerization and the monomer concentration

$$\frac{1}{\overline{DP}} = \frac{k_{tr-m}}{k_p} + \frac{k_{tr-s}[S]_0 + k_t}{k_p} \times \frac{1}{[M]_0}$$

INTRODUCTION

The cationic polymerizations are the polyaddition reactions in which the growing species are electrophilic. This kind of polymerization is commonly intiated by protonic acids, Lewis acids, alkylmetal compounds, etc. A large summary of initiators used at the cationic polymerization of styrene have been given by J.P. Kennedy(1).

Styrene was polymerized as cationic by $SnC1_4$(2), $TiC1_4$(3), $A1C1_3$(4) etc, which are Friedel-Crafts catalyts and water was used as a cocatalyst for these initiators. H_2S0_4(5) F_3CCOOH(6), $CC1_2HCOOH$ and $C1_3CCOOH$(7), $HC10_4$(8) which are the strong acids have been also used as initiator at the cationic polymerization of styrene.

Styrene had been previously polymerized by phosphorus pentoxide by R. Asami and N. Tokura(9). Liquid SO_2 was used as solvent in their works. But they didn't deal with the reaction mechanism. In this work, we tried to do this.

EXPERIMENTAL

Purification of Materials

Styrene: Styrene obtained through the courtesy of Petkim, Yarımca, was preserved in the Deep Freez adjusted to –30 °C. Before use, the styrene was purified by using the method of N. Kanoh et al(10).

Chloroform: The method suggested by S. Okamura(11) for the purification of ethylene chloride was used.

Ethanol: Ethanol used to precipitate the ploymers was provided by TEKEL (The administration of the Turkish Monopoly) and it was used without any purification.

Toluene: Toulene Trude mark "Merck" was used without any purification.

Preparation of Polymers:

The polymerization reactions were carried out at 0 °C in the chloroform solution in which the amount of P_20_5 was kept constant at a value of 0.036 mol 1^{-1} while the concentration of styrene was changed.

The duration of each reaction time was 60 minutes. The rate of polymerization was measured by means of the gravimetric method. The results are summarized in Table I.

Table I.

Effect of monomer concentration on the rate of polymerization carried out in the chloroform at 0°C. $[P_2 0_5]_0 = 0.036$ mol l^{-1}, Time of polymerization: 60 min.

$[M]_0$	$[M]$	$\frac{-d\,[M]}{dt} \times 10^5$ (mol l^{-1} sec^{-1})	$\log \left(\frac{-d\,[M]}{dt} \right)$	$\log\,[M]$	$[M]^2$
0.875	0.858	0.47	-5.33	-0.07	0.74
1.750	1.692	1.45	-4.84	0.23	2.86
2.188	2.085	2.86	-4.54	0.32	4.35
3.500	3.161	6.31	-4.20	0.50	9.90
4.375	3.618	14.50	-3.84	0.56	13.09

Limiting viscosity numbers of the polymers were measured in toluene at 25 °C. The results are summarized in Table II. A graph plotted, log (-d [M] /dt) versus log [M] is shown in Fig. 1. From the slope of the line it was found that the rate of the polymerization is a second order fonction of the concentration of styrene.

Table II

Variation of the viscosity average molecular weight with the monomer concentration. ($K = 4.4 x 10^{-2}$ ml g^{-1}, $\alpha = 0.65$(21))

$[M]_0$	$[\eta]$ (ml g^{-1})	$\bar{M}_v x 10^{-3}$	$1/\overline{DP}$	$1/[M]_0$
1.750	6.3	2.1	0.05	0.57
2.188	8.1	3.1	0.03	0.46
3.500	12.1	5.7	0.02	0.29
4.375	17.5	10.0	0.01	0.23

A graph plotted $1/\overline{DP}$ versus $1/[M]_0$ is shown in Fig. 2. From the slope of this line, the value of $(k_{tr-s}\,[S]_0 + k_t)/k_p$ was found to be 0.11.

Effect of Phosphorus Pentoxide:

By keeping the concentration of styrene constant, the polymerization reactions were conducted at three different temperatures (+20 °C, + 5 °C, -20 °C) for various amount of $P_2 0_5$ in chloroform. The duration

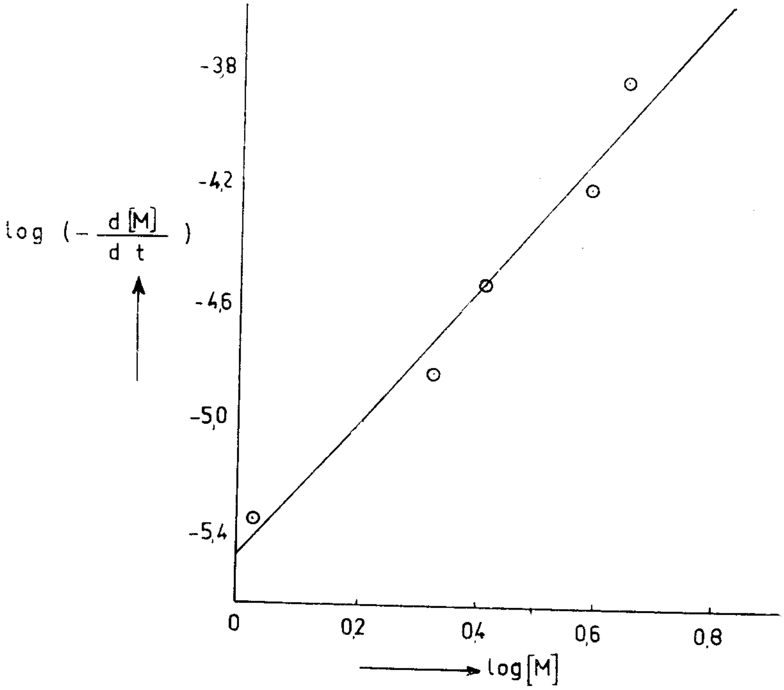


Fig. 1. A plot of log (–d [M]/dt) versus log [M]

of each reaction was 30 minutes. The rates of polymerization were calculated by gravimetric method. Viscosity moleculer weights of the polymers were measured by the Ubbelohde viscometer. The results are given in Table III.

Dependence of the rate of the polymerization on the concentration of $P_2 0_5$ is shown in Fig. 3. Fig. 3 implies that the rate of the polymerization is a first order function of the concentration of $P_2 0_5$. On the other hand the molecular weight of the polymers does not depend on the concentration of $P_2 0_5$ as seen from Table III.

From the slope of the lines in Fig. 3. the overall rate constants were calculated for three different temperatures by using the following rate equation

$$R_p = k\ [P_2 0_5]_o\ [M]_o^2 = k_1\ [P_2 0_5]_o$$

at + 20 °C; $k = 10.0 \times 10^{-4}\ l^2\ mol^{-2}\ sec^{-1}$

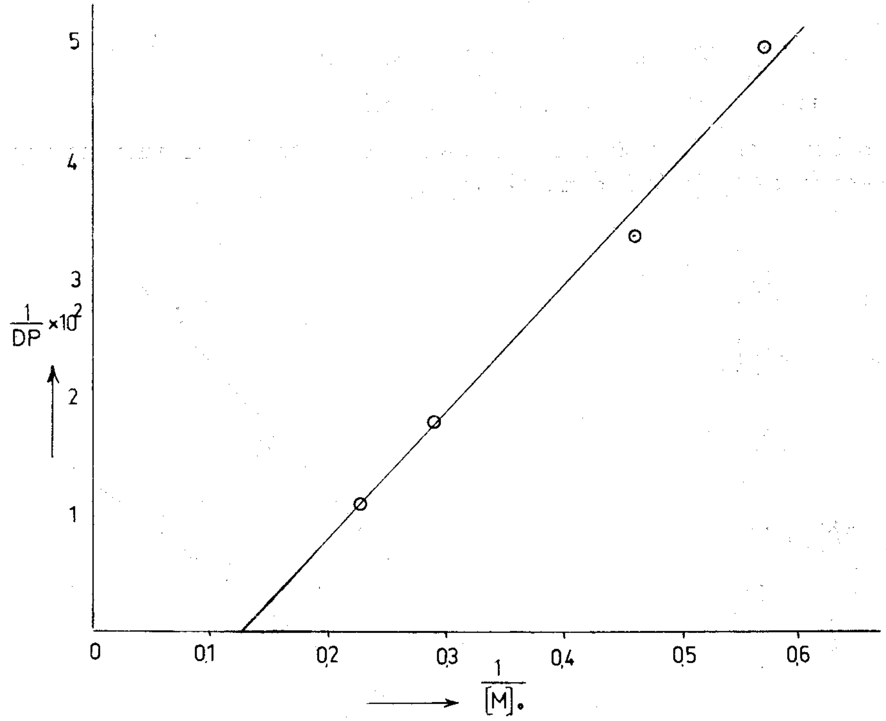


Fig. 2. A plot of $1/\overline{DP}$ versus $1/[M]_0$

Table III.

Effect of phosphorus pentoxide on the cationic polymerization of styrene in chloroform. $[M]_0 = 1.460$ mol l^{-1}, time; 30 min.

t °C	$[P_2O_5]_0$	$-\frac{d[M]}{dt} \times 10^5$ (mol l^{-1} sec^{-1})	$[\eta]$ (ml g^{-1})	$\bar{M}_v \times 10^{-3}$
+20	0.028	9.7	4.3	1.2
	0.480	12.4	4.5	1.2
	0.072	17.1	4.2	1.1
	0.127	28.4	5.0	1.5
	0.143	36.2	–	–
+5	0.054	7.1	5.8	1.8
	0.104	14.0	6.2	2.0
	0.136	22.0	5.5	1.6
	0.143	26.0	–	–
—20	0.048	0.2	–	–
	0.064	1.6	11.3	5.1
	0.101	2.0	10.8	4.8
	0.163	2.9	11.8	5.5

at + 5 °C; $k = 7.6 \times 10^{-4}\ l^2\ mol^{-2}\ sec^{-1}$

at — 20 °C; $k = 0.9 \times 10^{-4}\ l^2\ mol^{-2}\ sec^{-1}$

and from the graph plotted logk versus 1 /T, the total activation energy was found to be 46.1 kj mol^{-1} (Fig. 4).

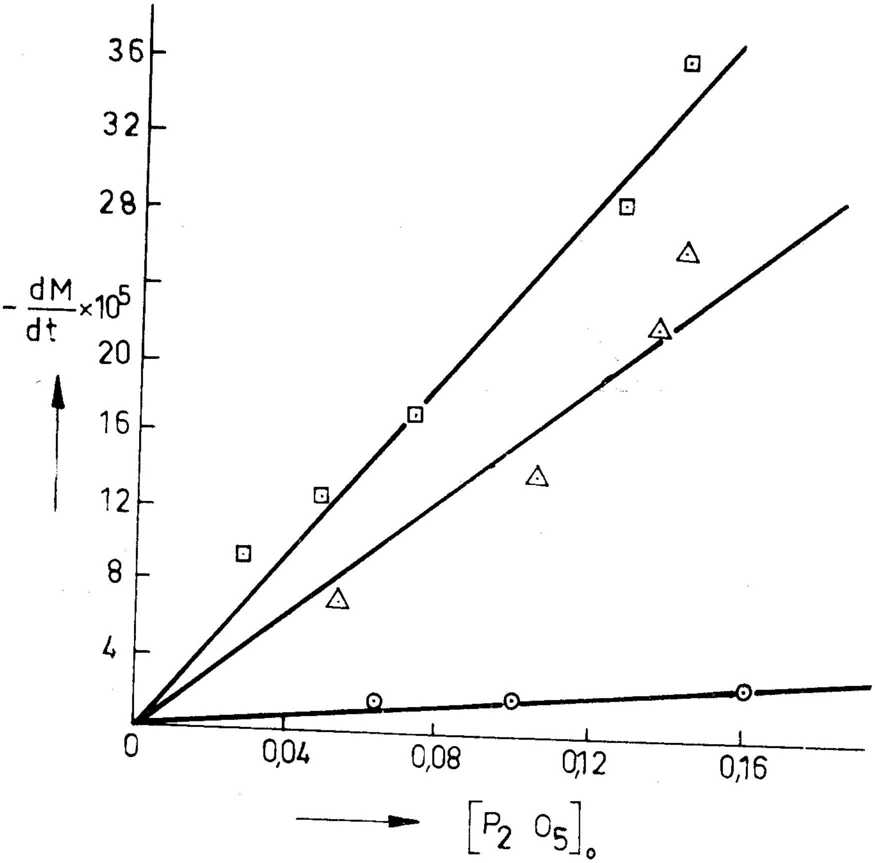


Fig. 3. Dependence of the rate of polymerization on the concentration of P_2O_5 at three different temperatures

Effect of Water Concentration:

Effect of water concentration on the rate and the molecular weights of the polymers was investigated.

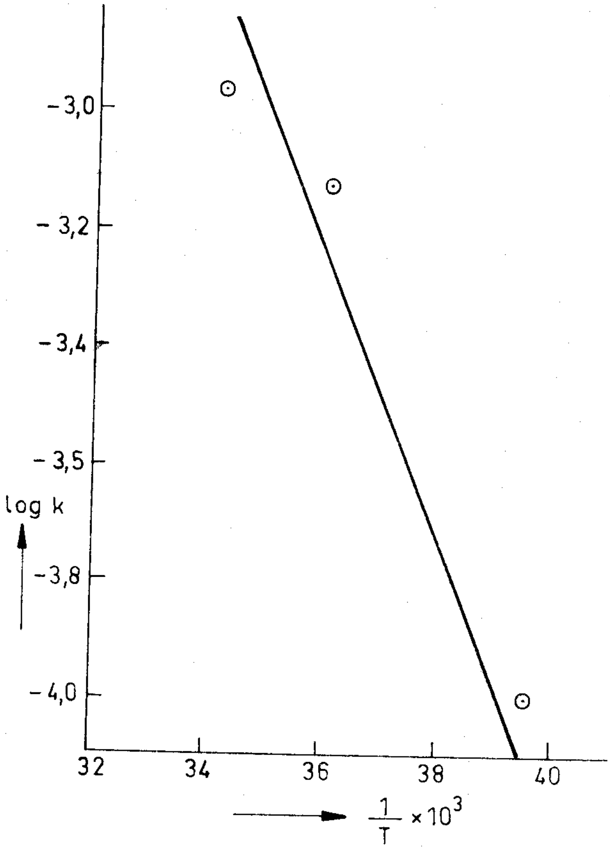


Fig. 4. A plot of log k versus 1/T

To do this, styrene was polymerized for 45 minutes in chloroform by changing the concentration of H_20. Rates of polymerization and the molecular weights of the polymers were measured.

The rusults are shown in Table IV and Fig. 5.

It is evident from these results that the concentration of H_20 effects the rate of the polymerization; as the concentration of H_20 increases the rate of the cationic polymerization increases passing through a maximum, then starts to decrease. At the maximum rate, the ratio of the concentration of H_20 to that of P_20_5 is 0.69

Table. IV.

Effect of H_20 concentration on the cationic polymerization of styrene at 5 °C in chloroform $[M]_0 = 1.460$ mol l^{-1}, $[P_20_5]_0 = 0.073$ mol l^{-1}; time: 45 mim.

$[H_20]$	Pol %	$-\frac{d[M]}{dt} \times 10^5$ (mol l^{-1} sec^{-1})	$\bar{M}_v x10^{-3}$
0	25.2	13.6	1.8
0.020	40.7	22.0	–
0.042	45.0	24.3	2.1
0.070	42.0	22.7	1.7
0.120	20.1	10.9	2.2
0.230	3.4	1.8	–

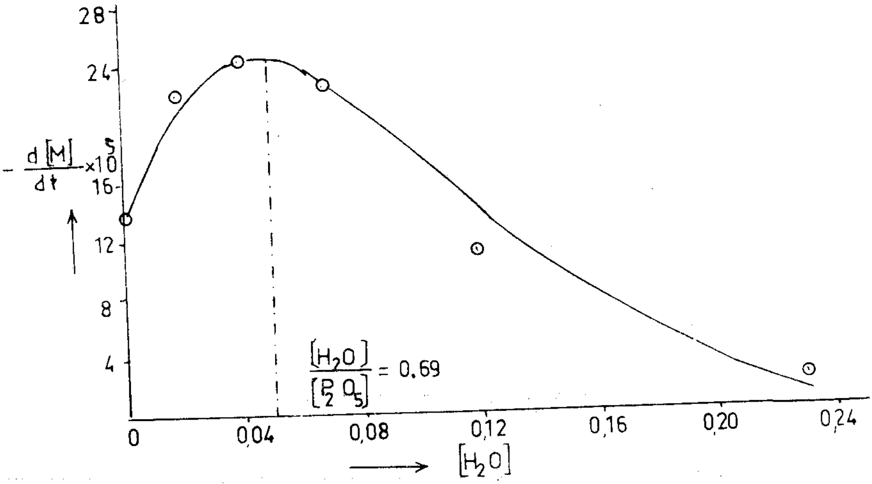


Fig. 5. The variation of the rate of polymerization with the concentration of H_20

DISCUSSION

The rate of polymerization is proportional to the second power of the monomer concentration. This result is similar to that of Peper(12), Jordan and Mathieson(4), Brow nand Mathieson(7) and Sakurada et al(13);

in their studies they have used $SnCl_4$, $AlCl_3$, CCl_2HCOOH and CCl_3 COOH, I_2 as catalyst.

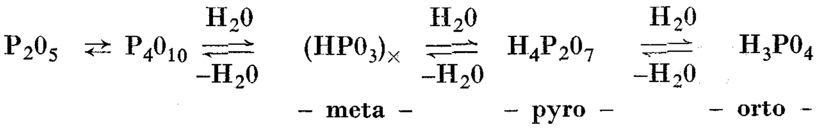
As the monomer concentration increased, molecular weights of polymers increased. It is seen from Fig. 2. that this increase is linear.

Since the intercept of the line $1/\overline{DP}$ against $1/[M]_o$ is smaller than zero, chain transfer to monomer doesn't take place. The slope of this straight line $(k_{tr-s}\,[S]_o + k_t)/k_p$ is equal to 0.11; for the cationic polymerization of styrene initiated by I_2(11) and $SnCl_4$(14), k_t/k_p is equal to $3.0 x 10^{-1}$ and $5.1 x 10^{-5}$ respectively. The value we have found is highly greater than these. This can be explained as that there is a chain transfer to the solvent.

The rate of polymerization is proportional to the first power of the catalyst concentration. This result is similar to that of Jordan and Mathieson(4), Brown(7), Colclough(2), in their studies they have used $AlCl_3$, CCl_2HCOOH and CCl_3 COOH, $SnCl_4$ as catalyst. It is seen that molecular weights of the polymers do not change with the catalyst concentration. One may say that chain transfer to the catalyst doesn't take place for this ploymerization reaction. This is similar to the results obtained at the cationic polymerization of styrene initiated by H_2SO_4(5), $HClO_4$(8) and α – methylstyrene catalyzed by H_2SO_4(15).

The rate of polymerization first increased as the concentration of water increased then decreased. The similar results were observed for the cationic polymerization of styrene catalyzed by $SnCl_4$(2), $AlCl_3$(16), $AlEt_3$–H_20(17) and for α – methylstyrene catalyzed by $BF_3\,(C_2H_5)_20$(18); but in the cationic polymerization of styrene catalyzed by H_2SO_4 the similar results were not observed(5).

The cationic polymerization of styrene catalyzed by P_20_5 can be carried out without using H_20; but since P_20_5 is hygroscopic, there must be very small amount of water in it. I can be obtained different kinds of phophoric acids according to the amount of water



$$P_20_5 \rightleftarrows P_40_{10} \underset{-H_20}{\overset{H_20}{\rightleftharpoons}} (HP0_3)_x \underset{-H_20}{\overset{H_20}{\rightleftharpoons}} H_4P_20_7 \underset{-H_20}{\overset{H_20}{\rightleftharpoons}} H_3P0_4$$

– meta – – pyro – – orto –

The strength of these acids are as follow(19)

$(HP0_3)_x > H_4P_20_7 > H_3P0_4$ % 100

$$\frac{[H_20]}{[P_20_5]} = 1, \text{ metaphosphoric acid}$$

$$\frac{[H_20]}{[P_20_5]} = 2, \text{ pyrophosphoric acid}$$

$$\frac{[H_20]}{[P_20_5]} = 3, \text{ ortophosphoric acid}^{(20)}$$

Metaphosphoric acid can be obtained by a little water. The proton which is necessary for cationic polymerization is suplied by metaphosphoric acid. Therefore, the factor which increase the concentration of metaphosphoric acid, increase the rate of polymerization. In this work, when $[H_20]/[P_20_5]$ is 0.69, the rate is maximum. Since P_20_5 is hygroscopic, we can think that P_20_5 may absorbe water from air before adding in it. Because of this reason, the ratio of $[H_20]/[P_20_5]$ will be greater than that value. When the adding water is icnreased in the media, the concentration of acid will increase, therefore the rate of polymerization will be maximum by increasing of acid concentration. When we add more water, the ratio of $[H_20]/[P_20_5]$ will be greater than 1, pyrophosphoric acid will start to occur and the rate of polymerization will decrease. If the ratio of $[H_20]/[P_20_5]$ is greater than 2, ortophosphoric acid will be arised and the rate of polymerization will be smaller. Although styrene can be polymerized by P_20_5 with 97 % conversion of monomer in liquid $S0_2$, it can be polymerized by ortophosphoric acid with 1 % conversion in the same circumstances(9).

The molecular weight of polymers wasn't changed by adding water, since all water in the media was absorbed by P_20_5, there are not free water molecules for transfer to water.

ÖZET

Fosfor pentoksit miktarı ve sıcaklık sabit tutularak değişik monomer konsantrasyonlarında polimerler hazırlandı. Polimerizasyon hızları hesaplandı. Polimerizasyon reaksiyonunun stiren konsantrasyonuna 2. mertebeden bağlı olduğu görüldü. 0 °C sıcaklıkta elde edilen polimerlerin molekül ağırlıkları limit viskozite sayısından bulunarak sayıca ortalama polimerizasyon dereceleri hesaplandı.

$1/\overline{DP} - 1/[M]_0$ doğrusunun eğiminden $(k_{tr-s}[S]_0 + k_t)/k_p$ oranı 0.11 olarak bulundu.

Üç ayrı sıcaklıkta, monomer konsantrasyonu sabit tutulup fosfor pentaoksit miktarı değiştirilerek yapılan deneylerden polimerizasyon hızının fosfor pentaoksit konsantrasyonuna birinci mertebeden bağlı olduğu görüldü.

Toplam hız sabitleri için

+ 20 °C da $k = 10.0 \times 10^{-4}\ l^2\ mol^{-2}\ sn^{-1}$
+ 5 °C da $k = 7.6 \times 10^{-4}\ l^2\ mol^{-2}\ sn^{-1}$
— 20 °C da $k = 0.9 \times 10^{-4}\ l^2\ mol^{-2}\ sn^{-1}$

değerleri ve toplam aktivasyon enerjisi için ise 46.1 kj mol^{-1} değeri bulundu.

Reaksiyon ortamına değişik miktarlarda su katılarak polimerizasyon yapıldı. Ortama katılan su miktarı ile önce polimerizasyon hızının arttığı, sonra bir maksimumdan geçerek azalmaya başladığı ve maksimum hızda $[H_2O]/[P_2O_5]$ oranının 0.69 olduğu belirlendi. Ortama katılan su polimerizasyon hızını etkilediği halde, elde edilen polimerlerin molekül ağırlıklarını etkilememiştir.

REFERENCES

[1] **J.P. Kennedy,** Cationic Polymerization of Olefins, John Wiley and Sons, Canada, 1975, p. 230.

[2] **R.O. Colclough and F.S. Dainton.** Trans. Faraday Soc., 54, 886 (1958).

[3] **P.H. Plesch,** J. Chem. Soc., 1653 (1953).

[4] **D.O. Jordan and A. R. Mathieson,** J. Chem. Soc., 611 (1952).

[5] **D.C. Peper,** paper presented at International Symposium on Macromolecular Chemistry, Wieşbaden, 1959 paper III, A9.

[6] **J.J. Throssell, S.P. Sood, M. Szvarc and V. Stannett,** J. Am. Chem. Soc., 78, 1122 (1956).

[7] **C.P. Brown and A.R. Mathieson.,** J. Chem. Soc., 3612 (1957).

[8] **A. Gandini and P.H. Plesch,** J. Chem. Soc., 4826 (1965).

[9] **R. Asami and N. Tokura,** J. Polymer Sci., 42, 553 (1960).

[10] **N. Kanoh, T. Higashimura and S. Okamura,** Makromol. Chem., 56, 65 (1962).

[11] **S. Okamura, N. Kanoh and T. Higashimura,** Makromol. Chem., 47, 19 (1961).

[12] **D.C. Peper,** Trans. Faraday Soc., 45, 404 (1949).

[13] **I. Sakurada. N. Ise, Y. Taraka and Y. Hayashi,** J. Polymer Sci., A-1, 4, 2081 (1966).

[14] **G.F. Endres. V.G. Kamath and C.G. Overberger,** J. Am. Chem. Soc., 84, 4813 (1962).

[15] **R.G. Heiligmann,** J. Polymer Sci., 6, 155 (1950).

[16] **D.O. Jordan and F.G. Treloar,** J. Chem. Soc., 734 (1961).

[17] **T. Saegua, H. Imai and J. Furukawa,** Makromol. Chem., 79, 207 (1964).

[18] **D.J. Worsfold and S. Bywater,** J. Am. Chem. Soc., 79, 4917 (1957).

[19] **Kirk-Othmer,** Encyclopedia of Chemical Technology Vol. 15, p. 270., (1964).

[20] **Kirk-Othmer,** Encyclopedia of Chemical Technology Vol. 15, p. 261., (1964)

[21] **J. Brandrup and E.H. Immergut,** "Polymer Handbook" IV–17, Interscience Publishers Company, New–York, (1975).