

SOME KINETIC PARAMETERS ON THE CATIONIC POLYMERIZATION OF α -METYLSTRENE (III)

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(Received in June 1985, Accepted December 1985)

SUMMARY

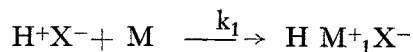
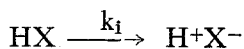
H₂SO₄ initiated cationic polymerization of α -methylstyrene was carried out in chloroform. The effect of temperature and monomer concentration on rate of polymerization and on the molecular weight of poly α -methylstyrene were studied. The total activation energy of the reaction was found to be - 32.6 kJ mol⁻¹.

Also assuming that the transfer reactions were negligible, it was obtained that k_p/k_t was equal to 2.64×10^2 .

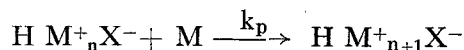
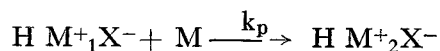
INTRODUCTION

The kinetic model for the cationic polymerization reactions is expressed as

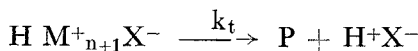
Initiation:



Propagation:



Termination:



If ionization is the slower step, the rate of initiation is given as

$$R_i = k_i[\text{C}] \quad (1)$$

where $[\text{C}]$ is the concentration of HX and k_i is the ionization constant. If the formation of the carbonium ions is the slower step, then, R_i is given by

$$R_i = k_1[\text{C}] [\text{M}] \quad (2)$$

The rate of consumption of the monomer, namely the propagation rate, is given by

$$R_p = - \frac{d[\text{M}]}{dt} = k_p[\text{M}^{+}] [\text{M}] \quad (3)$$

where $[\text{M}^{+}]$ is the total concentration of the polymer ions in the reaction mass.

For the termination step, the termination rate can be written

$$R_t = \frac{d[\text{P}]}{dt} = k_t[\text{M}^{+}] \quad (4)$$

where P denotes polymer.

Applying the steady state approximation to the polymer ion concentration and assuming that the formation of the carbonium ions is the slower step. Eq. 2 and Eq. 4 may be equated to solve for $[\text{M}^{+}]$

$$k_1[\text{C}] [\text{M}] = k_t[\text{M}^{+}] \quad (5)$$

This gives

$$[\text{M}^{+}] = \frac{k_1}{k_t} [\text{C}] [\text{M}]$$

If $[\text{M}^{+}]$ is substituted in Eq. 3, one has

$$R_p = - \frac{d[\text{M}]}{dt} = \frac{k_p k_1}{k_t} [\text{C}] [\text{M}]^2 \quad (6)$$

Since the degree of polymerization ($\overline{\text{DP}}$) is

$$\overline{\text{DP}} = \frac{-d[\text{M}] / dt}{d[\text{P}] / dt}$$

we obtain

$$\overline{DP} = \frac{k_p[M^+][M]}{k_t[M^+]} = \frac{k_p}{k_t} [M] \quad (7)$$

Here we assume that the transfer reactions are negligible.

EXPERIMENTAL

Purification of materials was done as described in the reference (Heiligmann 1952). The polymerization apparatus consisted of a conventional three-necked flask fitted with stirrer, thermometer and micropipette. Dry ice-acetone was used as an external cooling medium. Molecular weight of polymers was calculated from Mark Hauwink equation by using Ubbelohde viscometer at 30°C in benzene.

RESULTS

To find out the total activation energy of cationic polymerization reaction between α -methylstyrene and H_2SO_4 , the effect of temperature on the polymerization rate was studied. The experimental results are summarized in Table 1.

Table 1. Effect of temperature on the rate of polymerization in chloroform. Time = 1 hour. $[M]_0 = 1,026 \text{ mol l}^{-1}$, $[H_2SO_4]_0 = 0,025 \text{ mol l}^{-1}$

Temperature K	Pol. %	$R_p \times 10^5$ ($\text{mol l}^{-1} \text{ sec}^{-1}$)	$\log R_p$
243	4,23	1,2	- 4,92
233	8,67	2,5	- 4,60
223	15,03	4,6	- 4,33

The total activation energy of polymerization reaction was calculated from the conventional Arrhenius equation. For this reason $\log R_p$ was plotted against $1/T$ (Figure 1).

The total activation energy of the reaction was found to be $-32.6 \text{ kJ mol}^{-1}$ between 243 K and 213 K from the slope of the straight line in Figure 1.

Energy term $E_{\overline{DP}}$ for the polymerization degree was calculated to find out the effect of temperature on the molecular weight of poly α -methylstyrene. Results are shown in Table II.

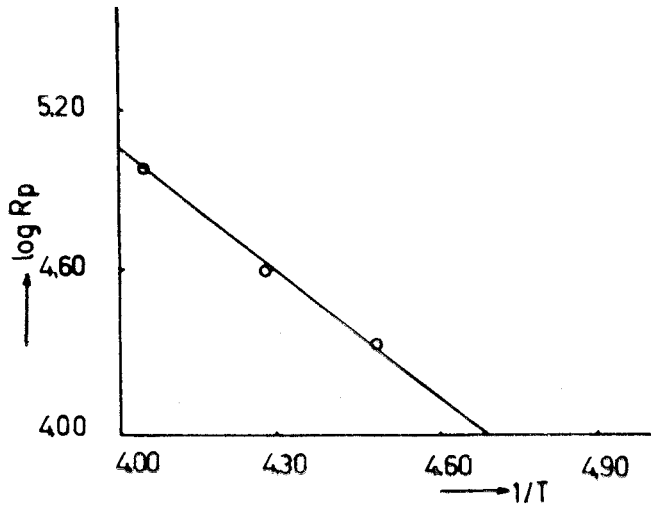


Figure 1: Variation of $\log R_p$ against $1/T$

Table II. Effect of temperature on the molecular weight of poly α - methylstyrene in chloroform. $[M]_0 = 1,026 \text{ mol l}^{-1}$, $[H_2SO_4]_0 = 0,025 \text{ mol l}^{-1}$, Time = 1 hour

Temperature K	$\bar{M}_v \times 10^{-3}$	\bar{DP}	Log \bar{DP}
233	19	161	2,20
223	27	229	2,36
213	32	271	2,43

The plot of $\log \bar{DP}$ against $1/T$ is shown in Figure 11. Energy term $E_{\bar{DP}}$ was calculated from the slope of straight line in Figure II in the similar way to the total activation energy.

In the other experiment, the effect of monomer concentration on the molecular weight of poly α - methylstyrene was studied and the degree of polymerization was calculated. Results are shown in Table III.

When the monomer concentration was under $0,719 \text{ mol l}^{-1}$, polymer could not be obtained.

If the degree of polymerization (\bar{DP}) is plotted against monomer concentration $[M]_0$ (Figure III), it is seen that k_p/k_t is equal to $2,64 \times 10^2$.

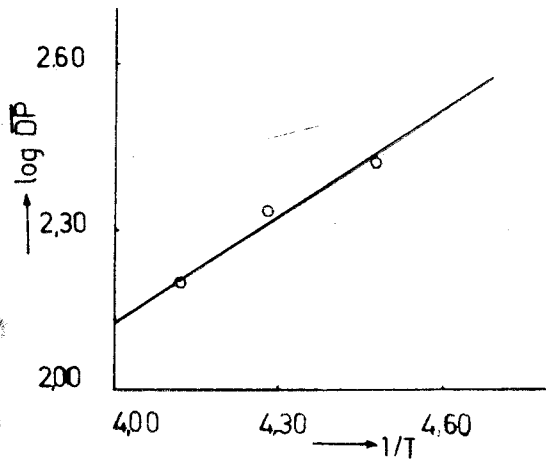


Figure II: Variaton of polymerization degree against temperature

Table III. Effect of monomer concentration on the molecular weight of poly α - methylstyrene in chloroform. T = 223 K, time = 1 hour.

$[M]_0$ mol l ⁻¹	$M_v \times 10^{-3}$	\overline{DP}
0,719	16	137
0,821	22	186
0,927	25	212
1,026	27	229

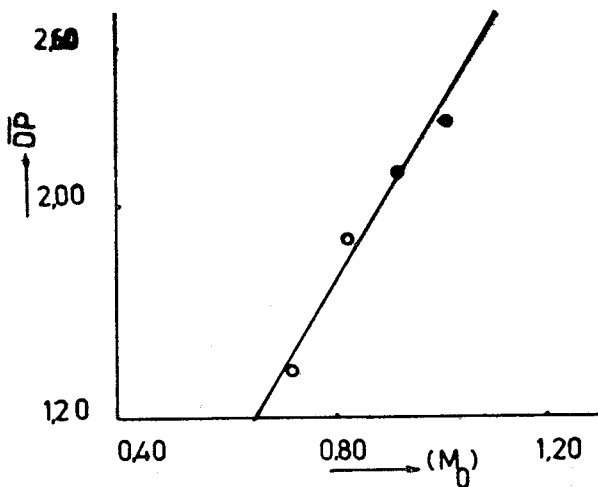


Figure III: Variaton of polymerization degree wiht monomer concentration

DISCUSSION

Ceiling temperature of α - methylstyrene is about the room temperature, so the polymers having high molecular weight cannot be obtained above the room temperature (Dainton 1948). We obtained the similar results. Both the molecular weight of poly α -methylstyrene and the polymerization rate increased as the temperature decreased.

The total activation energy E_A for this polymerization reaction was found to be - 32.6 kJ mol⁻¹. This shows that the rate of polymerization reaction increases as the temperature decreases. Similar results were obtained by the other workers. Roberts and Jessup (1951) have measured the heat of polymerization of α - methylstyrene and found it -37.9 kJ mol⁻¹.

For the α - methylstyrene - H₂SO₄ system, log \overline{DP} is linear with 1/T and the energy term $E_{\overline{DP}}$ for degree of polymerization was calculated as -11.5 kJ mol⁻¹. This means that high molecular weight of poly α - methylstyrene can be obtained at low temperatures. This value is good agreement with the value found by Brown and Mathieson for the trichloroacetic acid - ethyl bromide system (Brown 1958).

When the effect of monomer concentration on the molecular weight of poly α - methylstyrene was studied, it was seen that the molecular weight of poly α - methylstyrene increased as the monomer concentration increased. Also, when the transfer reactions are negligible, the value of k_p/k_t was found as $2,64 \times 10^2$.

ÖZET

Bu çalışmada α - metilstiren H₂SO₄ ile kloroformda katyonik olarak polimerleştirildi. Poli α - metilstirenin molekül ağırlığı ve polimerizasyon hızı üzerine sıcaklık ve monomer konsantrasyonunun etkisi araştırıldı. Reaksiyonun aktivasyon enerjisi - 32.6 kJ mol⁻¹ olarak bulundu.

Ayrıca, transfer reaksiyonlarının ihmal edilebileceği kabul edilerek, k_p/k_t için $2,64 \times 10^2$ değeri bulundu.

ACKNOWLEDGEMENTS

We are grateful to TUBİTAK-TUMKA for the the support of this project.

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