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by

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9

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Studies on the Cationic Polymerization of α -Methyl Styrene Catalyzed by Sulfuric Acid (II)

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SUMMARY

In this study α -methyl styrene has been polymerized using sulfuric acid as catalyst. The effects of catalyst and cocatalyst (water) concentration, type of solvent were investigated.

It has been found that the rate of the polymerization increases linearly with the catalyst concentration. On the other hand, molecular weight of the polymer was not effected by the catalyst concentration. α -methyl styrene has also been polymerized using different amounts of water as cocatalyst.

Our results showed that as the water concentration was increased the rate of polymerization and the molecular weight of the polymer decreased.

α -Methyl styrene has been polymerized at two different temperatures by using ethylene chloride and methylene chloride as solvent. Rate of polymerization and molecular weight of the polymers prepared in ethylene chloride were found greater than that prepared in methylene chloride.

INTRODUCTION

In the previous study the effect of temperature, time of polymerization and the monomer concentration on the rate of polymerization and on the molecular weight of the polymer had been investigated [1]. It will be of interest to search for the other variables effecting the reaction, to investigate the kinetic aspects of the sulfuric acid catalyzed

cationic polymerization of α -methyl styrene and compare it with the known characteristic of a system catalyzed by a typical electrophilic metal halide.

EXPERIMENTAL and RESULT

Purification of the materials and the preparation of poly α -methyl styrene were the same as that described previously [1].

Molecular weight of the polymers was determined by the viscosity measurements.

The specific viscosities of poly α -methyl styrene solutions were measured for four different concentrations in benzene at 30 °C by using Ubbelohde viscometer.

Percent polymerizations were determined by the gravimetric estimation of the polymers. All the experimental results are summarized in the following Tables and Figures.

Table 1

Effect of Catalyst Concentration on the Rate of Polymerization, at -60°C
 $[\text{M}]_0 = 0.9235 \text{ mol/l}$; $[\text{CH}_2\text{Cl}_2] = 13.4692 \text{ mol/l}$; time = 1 hr.

exp no.	$[\text{H}_2\text{SO}_4]$ (mol/l)	Pol %	$R_p \times 10^6$ (mol/l sec.)
1	12.00×10^{-3}	20.57	52.7
2	7.70×10^{-3}	9.92	25.4
3	3.80×10^{-3}	2.06	5.3
4	3.22×10^{-3}	0.53	1.4
5	2.50×10^{-3}	—	—

The plot of the rate of polymerization against catalyst concentration is given in Figure 1.

α -methyl styrene was not polymerized at the concentration of $12 \times 10^{-3}\text{M}$ H_2O in the period of one hour time, then H_2O concentration was decreased to $6.77 \times 10^{-3}\text{M}$, at the end of two and half an hour time poly α -methyl styrene was not obtained too, but at and below the concentration of $5.84 \times 10^{-3}\text{M}$ H_2O , the polymers were obtained as to be seen in Table III.

The effect of solvent on the rate of polymerization and on the molecular weight of the polymer was determined by preparing poly α -methyl

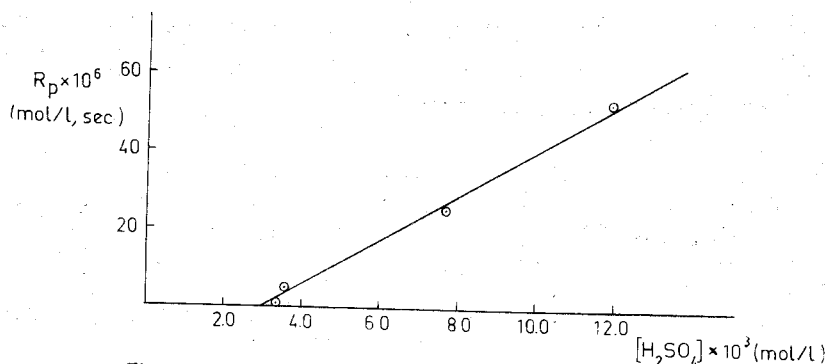


Fig 1 Variation of the Rate of polymerization with catalyst concentration

Table II

Effect of Catalyst Concentration on the Molecular weight of poly α -Methyl styrene, at -160°C ;
 $[M]_0 = 0.9235$ mol/l time = 1 hr.

exp no.	$[H_2SO_4]$ (mol/l)	\overline{M}_v	\overline{DP}
1.	12.00×10^{-3}	61050	517
2.	7.70×10^{-3}	60128	506
3.	3.80×10^{-3}	59722	505
4.	3.22×10^{-3}	59560	503

Table III

Effect of Co-catalyst Concentration on the Rate of Polymerization, at -60°C
 $[M]_0 = 0.9235$ mol/l ; $[H_2SO_4] = 0.0076$ mol/l ; time = 1 hr.

exp no.	$[H_2O]$ (mol/l)	Pol %	$R_p \times 10^6$ (mol/l, sec.)
1	1.20×10^{-3}	16.24	41.7
2	3.07×10^{-3}	3.37	8.6
3	4.92×10^{-3}	2.75	7.0
4	5.84×10^{-3}	0.76	1.9

Table IV

Effect of Co-catalyst Concentration on the Molecular Weight of poly α -Methyl styrene, at -60°C
 $[M]_0 = 0.9235$ mol/l ; $[H_2SO_4] = 0.0076$ mol/l ; time = 1 hr.

exp no.	$[H_2O]$ (mol/l)	\overline{M}_v	\overline{DP}
1	1.20×10^{-3}	65614	555
2	3.07×10^{-3}	60614	513
3	4.92×10^{-3}	50516	427
4	5.84×10^{-3}	41514	351

styrene at two different temperatures in methylene chloride and ethylene chloride.

The results are shown in Table V

Table V

Effect of Solvent on the Rate of Polymerization and on the Molecular Weight of the Polymer
 $[M]_0 = 0.9235 \text{ mol/l}$; time = 1 hr.; $[H_2SO_4] = 0.0105 \text{ mol/l}$

Solvent	t°C	Pol %	$R_p \times 10^6 (\text{mol/l, esc})$	\overline{M}_v
Ethylene Chloride	-25	9.35	23.0	4093
	-30	12.77	32.8	4937
Methylene Chloride	-25	2.67	6.8	1679
	-30	4.09	10.5	2623

DISCUSSION

The sulfuric acid catalyzed polymerization of α -methyl styrene has been studied by some workers.

Tiffeneau [2] has used 80 % H_2SO_4 at $0^\circ C$ and obtained dimer. At the room temperature, the saturated dimer was prepared by using 80 % H_2SO_4 . The amount of the saturated polymer increases with temperature [3]. High molecular weight polymer was prepared at low temperature (0, $-70^\circ C$) by using sulfuric acid [4].

In this study, the effects of the catalyst concentration, co-catalyst concentration and the effect of solvent on the molecular weight as well as on the rate of polymerization have been investigated.

Effect of the sulfuric acid concentration on the rate of polymerization is seen directly in Table I and Figure 1.

It will be seen from the data presented in Figure 1 that the rate of the sulfuric acid catalyzed polymerization of α -methyl styrene follows first order kinetic with respect to catalyst concentration.

We have observed that, poly α -methyl styrene was not obtained below the concentration of $3 \times 10^{-3} M H_2SO_4$ (see Table I)

In our experimental conditions this is the critical catalyst concentration above which the reaction can take place.

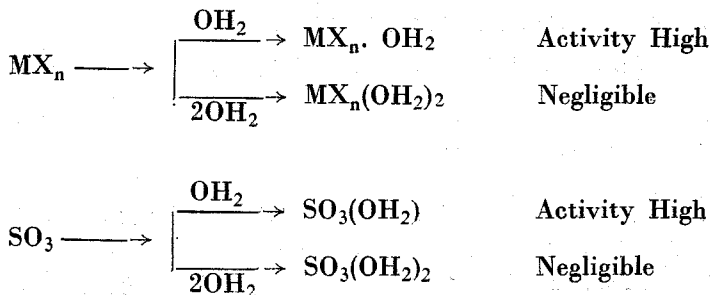
It will be seen from the data given in Table II that the catalyst concentration does not effect the molecular weight of poly α -methyl

styrene. We can come to this conclusion that transfer to catalyst is not, possible other wise catalyst will enter to the structure and terminate the polymerization, so the molecular weight of the polymer will be decreased. This agrees well with the data published by D.J. Worsfold and S. Bywater [5]. They have studied on BF_3 catalyzed polymerization of α -methyl styrene in ethylene chloride.

Change of the rate of polymerization with co-catalyst concentration is seen in Table III. We have observed that $6 \times 10^{-3} \text{M}$ H_2O is the maximum co-catalyst concentration at which polymerization reaction can not take place.

Water acts as co-catalyst when Friedel-Crafts catalyst is used. Catalyst-co-catalyst complex occurs due to the monohydrate -dihydrate reactions between catalyst and co-catalyst. Anhydrite of sulfuric acid (SO_3) can take as well as monohydrate or dihydrate.

Let us show MX_n as Friedel Crafts catalyst



Percentage of acid decreases as water concentration increases, that is dihydrate form is more then monohydrate. Number of the carbonium ions necessary to initiate polymerization decreases since dihydrate form gives proton difficultly then monohydrate form; due to the decreases in the number of active centers rate of polymerization decreases.

It is seen from the data given in Table IV that molecular weight of the polymers does not so much effected from co-catalyst concentration when its concentration is low. If water concentration is taken high, then molecular weight of the polymer will be decreased. It can he concluded that transfer to water seems likely.

The data for the polymers prepared at -25°C and -35°C using two different solvents keeping other conditions constant are given in Table V. It is seen from the data that the polymerization in ethylene chloride proceeds faster than that in methylene chloride. Dielectric constant of ethylene chloride is higher than that of methylene chloride, solvation power of solvent increases as the dielectric constant of solvent increases; polymeric ion pairs grow faster as the dielectric constant increases. Monomer can easily add to the polymeric chain since distance between carbonium ion and its gegen ion increases. Rate of the polymerization and the molecular weight of the polymer increases since more monomer can be added to the polymeric chain.

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ÖZET

Bu çalışmada katalizör olarak sülfürik asit kullanılarak α -metil stiren polimerleştirilmiştir. Katalizör ve kokatalizör (su) konsantrasyonunun çözücü cinsinin etkileri araştırılmıştır.

Polimerizasyon hızının katalizör konsantrasyonu ile doğrusal olarak değiştiği görülmüştür. Öte yandan molekül ağırlığı katalizör konsantrasyonundan etkilenmemiştir.

α -metil stiren ko-katalizör olarak farklı miktarda su kullanılarak da polimerleştirilmiştir. Deneylemizde su konsantrasyonu arttıkça polimerizasyon hızının ve polimerin molekül ağırlığının küçüldüğü görülmüştür.

Çözücü olarak etilen klorür ve metilen klorür kullanılarak iki ayrı sıcaklıkta α -metil stiren polimerleştirilmiş, etilen klorürde reaksiyon hızının ve polimerin molekül ağırlığının metilen klorürdekinden daha büyük olduğu görülmüştür.