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by

E. ÖZDEMİR and E. PULAT

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TURQUIE

Cationic Polymerization of α-Methyl Styrene Catalysed by Sulphuric Acid (1)

E. ÖZDEMİR and E. PULAT*

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

*Chemistry Department, Faculty of Science, University of Ankara-Turkey

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SUMMARY

Cationic Polymerization of α- methylstyrene was carried out in chloroform by using H_2SO_4 as catalyst. The effect of temperature, monomer and catalyst concentrations were studied. The dependence of the initial rates on the initial monomer $[M]_0$ and catalyst $[C]_0$ concentrations is $-d[M]/dt = k\,[M]_0\,[C]_0$ for chloroform solution. On the other hand, rate of polymerization increases to a certain temperature and then decreases.

It was found that molecular weight of the polymers increases with the monomer concentration and temperature, but it isn't dependent on the catalyst concentration.

INTRODUCTION

α- Methylstyrene is cationically polymerized more rapidly than styrene. The overall rate of polymerization of *α*- methylstyrene is greater than that of styrene under the same conditions (1) These facts reflect the greater basicity of the *α*- methylstyrene monomer; measurements of its proton affinity show that it is much higher than that of styrene.

Since the heat of polymerization of *α*- methyl styrene is known to be 8 kcal; this would lead to the conclusion that the ceiling temperature for polymerization would be somewhat above room temperature (2). Because of this reason the polymers having high molecular wright cannot be obtained at room temparatures, Whereas at room temparatures *α*- methylstyrene forms mainly dimers (3). The molecular weight of the polymers obtained by Heiligmann and coworkers at temperatures between 0°C and -130°C using $AlCl_3$ as catalyst and ethylchloride as solvent was found to increase rapidly with decreasing temperature (4).

Interesting results have been reported on the polymerization of α-methylstyrene at -78°C catalysed by boron fluoride etherate (5).

EXPERIMENTAL

a) Purification of materials: α- Methylstyrene and chloroform were dried over $CaCl_2$ and distilled before using them.

Methanol was used as precipitant without any purification before use.

b) Preparation of polymers: The polymerization apparatus consisted of a conventional three-necked flask fitted with stirrer, thermometer and micropipette. Dryice- acetone was used as an external cooling medium. After cooling the monomer and solvent in the three-necked flask, the sulphuric acid was added to the stirred mixture. The flask wasn't opened to a special polymerization time, then methanol was added to the polymer solution, white precipate filtered, washed and dried in vacuum oven at 60°C.

To find out the molecular weight of poly α-methyl-styrene, viscosity measurements were carried out by using Ubbelohde viscometer at 30°C in benzene. Molecular weight of the products was calculated from Mark-Hauwink equation where K and α were 1.7×10^{-5} and 0.85 respectively.

RESULTS

All the experimental results are summarized in the following tables.

Table I

Effect of Temperature on the Rate of Polymerization and on the Molecullar Weight.

Temperature °C	Pol %	$Rp \times 10^5$ (mol l^{-1} sec^{-1})	$\bar{M}_v \times 10^{-3}$
-30	4.23	1.2	
-40	8.67	2.5	19
-50	15.03	4.6	27
-60	15.80	4.5	32
-65	9.01	2.6	39

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

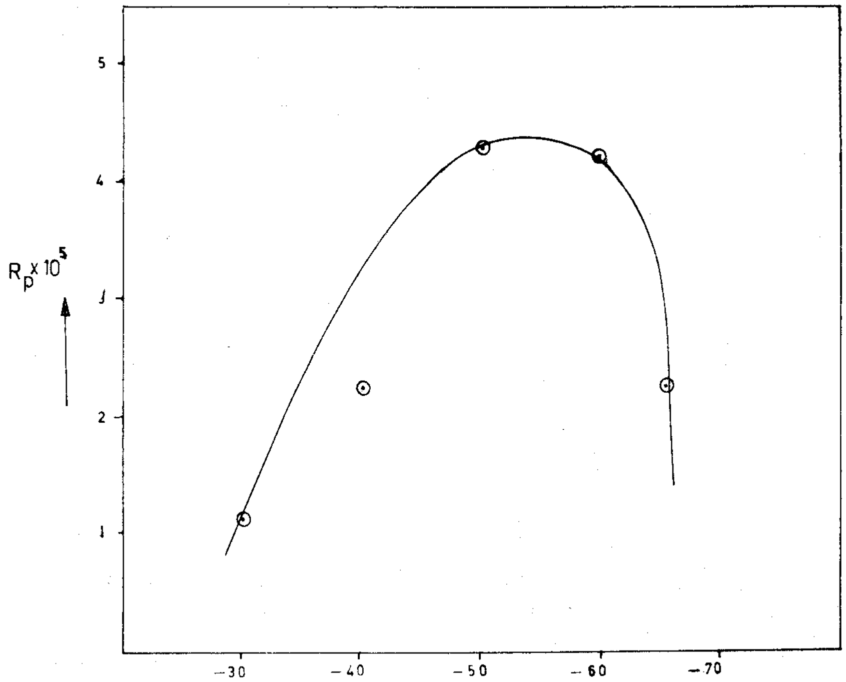

Figure 1, Variation of the rate of polymerization with temperature.

Table II

Effect of monomer oncentration on the rate of polymerization and on the molecular weight of poly-α-methylstyrene, at -50°C, $[H_2SO_4]_0 = 0.025$ mol l^{-1}; time = 1 hour

$[M]_0$	$[M]^2_0$	Pol %	$Rp \times 10^5$ (mol l^{-1} sec^{-1})	$\bar{M}_v \times 10^{-3}$
0.501	0.2513	0.85	0.2	—
0.719	0.5169	3.91	0.8	16
0.821	0.674	9.61	2.7	22
0.927	0.859	13.90	4.0	25
1.026	1.052	16.03	4.7	27

As can be seen from Figure 2, the plot of R_p against $[M]^2_0$ gives a straight line. This implies that the rate of polymerization is proportional to the second power of the monomer concentration.

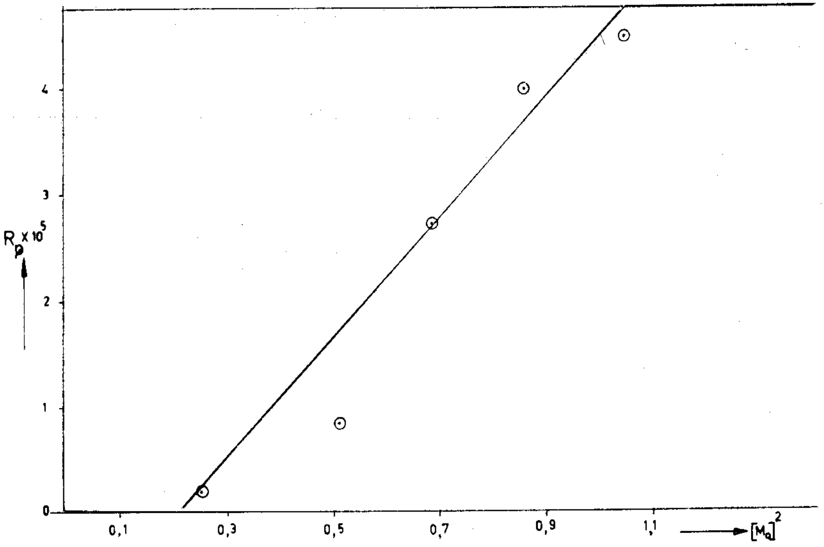

Figure 2, Variation of the rate of polymerization with monomer concentration.

We can also see that there is a critical monomer concentration below which poly *a*- methylstyrene cannot be obtained under these conditions.

It is seen that the molecular weight of poly *a*- methylstyrene increases as the monomer concentration increases.

Table III

Effect of catalyst concentration on the rate of polymerization and on the molecular weight of poly α- methylstyrene, at -50°C. $[M]_0 = 1.025$ mol l^{-1}; time = 1 hour.

$[H_2SO_4]_0$ (mol l^{-1})	Pol %	$Rp \times 10^5$ (mol l^{-1} sec^{-1})	$\bar{M}_v \times 10^{-3}$
0.0245	16.03	4.5	27
0.0491	34.47	9.8	26
0.0735	47.38	13.6	26
0.0979	70.15	19.9	26

Since the plot of the rate of polymerization against catalyst concentration [c] gives a straight line, the polymerization rate is proportional to the first power of the catalyst concentration (Fig. 3).

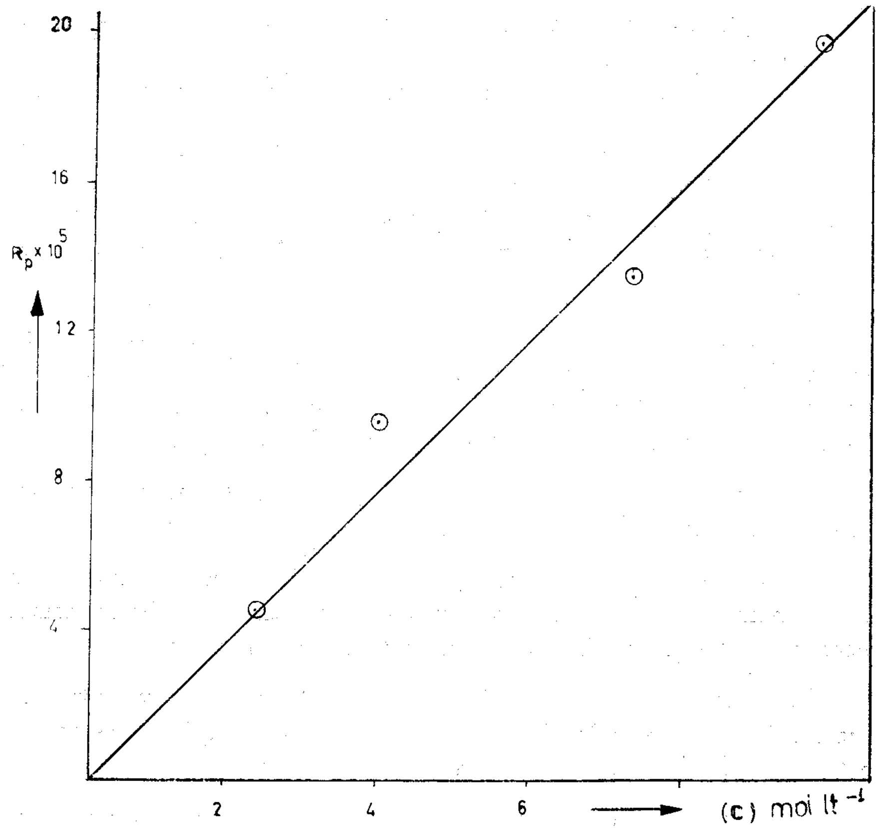

Figure 3, Effect of catalyst concentration on the rate of polymerization.

We can see that the molecular weight of poly *α*- methylstyrene isn't effected by the concentration of the catalyst (H_2SO_4)

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. The polymers formed at temperatures near room temperature were found to consist of dimers and trimers when the chloracetic acids were used as catalyst (3). Similar results were obtained by Dainton and Tomlinson (6) using stannic chloride. To prepare high molecular weight polymers, low temperature is required. This can be seen in this work. The molecular weight of poly α- methylstyrene and the reaction rate increases as the temperature decreases.

By lowering the temperature of cationic polymerization, the transfer rate and termination rate are reduced considerably. Another very important reason is that at low temperatures, the side reactions are also considerably reduced and the effect of residual impurities in the reaction mass is minimized.

It is seen that the molecular weight of poly α- methylstyrene and polymerization rate increase as the monomer concentration increases and under these polymerization conditions there is a critical monomer concentration below which polymer cannot be obtained.

The rate of polymerization of poly α- methylstyrene is proportional to the second power of the monomer concentration.

Since the molecular weight of poly α-methylstyrene changes with the monomer concentration, we can say that transfer to the monomer does not take place, therefore termination predominates.

The rate of polymerization increaseses as the catalyst concentration increases, but the molecular weight of poly α- methylstyrene is not effected with changing of the catalyst concentration.

The rate of polymerization is proportional to the first power of the catalyst concentration. This reasults is similar to that of Worsfold and S. Bywater where BF_3 was used as catalyst (5).

ÖZET

Katalizör olarak sülfürik asit kullanılarak α- metilstirenin katyonik polimerizasyonu yapıldı. Sıcaklık, monomer ve katalizör konsantrasyonlarının etkisi araştırıldı. Kloroform içindeki reaksiyon hızı $- d[M]/dt = k\,[M]^2_0[C]_0$ olarak bulundu. Diğer taraftan, polimerizasyon hızı belirli bir sıcaklığa kadar artmakta daha sonra azalmaktadır.

Polimerin molekül ağırlığının, monomer konsantrasyonunun artması ve sıcaklığın azalmasıyla arttığı gözlendi.

Polimerin molekül ağırlığı katalizör konsantrasyonuna bağımlı değildir.

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