COMMUNICATIONS

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

Série B: Chimie

TOME 27 ANNÉE : 1981

A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

Studies on the Cationic Polymerization of α– Methyl Styrene Catalyzed by Sulfuric Acid. (1)

by

O. ŞANLI and E. PULAT

15

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

Communications de la Faculté des Sciences de l'Université 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.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté des Sciences de l'Université 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, les 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.

DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

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

O.ŞANLI and E.PULAT*

State Engineering and Architectural Acedemy of Ankara, Faculty of Chemical and Management Engineering, Maltepe - Ankara - Turkey

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

(Received December 20, 1981; accepted December 30, 1981)

SUMMARY

In this study α -methy styrene has been polymerized in the presence of sulfuric acid.

The effect of polymerization time, temperature, monomer concentration on the rate of polymerization and molecular weight of the polymer were investigated.

α -Methyl styrene was polymerized at five different temperatures (–40 °C, –50 °C, –60 °C, –70 °C, –78 °C) and it was obcerved that the molecular weight of the polymers increases as the temperature decreases. On the other hand, rate of polymerization increases to a certain temperature and then decreases.

The relation of the limiting viscosity number and temperature was found as

$$\log [\eta] = 0.698 \times 10^3 \times \frac{1}{T} - 4.0626$$

It was found that the molecular weight of the polymers does not change by changing the polmerization time.

α -Methyl styrene was polymerized taking different monomer concentration.

It was found that as the monomer concentration increases rate of polymerization and degree of polymerization increase. Rate of polymerization changes with the second power of monomer concentration. It was concluded that termination with chain transfer to monomer does not take place.

INTRODUCTION

α -Methyl styrene has been homopolimerized by the solution of Friedel Crafts catalyst in organic solvents at temperatures as low as -130 °C to molecular weight 84.000 [5].

However there is a noticeable absence of detailed information on the corresponding effect of mineral acids under similar conditions. Klages using phosphoric acid as catalyst obtained an unsaturated polymeric product of low molecular weight [8]. Tiffeneau reported that the use of concentrated sulfuric acid as catalyst yeilded a saturated dimer [2].

Moderetely high polymers have been prepared by Heiligmann [3] from α -methyl styrene at low temperatures using sulfuric acid as catalyst. Therefore it was considered of interest to obtain data which would permit definition of general characteristics of mineral acid catalysed polymerization and compare it with the known caracteristics of a system catalyzed by a typical electrophlic metal halide.

EXPERIMENTAL

a) Purification of Materials: α -Methyl styrene used as monomer was distilled and dried over anhydrous potasium carbonate before use [3].

Methylene chloride used as solvent was dried over anhydrous potasium carbonate, methanol was used as precipitant and purified by distilling before use.

b) Preparation of Polymers: The polymerization apparatus consisted of a conventional three necked flask fitted with stirrer, termometer and micro pipette. Dry ice-acetone was employed as an external cooling medium and the flask was not opened after initial mixing of the reactants. In carrying out the experiment the monomer and solvent were precooled to the desired temperature, and the acid catalyst was edded to the stirred mixture.

Products were obtained by discharging the clear polymer solution into methanol, white precipitate filtered, washed and dried in vacuum oven at 60 °C.

Viscosity measurements were carried out by using Ubbelohde viscometer at 30 ° C in benzene. Molecular weight of the products was calculated, from Mark–Houwink equation where K and α were 1.7×10^{-5} and 0.87 respectively [7].

RESULTS

All the experimental results are summarized in the following Tables.

Table I

Effect of Temperature on the Rate of Polymerization and on the Molecular Weight. $[M]_o = 92.35 \times 10^{-2}$ mol l^{-1}; $[H_2SO_4] = 1.05 \times 10^{-2}$ mol l^{-1} time=1 hour

Temperature °C	pol %	$R_p \times 10^6$ (mol l^{-1}sec.$^{-1}$)	$[\eta]$ (dl / g)	$\bar{M}_v \times 10^{-3}$
–40	4.3419	11.15	0.0825	17
–50	6.6777	17.15	0.1219	27
–60	7.0770	18.10	0.2340	57
–70	3.0452	7.83	0.2370	58
–78	1.8523	4.75	0.3274	84

Table II

Effect of Polymerization Time on the Molecular Weight of the Polymer $[M]_o = 92.35 \times 10^{-2}$ mol l^{-1} $[H_2SO_4] = 1{,}08 \times 10^{-2}$ mol l^{-1}; at –60°C

(Time (min)	Pol %	$\bar{M}_v \times 10^{-3}$
30	4.3920	53
60	7.0770	57
90	10.4260	60
120	13.1000	63

Table III

Effect of Monomer Concentration on the Rate of Polymerization, at –60°C, $[H_2SO_4] = 1.25 \times 10^{-2}$ mol l^{-1}, time = 1 hour

$[M]_o \times 10^2$	Pol %	$R_p \times 10^6$	$R_p \times 10^6 / [M]_o$
51.30	4.1500	3.84	7.49
76.95	6.8940	16.72	21.72
87.21	11.4930	27.80	31.88
92.34	11.7920	30.20	32.70
102.60	13.7710	39.20	38.20

Below the monomer concentration of 0.4 mol l^{-1} for the specified polymerization condition polymer can not be obtained (Fig 2)

It was seen from Figure 2 that rate of polymerization changes with the second power of monomer concentration.

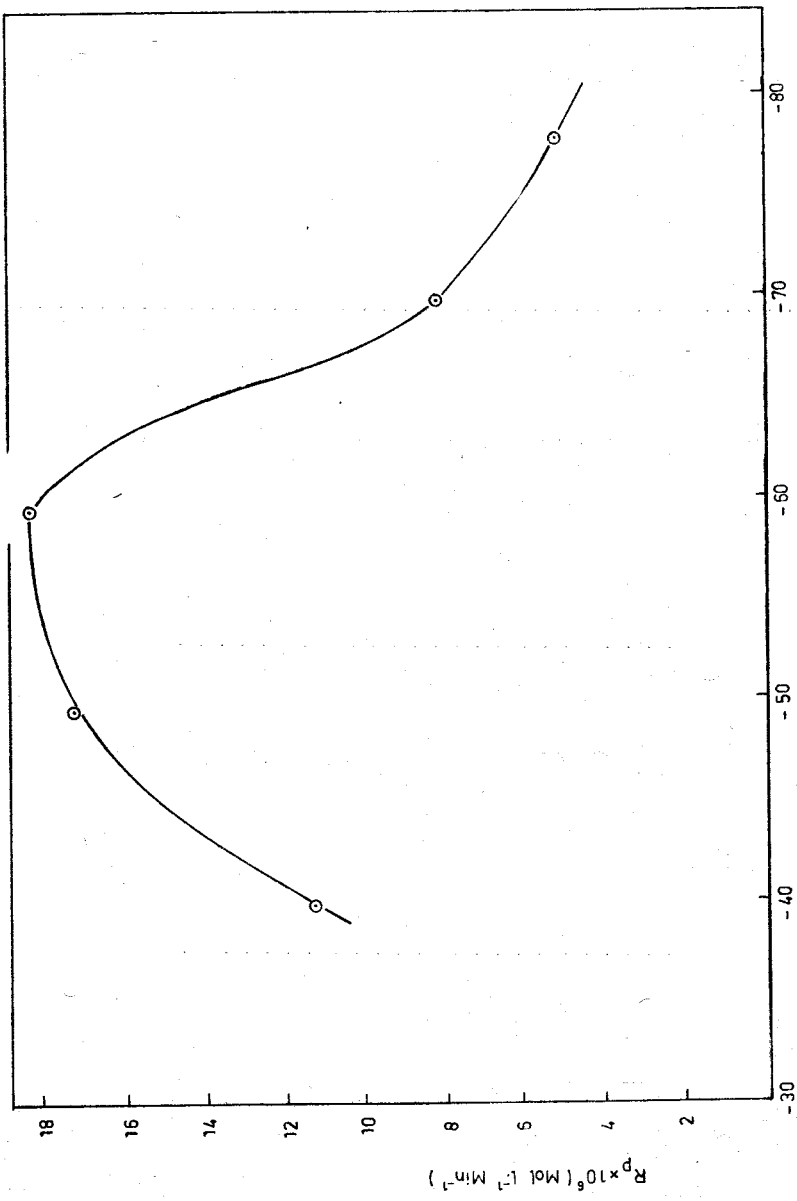

Figure 1 Variation of the Rate of Polymerization with Temperature

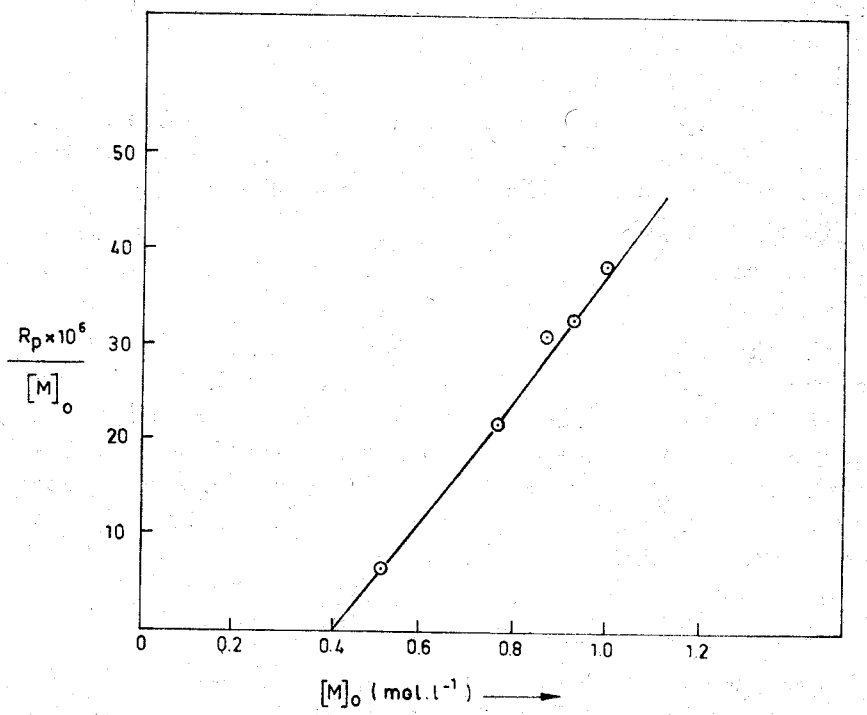

Figure 2: Variation of the Rate of Polymerization with Monomer Concentration

DISCUSSION

Heat of polymerization of α -methyl styrene is about 8 kcal / mol. Ceeling temperature corresponding to this heat of polymerization is above the room temperature. That is about the room temperature, depolymerization reaction proceeds with the polymerization reaction and high molecular weight polymers can not be ontained. To prepare high molecular weight polymers, low temperature and cationic catalysts are required. This can be seen also in this study. As the temperature decreases molecular weight of the polymers increases. As the temperature deareases dielectric constant of the solvent increases, so ion pairs dissociate to free ions. In the propagation reaction, free ions will be important comparing with the ion pairs and they can take more monomer.

This results are in correspondence with the aluminuim chloride catalyzed polymerization of α -methyl styrene [5] and the previous study of Heiligmann [3].

It is seen that molecular weights of the polymers do not change with the polymerization time. This result is similar to the radicalic polymerization in same way but differ from condensation polymerization.

At the specified polymerization conditions it is found that there is a critical monomer concentration below which polymer can not be obtained.

The rate of polymerization is proportional to the second power of the monomer concentration. This result is similar to that of Worsfold [6] and S.Bywater [6] where BF_3 was used as catalyst, but differs from that of Jordan and Mathieson [4] In their studies $AlCl_3$ and carbontetra chloride were used as catalyst and solvent respectively. In these circumstances the rate of polymerization is proportional to the first power of the monomer concentration.

ÖZET

Bu çalışmada α -metil stiren sülfirik asit yanında polimerleştirildi. Polimerizasyon süresi, sıcaklık ve monomer konsantrasyonunun polimerizasyon hızı ve molekül ağırlığına etkisi araştırıldı.

α -Metil stiren beş ayrı sıcaklıkta (–40 °C, –50 °C, –60 °C, –70 °C, –78 °C) polimerleştirildi. Sıcaklık düştükçe molekül ağırlığının arttığı gözlendi. Öte yandan polimerizasyon hızında, belli bir sıcaklığa kadar artma, sonra da azalma gözlendi.

Limit viskozite sayısı ile sıcaklık arasında

$$\log [\eta] = 0.698 \times 10^3 \times \frac{1}{T} - 4.0626$$

bağıntısının olduğu saptandı.

Polimerizasyon süresi ile polimerin molekül ağırlığında bir değişme olmadığı gözlendi.

Farklı monomer konsantrasyonlarında α -metil stiren polimerleştirildi, polimerizasyon hızı ve polimerizasyon derecesinin monomer konsantrasyonu ile arttığı, hızın monomer konsantrasyonunun ikinci kuvvetiyle orantılı olarak değiştiği ve böylece sonlanmanın monomere transfer ile olmadığı sonucuna varıldı.

REFERENCES

[1] C.P.Brown and A.R.Mathieson, J.Chem. Soc., 3445, 3507 (1958)
[2] M.Tiffeneau, Ann. Chim. (8) 10, 145 (1907)

[3] Randall, G.Heiligmann, J.Polymer Sci., 6, 155–164 (1962)

[4] D.V.Jordan and A.R.Mathieson, J.Chem. Soc., 2354 (1952)

[5] A.B.Hersberger, J.C.Reid and R.G.Heiligmann, Ind. Eng. Chem. 37, 1073 (1945)

[6] D.J.Worsfald and S.Bywater, J.Am. Chem. Soc., 79, 4917 (1957)

[7] L. A. Wall; J. Appl. Polymer Sci., 2, 134 (1959)

[8] Klages, A. Ber., 35, 2639 (1902)

Prix de l'abonnement annuel

Turquie : 15 TL; Étranger: 30 TL.
Prix de ce numéro : 5 TL (pour la vente en Turquie).
Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı Ankara, Turquie.

Ankara Üniversitesi Basımevi, Ankara – 1982