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by

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TURQUIE

Solvent Effect on The Cationic Polymerization of α- Methylstyrene (11)

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SUMMARY

α- Methylstyrene was polymerized in the pur and mixed solvents, using sulphuric acid as catalyst.

Rate of polymerization increased as dielectric constant of the solvents increased.

The molecular weight of poly α- methylstyrene did not change in the pur and mixed solvents.

It was also seen that the plots of log R_p against D and (D–1) /(2D+1) gave the straight lines.

INTRODUCTION

Rate of cationic polymerization depends on the counterion, temperature and the type of monomer and solvent (1). The formation and stabilization of a carbonium ion depends on the nature of R in the vinly monomer ($CH_2 = CHR$). For this reason cationic initiation is usually limited to monomers with electron-donating groups which help to stabilize the delocalization of the positive charge. Reactions can be extremely rapid when strong initiators such as BF_3, H_2SO_4 are used, and produce long chain polymer at low temperatures. Both molecular weight of polymer and reaction rate decrease as temperature increases.

For a given monomer and catalyst, rate of polymerization will depend on the rate constants of initiation (k_i), propagation (k_p) and termination (k_t)

Propagation also depends greatly on the position and type of the gegen-ion associated with the chain carrier. The position of the gegen-ion can be altered by varying dielectric constant of the solvent. When dielectric constant of solvent increases, ion pairs dissosiate to free ions. As free ions propagate faster than a tight ion pair, the increase in the free ion concentration by changing dielectric constant is reflected as an increase in k_p. (2).

EXPERIMENTAL

a) Purification of materials: α- Methylstyrene and the solvents were dried over $CaCl_2$ overnigth and distilled before use.

Methanol used as precipitant was purified by distilling before use.

b) Preparation of polymers: Poly α- methylstyrene was obtained in the three-necked flask fitted with stirrer, thermometer and micropipette. Dryice-acetone was used to cool down the reaction container.

The polymer were isolated from the reaction mixture by precipitation with methanol, and dried in vacuum at 60°C.

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

RESULTS

All the experimental results are summarized in the following tables.

Table I

Effect of Solvent on the Rate of Polymerization of α- Methylstyrene, at 50°C
$[M]_0 = 1.026$ mol l^{-1}; $[H_2SO_4]_0 = 0.025$ mol l^{-1}; time = 1 hour

Solvent	Dielectric Constant (D)	Pol %	$R_p \times 10^5$ (mol l^{-1} sec^{-1})
Toluene	2.43	6.50	1.8
Chloroform	6.76	16.03	4.6
Methylenedichloride	9.20	25.30	7.2

Table II

Effect of Mixed Solvents on the Polimerization Rate and on the Molecular Weight of Poly α-Methylstyrene; at 50°C.

$[M]_0 = 1.026$ mol l^{-1}; $[H_2SO_4]_0 = 0.025$ mol l^{-1}; time = 1 hour. A: Chloroform, B: Methylene Dichloride, C: Toluene

Mixed Solvent		Pol %		$R_p x10^5$(mol $l^{-1}sec^{-1}$		$\bar{M}_v \times 10^{-3}$	
A (ml)	B or C (ml)	A+B	A + C	A + B	A + C	A + B	A + C
65	0	16.03	16.03	4.6	4.6	27	27
45	20	18.90	12.34	5.4	3.5	27	26
25	40	22.60	9.33	6.4	2.6	27	26
10	55	24.48	7.59	6.9	2.1	28	25
0	65	25.30	6.50	7.2	1.8	28	26

As can be seen from Tables I and II that the rate of polymerization increases as dielectric constant of the solvent increases.

The plots log R_p against D and (D-1)/(2D+1) give the straight lines (Figure 1 and 2).

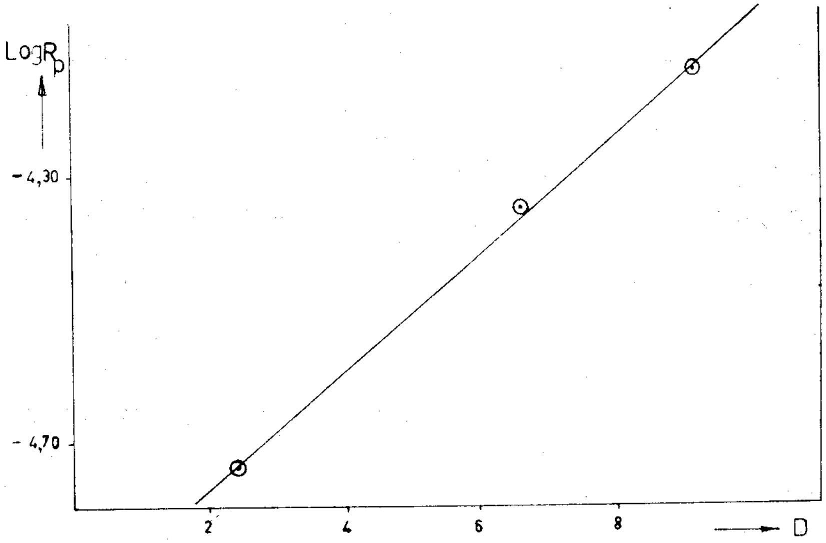

Figure 1. Variation of the rate of polymerization with dielectric constant of solvent.

When methylene dicloride is added to chloroform, dielectric consconstant of the mixed solvent increases (3). In contrast, when toluene is added to it, dielectric constant of the mixed solvend decreases.

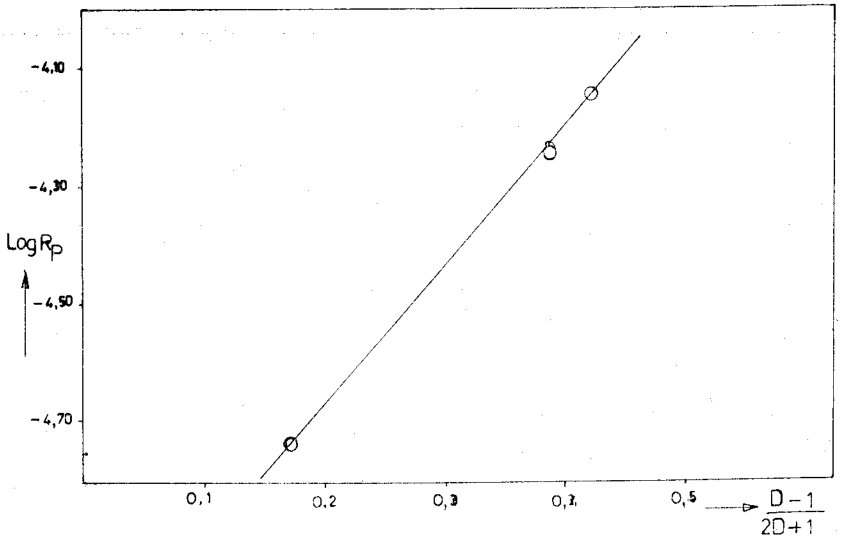

Figure 2. Variation of the rate of polymerization with (D-1) /(2D+1)

The molecular weight of poly α- methylstyrene doesn't change with changing of the dielectric constant of the solvent.

DISCUSSION

From the experimental results, we have seen that rate of polymerisation of α- methylstyrene is effected by the change of dielectric constant of the solvent, on the other hand molecular weight of the polymer does not change.

This can be explained as follows:

The various stages of the ionization producing carbonium ions can be represented as

RX	$\leftrightarrow$ $R^+ X^-$	$\leftrightarrow$ $R^+ // X^-$	$\leftrightarrow$ $R^+ \leftrightarrow X^-$
covalent	intimate ion–pair	Solvent seperated ion–pair	free ions

The increasing polarity of the solvent alters the distance between the ions from an intimate ion pair, through a solvent seperated ion pair for a state of complete dissociation. The seperation of the ions lowers the steric restrictions to the incoming monomer so that free ions exert little stereo-regulation on the propagation.

The difference between the radical and the cationic polymerization lies in the fact that in the latter, initiation is very fast and propagation is the rate determining step. It has been shown experimentally (4) that carbonium ions are much less stable than the corresponding radicals. This implies that the lifetime of a polymer cation is much shorter than the correspending polymer radical.

ÖZET

α- Metilstiren, saf ve karışık çözücüler (kloroform-metilenklorür ve kloroform-toluen) içinde katalizör olarak H_2SO_4 kullanılarak -50°C de polimerleştirildi.

Karışık çözücülerde olduğu gibi saf çözücülerde de, çözücünün dielektrik sabiti arttıkça polimerizasyon hızı artmaktadır.

Poli α- Metilstirenin molekül ağırlığı hem saf çözücülerde hem de karışık çözücülerde çözücülerin dielektrik sabiti ile fazla değişmedi.

Ayrıca D–log R_p ve (D-1) /(2D + 1)— log $R_p$grafiklerinin bir doğru verdiği görüldü.

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