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## SOLVATION EFFECT OF AROMATIC DILUENTS ON THE CATIONIC POLYMERIZATION OF STYRENE

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Cationic polymerization of styrene in benzene, toluene and xylene has been carried out at 10-12° using anhydrous  $AlCl_3$  as the catalyst. The efficiency of propagating species in different aromatic diluents has been found in the following order. Xylene > toluene > benzene. Diluents help not only the initiation of cationic polymerization of styrene, but also partially serve as chain transfer agent. The molecular weight of the polymer, degree of polymerization, chain transfer constant and monomer transfer constant may vary diluent to diluent. The values of chain transfer constant measured for benzene, toluene and xylene are respectively  $8 \times 10^{-3}$ ,  $14 \times 10^{-3}$  and  $30 \times 10^{-3}$ . The value of monomer transfer constant determined for styrene is  $10 \times 10^{-3}$ .

**Key words :** Diluents, Dielectric constant, Monomer chain transfer constant.

### INTRODUCTION

It has been noted that the nature of reaction medium (diluents) plays a significant role in the cationic polymerization of olefinic monomers at low temperature using Friedel Crafts catalysts. The change in reaction medium affects the rate of propagation as well as termination of the growing polymer chain and degree of polymerization. It also helps in controlling the molecular weight (size of polymer chain) of the polymer. In our earlier paper [1] we have reported the cationic polymerization of  $\alpha$ -methyl styrene in benzene, toluene and xylene using anhydrous  $AlCl_3$  as initiator. It has been observed that not only solvents facilitate the initiation of cationic polymerization of  $\alpha$ -methyl styrene but also partially serve as a chain transfer agent. This paper describes the solvation effect of aromatic diluents (benzene, toluene and xylene) on the cationic polymerization of styrene using anhydrous  $AlCl_3$  as catalyst and determination of their chain transfer constant.

### EXPERIMENTAL

**Material.** Styrene (E. Merck) was washed with 5-6% aqueous sodium hydroxide to remove the inhibitor, dried over calcium chloride and distilled. Anhydrous aluminium chloride (BHH) was used without further purification. Laboratory reagent grade benzene, toluene and xylene were distilled before use.

**Procedure of polymerization.** Styrene was polymerized according to the procedure given else where [2-3] in a 3-neck round bottom flask fitted with a funnel, a stirrer and a thermometer. The flask was kept in ice cold bath for maintaining required temperature. Known quantities of styrene and solvent as mentioned in Table 1, 2 and 3 are added to the reaction flasks. The contents were stirred for 15 minutes

and then 2.5 gm anhydrous aluminium chloride was added gradually. The addition of aluminium chloride raised the temperature of the reactants which was maintained at 10-12°. It was stirred for 4 1/4 hours and then an aqueous solution of methanol was added to stop the reaction. This was then transferred to separating funnel and shaken with methanol to remove the catalyst residue. The lower layer was collected. The solvent and unreacted monomer were distilled off. A semi solid amber colour resinous product soluble in common organic solvents is obtained. The viscosity of dilute solutions of polystyrene prepared in toluene was measured at  $30 \pm 0.5^\circ$  using an Ostwald type viscometer.

### RESULTS AND DISCUSSION

The detailed results of solvation of effect of aromatic diluents on the cationic polymerization of styrene in benzene, toluene and xylene are shown in Table 1, 2 and 3 respectively. In Fig. 1, % conversion of styrene vs % of aromatic solvent in feed has been plotted. From these figures it is evident that rate of conversion of styrene into its polymer increases with increase in concentration of solvent. The percentage conversion obtained by polymerizing styrene in the absence of any solvent is lower (24%) as compared with the percentage conversion obtained by polymerizing in benzene (60-90%), toluene (62-93%) and xylene (66-96%) at different solvent monomer ratios. These plots also indicate that rate of polymerization of styrene is higher in xylene than in toluene and benzene as indicated in the following order. Xylene > toluene > benzene.

It might be due to the fact that the propagating species (solvent separated ion pair and free ions) produced by the polymerization of styrene in xylene are more efficient than



Table 1. Cationic polymerization of styrene in benzene using 5% anhydrous  $\text{AlCl}_3$  as the catalyst at  $10-12^\circ$  for  $4\frac{1}{2}$  hours.

Exp. No.	Styrene [M] moles/l	Benzene [S] miles/l	Conversion of styrene %	$[\eta]$ dl/g	Mn	DP
1.	1.7020	9.0773	90.00	0.032	3370	32.40
2.	3.4897	6.9793	82.05	0.036	3970	38.17
3.	4.2990	5.7322	77.00	0.039	4436	42.65
4.	5.1561	4.6010	68.67	0.050	6265	60.24
5.	6.9510	2.3170	59.47	0.063	8626	83.04
6.	8.7500	—	24.24	0.071	10195	98.03

Table 2. Cationic polymerization of styrene in toluene using 5% anhydrous  $\text{AlCl}_3$  as the catalyst at  $10-12^\circ$  for  $4\frac{1}{2}$  hours.

Exp. No.	Styrene [M] moles/l	Benzene [S] miles/l	Conversion of styrene %	$[\eta]$ dl/g	Mn	DP
1.	1.6816	7.6038	93.40	0.028	2800	26.92
2.	3.4578	5.8628	89.4	0.031	3225	31.01
3.	4.2666	4.8231	82.00	0.033	3518	33.82
4.	5.1454	3.8777	72.67	0.045	5412	52.04
5.	6.9296	1.9584	62.00	0.051	6440	61.92
6.	5.7500	—	24.24	0.071	10195	98.03

Table 3. Cationic polymerization of styrene in xylene using 5% anhydrous  $\text{AlCl}_3$  as the catalyst at  $10-12^\circ$  for  $4\frac{1}{2}$  hours.

Exp. No.	Styrene [M] moles/l	Benzene [S] miles/l	Conversion of styrene %	$[\eta]$ dl/g	Mn	DP
1.	1.6722	6.5626	96.4	0.020	1755	16.87
2.	3.4426	5.0664	90.40	0.023	2131	20.49
3.	4.2514	4.1712	85.84	0.026	2526	24.29
4.	5.1306	3.3559	80.33	0.033	3518	33.82
5.	6.9195	1.6972	66.30	0.036	3970	38.17
6.	5.7500	—	24.24	0.071	10195	98.03

produced in toluene and benzene. This efficiency of propagating species is due to the dielectric constants of benzene ( $\epsilon = 2.2628$  at  $25^\circ$ ) toluene ( $\epsilon = 2.3661$  at  $25^\circ$ ) xylene ( $\epsilon = 2.374$  at  $25^\circ$ ). The dielectric constant enhances the efficiency of propagating species. Now this may be said that solvents are advantageous for obtaining maximum yield and the polymer of same molecular range in cationic polymerization of electron donating monomers.

The number average molecular weight Mn was determined by using the following intrinsic viscosity-molecular weight relationship [4]

$$[\eta] = 0.923 \times 10^{-4} \text{Mn}^{0.72}$$

where intrinsic viscosity (in dl/g) is the intercept of the plot  $\eta_{sp}/c$  against  $C$ .  $\eta_{sp}$  and  $C$  being respectively the specific viscosity and concentration of solution of polymer

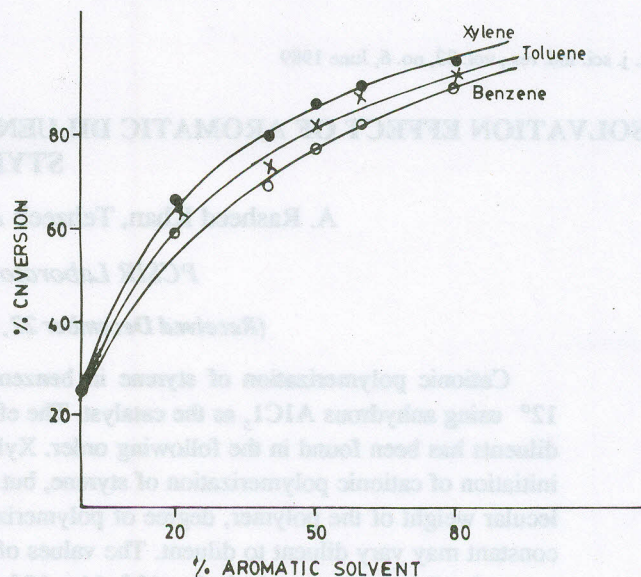


Fig. 1. Plot showing % conversion of styrene in cationic polymerization in the presence of benzene (O), toluene (x) and xylene (O) using  $\text{AlCl}_3$  as a catalyst at  $10-12^\circ$  for  $4\frac{1}{2}$  hours.

samples expressed in percentage. The viscosity of dilute solutions of polystyrene prepared in toluene was measured at  $30 \pm 0.5^\circ$ . The intrinsic viscosity of polystyrene prepared in the absence of any solvent was measured as 0.07 dl/g giving number average molecular weight of 10195. The intrinsic viscosities of polystyrene prepared in benzene were found to range from 0.036 to 0.063 dl/g whereas the intrinsic viscosities of polystyrene prepared in toluene and xylene were measured to range from 0.028 to 0.045 dl/g and from 0.02 to 0.033 dl/g respectively. The molecular weight calculated from the values of viscosities were found for benzene, toluene and xylene as 3970-8686, 2800-5412 and 1755-3518. These results indicate that solvents (diluent) act as chain transfer agents in the cationic polymerization of styrene. It is because of the facility of Friedel Crafts alkylation reactions on aromatic compounds [5-7]. Further the degree of polymerization (DP) of styrene in aromatic solvents gets decreased with increase in concentration of diluent and is found higher in the solvent possessing the lower dielectric constant. From rate of formation of polymer, its number average molecular weight and degree of polymerization, it may be concluded that not only aromatic solvents serve as reaction medium but also helps in the transfer and premature termination (by the transfer of hydrogen from diluents) of growing polymer chain of styrene. The premature termination of growing polymer chain reduce the molecular weight and form resinous product of small chain and low softening point. The chain transfer constant due to the reaction (diluent) have been determined by using the following equation of Mayo [8].

$$\frac{1}{\text{DP}} = \frac{(K_1 K_2)^{1/2} [B]^{1/2}}{K_2 [M]^{1/2}} + \frac{K_4}{K_2} + C_s \frac{[S]}{[M]}$$



where  $[B]$ ,  $[M]$  and  $[S]$  are the concentration of initiator, monomer and diluent,  $DP$  is the degree of polymerization  $K_4/K_2$  or  $CM$  is the monomer transfer constant and  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$  are the rate constant for initiation, propagation, termination and monomer transfer respectively. At a fixed concentration of  $AlCl_3$  in each experiment, the first term of the equation may be neglected. The slope of the  $1/DP$  against  $[S]/[M]$  in Fig. 2, determines the value of chain transfer constant ( $C_s$ ) and intercept of this plot meas-

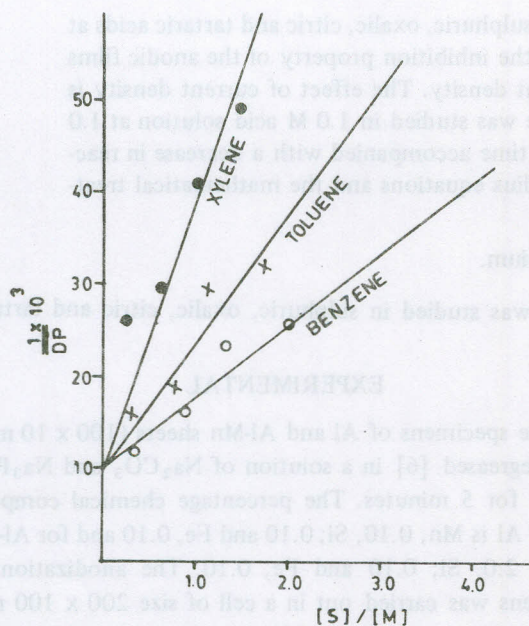


Fig. 2. Effect of benzene (O), toluene (x) and xylene (O) on the degree of polymerization of styrene for the cationic polymerization using  $AlCl_3$  as a catalyst at  $10-12^\circ$  for  $4\frac{1}{2}$  hours.

ures the value of monomer transfer constant ( $C_M$ ). Thus the chain transfer constant obtained from these plots for benzene is  $8 \times 10^{-3}$  whereas for toluene and xylene, these values are respectively  $14.0 \times 10^{-3}$  and  $30.0 \times 10^{-3}$ . Further the value of  $C_M$  obtained from the intercept is  $10 \times 10^{-3}$ . These results indicate that chain transfer constant, monomer transfer constant and degree of polymerization may vary with solvents used as reaction medium. Survey of the literature provides information about the variation in value of  $C_M$  with the

change of reaction medium temperature and catalyst. These are as for  $SnCl_4$  - benzene system at  $30^\circ$  it is  $18.8 \times 10^{-3}$  [9] for  $FeCl_3$  - benzene system at  $30^\circ$  it is  $12 \times 10^{-3}$  [10] for  $TiCl_4$  - benzene system at  $30^\circ$ , it is  $20 \times 10^{-3}$  [11], for  $SnCl_4$  -  $C_2H_5$  - Br system at  $63^\circ$  it is  $0.2 \times 10^{-3}$  [10]. These findings clearly show that the size of the chain may be controlled by using specific solvent of specific dielectric constant as reaction medium. These solvents not only produce solvation effect but also serve as chain transfer agent. Briefly speaking, in carbonium ion initiated polymerization two types of propagating species control the rate of reaction. These are an ionpair and a free ion which are in equilibrium with each other. The propagating species produced in different solvents of different dielectric constant are of different efficiency. Hence diluents in cationic polymerization of vinyl monomers are very significant and advantageous for getting the polymer of uniform molecular weight.

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