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Preliminary Study of Cationic Copolymerization of α-Methylstyrene and Isobutyl Vinyl Ether

3. Homopolymerization of α-Methyl Styrene Using *t* BuCl/Et₂AlCl Initiator System

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SUMMARY

α-Methyl styrene polymerization was carried out using t-BuCl/Et_2AlCl/CH_2Cl_2 system in the temperature range of 0° to -63.5°C. The effect of temperature on yield and molecular weights of Poly α-Methyl styrene was determined. Based on Arrhenius plots, average activation energies of molecular weights were determined to be -9.2 ± 1.0 K cal/mole. (0° to 40°C) and 0 ± 0.5 K cal/mole (-40° to -63.5°C). These were postulated to reflect the molecular weight governing mechanisms such as transfer to monomer and termination respectively.

INTRODUCTION

α-Methyl styrene (α-MS) undergoes ready polymerization by either cationic or anionic initiation at low temperatures. The published literature on α-MS polymerization has been extensively reviewed (BYWATER,1963, KENNEDY, 1975). IMANISHI (1964) reported some initial work on the mechanism of homopolymerization of α-MS using BF_3-etherate and CH_2Cl_2 or CH_3Cl solvent. He suggested presence of both transfer to monomer and termination as molecular weight governing reactions. TRIVEDI (1980) carried out homopolymerization of α-MS using "H_2O"/$EtAlCl_2/CH_3Cl$ system in the temperature range from -30° to -90°C and obtained high conversions. Based on the available data, it was postulated that the termination was probably negligible while transfer to monomer was the major molecular weight controlling event.

In this paper, we report data obtained in α-MS polymerization using t-BuCl/Et_2AlCl/CH_2Cl_2 system. The effect of temperature on the yield and molecular weight was evaluated.

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EXPERIMENTAL

α-MS (E. Merck) was washed with 10% NaOH solution and then with distilled water. It was dried over anhydrous Na_2SO_4, refluxed over CaH_2 for 4 hours and then distilled at reduced pressure under nitrogen atmosphere (48°C/10 mm Hg). CH_2Cl_2 was refluxed over CaH_2 for 6 hours and then distilled at atmospheric pressure under nitrogen atmosphere (40°C). t-BuCl was prepared using standard procedure and distilled over CaH_2 at atmospheric pressure under nitrogen (50°C). Et_2AlCl (Ethyl Corporation) was used as received.

Polymerization was carried out under nitrogen atmosphere in a four necked flask fitted with a thermometer, nitrogen inlet, stirrer and an inlet fitted with syringe for transferring reactants. The required amounts of α-MS, CH_2Cl_2, t-BuCl were transferred to a bottle capped with a rubber septum in a dry box. The mixture was then transferred to the cooled flask under nitrogen and at the desired temperature and Et_2AlCl solution in benzene was added. The reaction was quenched after 10 minutes by addition of MeOH. The polymer was precipitated in excess MeOH filtered and dried.

The polymer was further purified by dissolving in benzene, reprecipitating in MeOH and drying in vacuum oven at 60°C/10 mm Hg. The $\bar{M}v$ was determined using Ubbelohde viscometer in toluene at 30 C and calculated using equation: $[\eta] = 10.8 \times 10^{-5} \bar{M}v^{0.71}$.

RESULTS AND DISCUSSION

Table 1 shows the yield and molecular weights of Poly(α-MS) prepared in the temperature range from 0°C to -63.5°C. The yield of Poly(α-MS) tends to decrease below -30°C. This is probably due to a decrease in initiation at lower temperatures.

TABLE 1

EFFECT OF TEMPERATURE ON YIELD AND $\bar{M}v$ OF POLY(α-MS)

Temp°C	Yield %	Mv x 10^{-3}
0	13.5	10.8
-11	4.3	20.6
-22.5	15.9	47.7
-30	16.9	37.1
-40	6.9	82.4
-48	3.5	79.1
-63.5	5.6	84.3

[α-MS] = 1.87M $[Et_2AlCl] = 1.8 \times 10^{-2}M$ [t-BuCl] = $1 \times 10^{-3}M$ $[CH_2Cl_2]$ = 100 ml

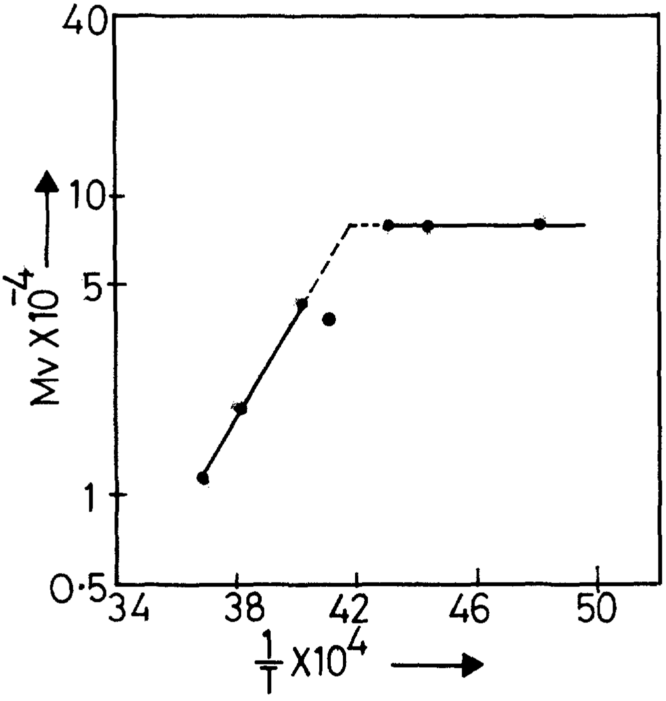

Figure: Effect of Temperature on Molecular Weight

A plot of log $\overline{M}v$ Vs 1/T (Arrhenius plot) is shown in figure. Activation energies of molecular weight $\Delta E\overline{M}v$ were calculated from slopes and were found to be -9.2 ± 1.0 K cal/mole (0° to -40°C) and 0 ± 0.5 K cal/mole (-40°C to -63.5°C).

In cationic polymerization of olefins activation energies of transfer to monomer, termination and propagation usually are $Etr > Et > Ep$ (SAWADA, 1972). The activation energies obtained from Arrhenius slopes, thus, may be postulated to reflect $\Delta Ep - \Delta Etr$ and $\Delta Ep - \Delta Et$ or a combination of the two.

As in isobutylene polymerization, since the solvent and initiator systems are similar for both, activation energy $\Delta E\overline{M}v = -9.2 \pm 1.0$ K cal/mole may be postulated to reflect the molecular weight governing mechanism, which is transfer to monomer, i.e. $\Delta EMv = \Delta Ep - \Delta Etr$.

The lower activation energy of $\Delta E\bar{M}v = 0 \pm 0.5$ K cal/mole may be postulated to reflect the molecular weight governing mechanism, which is termination i.e. $\Delta E\bar{M}v = \Delta Ep - \Delta Et$. Such a postulate seems reasonable in view of the vast amount of data generated for related systems (KENNEDY, TRIVEDI, 1978).

TABLE 2

MOLECULAR WEIGHT CONTROL IN -MS POLYMERIZATION

$\Delta E\bar{M}v$ K cal/mole	Molecular weight controlling mechanism	Initiator System/ Temperature Range
-9.2 ± 1.0	Transfer to monomer	t-BuCl/Et$_2$AlCl/CH$_2$Cl$_2$ 0° to -40°C
-3.6 ± 0.5	Transfer to monomer + termination	"H$_2$O"/EtAlCl$_2$/CH$_3$Cl -30° to -90°C
0 ± 0.5	Termination	t-BuCl/Et$_2$AlCl/CH$_2$Cl$_2$ -40° to -63.5°C

It is interesting to note that $\Delta E\bar{M}n = -3.6 \pm 0.5$ K cal/mole for poly(α-MS)polymerization using "H_2O"/$EtAlCl_2$/CH_3Cl in the temperature range of -30°C to -90°C (Table 2). Such an intermediate activation energy may be presumed to reflect a molecular weight governing mechanism which is a combination of termination and transfer as was also the case for isobutylene polymerization.

The $\Delta E\bar{M}v$ may thus provide a simple diagnostic tool for α-MS polymerization system. In co-polymerization reactions like grafting, block polymerization etc., the importance of termination reaction cannot be underestimated. For such systems knowledge of $\Delta E\bar{M}v$ can facilitate in the selection of reaction parameters like temperature, initiator system and solvent for achieving the highest control.

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