

The A-Oligomerization of the α -Methylstyrol with the Presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ Catalyst and Small Amount of 1,4-Benzoxinone

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Abstract:

The cation polymerization of α -Methylstyrol with the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ was carried out at the presence of 1,4-benzoquinone and it was shown that when the small amount of 1,4-benzoxinone was added the process was accelerated, the received polymer macromolecules also contained 1,4-dihydroxybenzene manganese. It has been revealed that the complex transport of loads between the α -methylstyrene and quinone molecules is formed that plays a crucial role both in excitement and stretching stages. Values of kinetic and activation parameters of cation polymerization of 1,4-benzoxinone were obtained by the transmission of the load between α -methylstyrol and quinone molecules.

Key words: 1-alkenes, α -methylstyrol, complex transmitted by load, poly- α -methylstyrene.

INTRODUCTION

The electron nature of the monomers in the monomer couple used in the oligomerization of 1-Alkenes and α -methylstyrene with alkylmethacrylates differs. It is known that complexes (Complex of high transmission) are formed by transmitting electrons and electroacceptor naturally occurring monomer molecules, while the last complexes can dramatically increase the velocity of these stages by participating in both the excitement and the stretch of the chain [1-3]. Polymerization of α -methylstyrene by $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$ catalyst and small amount the addition of 1,4-benzoxynone (BX) for the purpose of obtaining polyfunctional additives to confirm receipt of complex of high transmission between monomer couplings and containing dihydroxyphenylated fragments in the above-mentioned systems studied.

EXPERIMENTAL PART

The process's kinetics have been studied in a vacuum (10^{-3} - 10^{-4} tor) dilatometrically by changing the reaction conditions [4]. $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$ is taken as a catalyst and benzene as a solvent. A pre-graded dilatometer with a special design has been used to allow the catalyst solution to be inserted into the system after vacuuming. The dilatometer is primarily blown up with dry and purified nitrogen gas, filled with benzene solution of α -methylstyrene and 1,4-benzoquinone. In the upper part of the dilatometer, the catalyst's benzene solution is placed. Then three times process of degasification is carried out by using liquid nitrogen and vacuum conditions (10^{-3} - 10^{-4} tor). After these operations, the dilatometer is placed on the ultra-thermostat and after the required temperature is reached, the catalyst solution is added to the solution with monomers and depending on the time, the decrease in the volume of reaction

mixture in the dilatometer. Composition and structure of synthesized compounds were investigated by methods of Infrared and Nuclear magnetic resonance spectroscopy and elementary analysis methods. It has been done in Infrared Spectra Specord M 80 (Carl Zeiss Jena) and Spectroscopy FTIR Nicolet on 10 devices. Nuclear magnetic resonance spectra were plotted on the 300 MHz "Bruker" device using CCl_4 . 90 MHz PerkinElmer has been used to explore some moments.

DISCUSSION OF RESULTS

The results of the research have been presented in Figure 1 and Table 1.

It is clear that the α -methylstyrene by $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$ takes place at constant speeds at the cation polymerization induction period and in the initial reaction time. Increasing the density of BX added to the system in the range of $0.007 \div 0.045$ mol / l ($[\text{MSt}]_0 = 0.64$ mol/l, $[\text{cat}]_0 = 0.0064 \cdot 10^{-2}$ mol/l, T=303K,) reduced induction time and polymer Resulting in an increase in the total speed of the transaction.

Figure 1. The effect of addition small amount 1,4-benzoxinone and cation polymerization of the participation of in the presence of α -Methylstyrene T=303K, $[\text{MSt}]_0 = 0.64$ mol/l, $[\text{cat}]_0 = 0.0064$ mol/l, , $[\text{BX}]_0$, mol/l: 0(1), 0.007 (2), 0.02(3), 0.03 (4) \vee 0.045 (5)

Results from Table 1 show that the presence of BX at 0.02 mol / l in the reaction mixture causes the process to accelerate to 1.3 times. In this case, the transformation of the monomer reaches 85% within 24 hours. The decrease in induction is also observed the total increasing of MSP polymerization (V_p) in the system is recorded while increasing time of the monomer and catalyst thicknesses. The compositions of the α -polymerization reaction of the α -

methylstyrene have also been determined and clarified that the process is expressed in the following kinetic equation:

$$V_p = k \cdot [MSt] \cdot [BX]^2 \cdot [BF_3 \cdot O(C_2H_5)_2]$$

Table 1

The results of the investigation of the formal kinetics of cation polymerization with the presence of a -Metylstyrol BF₃-O (C₂H₅)₂ catalyst and a small amount of 1,4-benzoxinone (soluble benzene)

| № | Initial thickness x·10 ² , mol/l | | | T, K | W ₀ ·10 ⁵ mol/l·sec | T ind./min |
|---|---|--------------------|-------------------|------|--|---------------|
| | [MSt] ₀ | [cat] ₀ | [BX] ₀ | | | |

E=56.1 kC/mol

The elevation of the temperature from ([MSt]₀-0.64 mol/l, [Cat]₀-0.0064 mol/l, [BX]₀-0.03 mol/l) is formed for the total polymerization rate. This results in an increase of from 8.40 10⁻⁵ ~ 16.3×10⁻⁵ (~ 2 times). In this temperature range, the velocity constant (k) of the polymerization of MSt also increases approximately by 2 times.

It should be noted that the reduction of the induction time during the polymerization of α-methylstyrene in the presence of BF₃-O (C₂H₅)₂ catalyst with the addition of a small amount of BX also depends on the mixing sequence of the reagents. Thus, when the BX + catalyst mixture was added to the MSt solution (3 ÷ 5 min), the rate of reaction (3 · 10⁻⁵ mol / l), MSF without BX, then BF₃-O (C₂H₅)₂ The polymerization rate (2.4 ± 10⁻⁵ mol / ls·sec) differs very little. If a small amount of BX was previously added to the α-methylstyrene solution, then the BF₃-O (C₂H₅)₂ solution was added to the resulting mixture, with considerable decrease in induction and an increase in the overall polymerization rate is observed.

Since 1,4-Benzoxinone is a powerful electroacceptor coupling, It generates intermediate complexes with MSt. The

resulting intermediate weak molecular complex taking place both at the excitement and at the stretching of the chain, Intensifies them, resulting in a decrease in induction time and a tendency to increase the overall rate of polymerization.

The formation of the complex between the α -Methylstyrol (donor) and 1,4-benzoxinone (acceptor) molecules is confirmed by PMR spectroscopy (Figure 2). From this picture and Table 2, it is clear from the table that the maximal displacement of the xinsone molecule to the protons in the $\text{HC}=\text{CH}$ -fragment is recorded in the equidistant mix of donor-acceptor-type monomers (MSt and BX).

Table 2

MSt ... The results obtained from PMR spectroscopy for the determination of BX complex complexity constant.

| [BX], mol/l | [MSt], mol/l | CH=CH Connection (xinson) m.h. | $\Delta\delta$, m.h. | $1/\Delta\delta$ | $I/[\text{MSt}]$ |
|----------------|-----------------|--------------------------------------|--------------------------|------------------|------------------|
|----------------|-----------------|--------------------------------------|--------------------------|------------------|------------------|

($\Delta\delta = 0.03$ mh) for the 1,4-Benzoxinone protons ($\delta = 6.66$ mh) to the strong field $\Delta\delta = 0.06$ mh, and for α -methylstyrene monomer $\text{CH}_2 =$ protons ($\delta = 5.60$ mh) displacement to the weak area ($\Delta\delta = 0.03$ m.h.) is observed. The signal of the protons of the CH_2 group in the free α -methylstyrene molecule is recorded as triplet.

The prices for their spin-spin interactions are $J_1 = 18$ and $J_2 = 11$ Hz. In the PMR-spectrum of MSt and BX constants are consistent.

Figure 2. PMR spectra: 1) 1.0% solution of α -methylstyrene in CDCl_3 , 1.0% solution of 1,4-benzoxinone in CDCl_3 ; 3) Auxiliary mixture of α -methylstyrene 1,4-benzoxynone in CDCl_3 % decreases to 16 Hz and 9.5Hz respectively.

Such a change in the chemical shift and spin-spin interaction interactions proves the emergence of a donor-acceptor-type weak molecular complex by transporting the α -methylstyrene and 1,4-benzoquinone molecules.

($[\text{MSt}] \gg [\text{BX}]$) to determine the value of the complex formation constant (K) between α -methylstyrene and 1,4-benzoquinone, keeping the solubility of the acceptor at different proportions of these compounds and significantly reducing the thickness of the electrodeanomeric monomer PMR spectra are plotted and indicators derived from such spectra are given at the table 2.

Based on the 1,4-Benzoquinone double-acting symmetric protons, the graph of dependence of $1/\Delta\delta\text{-f}(1/[\text{MSt}])$ was calculated based on the graph of dependence (Fig. 3) and the computing stability constant (K) calculated using the known Kettlear equation:

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_0} + \frac{1}{\Delta\delta_0 \cdot K} \cdot \frac{1}{[\text{MSt}]}$$

$\Delta\delta$ - Difference of chemical displacement for BX, m.h.

$\Delta\delta_0$ - the difference of chemical displacement for BX molecules in the complex, m.h.

For this system it was found that $K = 0.11 \text{ lmlm}^{-1}$.

Thus, the formation of intermediate donor-acceptor-type weak molecular complexes occurs through transmission of the load between α -methylstyrene and 1,4-benzoquinone. Existence of such complexes between joint monomer molecules is one of the key factors determining the mechanism of the joint polymerization process, the value of the kinetic parameters, the second structure and the molecular mass index.

Figure 3. Determination of 1,4-benzoquinone complex-fixing constant of α -methylstyrene

RESULTS:

1-The cation polymerization of α -Methylstyrol with the presence of $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ was carried out at the presence of 1,4-benzoquinone and it was shown that when the small amount of 1,4-benzoxinone was added the process was accelerated, the received polymer macromolecules also contained 1,4-dihydroxybenzene manganese.

2-It has been revealed that the complex transport of loads between the α -methylstyrene and quinone molecules is formed that plays a crucial role both in excitement and stretching stages. Values of kinetic and activation parameters of cation polymerization of 1,4-benzoxinone were obtained by the transmission of the load between α -methylstyrol and quinone molecules.

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