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Investigation of the $TiCl_4$ reaction order in quasiliving styrene polymerization with 1-phenylethyl chloride/ $TiCl_4/Bu_2O$

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Summary

The reaction order with respect to $TiCl_4$ was investigated in the quasiliving polymerization of styrene using a 1-phenylethyl chloride/$TiCl_4/Bu_2O$ initiating system in mixture of 1,2-dichloroethane and *n*-hexane (55:45 v/v) at $-15\ ^0C$. It was found out that the reactions order with respect to $TiCl_4$ was closer to 1. A mechanistic scheme to explain the kinetic behavior of quasiliving styrene polymerization in 1-phenylethyl chloride/$TiCl_4/Bu_2O$ is proposed.

Introduction

For the past years a kinetic and mechanistic study of quasiliving cationic polymerization of isobutylene has been conducted rather intensively [1-14]. It has recently been postulated that most of the living polymerizations reported until now (including living cationic polymerization) are quasiliving polymerizations, which denotes existence of reversible equilibrium between dormant and active species [15, 16]. The most kinetic investigations are concerning the systems based on $TiCl_4$ which always have first-order dependence with respect to initiator (I) and monomer, but apparent zero order monomer dependence has also been reported [17, 18]. There is a serious difference in the kinetic order of isobutylene polymerization on $TiCl_4$ concentration, obtained by various research groups. The kinetic studies, carried out in the 1,4-bis(2-chloro-2-propil)benzene (DiCumCl)/$TiCl_4$/di-*tert*-butylpyridine (DTBP) [6], DiCumCl/$TiCl_4$/pyridine [4], t-Bu-m-DiCumCl/$TiCl_4$/2,4-dimethylpyridine [5] systems, showed that the kinetic order of the polymerization with respect to $TiCl_4$ concentration is two. Puskas et al. [2, 3] reported that in the 2,4,4-trimethyl-2-chloropentane (TMPCl)/$TiCl_4$/DTBP system at $[TiCl_4]>[TMPCl]$ the kinetic order on $[TiCl_4]$ equals two, but at $[TiCl_4]<[TMPCl]$ - unity. However, it has recently been shown that in the polymerization of isobutylene, using the t-Bu-m-DiCumCl/$TiCl_4$/2,4-dimethylpyridine system at $[TiCl_4]<[I]$, the kinetic order of reaction with respect to $[TiCl_4]$ is quite close to 2 [7]. In addition, in the article [9] it was reported about the dependence of the first order on $TiCl_4$ concentration during the isobutylene polymerization using $H_2O/TiCl_4$/electron donor (ED) systems in the presence of strong electron donors, and about the dependence of the second order with respect to $[TiCl_4]$ in the presence of weak ED.

$TiCl_4$ is used rather often for co-initiation of the quasiliving polymerization of styrene and its derivatives [19-26]. But only the articles [19, 20] inform about the second-order dependence on [$TiCl_4$] for the styrene polymerization by TMPCl/$TiCl_4$/DTBP initiating system at [$TiCl_4$]>>[TMPCl]. There is no information in the literature concerning the kinetic order determination of the styrene polymerization with $TiCl_4$ at [$TiCl_4$]~[I]. These facts are evidence of necessity to obtain new experimental data, dealt with the reaction order for [$TiCl_4$], and to understand the polymerization mechanism more deeply. That is why the investigation of the styrene polymerization kinetics at [$TiCl_4$]~[I] is of considerable interest.

Experimental

Materials

1-Phenylethyl chloride was prepared by bubbling of HCl through a solution of styrene in CH_2Cl_2 and purified by distillation from CaH_2 under reduced pressure. The reaction was monitored by ^{1}H NMR. The source and purification of all other reagents have been previously reported [26].

Instruments

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) in THF using Waters GPC instrument with three Ultrastyragel columns ($3 \cdot 10^3$Å, $3 \cdot 10^4$Å, $3 \cdot 10^5$Å). The calculation of molecular weight and polydispersity was based on polystyrene standards. ^{1}H NMR spectra were recorded at 100 MHz in CD_2Cl_2 on Tesla 567A spectrometer.

Polymerization

Polymerization experiments have been carried out under a dry argon atmosphere using large test tubes. The reaction was initiated with adding a solution of $TiCl_4$ to a mixture of a total volume 45 mL consisting of styrene, 1- phenylethyl chloride and dibutyl ether in mixture of 1,2-dichloroethane and *n*-hexane (55:45 v/v) at –15 ^{0}C. Specific reaction conditions are listed in the figure captions. The reaction was quenched by pre-cooled ethanol. The quenched reaction mixtures were washed with 0.5 M nitric acid and deionized water to remove the titanium–containing residues, evaporated to dryness under reduced pressure, and dried in vacuum overnight to give the product polymers.

Results and discussion

We have recently shown that in the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system the quasiliving cationic polymerization of styrene takes place [26, 27]. In this work the styrene polymerization was studied with the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system at –15 ^{0}C in 1,2-dichloroethane/hexane mixture at the ratio [$TiCl_4$]:[I] from 1:1 to 6:1. The plot of M_n versus conversion is shown in figure 1.

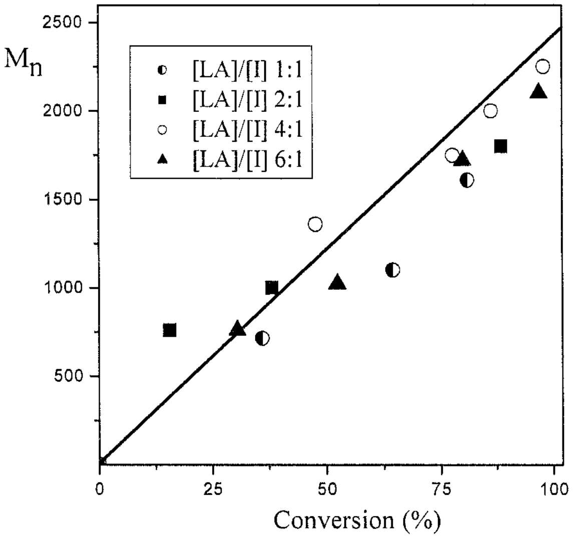


Figure 1. Molecular weights as function of monomer conversion in the polymerization of styrene with 1-phenylethyl chloride/$TiCl_4$/Bu_2O/ –15 ^0C at various concentration of $TiCl_4$; $[M]_0$ 0.82 M; $[I]_0$ $3.5 \cdot 10^{-2}$ M; $[TiCl_4]=2[Bu_2O]$. The straight line corresponds to theoretically calculated M_n values.

As it is seen in the figure 1, the M_ns increase linearly with conversion, which indicates the absence of chain transfer. Slightly low values of experimental M_ns in comparison with the calculated ones could be explained by the simultaneous initiation by the protic impurities. An undergoing of such process is rather possible, because we have shown that in the $H_2O/TiCl_4/Bu_2O$ system, the water is an effective initiator of the styrene cationic polymerization [28]. It's interesting that MWD of a polymer has been monomodal and rather narrow at the styrene polymerization both in the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system in different initiator concentrations (1, 2 in figure 2) and in the $H_2O/TiCl_4/Bu_2O$ system (3 in figure 2). This fact proves a close rate of initiation with H_2O and 1-phenylethyl chloride during the styrene polymerization in the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system.

Figure 3 shows the first-order dependences with respect to monomer for the styrene polymerization using the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system at different concentrations of $TiCl_4$. These dependences display the absence of irreversible chain termination in the examined interval of the $TiCl_4$ concentrations. The apparent rate constant for propagation ($k_{p\ app}$) was determined by the slope of the lines in the $\ln([M]_0/[M])$ versus polymerization time. It resulted in $0.67 \cdot 10^{-2}$ $1.1 \cdot 10^{-2}$; $2.1 \cdot 10^{-2}$ and $3.9 \cdot 10^{-2}$ min^{-1} for the $TiCl_4$ concentrations 0.035 M, 0.07 M; 0.14 M; 0.21 M respectively. The obtained values of $k_{p\ app}$s were used to determine a kinetic order of polymerization on $[TiCl_4]$.

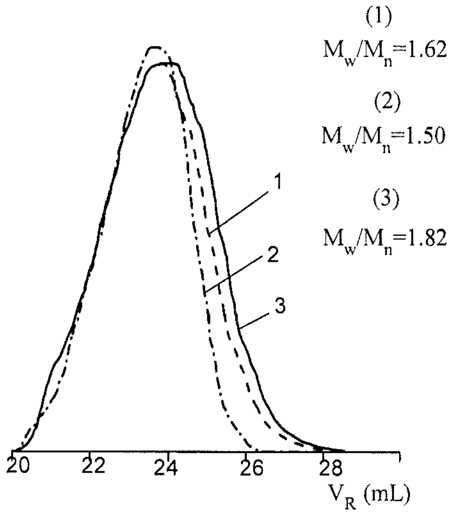


Figure 2. GPC traces of polystyrene obtained by the 1-phenylethyl chloride/$TiCl_4$/Bu_2O/ –15 °C system at [I] 0.0175 M (1) and 0.035 M (2); and by the H_2O/$TiCl_4$/Bu_2O/–15 °C (3) system at [H_2O] 0,035 M; $[M]_0$ 0.82 M; [$TiCl_4$] 0.14 M [Bu_2O] 0.28

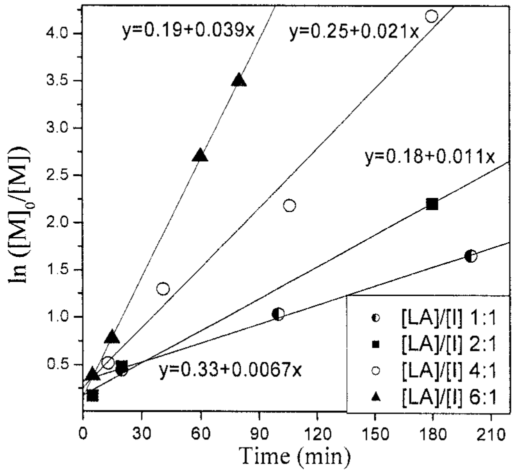


Figure 3. First-order plots for styrene polymerization with 1-phenylethyl chloride/$TiCl_4$/Bu_2O/ –15 °C at various concentration of $TiCl_4$; $[M]_0$ 0.82 M; $[I]_0$ $3.5 \cdot 10^{-2}$ M; [$TiCl_4$]=2[Bu_2O].

As it is seen in the figure 4, the kinetic order of the styrene polymerization with respect to titanium tetrachloride concentration in the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system is 1.01 that is very close to 1.

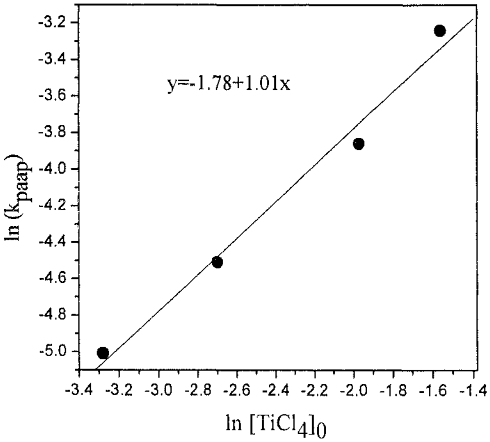
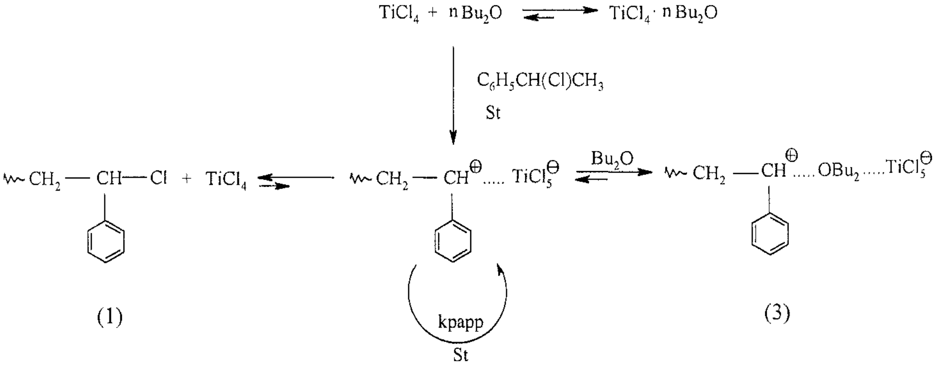


Figure 4. Reaction order of [$TiCl_4$] for styrene polymerization with 1-phenylethyl chloride/$TiCl_4$/Bu_2O/ –15 °C; $[M]_0$ 0.82 M; $[I]_0$ $3.5\cdot10^{-2}$ M; [$TiCl_4$]=2[Bu_2O].

Having included the fact that the first order kinetics on [$TiCl_4$] is observed in isobutylene polymerization if [$TiCl_4$]≥ [I] [2, 3], so we assumed that the initiation of polymerization, using the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system, is realized by small amount of $TiCl_4$, formed after dissociation of its complex with Bu_2O. In this case the instantaneous concentration of $TiCl_4$ is less in comparison with initiator concentration and, according to [2, 3], the kinetic order on [$TiCl_4$] is 1.

We have proposed the following mechanism of the styrene polymerization on the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system (scheme 1).



(1)

(2)

(3)

Scheme 1. Proposed mechanism for styrene polymerization with 1-phenylethyl chloride/TiCl4/Bu2O

We assumed, that dibutyl ether reacts with Lewis acid, decreasing its instantaneous concentration and promoting a suppression of side reactions with the participation of Lewis acid (irreversible termination, chain transfer). Co-initiation of polymerization was carried out with $TiCl_4$, formed after dissociation of $TiCl_4$ complexes with Bu_2O. The active propagating species exist in equilibrium with dormant (nonpropagation) chains (1 in scheme 1). On the other hand free dibutyl ether could interact with growing species by means of their solvation (3 in scheme 1). It leads to the decrease of the polymerization rate as well as to suppressing of side reactions. The participation of the species (3) in the chain growth is unlikely, otherwise the species (2) and (3) would differ in activity that would lead to bimodal MWD.

It has recently been shown [7] that in the t-Bu-m-DiCumCl/$TiCl_4$/2,4-dimethylpyridine system an essential mistake could appear while the determination of the kinetic order with $TiCl_4$ concentration when $[TiCl_4]<[I]$. The mistake is a result of the presence of protic impurities (HA), leading to the decrease of $TiCl_4$ concentration. The formation of a stable Lewis acid/ED complex also promoted the $TiCl_4$ concentration decrease. So for estimation of the effective $TiCl_4$ concentration ($[TiCl_4]_{eff}$) it was offered to use the following equations: $[TiCl_4]_{eff} = [TiCl_4]_0 - [TiCl_4 \cdot ED] - 2[EDH^+Ti_2Cl_8OH^-]$, when $[ED]>[HA]$ or $[TiCl_4]_{eff} = [TiCl_4]_0 - 2[ED]$, when $[ED]=[HA]$ [7]. However, the concentration of protic impurities is very difficult to estimate. On the other hand, if the $TiCl_4$ concentration is less the mistake in $[TiCl_4]_{eff}$ estimation is bigger.

In the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system H_2O is effective initiator of styrene cationic polymerization, dibutyl ether forms weak complexes with Lewis acid ($\Delta H \approx -6{,}0$ kcal·mol^{-1}) and doesn't participate in elimination of protic impurities [26-28]. As long as in all experiments $[TiCl_4]=2[Bu_2O]$, and co-initiation of polymerization is realized by $TiCl_4$, formed due to the dissociation of its complexes with Bu_2O, hence in the investigated system $[TiCl_4]_{eff} \sim [TiCl_4]_0$ with any $TiCl_4$ concentrations.

As a final note, it was found out that during the styrene polymerization in 1-phenylethyl chloride/$TiCl_4$/Bu_2O when $[TiCl_4]_{eff} < [I]$ the reaction order on $[TiCl_4]$ is 1. These results are in good agreement with the results, obtained during the kinetic order investigation for $TiCl_4$ concentration for isobutylene polymerization if $[TiCl_4]<[I]$ [2, 3]. On the contrary, while isobutylene polymerization in the t-Bu-m-DiCumCl/$TiCl_4$/2,4-dimethylpyridine system the kinetic order on $[TiCl_4]$ is 2 both for $[TiCl_4]>[I]$ and for $[TiCl_4]<[I]$ [7]. To understand the polymerization mechanism more deeply it is necessary to obtain new experimental data concerning the kinetic order for $[TiCl_4]$ when $[TiCl_4]<[I]$ during polymerization of isobutylene and styrene.

Conclusions

The kinetics of the quasiliving cationic polymerization of styrene using the 1-phenylethyl chloride/$TiCl_4$/Bu_2O initiating system was investigated and found out that the reactions order with respect to $[TiCl_4]$ is 1. The polymerization mechanism was proposed, based on the assumption that co-initiation of polymerization is realized by small amount of $TiCl_4$, formed after dissociation of its complexes with dibutyl ether. Free ether could solvate the growing species, suppressing a flowing of side reactions.

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