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Living cationic polymerization of styrene with 1-phenylethyl chloride/$TiCl_4$/Bu_2O

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Summary

Living polymerization of styrene was obtained in the system 1-phenylethyl chloride/$TiCl_4$/Bu_2O in mixture of 1,2-dichloroethane and *n*-hexane (55:45 v/v) at $-15\ ^0C$. The number–average molecular weights (M_n) of the polymers obtained increased in direct proportion to the monomer conversion and agreed well with the calculated values. The first-order kinetic plots were linear. The molecular weight distributions were narrow (M_w/M_n=1.46-1.56).

Introduction

The living polymerization is characterized by the absence of chain breaking processes such as termination and transfer reactions. Thus, it is the most effective method to synthesize polymers with controlled molecular weight (MW), narrow molecular weight distribution (MWD), as well as end-functionalized polymers. Sequential addition of different monomers leads to the formation block copolymers, whereas almost no homopolymer is formed. For the first time, the living cationic polymerization was carried out in the middle of 1980s. Higashimura et al. [1] were first to observe experimentally a living polymer formed in vinyl ether polymerization in 1984. In 1987, Faust and Kennedy [2] reported the living polymerization of isobutylene. The living cationic polymerization of styrene with the narrow MWD ($M_w/M_n<1.2$) was performed considerably later [3]. The difficulties were due to the nature of growing carbocation capable of undergoing chain transfer, termination, and other undesirable side reactions.

At the present time, numerous studies of living cationic polymerization (including polymerization of styrene) are conducted, aimed at both detailed investigation of the reaction mechanism and the search for new effective initiating systems [4-7]. For obtaining living polystyrene, systems on the basis of $SnCl_4$, BCl_3, $TiCl_4$ and $TiCl_3$(*i*-OPr) are used in the presence of various additives: ionic salts ($n$$Bu_4NCl$) and electron donors (ED), including proton traps (di-*tert*-butylpyridine and others) [3,4,8-10]. As a rule, strong EDs are used. In such cases, molar concentrations of Lewis acids are taken 2-20 higher than the sum of the initiator and ED concentrations, and rapid formation of a stable Lewis acid/ED complex takes place. In this case the main function of EDs is to react with protic impurities in the polymerization system. There is no information about living cationic polymerization of styrene in the presence of weak EDs. However, in our preliminary investigations, polymerization of styrene in the presence of relatively weak ED manifested the signs of living polymerization [11].

The purpose of this work is to study the process of cationic polymerization of styrene initiated with 1-phenylethyl chloride/$TiCl_4$ in the presence of dibutyl ether (Bu_2O) taken in excess to Lewis acid, and find out optimal system for realizing the living cationic polymerization.

Experimental

Materials

Styrene was treated with KOH or NaOH, dried with $CaCl_2$ and CaH_2, and twice distilled from CaH_2 under reduced pressure. *n*-Hexane and 1,2-dichloroethane were treated with sulphuric acid until the acid layer remained colorless, then washed with aqueous $NaHCO_3$, dried over $CaCl_2$, and distilled from CaH_2 (at least twice) under an inert atmosphere. 1-Phenylethyl chloride was prepared by bubbling of HCl through a solution of styrene in CH_2Cl_2. The reaction was monitored by ^1H NMR. 1-Phenylethyl chloride was purified by distillation from CaH_2 under reduced pressure. Dibutyl ether was dried over CaH_2 and twice distilled from CaH_2 under reduced pressure. $TiCl_4$ was distilled from copper shavings under reduced pressure.

Instruments

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) in THF using Waters GPC instrument with three Ultrastyragel columns ($3\cdot10^3$Å, $3\cdot10^4$Å, $3\cdot10^5$Å). The calculation of molecular weight and polydispersity was based on polystyrene standards. ^1H NMR spectra of the polymers 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 $TiCl_4$ in 1,2-dichloroethane (1.5 mL, 4 M) to a mixture of a total volume 45 mL consisting of styrene (4 ml), 1- phenylethyl chloride (0.2 mL) and dibutyl ether (2 mL) in mixture of 1,2-dichloroethane and *n*-hexane (55:45 v/v) at -15 ^{0}C. 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

Figure 1 shows the conversion -time relationships for styrene polymerization processes initiated with 1-phenylethyl chloride/$TiCl_4/Bu_2O$ at –15 ^0C in mixture of 1,2-dichloroethane and *n*-hexane. As it is seen in the figure, the polymerization rate is decreasing with increasing dibutyl ether concentration. At the same time, the maximum M_n value, which is controlled by the monomer to initiator ratio, $[M]_0/[I]_0$, is also decreasing from 4500 (for $[TiCl_4]$:$[Bu_2O]$ 1:1) to 2500 (for $[TiCl_4]$:$[Bu_2O]$ 1:2) (Figure 2). Simultaneously with the increase of the dibutyl ether concentration, MWD of the polymer begins to narrow (from 2 to 1.67-1.81).

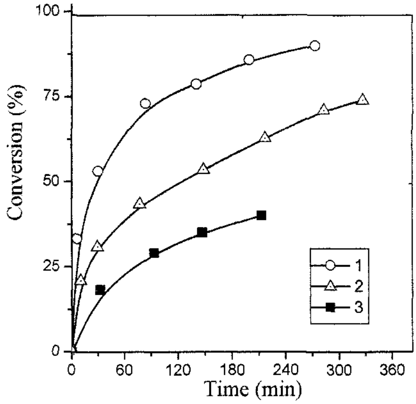

Figure 1. Dependence of monomer conversion as function of time in the polymerization of styrene at various concentration of dibutyl ether with 1-phenylethyl chloride/ $TiCl_4$/ Bu_2O/ –15 ^0C; $[M]_0$ 1,58 M; $[I]_0$ 1,8·10^{-2} M; $[TiCl_4]$ 3·10^{-2} M (1,2) and 6·10^{-2} M (3); $[Bu_2O]$ 3·10^{-2} M (1), 6·10^{-2} M (2), 0,18 (3).

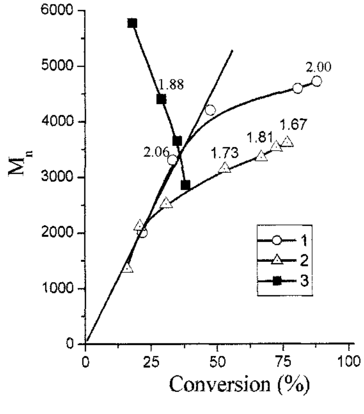

Figure 2. Molecular weights as function of monomer conversion in the polymerization of styrene with 1-phenylethyl chloride/ $TiCl_4/Bu_2O$ -15 ^0C at various concentration of

dibutyl ether; $[M]_0$ 1.58 M; $[I]_0$ $1.8 \cdot 10^{-2}$ M; $[TiCl_4]$ $3 \cdot 10^{-2}$ M (1,2) and $6 \cdot 10^{-2}$ M (3); $[Bu_2O]$ $3 \cdot 10^{-2}$ M (1), $6 \cdot 10^{-2}$ M (2), 0.18 (3). The numbers given above the graph points are MWD values. The straight line corresponds to theoretically calculated M_n values.

With a triple excess of dibutyl ether to Lewis acid, the M_n-conversion curve shows a dramatic change: the polymer M_n value decreases with increasing conversion. This behavior can be attributed to a conventional cationic polymerization proceeding in system. The fact that the M_n-conversion plot deviates from linear relationship in the later stage of the reaction can be explained by chain transfer. Note should be taken, that at high Bu_2O concentrations, the latter can induce elimination of β-protons provoking thereby chain transfer processes [12].

Taking into account the above findings, the 1-phenylethyl chloride/$TiCl_4$/Bu_2O system was investigated using the molar ratio of the components 1:4:8, respectively, and $[M]/[I] < 25$. The results are shown in Figure 3. As it is seen in the figure, the M_ns increase linearly with conversion, and the plot can be extrapolated to the origin, which indicates a polymerization mechanism without chain transfer processes. Within experimental error, all points of the plot fit the theoretical line built up based on the assumption that one polymer chain is formed per molecule of initiator. In addition, the linearity of the $\ln([M]_0/[M])$ versus time plot indicates the absence of termination processes.

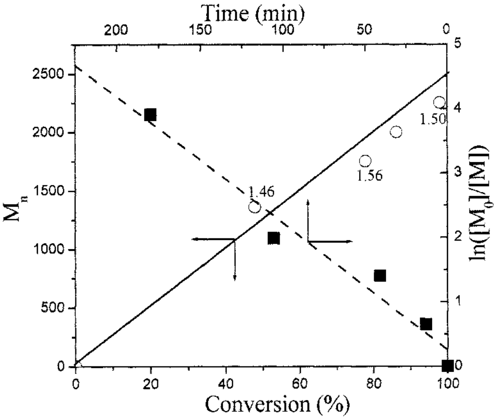

Figure 3. Molecular weights as function of monomer conversion, and $\ln([M]_0/[M])$ versus time in the polymerization of styrene with 1-phenylethyl chloride/$TiCl_4$/Bu_2O/ – 15 °C; $[M]_0$ 0.82 M; $[I]_0$ $3.5 \cdot 10^{-2}$ M; $[TiCl_4]$ 0.14 M $[Bu_2O]$ 0.28. The numbers given above the graph points are MWD values. The straight line corresponds to theoretically calculated M_n values.

The data presented above are evidence of living character of styrene polymerization under the conditions studied. Earlier we have found that that the lifetime of active species is longer than the time of complete conversion of the monomer [13]. This fact is an indication of a prevailing role of chain growth processes over those of irreversible chain termination. Molecular weight distributions of the polymers, obtained in this work, are rather narrow (M_w/M_n=1.46–1.56), see Figure 3.

^{1}H NMR spectroscopy of the polystyrene obtained by the living cationic polymerization with 1-phenylethyl chloride/$TiCl_4/Bu_2O$ system and quenched with ethanol indicated the presence of $-CH_2CH(C_6H_5)Cl$ end groups (broad *signal in the region of δ 4,2–4,4 ppm that is assignable to the methine proton of* the CH–Cl group). The number-average molecular weight of the polymers, determined by ^{1}H NMR (M_n=1700) is in good agreement with M_n, measured by gel permeation chromatography (M_n=1720). It is known that equilibrium exists between so-called dormant species (i.e. with covalent C-Cl bonds) and active ion pair species [4] .The absence of terminal ethoxide groups indicates a stronger interaction of chloride with the terminal carbon than with the Lewis acid. One of the main conditions for the living polymerization to be realized is that the abovementioned equilibrium be shifted toward the inactive dormant species. This provides low concentration of growing ends and small probability of side reactions to proceed.

The main function of EDs is often thought to be inactivation protic impurities in the polymerization system [14-16], similar to a proton trap. There are also other concepts about the role of EDs in living cationic polymerization, the main idea of which is stabilization of the active species by electron donors or by their complexes with Lewis acid [17].

We think that in the system studied, dibutyl ether forms a complex with the Lewis acid, decreasing thereby its electrophilic properties. It is known that changes in coinitiator acidity strongly affect the equilibrium between the dormant and active species. Hence, the MWD narrowing with the increasing concentration of dibutyl ether in the system studied can be associated with the increasing rate of the interconversion between the dormant and active species of polymerization. On the other hand, because of the low stability of the complex $TiCl_4{\cdot}OBu_2$ or $TiCl_4{\cdot}2OBu_2$ ($\Delta H \approx -6{,}0$ kcal·mol^{-1}), there are always free dibutyl ether molecules capable of complex formation with the growing ends, providing thereby their stabilization. However, in the presence of excessive concentrations of free dibutyl ether molecules, eliminatinon of β–protons can take place which provokes chain transfer processes. These issues, however, need to be investigated in more detail.

For the first time living cationic polymerization of styrene was carried out in the presence of excess of electron donor to Lewis acid. The obtained results confirm a theory of carbocationic stabilization by electron donors through weak nucleophilic interaction [18,19]. System 1-phenylethyl chloride/$TiCl_4/Bu_2O$, unlike other initiating systems based on $TiCl_4$, results in obtaining a polymer with more narrow MWD. Intermolecular alkylation, frequently taking place during polymerization of styrene in such systems, is absent [9,10,14]. The suggested initiating system, as the systems based on $SnCl_4$ [3,20], allows to carry out the living cationic polymerization of styrene by relatively high temperature.

Conclusions

The polymerization of styrene with the 1-phenylethyl chloride/$TiCl_4$ initiating system in the presence of excess of a weak electron donor (Bu_2O) afforded the living polymers with low polydispersity (M_w/M_n=1.46–1.56). Dibutyl ether in this system can interact with Lewis acid and, probably, with growing ends.

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