

Novel initiating system based on AlCl_3 etherate for quasiliving cationic polymerization of styrene

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Summary

Quasiliving cationic polymerization of styrene was obtained in the system 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{O}(\text{Bu})_2/\text{Bu}_2\text{O}$ in a mixture of 1,2-dichloroethane and *n*-hexane (55:45 v/v) at -15°C . The molecular weights of the polymers (M_n) increased in direct proportion to the monomer conversion. However, the experimental M_n s are essentially higher than theoretical ones, indicating that slow initiation relative to propagation takes place. The molecular weight distributions were broad ($M_w/M_n \sim 2.5$), probably due to the slow initiation and slow exchange between reversibly terminated and propagating species.

Introduction

Quasiliving cationic polymerization is one of the simplest and effective methods to synthesize polymers with controlled molecular weight, molecular weight distribution (MWD) and end-functionalized polymers [1-3]. It is known, that quasiliving cationic polymerization of styrene has been considered to be difficult to achieve, because of the low stability of the propagating carbocation. So only several systems for quasiliving cationic polymerization of styrene based on SnCl_4 [4], BCl_3 [5], TiCl_4 [6] and $\text{TiCl}_3(\text{O}i\text{-Pr})$ [7] are used. On the other hand, only titanium tetrachloride is used in the synthesis of triblock copolymers [3, 8-10]. Therefore at the present time the searches of new effective systems for quasiliving cationic polymerization of styrene and its block copolymerization with isobutylene are carried out rather intensively [3, 11-13].

Aluminum trichloride (AlCl_3) is one of the representative Lewis acids that are effective in cationic polymerization of styrene, isobutylene and other monomers [14]. However, AlCl_3 is very strong Lewis acid and so in the systems based on aluminum trichloride the propagation is very rapid and is accompanied by chain transfer and termination. At the present time AlCl_3 has not been used in quasiliving cationic polymerization of styrene, probably due to the lack of suitable initiators, higher Lewis acidity of AlCl_3 and its poor solubility in organic solvents.

However, our preliminary studies have revealed that when styrene polymerization is performed in the systems $\text{H}_2\text{O}/\text{AlCl}_3 \cdot \text{O}(\text{C}_6\text{H}_5)_2$ [15] and $\text{H}_2\text{O}/\text{AlCl}_3 \cdot \text{O}(\text{C}_4\text{H}_9)_2$ [16] the irreversible chain termination is absent, and M_n of the polymer increases with increasing its yield. Nevertheless, lower M_n value as compared to that calculated indicates that a chain transfer reaction is operated in the named systems. We also found out that a polymer with more narrow MWD is formed in styrene polymerization in the system $\text{H}_2\text{O}/\text{AlCl}_3 \cdot \text{O}(\text{C}_4\text{H}_9)_2$ than in 1-phenylethyl chloride/ $\text{AlCl}_3 \cdot \text{O}(\text{C}_4\text{H}_9)_2$ [17]. This publication reports on the achievements of quasilinging cationic polymerization of styrene with the AlCl_3 etherate based initiating systems.

Experimental

Materials

1-Phenylethyl chloride was prepared by bubbling of HCl through a solution of styrene in CH_2Cl_2 . 1-Phenylethyl alcohol and 2-phenyl-2-propanol were prepared by reaction of phenylmagnesium bromide with acetaldehyde and acetone in diethyl ether respectively. The reactions were monitored by ^1H NMR. The initiators were purified by distillation from CaH_2 (at least twice) under reduced pressure. Aluminum trichloride was purified by sublimation under argon atmosphere. $\text{AlCl}_3 \cdot \text{O}(\text{C}_4\text{H}_9)_2$ was synthesized by the reaction of aluminum trichloride with dibutyl ether in 1,2-dichloroethane. The source and purification of all other reagents have been previously reported [18].

Instruments

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) in THF using a Waters GPC instrument with three Ultrastaygel columns ($3 \cdot 10^3 \text{ \AA}$, $3 \cdot 10^4 \text{ \AA}$, $3 \cdot 10^5 \text{ \AA}$). The calculation of molecular weight and polydispersity was based on polystyrene standards. ^1H NMR spectra were recorded at 400 MHz in CDCl_3 on a Bruker AC-400 spectrometer.

Polymerization

The polymerizations were carried out under dry argon atmosphere using large test tubes. The reaction was initiated with adding a solution of $\text{AlCl}_3 \cdot \text{O}(\text{C}_4\text{H}_9)_2$ in 1,2-dichloroethane (1M) to a mixture of total volume 40 mL consisting of styrene, 1-phenylethyl chloride and dibutyl ether in the mixture of 1,2-dichloroethane and *n*-hexane (55:45 v/v) at -15°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 aluminium-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 M_n - monomer concentration relationships for styrene polymerization in the systems based on $\text{AlCl}_3 \cdot \text{O}(\text{C}_4\text{H}_9)_2$ at -15°C in the mixture of 1,2-dichloroethane and *n*-hexane. As it is seen in figure 1, the experimental M_n s are much

higher than theoretical values (dotted line in figure 1) and the MWD of the polymers is very broad (see figure 2) when styrene polymerization is performed in the system 1-phenylethyl chloride/ $\text{AlCl}_3 \cdot \text{OBu}_2$.

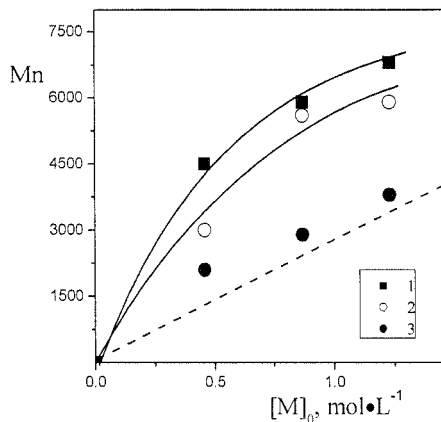


Figure 1. Molecular weights as function of monomer concentration in the polymerization of styrene in the presence of $\text{AlCl}_3 \cdot \text{OBu}_2$: $[\text{AlCl}_3 \cdot \text{OBu}_2] 5 \cdot 10^{-2} \text{ M}$; $[\text{I}] 3.8 \cdot 10^{-2} \text{ M}$; $[\text{I}] = 1$ -phenylethyl chloride (1); 1-phenylethyl alcohol (2); 2-phenyl-2-propanol (3); temperature = -15°C . The dotted line corresponds to theoretically calculated M_n values.

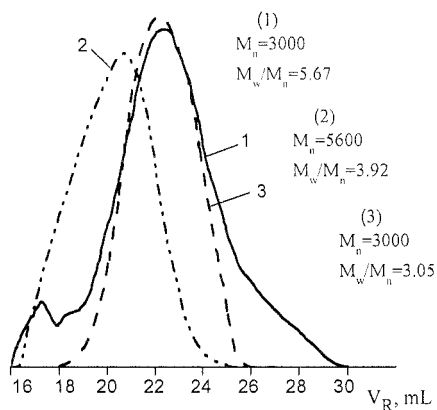


Figure 2. MWDs of the polystyrene obtained in the systems based on $\text{AlCl}_3 \cdot \text{OBu}_2$: $[\text{AlCl}_3 \cdot \text{OBu}_2] 5 \cdot 10^{-2} \text{ M}$; $[\text{I}] 4 \cdot 10^{-2} \text{ M}$; $[\text{I}] = 1$ -phenylethyl chloride (1); 1-phenylethyl alcohol (2); 2-phenyl-2-propanol (3); temperature = -15°C .

It has been found out that initiators containing donor groups ($-\text{OH}$) are promoting controlled polymerization of styrene and leading to polymers with more narrow MWD (figure 2). In the polymerization of styrene using the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2$ system molecular weight of the polymer increases linearly with the monomer

concentration, although the experimental M_n values are higher than theoretical ones and molecular weight distribution of the polymers are broad.

We think that in case of the initiators, containing donor groups, the *in situ* modification of the $AlCl_3$ Lewis acidity by the introduction of the electron-donating hydroxyl groups into the metal center takes place. This leads to acceleration of exchange reaction between active and "dormant" species (or according to a recent definition [19] between reversibly terminated and propagating species) and narrowing of the MWD of the polymers respectively. It is known that modulation of the acidity of $TiCl_4$ by the electron-donating alkoxy groups was in some cases effective to obtain quasiliving cationic polymerization of styrene [7], α -methylstyrene [20], indene [21] and isobutyl vinyl ether [22]. However, the molecular weight distribution of the polymer remains broad ($M_w/M_n \sim 3$). It is likely that in the investigated systems coexistence of free ions and ion pairs and relatively slow equilibrium rates between these species and reversible terminated chains may lead to broad MWD.

It should be noted, that the polymerization of styrene in the 2-phenyl-2-propanol/ $AlCl_3 \cdot OBu_2$ system was very fast, complete conversion was obtained in a few seconds and sampling or kinetic measurement during the polymerization had not been possible. On the other hand we also found out that with the increase of the dibutyl ether concentration ($[AlCl_3 \cdot OBu_2]:[OBu_2]$ 1:1), the polymerization rate decreases and the MWD of the polymers begins to narrow (from $M_w/M_n \sim 3$ to $M_w/M_n \sim 2.5$).

Taking into account the above findings, the 2-phenyl-2-propanol/ $AlCl_3 \cdot OBu_2/Bu_2O$ initiating system was investigated. The obtained results are shown in figure 3.

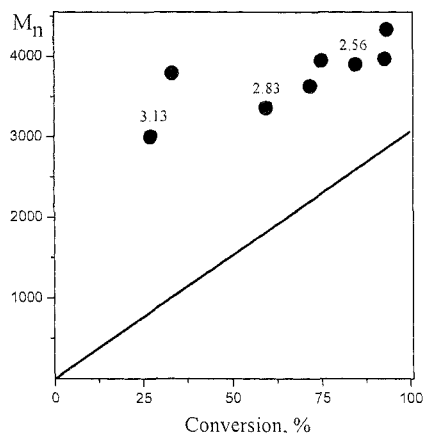


Figure 3. Molecular weight as function of monomer conversion in the polymerization of styrene with 2-phenyl-2-propanol/ $AlCl_3 \cdot OBu_2/Bu_2O$ at $-15^\circ C$: $[M]_0$ 1.0; $[AlCl_3 \cdot OBu_2]$ $4.7 \cdot 10^{-2}$ M; $[I]$ $3.5 \cdot 10^{-2}$ M; $[Bu_2O]$ $4.7 \cdot 10^{-2}$ M. The straight line corresponds to theoretically calculated M_n . The numbers adjacent to the experimental points are M_w/M_n values.

As it is seen in figure 3, the M_n s increase with conversion which indicates the absence of the chain transfer. However, experimental M_n s are essentially higher than theoretical ones, indicating that slow initiation relative to propagation takes place in the 2-phenyl-2-propanol/ $AlCl_3 \cdot OBu_2/Bu_2O$ initiating system [1, 23]. In other words in

this system the reaction of tertiary carbocations (formed from the initiator) with counterion is slower than their reaction with styrene that leads to polymer with higher M_n values and part of initiator remains unreacted [24, 25]. For proof the quasiliving character of the styrene polymerization in the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ system the series of IMA (incremental monomer addition) [1] experiments have also been carried out. The obtained results are collected in figure 4.

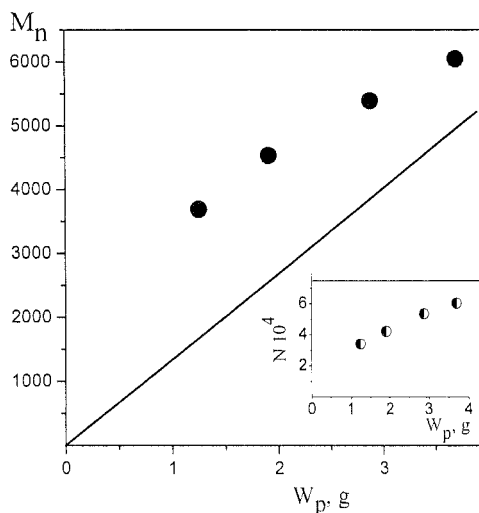


Figure 4. M_n versus weight of polymer (W_p) and number of polymer chains (N) versus W_p (inset) plots for the styrene polymerization in the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}/-15^\circ\text{C}$ system. IMA method: $[\text{I}] 4.6 \cdot 10^{-2} \text{ M}$; $[\text{AlCl}_3 \cdot \text{OBu}_2] 6.4 \cdot 10^{-2} \text{ M}$; $[\text{Bu}_2\text{O}] 6.4 \cdot 10^{-2} \text{ M}$; $[\Delta\text{M}] 0.84 \text{ M}$; $V_0 16 \text{ mL}$; $\Delta t 5 \text{ min}$.

It can be seen from figure 4, M_n is above the theoretical line and approaches to it with increasing of the weight of the polymer formed. Similarly, the number of polymer chains (N) increases by increasing the number of monomer increments. However, even after the four monomer additions observed M_n s are somewhat higher and, respectively, N is lower than the theoretical values ($I_{\text{eff}} \sim 80\%$). These results confirm that in the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ initiating system quasiliving cationic polymerization of styrene with slow initiation relative to propagation takes place.

Figure 5 shows the first-order dependence with respect to monomer for the styrene polymerization for two separate experiments using the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ system. As it is seen in the figure, the plot starting from the origin is curved. The curvature indicates that the concentration of propagating and reversibly terminated chains decreases more rapidly than formation of new chains by the slow initiation occurs. It is confirmed by ^1H NMR spectroscopy: chain coupling by intermolecular alkylation involving the propagating chains takes place (see below).

We also found out that when a fresh feed of styrene was added to the reaction mixture just before the initial increment had been completely polymerized the slower polymerization took place (table 1). This phenomenon is now under investigation in

more detail in our laboratory and will be discussed in a subsequent paper. It should be noted that after addition of the second monomer increment the M_n values increased in direct proportion to monomer conversion, however the MWD of obtained polymers remains broad (table 1).

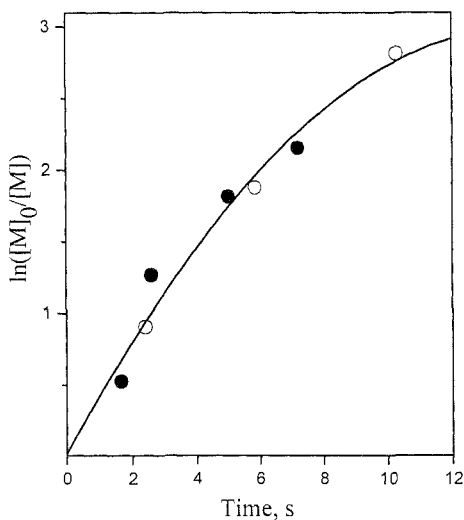


Figure 5. $\ln[M]_0/[M]$ vs. time plot for the polymerization of styrene with 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ at -15°C : $[M]_0$ 1.0; $[\text{AlCl}_3 \cdot \text{OBu}_2]$ $4.7 \cdot 10^{-2}$ M; $[\text{I}]$ $3.5 \cdot 10^{-2}$ M; $[\text{Bu}_2\text{O}]$ $4.7 \cdot 10^{-2}$ M.

Table 1. Characterization of polystyrene after the second monomer addition.

Time of addition of the second monomer increment (s)	Conversion (%)	M_n	M_w/M_n
original	94	3200	2.38
40	112	3325	—
79	124	3640	—
158	140	3750	—
300	153	4050	—
900	181	4200	2.38

Reaction conditions: $[\text{I}]$ $5.1 \cdot 10^{-2}$ M; $[\text{AlCl}_3 \cdot \text{OBu}_2]$ $6.8 \cdot 10^{-2}$ M; $[\text{Bu}_2\text{O}]$ $6.8 \cdot 10^{-2}$ M; $[\text{styrene}]_1$ 0.88 M; $[\text{styrene}]_2$ 0.48 M. Polymerization time for original sample: 40 s.

The terminal structure of the polystyrene obtained by quasiling cationic polymerization with the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ system was examined by ^1H NMR spectroscopy. In addition to the large absorption of the main-chain protons, the signals due to the end groups appeared, namely CH_3- ($\delta \sim 1$ ppm) at the α -end and $-\text{C}(\text{C}_6\text{H}_5)\text{H}-\text{Cl}$ at the ω -end (broad signal in the region of δ 4.2 – 4.5 ppm). The number-average end functionality (F_n) of the polymers, determined by the peak area ratio of the ω -methine to α -methyl protons, was about 0.65-0.8. At the same time

the ^1H NMR spectrum of obtained polymers shows the signal in the region of δ 3.2 – 3.6 ppm, which can be assigned to methine protons neighboring with two aromatic rings [26, 27], indicating that during the styrene polymerization with the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ system the intermolecular alkylation takes place. It is worth recalling that the presence in the synthesized polymers of the $-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{Cl}$ end groups confirms the modification of Lewis acid by donor hydroxyl groups by interaction of the initiator with metal halide at the styrene polymerization in the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ system.

In our opinion, the quasiliving cationic polymerization of styrene in the system 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ occurs due to the formation *in situ* of a weaker Lewis acid (AlCl_2OH). This leads to a shift in the equilibrium between propagating and reversibly terminated species towards formation of the latter, as well as to acceleration of exchange reactions between them, which favors the control of M_n s of polymers and narrowing its MWD. However, the molecular weight distribution of the polymer remains broad, probably due to the slow initiation and slow exchange between reversibly terminated and propagating species on the one hand. On the other hand high polydispersity of obtained polymers could be a result of intermolecular alkylation, which takes place during styrene polymerization in the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ initiating system. This leads to differently branched polystyrenes and limits the possibility of synthesizing well-defined polymers. At the same time, dibutyl ether forms fairly stable complex with the Lewis acid ($\Delta H \sim -36.5 \text{ kcal/mol}^{-1}$) [28] that leads to the suppression of the side processes involving the latter. Taking into account the high stability of the complex AlCl_3 with dibutyl ether it is unknown if free acid or its complex with ether participate in the co-initiation of polymerization. Recently we have also shown that in the 1-phenylethyl chloride/ $\text{TiCl}_4/\text{Bu}_2\text{O}$ initiating system at $[\text{TiCl}_4]:[\text{Bu}_2\text{O}]$ 2:1 quasiliving cationic polymerization of styrene takes place [18, 29]. We also found out that the styrene polymerization with 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ system flows rapidly even at $[\text{AlCl}_3 \cdot \text{OBu}_2]:[\text{Bu}_2\text{O}]$ 1:6 [30]. On the other hand, it is known, that free Lewis acid is needed for olefin polymerizations at least in the systems based on TiCl_4 in contrast to vinyl ethers polymerization [1, 31]. Therefore, to understand the polymerization mechanism more deeply it is necessary to obtain new experimental data.

Conclusions

Thus, the studies we have performed made it possible for the first time to realize quasiliving cationic polymerization of styrene in the presence of AlCl_3 etherate. We assume that in the 2-phenyl-2-propanol/ $\text{AlCl}_3 \cdot \text{OBu}_2/\text{Bu}_2\text{O}$ initiating system, the *in situ* modification of the AlCl_3 Lewis acidity flows by the introduction of the electron-donating hydroxyl groups into the metal center. This leads to a shift in the equilibrium between propagating and reversibly terminated species towards terminated species and to acceleration of exchange reactions between them, which favors the control of M_n s of polymers and narrowing their MWD.

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