Polymerization Processes in Ionic Liquids. Cationic Polymerization of Styrene

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Summary: There is an increasing interest in using ionic liquids as solvents for polymerization processes. Most published data deals with controlled radical polymerization. It has been shown that ionic liquids offer several advantages for conducting Atom Transfer Radical Polymerization (ATRP), such as good solubility of catalyst and improved k_p/k_t ratio. Ionic liquids are highly polar therefore they seem to be suitable solvents for conducting also ionic polymerization processes. In our preliminary communication we reported on cationic polymerization of styrene initiated by R-Cl/$TiCl_4$ system in ionic liquid. To clarify the mechanism of this process, racemization of optically active 1-phenylethyl choride (initiator and the model of dormant species) was studied and it was shown that in ionic liquid racemization proceeds even in the absence of coinitiator ($TiCl_4$). Because racemization proceeds through ionization of C–Cl bond, this explains the cationic polymerization of styrene initiated by R-Cl alone (in the absence of coinitiator). Chain transfer, however, cannot be eliminated, therefore polymerization is not controlled.

Keywords: cationic polymerization; ionic liquids; polystyrene

Introduction

Ionic liquids, organic salts that are liquid at ambient temperatures, have received much attention in many areas of chemistry due to their properties which make them attractive alternative to traditional solvents. [1] Due to such properties as negligible vapor pressure, ability to dissolve several inorganic and organometallic compounds as well as thermal and chemical stability, ionic liquids are used as solvents in organic synthesis. In recent years ionic liquids have been used also as solvents for polymer synthesis and there are several reviews that discuss the progress in this field. [2–5]

Most papers describing the application of ionic liquids for polymer synthesis deals with controlled radical polymerization processes, mainly Atom Transfer Radical Polymerization (ATRP). ATRP requires the presence of catalyst (most frequently copper salts) and ability of ionic liquids to dissolve catalyst offers significant advantage, although interesting kinetic effects (increasing of the ratio of rate constant of propagation to the rate constant of termination [6]) have also been observed for ATRP in ionic liquids.

One of the properties of ionic liquids is their high polarity therefore they seem to be suitable solvents for conducting also ionic polymerizations. There is, however, very little research activity concerning application of ionic liquids as solvents for polymerizations proceeding by ionic mechanism.

High polarity of ionic liquids should especially affect the course of those ionic polymerization processes that involve equilibrium between active and dormant species. Ionization should be favored in more polar solvents, as it was shown for example for the cationic polymerization of tetrahydrofuran initiated by triflic acid in organic

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solvents of different polarity. In those systems active species (tertiary oxonium ions) were in equilibrium with dormant species (macroesters) and relative proportions of both species depended strongly on solvent polarity. [7]

There are two reports in the literature concerning cationic polymerization of styrene in ionic liquid. Bis(oxalato)boric acid initiated efficiently cationic polymerization of styrene in N-Butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ionic liquid (96% conversion after 2h at 60 °C) while under the same conditions only very slow polymerization was observed in methylene chloride solution (15% conversion after 2h at 60 °C). [8] Authors, claim that the polymerization proceeded as living process and although indeed some features of living polymerization were observed, the living character of this polymerization has still to be confirmed.

In the preliminary report from our laboratory, the initiating system developed by Kennedy et al. [9] was applied for cationic polymerization of styrene and it was shown that polymerization required lower concentration of coinitiator ($TiCl_4$) than in organic solvents. [10] The interesting observation was that polymerization initiated with 1-phenylethyl chloride proceeded to high conversion even in the absence of coinitiator ($TiCl_4$) although it required higher temperatures (90 °C). That could imply that initiation involves ionization of C–Cl bond in 1-phenylethyl chloride proceeding in the solution in ionic liquid even in the absence of coinitiator. MALDI TOF analysis of polymers formed in polymerization initiated with 1-(p-methylphenyl)ethyl chloride (to distinguish between head-groups formed through ionization of initiator and head-groups formed by transfer) revealed that two populations of macromolecules were present, one containing p-methyl substituent in the head-group and the other having head-groups devoid of methyl substituent, thus apparently formed by transfer. Corresponding reaction pathways are shown in Scheme below:

To clarify the mechanism of this polymerization it is necessary to determine whether ionic liquids are sufficiently polar to bring about spontaneous ionization of C–Cl bond in 1-phenylethylchloride (which is an initiator but also the model of covalent species in propagation).

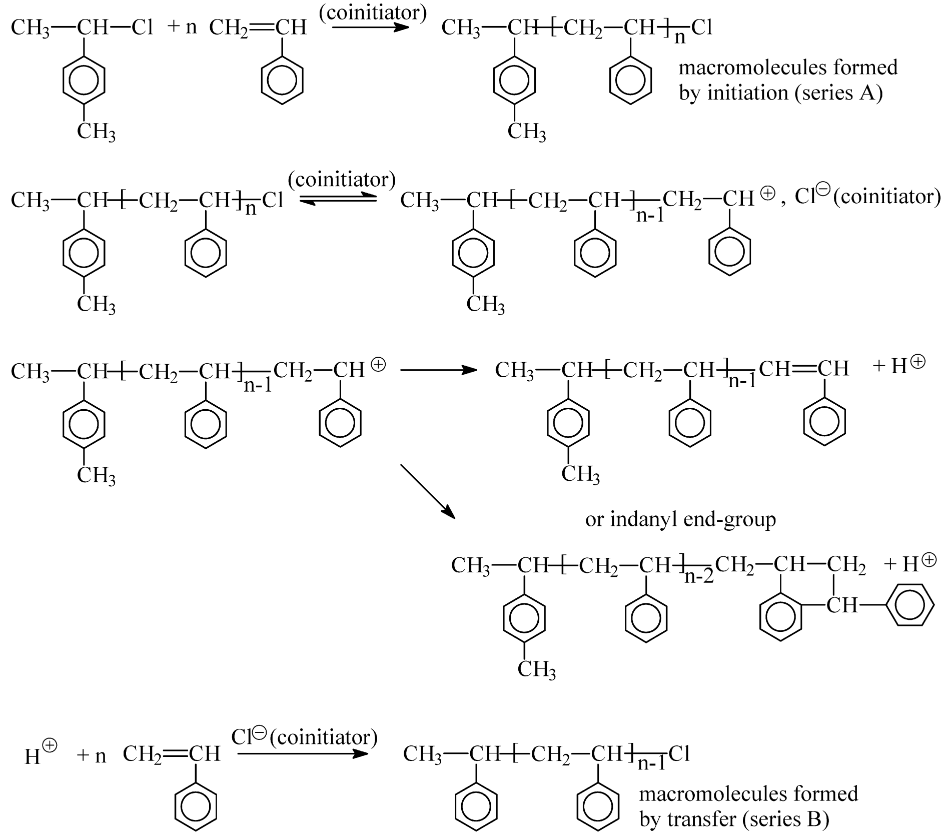
It is generally claimed that ionic liquids are highly polar. Although dielectric constant can not be measured directly because ionic liquids are electrolytes, polarity has been estimated by spectroscopic methods and it has been concluded that ionic liquids are indeed highly polar, their polarity (depending on structure of ionic liquids) being higher than that of acetonitrile or dimethylformamide but lower than methanol. [11,12] In a recently published paper on the basis of dielectric spectroscopy measurements it has been claimed, however, that results based on polarity sensitive dyes and fluorescent probes give too high values and that ionic liquid are medium polarity solvents, with a polarity comparable to that of higher alcohols (corresponding to dielectric constant in the range $\varepsilon = 10–15$). [13] Thus apparently results strongly depend on the method applied to estimate polarity.

In order to estimate whether the polarity of ionic liquid is sufficient to cause spontaneous ionization of C–Cl bond in the particular system studied, we investigated the racemization of optically active 1-phenylethylchloride. If, at the given conditions, C–Cl bond underwent ionization then racemization should be observed (cf Scheme 2). If there were no ionization, the racemization should not occur.

In the present paper we report on the behavior of optically active 1-phenylethyl chloride in solution in ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate – [bmim][PF_6]) and correlate these results with a results of polymerization experiments.

Racemization of Optically Active 1-Phenylethyl Chloride

When optically active 1-phenylethyl chloride ($[\alpha]_D = +65.4°$) was dissolved in [bmim][PF_6] (7.7×10^{-4} mol of chloride

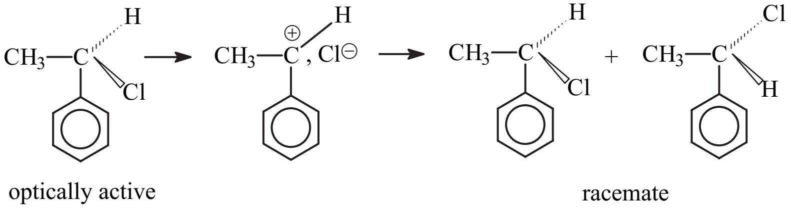


Scheme 1.

in 1 g of [bmim][PF_6] i.e approximately 0.55 mol/L solution) no change of optical rotation was observed at 25 °C for 24h. At 60 °C a slow racemization was observed, the optical rotation decreased to 50% of the starting value in about 400 min. At 80 °C racemization was much faster, almost complete racemization occurred within 60 min.

Racemization should be of the first order with respect to optically active 1-phenylethyl chloride and indeed the kinetic plot in semi-logarithmic coordinates is linear as shown in Fig. 1. Rate coefficient for racemization is equal to $k = 7.2 \times 10^{-3}\ s^{-1}$ at 80 °C. Racemization proceeded much faster in the presence of $TiCl_4$, even at lower temperatures, indicating that indeed coinitiator facilitates ionization of C–Cl bond.

For comparison, the changes in optical rotation of the solution of optically active 1-phenyletyl chloride were followed in the



Scheme 2.

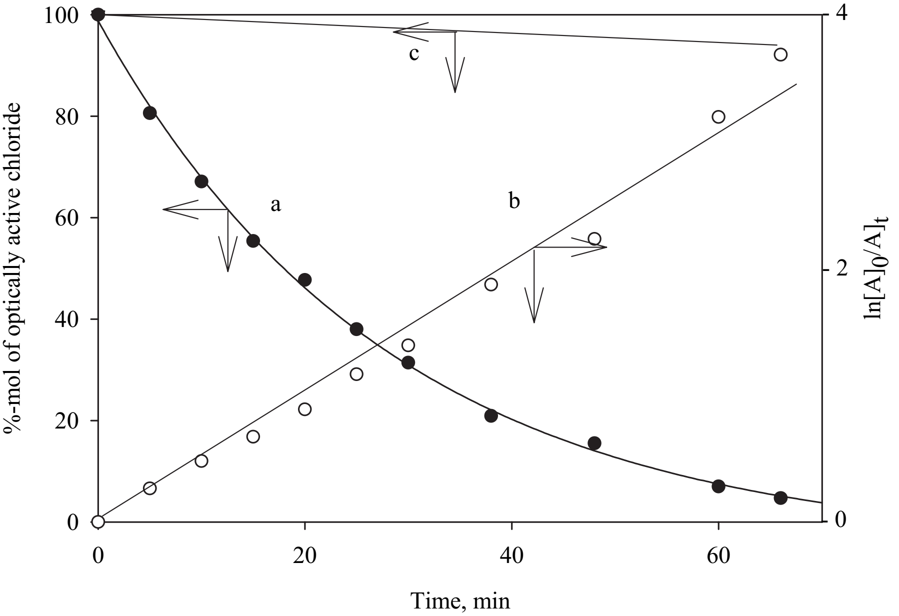


Figure 1.
Racemization of optically active 1-phenylethyl chloride in solution in [bmim][PF_6] (polarimetry). a – decrease of optical rotation of a solution of 7.7×10^{-4} mol of chloride in 1 g. of [bmim][PF_6] at 80 °C, b – semilogarithmic plot of the data of plot a), c - decrease of optical rotation of a solution of 7.7×10^{-4} mol of chloride in 1 g. of [bmim][PF_6] at 60 °C.

absence of coinitiator in chlorobenzene. There was no change of optical rotation at 80 °C for 48 h indicating that no racemization occurs at those conditions in organic solvent of medium polarity ($\varepsilon = 5.7$).

Those results show, that ionization of C–Cl bond in 1-phenylethyl chloride is indeed facilitated in ionic liquids as compared to organic solvents of medium polarity and consequently that cationic styrene polymerization involving ionization of this bond both in initiation and in propagation step, is possible in ionic liquid even in the absence of coinitiator. This is in line with results of recently published paper concerning carbocation-forming reactions in ionic liquids. [14]

In the cationic polymerization of styrene, chain transfer occurs by transfer of proton to monomer molecules (with a formation of unsaturated and/or indanyl end-groups), leading to formation of new population of macromolecules. In the system described by Kennedy et al. [8], chain transfer could be suppressed and polymerization proceeded as living/controlled process. This, however, required relatively high concentration of $TiCl_4$ coinitiator (about one order of magnitude higher than concentration of initiator) and addition of common-ion salt (tetraalkylammonium chloride).

The necessary requirement for controlled polymerization in this system (but also in other systems) is that both activation and deactivation reactions are fast as compared to propagation. This requirement was apparently fulfilled in the system described by Kennedy et al. because polymerization showed the features of living/controlled polymerization ($DP_n = ([M]_0 - [M]_t)/[I]_0$, low dispersity).

As shown in the present paper, ionization of C–Cl bond (corresponding to activation step in controlled polymerization scheme) occurs in [bmim][PF_6] in the absence of coinitiator. The question remains, however, whether this process is

Table 1.
Polymerization of styrene with 1-(p-methylphenyl)ethyl chloride as initiator in [bmim][PF_6] in the absence of coinitiator at 90 °C.

No	Time, h	Conversion, %	M_n calcd	M_n GPC	M_w/M_n
ST 1	24	85	2.8×10^3 (for 85% conversion)	5.3×10^3 [c)] 1.1×10^6 [c)]	2.3
ST 7[a)]	24	90	2.65×10^3 (for 90% conversion)	4.1×10^3	2.0
ST 13[b)]	5 × 24	15	4.1×10^2 (for 15% conversion)	1.0×10^3 [c)] 1.0×10^6 [c)]	1.06

[a)] polymerization in the presence of radical inhibitor: hydroquinone (50%-mol with respect to initiator).

[b)] polymerization in the presence of proton sponge (1,8-bis(dimethyloamino)naphthalin): (140%-mol with respect to initiator).

[c)] bimodal molecular weight distribution.

fast enough to ensure fast equilibration of active and dormant species.

Polymerization of Styrene

Results of polymerization of styrene with 1-(p-methylphenyl)ethyl chloride as initiator in [bmim][PF_6] in the absence of coinitiator at 90 °C are shown in Table 1. The p-methyl substituted initiator was used in order to distinguish between head groups formed by initiation and by transfer (although the reactivity of p-methyl substituted initiator may be different then the reactivity of unsubstituted analogue due to the inductive effect of substituent).

GPC traces for samples ST 1, ST 7 and ST 13 are shown in Fig. 2.

Polymerization with no additives (ST 1) leads to bimodal weight distribution. In addition to medium molecular weight polymer (main fraction), some high molecular weight polymer is formed (elution volume ~ 10 mL). We assumed that this high molecular weight fraction can be formed by radical mechanism (thermal initiation or initiation by impurities due to relatively high temperature of polymerization). This was indeed confirmed by results of experiment ST 7. In the presence of radical inhibitor the position of peak of the main fraction remains essentially unchanged while high molecular weight peak disappears. In the presence of proton sponge (experiment ST 13) results are

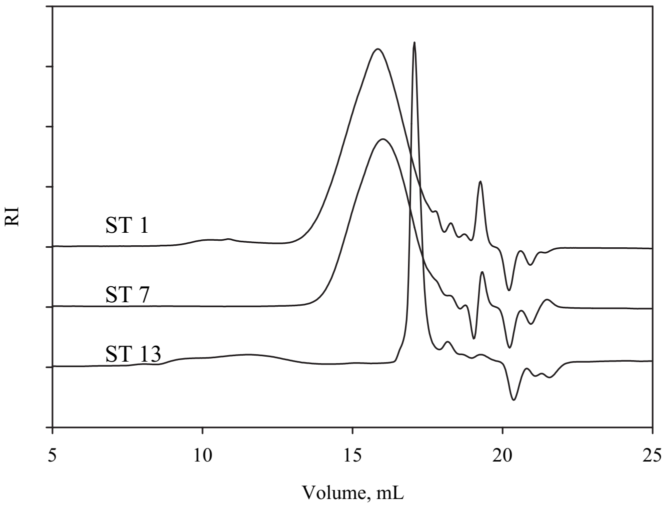


Figure 2.
GPC traces of polystyrene: samples ST 1, ST 7 and ST 13 (cf. Table 1).

different. Polymerization is very slow (15% conversion after 5 × 24 h), some high molecular weight fraction is formed (no radical inhibitor was added in this experiment) and the main fraction gives narrow peak ($M_w/M_n < 1.1$) although M_n value is still higher than the calculated value. For longer reaction times (2 weeks) some broadening of lower molecular weight peak is observed but further polymerization leads mainly to the high molecular weight polymer ($M_n \sim 10^6$) apparently by radical mechanism.

Analysis of MALDI TOF spectra of polymers shows that in the absence of proton sponge (ST 1, ST 7) the main fraction (medium molecular weight fraction) consist of macromolecules containing both types of head-groups: $CH_3CH(CH_3C_6H_4)$– groups formed by initiation and $CH_3CH(C_6H_5)$– groups formed by transfer (cf Scheme 1). On the other hand, polymer formed in the presence of proton sponge is composed exclusively of macromolecules containing $CH_3CH(CH_3C_6H_4)$– groups formed by initiation. MALDI TOF spectra are shown in Figure 3.

Results of polymerization experiments may be summarized as follows.

At 90 °C cationic polymerization of styrene is initiated by ionization of C–Cl bond in 1-phenylethyl chloride (or its p-methyl substituted analogue) even in the absence of coinitiator (Lewis acid). Formation of two populations of macromolecules (as evidenced by MALDI TOF spectra of products) indicates that transfer to monomer proceeds and significant fraction of polymer is formed by transfer. In addition some high molecular weight fraction is formed, apparently by radical mechanism, because this fraction is eliminated in the presence of radical inhibitor (as in ST 7).

If proton sponge is added in order to prohibit formation of polymer by transfer

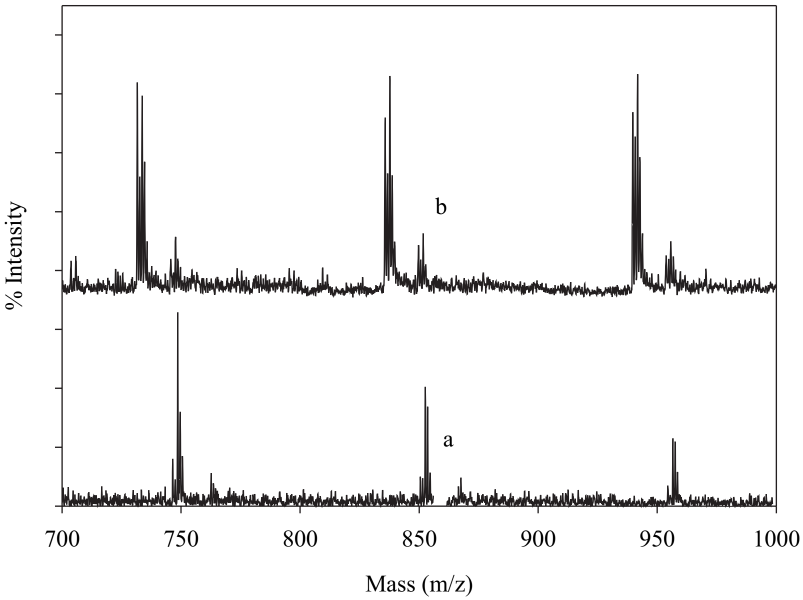


Figure 3.

MALDI TOF spectra of polystyrenes obtained: a -in the presence of proton sponge (ST 13), b – in the absence of proton sponge (ST 7). The expanded fragment of the spectrum shown (m/z = 700–1000). In spectrum b, the series of higher intensity peaks separated by 104 molar mass units corresponds to macromolecules containing $CH_3CH(C_6H_5)$- head groups and unsaturated or indanyl end-groups (not distinguished by MALDI TOF). The series of lower intensity peaks (also separated by 104 molar mass units) corresponds to macromolecules containing $CH_3CH(CH_3C_6H_4)$- head groups and unsaturated or indanyl end-groups. Only the later series is present in spectrum b.

(as in ST 13) polymerization proceeds slowly to a limited conversion and polymer is formed only by initiation. If the reaction time is prolonged, there is apparently no further cationic polymerization, although styrene polymerize further by radical mechanism to high molecular weight polymer.

Combining those results with results of the measurements of the rate of racemization of optically active 1-phenylethyl chloride one may reach a conclusion that although cationic polymerization of styrene in ionic liquid may be initiated by 1-phenylethyl chloride (or its p-methyl substituted analogue) alone (in the absence of any coinitiator) the conditions are not suitable for controlled polymerization. Rate of isomerization of optically active phenylethyl chloride is a measure of not only the rate of initiation but also of the rate of activation of dormant species. Comparing the rate of isomerization and the overall rate of polymerization, one comes to the conclusion that ionization rate is not high enough to ensure sufficiently fast initiation and sufficiently fast activation of dormant species.

Low rate of initiation explains why in all cases observed M_n values were higher than calculated values. Low rate of activation of dormant species may be a reason why chain transfer cannot be eliminated.

Conclusion

High polarity of ionic liquids facilitates ionization of C–Cl bond in 1-phenylethyl chloride. Cationic polymerization of styrene even in the absence of coinitiator may be initiated by this initiator and proceeds to nearly complete conversion, although only at higher temperatures (90 °C). Ionization of C–Cl bond even at this temperature, however, is not sufficiently fast to ensure fast initiation and fast activation of dormant species and therefore polymerization is not controlled.

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