Anion Complexation of Vinylimidazolium Salts and Its Influence on Polymerization

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ABSTRACT: To improve water solubility of 1-butyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide ([bvim]-[Tf_2N]) the complexation with β-Cyclodextrin (β-CD) was carried out. Investigations of conductivity measurements, NMR and microcalorimetry show that β-CD forms exclusively host−guest complexes with the anion bis(trifluoromethylsulfonyl)imide (Tf_2N^-). The received spatially separated ion pairs create quasi "naked" vinylimidazolium cations which do not polymerize in water by radical mechanism. Only in the presence of foreign salt is the cation−cation repulsion compensated and polymerization occurs.

Introduction

Free radical polymerization of *N*-vinylimidazolium cations in water has been well established for decades. The polymerization proceeds rapidly since the electrostatic repulsion of the vinyl cations is compensated by the counterions. The resulting polycations are of broad interest because of their many practical applications, e.g., in cosmetics or as flocculants.[1−3]

Recently, ionic liquids became popular because of serious properties such as no vapor pressure and their potential as a solvent for polar substrates. In the present study, we were encouraged to polymerize a vinylimidazolium cation with bis(trifluoromethylsulfonyl)imide as counterion which represents a typical momomeric ionic liquid.[4−9]

According to our interest in the use of cyclodextrins (CDs) in polymer chemistry,[10−14] we intended to complex this ionic liquid with β-cyclodextrin (β-CD) to achieve high water solubility. Thus, in this study, we wish to report the polymerization behavior of a CD-complexed ionic liquid in water as a reaction medium. 1-Butyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide ([bvim][Tf_2N]) (**2**) represents a typical polymerizable ionic liquid. The salt was found to be nearly insoluble in water (5 mg/mL). We therefore investigated the formation of a CD-complex of [bvim][Tf_2N], which is an established method to improve the water solubility of hydrophobic guests.

Results and Discussion

The complexation of an organic salt with β-CD influences ionic mobility, which is correlated with electrical conductivity.

As expected the conductivities decreased strongly with increasing β-CD concentration, indicating the reduced mobility of the host−guest complex.

However, not only the complexation but also the stoichiometry can be pursued with this method. The inflection point at an equimolar concentration of β-CD (3.3 mmol L^{-1}) is due to the formation of a complex with a 1:1 stoichiometry (Figure 1).[15] It was not yet clear whether either the cation or the anion was complexed preferentially with CD. However, a statistical mixture of anion and cation complexes cannot be expected because of the nearly perfect equimolar host guest formation. Thus, for better understanding of the complex system, detailed NMR analysis was carried out.

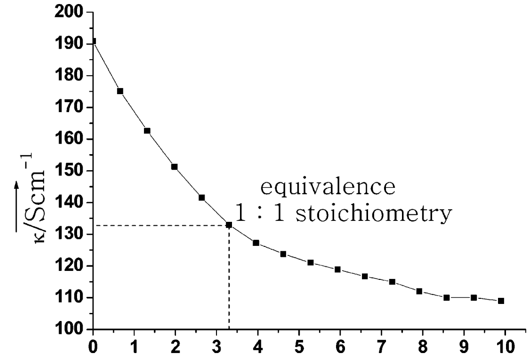

Figure 1. Electrical conductivity of aqueous solutions of [bvim][Tf_2N] (3.3 mmol L^{-1}) depending on the concentration of β-CD at 298 K.

The established method of continuous component variations according to Job and Blanda[16−18] was used to confirm the complex stoichiometry (see Supporting Information). It was surprisingly found that no shift of proton signals of the cation took place in presence of β-CD.

In contrast, a significant influence of β-CD on the fluorine signals of the anion on the ^{19}F NMR spectra was found. Also a 2D-ROESY NMR spectrum supports the above-described assumption that only the anion is involved in the complex formation because of the missing signals between the cation and β-CD (see Supporting Information). The hydrophobic cavity of the CD causes the hydrophobic interactions with the guest which leads to characteristic ^{19}F NMR shifts. For example the signals of the bis(trifluoromethyl) group are shifted from −79.67 ppm (in water) to −79.07 ppm (in the CD complex).

Thus, only the ^{19}F NMR spectra of the complexed anion supply an ideal Job diagram. The maximum at 0.5 confirms clearly a complex stoichiometry of 1:1 as mentioned above (Figure 2).

The complexation results in a spatial separation of the ion pair (Scheme 1). It was calculated semiempirically on an AM-1 level, which confirmed a bond angle for S−N−S atoms of 180° (see Supporting Information).

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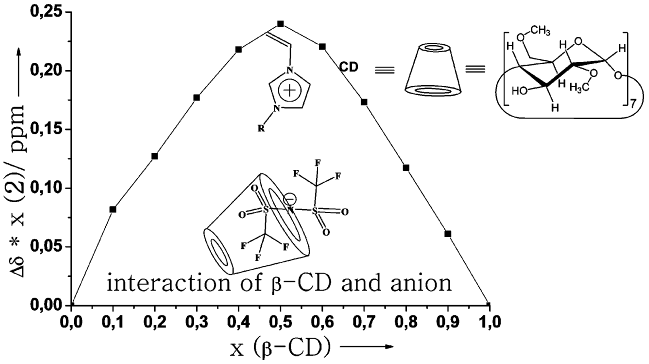


Figure 2. Job diagram of the monomer **2**. Chemical shift of the six fluoric atoms in $^{-}N(SO_2-CF_3)_2$: x = mole fraction; $\Delta\delta$ = changing of the chemical shift.

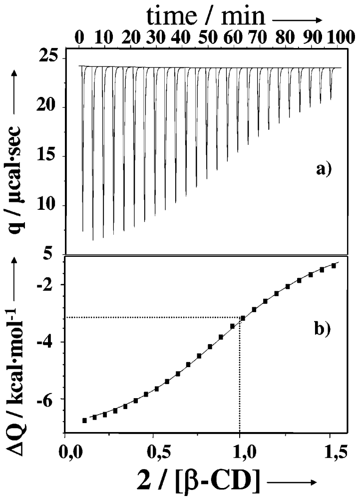


Figure 3. (a) Heat flow q as a function of time detected by a microcalorimeter upon the addition of a 8 mM solution of **2** to a 1 mM solution of β-CD. (b) Inclusion enthalpies in dependence of the molar ratio calculated by the integration of the heat flows q for the consecutive peaks.

Scheme 1. Host−Guest Complex Formation of [bvim][Tf$_2$N] with β-CD at 298 K in Water

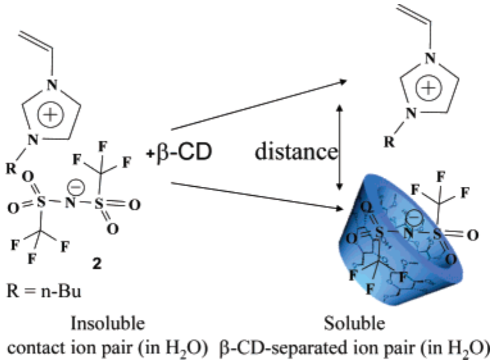
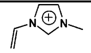
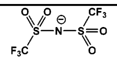
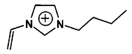
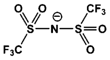
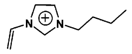
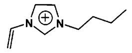
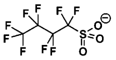
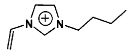
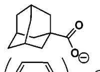
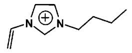
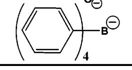


Table 1. Comparison of the Complex Stability Constant of Different Ionic Liquids

Ionic liquid			
Number	Cation	Anion	K_s [M^{-1}]
1			8190
2			8100
3		$^{\ominus}PF_6$	289
4			21000
5			5300
6			no complexation

A very versatile and accurate method for the determination of thermodynamic binding data is titration by use of microcalorimetry.[19] ΔG, ΔH, and ΔS could be obtained very accurately within one experiment. Also the complex formation constant K_s can be determined. Figure 3a shows the heat flow as a function of time for a microcalorimetric titration. All injections show negative heat flow signals, which indicate exothermal complex formation. An excellent fit of the integrated signals received from nonlinear regression by the binding curve was found (Figure 3b). The inflection point at a molar ratio of 1.0 shows the same 1:1 stoichiometry as discussed above. Although some water molecules are released from β-CD cavity during the complex formation, the experimentally determined entropy is clearly negative. This results from the increased order and reduced mobility of the Tf_2N^--β-CD system. Also the non coordinating behavior, which is due to the distributed negative charge in the molecule, leads to this entropy decrease.

The estimated stabilities of the inclusion complexes of the anion of [bvim][Tf$_2$N] with β-CD was Ks = 8100 ± 64 M^{-1}, which is relatively high compared to other guests in supramolecular chemistry. For example, if the Tf_2N^- anion is replaced by PF_6^-, we receive a much lower complex stability constant of only 289 ± 11 M^{-1} (Table 1). This value is exclusively caused by the weak complexation of β-CD with the imidazolium cation. Replacing the Tf_2N^- anion by nonafluorobutansulfonate [NfO$^-$] anion, we got a constant of 21000 ± 330 M^{-1} which indicates a very strong interaction of the anion with the β-CD cavity. Table 1 also illustrates the behavior of hydrophilic anions like adamantylcarboxylat, which belongs to the best guests of β-CD known so far.[20] However, the K_s value is 5300 M^{-1}, which is lower than the determined value for the Tf_2N^- and NfO$^-$ anions. The table shows also that, a change of the cation structure to 1-methyl-3-vinylimidazolium leads to no change of the stability constant, since only the anion is incorporated into the CD cavity.

Very large hydrophobic anions such as tetraphenylborate $(Ph)_4B^-$ do not form host−guest complexes because of sterical factors. They remain completely insoluble in water. These results show indirectly the outstanding inclination of the Tf_2N^- and NfO$^-$ anion to form host−guest complexes with β-CD.

The uncomplexed vinyl monomer (**2**) was easily polymerized in organic solvents like *tert*-butanol. Surprisingly, several attempts to polymerize the β-CD complexed ionic liquid in water were not successful by free radical initiation. In this context, the variation of some experimental parameters like temperature and initiator were ineffective in all cases.

The postulated reason for this high monomer stability toward polymerization is a result of spatial ion pair separation which leads to quasi “naked vinylimidazolium cations” caused by the complex formation. This β-CD-effect is indicated in Scheme 1. Obviously the increased mean distance of vinylimidazolium cation and complexed anion leads to a strong electrostatic repulsion between the vinylimidazolium cations and thus, no polymerization takes place. Accordingly, this effect should be compensated with some addition of foreign salt. We therefore added LiCl to the solution. The addition of the salt leads to shielding of the charges of the monomers in solution. The Cl$^-$ anions are localized close to the vinylimidazolium cations, whereby the repulsion of the monomers is partially compensated.

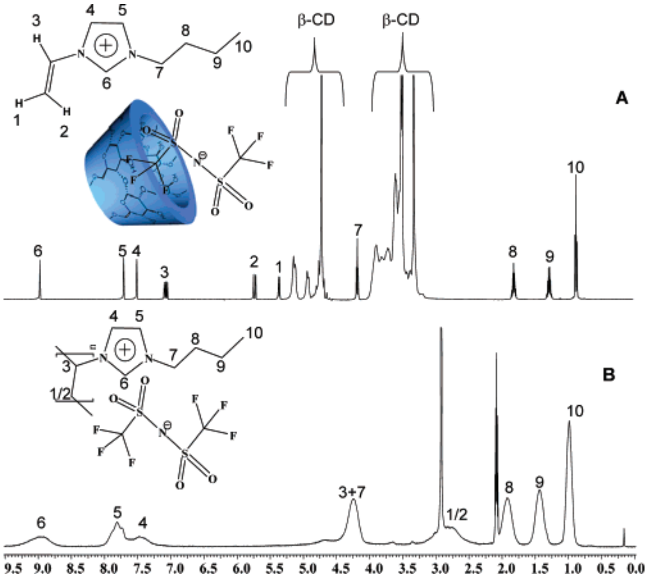


Figure 4. NMR-spectra after the polymerization of CD-complexed **2**: (A) spectrum for the polymerization without LiCl; (B) spectrum with LiCl.

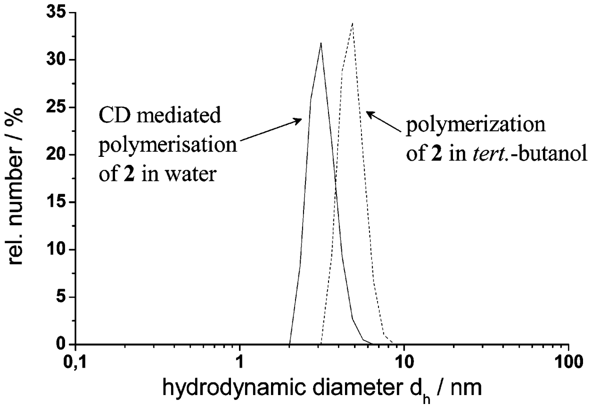


Figure 5. Hydrodynamic diameter of the polyelectrolytes, which were polymerized either in water by CD complexation or in *tert*-butanol.

As postulated, the polymerization of [bvim][Tf_2N] could be carried out easily (Figure 4).

While the absence of LiCl led to no conversion and polymerization respectively, Figure 4B shows the successful polymerization in presence of LiCl recognizable at the broad signals, which are typical for polymers.

The polyelectrolyte could be also characterized through dynamic light scattering measurements (DLS) in DMF. Figure 5 shows the hydrodynamic diameter for the polyelectrolytes, which were radically polymerized in water by CD complexation and in *tert*-butanol. The results indicate that the polymerizations do not differ so much. While the maximum of the diameter of the CD mediated polymerization is at 3.12 nm, the diameter amount to 4.85 nm for the polymerization in *tert*-butanol. This implicate that the polymerization in organic solvents proceed with higher molecular weights. This may be a result of different polymerization conditions.

It has been shown that vinylimidazolium cations containing bis(trifluoromethylsulfonyl)imide as conjugated anions are able to form host−guest complexes with β-CD. We have proved through conductivity, NMR measurement and microcalorimetry that only the anions are enclosed in the cavity of β-CD with a high complex stability constant of 8100 ± 64 M^{-1}. The obtained quasi-naked vinylimidazolium cations could not be polymerized radically under usual conditions. Only after the addition of a foreign salt did a polymerization take place. Further investigations are ongoing to explore this interesting field of polymer chemistry.

Supporting Information Available: Text giving experimental preparations and characterization of the described compounds and description of the different methods for proving the complexation, Figure 5S, showing the structure of [bvim][Tf_2N] from a semiempirical calculation, Figure 6, showing a 2D-ROESY spectrum of β-CD complexed imide, and Scheme 2, showing the intended polymerization paths. This material is available free of charge via the Internet at http://pubs.acs.org.

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