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Supramolecular Controlled Pseudo-LCST Effects of Cyclodextrin-Complexed Poly(ionic liquids)

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ABSTRACT: We investigated the complexation of monomeric 1-butyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide ([bvim][Tf$_2$N]) with different cyclodextrins (CDs) in water. Furthermore, we discovered that the poly([bvim][Tf$_2$N]) **1** showed a pseudo-LCST (lower critical solution temperature) effect in the presence of CD. It was shown that the CD ring complexates only the polymer anion and slips off at higher temperature where the poly(ionic liquid) becomes insoluble in water. We were encouraged to prove this effect by turbidity measurements, microcalorimetric titrations, dynamic light scattering, and enzymatic scission of the CD.

Introduction

Numerous investigations were made to study the LCST (lower critical solution temperature) behavior of some polymers like poly(*N*-isopropylacrylamide).[1–4] Potential applications of these materials are in the medical and biochemical field. We recently observed pseudo-LCST effects of certain cyclodextrin (CD)-complexed polymers.[5,6] This pseudo-LCST behavior was found to be a result of thermally controlled reversible complexation of suitable polymer side groups with CD. However, up to now, this interesting phenomenon was observed exclusively in the case of nonionic polymers. Now, in the present paper, we describe an unexpected pseudo-LCST effect based on a hydrophobic polyelectrolyte in combination with CD as the anion-host.

The herewith described pseudo-LCST effect of a poly(ionic liquid) is based on solubility change of poly(1-vinyl-3-butylimidazolium) bis(trifluoromethylsulfonyl)imide ([vbim][Tf$_2$N]) **1** due to supramolecular CD effects.

Results and Discussion

Ionic liquids became popular because of unusual properties like virtually no vapor pressure and potential use as solvent for polar substrates.[7–11] These special characteristics open a wide field of applications, including the use of ionic liquids in polymer chemistry.[12]

In our interest, we investigated the complex formation and solubility behavior of poly(ionic liquids). The radical polymerization of the monomeric ionic liquid 1-vinyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide ([vbim][Tf$_2$N]) can be easily accomplished either in water in the presence of CD or in organic solvents like *tert*-butanol without CD.[13] It is not possible to polymerize the monomeric hydrophobic ionic liquid in water without CD. Like the monomeric ionic liquid, the resulting hydrophobic and solid poly(ionic liquid) **1** are able to form water-soluble host−guest complexes with CD. Both monomeric and polymeric ionic liquids are not water soluble; however, the monomeric ionic liquid has a residual solubility of nearly 5 mg/L. To understand this supramolecular interaction, it is essential to determine the stability of these CD complexes.

In our previous work, we characterized the complexation of [vbim][Tf$_2$N] by different methods in which only the anions are the preferred guest components,[13] while also the complexation of cations of PF$_6$−ionic liquid surfactants was reported.[14] We determined a 1:1 stoichiometry of CD as the host with hydrophobic anions like the bis(trifluoromethylsulfonyl)imide anion as the guest and very high complex stability constants for these complexes.[13]

The hydrophobic cavity of the CD causes the hydrophobic interactions with the guest which lead to characteristic ^{19}F NMR shifts of the fluorine atoms of the anion. As an example, the NMR signals of the bis(trifluoromethyl) group are shifted from −79.67 ppm (in water) to −79.09 ppm (in CD complex) (Figure 1). 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.

A very versatile and accurate method for the determination of thermodynamic binding data is titration by use of microcalorimetry.[15] ΔG, ΔH, ΔS, and the complex formation constant *K*s can be obtained very accurately within one experiment.

The estimated stability of the inclusion complexes of the anion of monomeric [vbim][Tf$_2$N] at room temperature with RAMEB-CD (randomly methylated β-CD = CD) was $Ks = 8100 \pm 64$ M^{-1} which is relatively high compared to other guests in CD chemistry. Furthermore, we investigated the complex formation of the monomeric [vbim][Tf$_2$N] with different CDs as host molecules. Table 1 summarizes the complex stability constants of monomeric [vbim][Tf$_2$N] with different CDs.

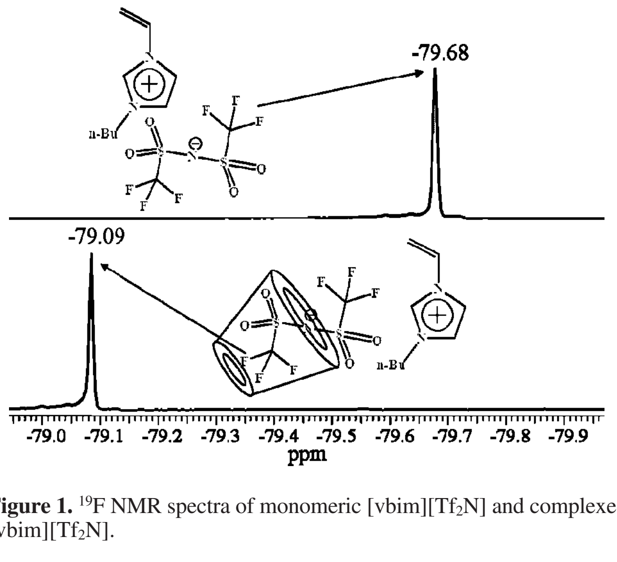

Figure 1. ^{19}F NMR spectra of monomeric [vbim][Tf$_2$N] and complexed [vbim][Tf$_2$N].

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Table 1. Comparison of the Complex Stability Constant of Monomeric [vbim][Tf_2N] with Different Cyclodextrins as Host Molecules

cyclodextrin	*K*s/M^{-1a}
α-CD	25
β-CD	3230
γ-CD	170
RAMEB-CD	8100

[a] Determined by microcalorimetry.

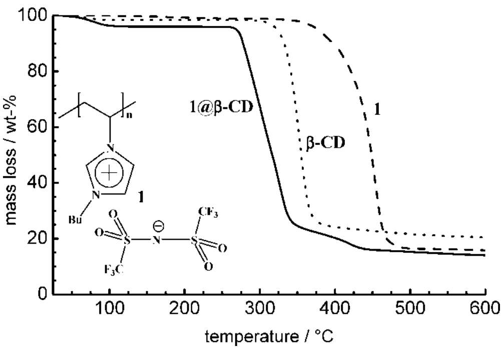


Figure 2. TGA curves obtained for: RAMEB-CD, poly([vbim][Tf_2N]) (**1**), and a complex of both.

While α- and *γ*-CD show only low constants regarding the anion of [vbim][Tf_2N], both *β*- and RAMEB-CD have an outstanding complex stability constant. Obviously, α- and *γ*-CD are either too small or too big to include the $[Tf_2N]^-$ anion perfectly into the cavity.

To prove the complexation of the anions in poly([vbim]-[Tf_2N]) **1**, the thermal stability of polymeric [vbim][Tf_2N] was evaluated by using TGA analysis, and the results were compared with the stabilities of pure RAMEB-CD and the CD complexed poly([vbim][Tf_2N]) (Figure 2). It is interesting to note that the complex between the polyelectrolyte **1** and CD has a clearly lower thermal stability than both pure **1** and RAMEB-CD, which is unusual.[16,17] The inclusion of the anion Tf_2N^- into the cavity of RAMEB-CD leads to a spatial separation of the ion pair. Thus, the distance between Tf_2N^- and $vbim^+$ increases which leads to higher total energies in comparison to the ion pair. This may be the main reason for the relatively low decomposition temperature of the anion-complexed salt.

The obtained solid poly(ionic liquid) **1** with a MW of 8.000 g/mol (Polystyrol as a standard) shows a "pseudo"-LCST effect in the presence of RAMEB-CD. By heating the clear aqueous solution of the complexed polyelectrolyte poly[vbim][Tf_2N] **1** over 45 °C, the solution clouded suddenly. Cooling the solution, the turbid dispersion became completely transparent again. This results from the thermoreversible complexation and decomplexation of the anion of the poly(ionic liquid) (Scheme 1). To determine the behavior of the various systems, some turbidity measurements were carried out (Figure 3).

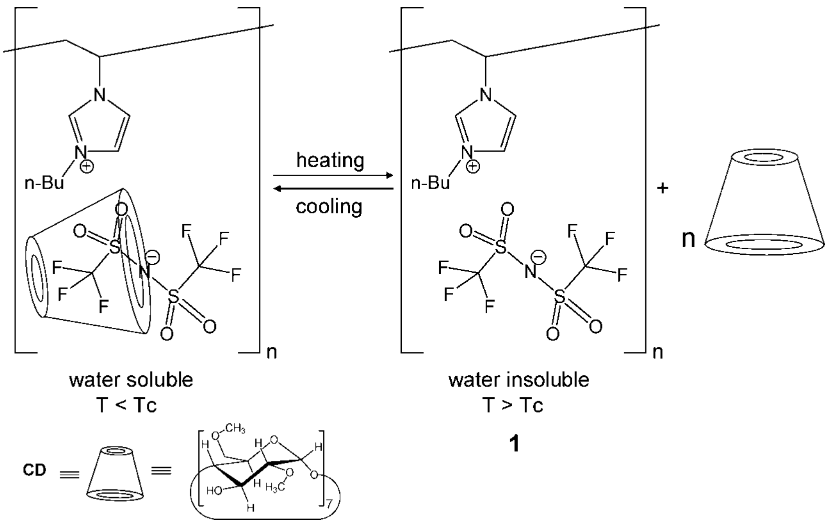
The reduction of the transparency of complexed **1** is a result of slipping off of the CD while heating. **1** gets insoluble and precipitates. During the following cooling, **1** reforms host−guest complexes which lead to water solubility. In contrast to CD-complexed **1**, the free polyelectrolyte is not water soluble over the whole temperature range. This behavior is due to the formation and scission of noncovalent interactions between CD and the anions of poly[vbim][Tf_2N].

Another interesting point shown in Figure 3 is the focus on the dependence of the pseudo-LCST on the CD concentration. With rising CD concentration, the LCST value increases significantly and shows phase transition temperatures of 48 to 62 °C. This is due to the equilibration of the complex formation. The higher the CD concentration, the stronger the equilibration moves toward the complex formation. In contrast to the LCST behavior that is commonly reported for polymer systems, based on hydrogen bond effects, the effect reported here is due to entropy driven decomplexation from the anions at higher temperatures.

To understand this temperature dependence of the complexation process, microcalorimetric titrations between 20 and 70 °C were carried out for a monomeric ionic liquid (Table 2). At 20 °C, the complex stability constant is relatively high (Ks = 10 200 M^{-1}). However, at 70 °C, the Ks value becomes much lower (Ks = 1170 M^{-1}). This is nearly an order of magnitude. It is interesting to note that the entropy is negative during the complexation process. Since the complexation process is an exothermic equilibration reaction, it strongly depends on temperature as described above. Thus, with rising temperature, Ks decreases (Figure 4).

In the case of the polymeric ionic liquid **1**, the complex stability constant is definitely lower than the monomeric ionic liquid so that an increase in temperature leads to a decomplexation of CD from the anion of **1**. To prove this mechanistic postulation, we demonstrated that this precipitated polymer shows only weak or no CD signals in the IR spectrum, while the original complexed poly(ionic liquid) shows strong signals of the CD ring at about 3392 cm^{-1} (see Supporting Information). The results confirm the postulated pseudo-LCST mechanism

Scheme 1. Pseudo-LCST Behavior of Poly[vbim][Tf_2N] (1)



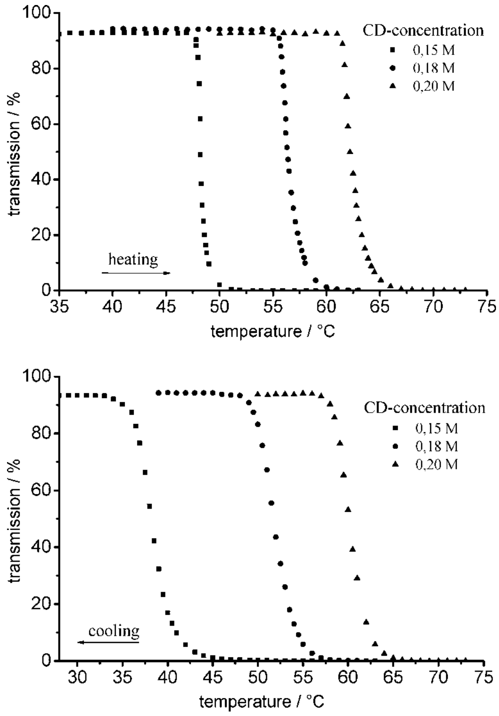


Figure 3. Dependence of the LCST value of solutions of **1** ($c = 50$ mM of the polymer in water) on CD concentration.

Table 2. Comparison of the Thermodynamic Data of Complex Formation of Monomeric [vbim][Tf_2N] with CD at Different Temperatures

temperature/°C	Ks/M^{-1}	ΔH/kJ·mol^{-1}	$T\Delta S$ /kJ·mol^{-1}
20	10200	−31.05	−8.56
30	6890	−35.79	−13.44
40	4370	−39.43	−17.55
50	2650	−44.31	−23.11
60	1740	−48.33	−27.59
70	1170	−49.79	−29.56

that deviates from the classical LCST behavior. In comparison to the poly(ionic liquids), the monomeric salts do not show any LCST effects.

Additionally, the temperature-dependent hydrodynamic diameter d_h of complexed **1** was measured by use of dynamic light scattering (DLS) (Figure 5). The d_h value was measured before and after reaching the LCST. Figure 3 exhibits clearly that the hydrodynamic diameter increases by approaching the LCST. At the temperature of 56 °C, we measured a hydrodynamic diameter of nearly 2.5 nm, and the solution became clear. At the equilibration of the LCST at 57 °C, d_h increases to 15.7 nm due to intermolecular aggregation. Finally, the CD slips off from the poly(ionic liquid), and the hydrophobic polymer chains aggregate to large particles at temperatures above 57 °C and form a turbid dispersion.

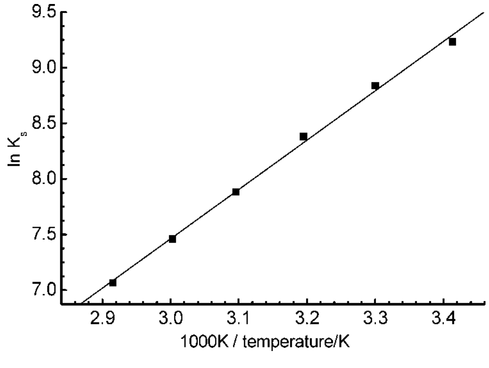


Figure 4. Temperature dependence of the complex stability constant Ks.

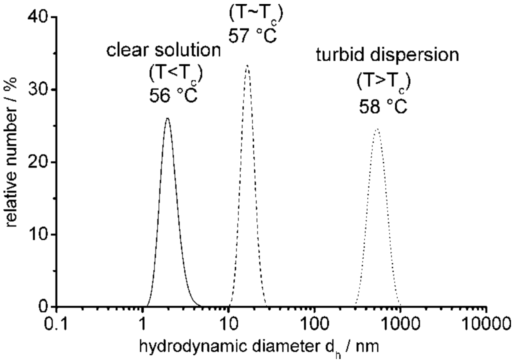


Figure 5. Hydrodynamic diameter before and after reaching the LCST.

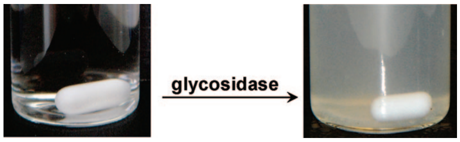


Figure 6. Enzymatic scission of CD from CD-complexed **1**.

Another important and interesting proof of the existence of CD-complexed poly(ionic liquid) is the enzymatic scission of CD by a glycosidase. After a reaction time of 24 h **1** begins to precipitate due to degradation of the CD (Figure 6).

It can be concluded from the above-described results that CD forms stable complexes with the counterion of poly(vinylimidazolium) salts at room temperature. At higher temperatures, the CD slips off from the anion and the resulting noncomplexed polymer precipitates.

Similarly, also by addition of the enzyme, glycosidase is also responsible for cleavage of the CD ring, whereby the polymer precipitates. This pseudo-LCST effect of poly(ionic liquids) may open new applications, e.g., for the design of temperature-sensitive gels.

Supporting Information Available: Experimental preparations and characterization of the described compounds and description of the different methods for proving the complexation. This material is available free of charge via the Internet at http://pubs.acs.org.

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